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3.3.2

Number of research papers per teachers in the Journals notified on UGC website during the last five years (10)

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A GRADE C.GPA. 3.24., BY NAAC

3.3.2 Number of research papers per teachers in the Journals notified on UGC website during the last five years (10)

S.N.	Title Of Paper	Name Of The Author/S	Department Of The Teacher	Name Of Journal	Page No.
1.	Isolation Of High Yielding, Nutritionally Improved Chickpea Mutant Lines Through Induced Mutagenesis Using Gamma Rays And Ems	Deepak Koche And Archana Joshi Saha	Botany	International Journal Of Tropical Agriculture Volume 39,	**1**
2.	An Update On Role Of Salicylic Acid (Sa) In Abiotic Stress Tolerance In Crop Plants: A Review	Deepak Koche , Ruchita Gandhi, Shubham Rathod, Rupali Shirsat	Botany	Agbir Vol.37	10
3.	Correlating Medicarpin Content Of Chickpea Cultivars As A Key Defense Compound Against Fusarium Wilt	S. B. Chavan And D. K. Koche	Botany	Res. On Crops	17
4.	Nutritional Profiling Of Wild Areal Tubers Of Dioscorea Bulbifera L. From Maharashtra, India	Ruchita Gandhi , Tripty Jagtap , Neha Kopare , Rupali Shirsat , Deepak Koche	Botany	International Journal Of Botany Studies	22
5.	Physico-Chemical, Fluorescent And Phytochemical Analysis Ofanisochilus Carnosus (L.F.) Wall: A Lamiaceae Herb Frommaharashtra, India	Ruchita R. Gandhi, Neha P. Kopare, Shubham A. Rathod,Rupali P. Shirsat And Deepak K. Koche	Botany	Indian J. Applied & Pure Bio. Vol. 37(1),	27
6.	Antimicrobial Activities Of 3-Aryl-4-S-Benzyl-6-Phenylimino2-Hepta-O-Acetyl-B-D-Maltosylimino-2,3-Dihydro-1,3,5- Thiadiazines (Hydrochloride)	Yadgire Av	Chemistry	International Journal Of Life Sciences2320-7817	39
7.	Synthesis Of 1,3,4-Thiadiazole Lactosylamino Derivatives As Antimicrobials	Sharayu M. Thorat, Mamata T. Sangole	Chemistry	Indian Journal Of Heterocyclic Chemistry	43
8.	Investigation Of Physicochemical And Medicinal Properties Of Oil Seed Of Certain Wild Plant Species Of Gadchiroli District Of Maharashtra	Dr. M. T. Sangole,Rajiv B. Dange	Chemistry	Juni Khyat	49
9.	Green Multicomponent Method For Synthesis Of Substituted	Pawar Mahesh A And Kadu Ss	Chemistry	International Journal Of Life Sciences2320-	54

	Derivatives 2-Amino Chromenes By Using Na2co3 As A Catalyst			7817	
10.	N-Tosylhydrazone As An Oxidizing Directing Group For The Redox-Neutral Access To Isoquinolines Via Cp*Co(Iii)-Catalyzed C−H/N−N Activation	D. S. Deshmukh, N. Gangwar, B. M. Bhanage	Chemistry	Journal Of The Indian Chemical Society	58
11.	A Study Of Routing Protocol In Wireless Sensor Network	Dr. Santosh Madhusing Chavan	Computer Science	Journal Of The Maharaja Sayajirao University Of Baroda	69
12.	A Study Of Cryptography And Techniques Of Cryptography	Dr.Santosh Madhusing Chavan, Dr. Shyamsundar Ashokrao Abuj	Computer Science	Wesleyan Journal Of Research	78
13.	Design And Development Of Microcontroller Base Pulse Oximeter	Niteen Sridhar Mohod	Electronics	Aayushi International Interdisciplinary Research Journal	87
14.	Utilization Of Green Electricity For Operation Of A Miniature Electronic Circuits	G. S. Wajire	Electronics	Internation Journal Of Scientific Research In Science And Technology	89
15.	Remote Sensing And Gis Based Extensive Morphotectonic Analysis Of Tapti River Basin, Peninsular India	Shubhendu Shekhar,Y.K. Mawale, P. M. Giri , R. S. Jaipurkar , And Neelratan Singh	Geology	Journal Of Scientific Research	94
16.	Lithological Controls On The Groundwater Fluoride Enrichment In Central India	Madhavi Dubey · Satish Deshpande · Satyajit Gaikwad · Ganesh Gaikwad · Ashish Dongre	Geology	Arabian Journal Of Geosciences	102
17.	Effect Of Synthesis Techniques On Vuv Properties Of Eu3+ Doped Yvo4 Phosphors: A Comparative Study	R. G. Korpe , N. S. Bajaj , G. V. Korpe , S. K. Omanwar	Physics	International Journal Of Scientific Research In Science And Technology	121
18.	Novel Molten Salts Synthesis And Photoluminescence Properties Of Eu (Iii)Doped Y2o3 Phosphor	K. A. Koparkar, N.S. Bajaj, S. K. Omanwar Pg. No. 476-479	Physics	International Journal Of Scientific Research In Science And Technology	128
19.	Aldo-Keto Gel Synthesis And Photoluminescence Properties Of Yvo4: Eu3+Microspherek.	A. Koparkar, G. V. Korpe, S. K. Omanwar Pg. No. 480-483	Physics	International Journal Of Scientific Research In Science And Technology,	132
20.	Impact Of Synthetic Pyrethroid On Dna Rna And Dna/Rna Ratio On Freshwater Fish Channa	Dr.U.P. Lande	Zoology	Worldwide Internation Inter Disciplinary Research Journal	141

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ISOLATION OF HIGH YIELDING, NUTRITIONALLY IMPROVED CHICKPEA MUTANT LINES THROUGH INDUCED MUTAGENESIS USING GAMMA RAYS AND EMS

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Abstract: Chickpea (*Cicer arietinum* L.) is one of the major pulse crops in India. It is a major source of protein for populations that are vegetarian by choice or unaffordability of animal proteins. Chickpea cultivar 'Vijay' is a very old variety that is still popular among farmers of Maharashtra State. There is a scope to improve this cultivar in terms of yield and nutritional value. The present attempt focused on development of mutant lines with improved yield and nutrition using induced mutation. The Chickpea variety- 'Vijay' was treated with different doses of gamma rays (300Gy, 400 Gy, 500 Gy) and EMS (0.2%, 0.3%, 0.4%) and sown to grow M_1 generation. The M_1 was harvested on single plant basis and sown in next season as plant to row progeny to grow M_2 generation. M_2 generation was visually screened thoroughly for different types of mutations. Additionally the M_2 harvest was also screened for protein content using calorimentric methods. Total 171 mutants were selected based on yield, nutrition and earliness. These mutants were sown as plant to row in M_3 generation to study the breeding behavior. Out of these, 12 mutant lines were found to have higher yield than control Vijay, including 07 lines with bold seeds and one line with earliness in M_3 generation. The selected lines will be forwarded to advance generation (M_4 to M_6) to stabilize the yield contributing characters and then will be evaluated in various trials.

Keywords: *Cicer arietinum* L., Germplasm, Gamma rays, EMS, Mutant.

INTRODUCTION

Chickpea (*Cicer arietinum* L.) is the second largest pulse crop, grown in over 50 countries, and traded across the globe [1]. Chickpea is valued and accepted globally for its nutritive seed composition and protein content as a substitute for animal protein [2]. Mutation breeding is an effective tool and playing vital role in crop improvement since its inception in agriculture. Induced mutation technique has proved to be successful for improving different traits in a wide variety of crops especially pulses. To date, more than 3,274 varieties in more than 224 plant species derived from mutagenesis programs have been officially released as listed in the FAO/IAEA Mutant Varieties Database (MVD). Among these, 493 mutant varieties of pulses are registered, with 21 improved chickpea mutants released for cultivation [3, 4].

Mutation breeding is an additional advantage when there is a case of improvement of a good variety as it has to alter just one or two traits [5]. Genetic variability can be effectively induced through mutation and its practical applications are well recognized [6, 7]. Considering the rapidly increasing population and declining per capita pulses consumption in India, while also considering comparatively large area under its cultivation then other pulses, the chickpea production statistics over the last decade is not sufficient to meet the growing demand. Therefore, attempts are needed to

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crack the stagnation of chickpea productivity by developing high yielding and better adapted varieties. The main purpose of this work was to evaluate the mutagenicity of gamma rays, EMS doses employed and the magnitude of variability induced in various morphological and quantitative traits of the chickpea variety- Vijay for the practicable selection based on yield attributing characters and nutrition.

MATERIAL AND METHODS

The study was aimed to develop the Chickpea mutant with high yield potential and high nutrition. For this a *Desi* variety- Vijay was selected, and germplasm was procured from Mahatma Phule Agriculture University, Rahuri (MS). After screening of the seed material for purity, they were treated with gamma rays and EMS. Each treatment of mutagen included about 300 seeds. The doses selected were [gamma rays- 300, 400 and 500 Gy and EMS 0.2, 0.3, and 0.4 %]. The treated material was then sown in field during mid of October 2015. Standard agricultural practices were followed throughout the cultivation. After germination, the growing progeny was monitored for germination and survival rate and physiological variation if any. The M_1 population was harvested during January-February 2016. In October 2016, M_2 generation was grown and closely monitored for different morphological variations. The plant types with high yield, bold seeds and other economic characters were marked and harvested separately from progeny of each treatment. The M_2 progeny was harvested during February- March 2017. The M_2 selections were grown as M3 progeny on plant to row basis (during October 2017). After germination, each line was monitored closely for the traits under observations and noted. The M3 progeny was harvested during February – March 2018. After harvest, number of seeds per plant, 100 seed weight was noted and protein content [8] of each seed sample was analyzed.

RESULTS AND DISCUSSION

Total 12 high yielding mutants were selected from M_2 population of variety Vijay for their yield performance to observe and evaluate their breeding nature in M_3. All of them were found segregating in M_3 for their yield character. However, few of them showed interesting results in terms of their average yield, 100 seed weight and boldness of seeds. The data of performance of high yielding mutant lines is presented in table 1.

Mutant 1(14-03) with total 20 plants showed segregation in yield and yield contributing characters but observed to be early flowering and early maturing as compare to control (by 8 days) (Fig. 2). Mutant 11(04-03) with 10 plants respectively in M_3 showed segregation in yield but the average yield and seed weight was found to be slight higher than control. Mutant 17(03-01) does not showed any stability in selected characters. Mutant 17(04-01) with 10 plants in M_3 showed segregation in M_3 generation for yield, but interestingly the average seed yield was double than control with slight increase in 100 seed weight. Mutant 16(06-22) was found to be true breeding for yield characters with average seed yield nearly 3 times than control. 100 seed weight and protein content was also found to slight higher than control.

Mutant 16(07-01) showed segregation in yield character in terms of seed number, however most of these plants showed higher seed weight and bold size. Mutant 16(04-11) plants also showed segregation in yield, with average seed yield less than control but average seed weigh (24.78g) per 100 seeds and increased protein content (18.45 mg/g to 21.82 mg/g) was seen.

Mutant 11(04-11) with 26 M_3 plants showed segregation in yield as compare to its M_2 performances. But their average yield was nearly same as that of control. Moreover, seeds of all these plants were bolder than control (100 seed weight 25.38g; Fig. 1) with sizable increase in protein content. Mutants 11(04-12) A, B & C with about 50 plants in M_3 showed segregation in M3 for yield but seeds of entire progeny were found to be bold, where 100 seed weight were found to be nearly 04 to 06 gm more than control. Mutant 16(06-09) also showed segregation in yield characters averaging less than control in terms of number of seed grains buts its seed size was bold (100 seed weight 23.81g) with increase in protein content (table 1).

The use of induced mutations has played a key role in the improvement of superior plant varieties especially pulses. A large number of improved mutant varieties have been released for commercial cultivation [9,10]. In releasing mutant varieties of Chickpea, India is contributing immensely through the efforts of Indian Agriculture research Institute, its sub-centers and collaboration with several State Agriculture Universities [11]. In some earlier reports [12] similar results in chickpea breeding were noted that reported segregating lines till M_4 generation but showed stability from M_5 onwards to develop a superior line with high yield and high protein content. Few workers [13] reported the isolation of high yielding bold seeded mutant lines of chickpea using gamma rays and EMS. Development of bold seeded Kabuli cultivar "CM2008" also revealed the same procedure [14,15]. Some workers have used EMS and SA as mutagen and isolated the desired mutant lines especially high yielding and yield contributing characters [16, 17]. Thus, results of the present study are in line, however, needs evaluation at least up to M_6 or M_7 to observe the stability of mutants for yield and yield contributing characters. From the results discussed, it is clear that the lower doses (300 Gy) are found to be more effective inducing high degree of defined mutations as compare to their counter higher doses of gamma radiations. No selections were recorded from EMS progeny. Further on the basis of yield performances and protein content analysis it could be stated that, the selected mutant lines are potential sources for developing the new improved variety.

Table 1: M_3 Performance of high yielding mutants isolated from M_2 progeny of Var- Vijay

Variety	*Treatment/ Dose*	*M_2 plant no. (Seed plant^{-1}/ 100 Seed wt.*	*M_3 Plant no.*	*Seeds/ plant*	*100 Seed wt. (gm)*	*Protein content*
Vijay	Control			74.89	18.12	18.28 ± 0.53
	Gamma rays					
	300 Gy	01 (14-03) [680/17.32]	1(14-03)-1	58	18.22	18.56
			1(14-03)-2	89	18.54	18.48
			1(14-03)-3	102	18.52	18.39
			1(14-03)-4	150	18.78	18.62
			1(14-03)- 5	130	18.52	18.56
			1(14-03)-6	111	18.38	18.42
			1(14-03)- 7	124	18.70	18.42
			1(14-03)-8	78	18.23	18.45
			1(14-03)-9	57	18.52	18.65
			1(14-03)-10	65	18.50	18.38
			1(14-03)-11	79	18.25	18.48
			1(14-03)- 12	164	18.63	18.58
			1(14-03)- 13	162	18.65	18.65
			1(14-03)- 18	215	17.80	18.45
			1(14-03)-19	110	18.25	18.42
			1(14-03)-20	108	17.89	18.28
			Total Plant= 20	Avr= 87.02	Avr= 18.40	Avr= 18.26
		11 (04-03) [465/18.02]	11 (04-03)-1	85	18.52	18.52
			11 (04-03)-2	48	18.28	18.33
			11 (04-03)-3	69	18.39	18.45
			11 (04-03)-4	55	18.25	18.29
			11 (04-03)-5	89	17.88	18.33
			11 (04-03)-6	92	18.62	18.42
			11 (04-03)-7	167	18.72	18.39
			11 (04-03)-8	152	18.80	18.45
			11 (04-03)-9	160	18.93	18.52

Variety	*Treatment/ Dose*	*M_2 plant no. (Seed plant^{-1}/ 100 Seed wt.*	*M_3 Plant no.*	*Seeds/ plant*	*100 Seed wt. (gm)*	*Protein content*
			11 (04-03)-10	101	18.38	18.45
			Total Plant= 20	Avr= 87.40	Avr= 18.33	Avr= 18.41
		17(03-01) [1026/17.30]	17(03-01)-1	115	19.30	18.58
			17(03-01)-2	108	18.45	18.46
			17(03-01)-3	40	18.00	18.45
			17(03-01)-4	46	17.90	18.42
			17(03-01)-5	168	18.50	18.42
			17(03-01)-6	108	16.80	18.66
			17(03-01)-7	62	17.85	18.36
			17(03-01)-8	118	18.00	18.64
			17(03-01)-9	102	18.22	18.22
			17(03-01)-10	70	19.40	18.45
			17(03-01)-11	135	18.50	18.98
			17(03-01)-12	98	17.80	18.43
			17(03-01)-13	50	19.20	18.52
			17(03-01)-14	102	20.70	18.54
			17(03-01)-15	175	19.60	18.28
			17(03-01)-16	115	18.95	18.33
			17(03-01)-17	165	19.45	18.46
			17(03-01)-18	65	18.60	18.36
			17(03-01)-19	142	19.70	18.78
			17(03-01)-20	40	20.00	18.48
			17(03-01)-21	85	18.20	18.46
			17(03-01)-22	85	20.18	18.48
			17(03-01)-23	52	19.00	18.58
			17(03-01)-24	82	19.05	18.96
			17(03-01)-25	25	19.08	18.56
			Total Plants= 25	Avr= 94.12	Avr= 18.81	Avr= 18.51
		17(04 – 01) [305/18.80]	17 (04- 01)- 1	102	18.03	18.38
			17 (04- 01)- 2	120	18.50	18.40
			17 (04- 01)- 3	325	19.02	18.42
			17 (04- 01)- 4	107	18.60	18.55
			17 (04- 01)- 5	109	18.30	18.54
			17 (04- 01)- 6	212	18.20	18.87
			17 (04- 01)- 7	305	19.50	18.48
			17 (04- 01)- 8	98	18.30	18.79
			17 (04- 01)- 9	268	17.90	18.44
			17 (04- 01)- 10	102	18.30	18.38
			Total plants= 10	Avr= 164	Avr= 18.46	Avr= 18.52
		16(06- 22) [320/18.08]	16(06- 22)- 01	105	18.30	18.44
			16(06- 22)- 02	98	18.06	18.48
			16(06- 22)- 03	97	18.00	18.58
			16(06- 22)- 04	432	20.27	18.85
			16(06- 22)-05	105	18.70	18.53
			16(06- 22)- 06	303	18.50	18.32
			16(06- 22)- 07	412	18.60	18.38
			16(06- 22)- 08	93	17.80	18.42

Variety	*Treatment/ Dose*	*M_2 plant no. (Seed plant^{-1}/ 100 Seed wt.*	*M_3 Plant no.*	*Seeds/ plant*	*100 Seed wt. (gm)*	*Protein content*
			16(06- 22)- 09	103	18.02	18.47
			16(06- 22)- 10	100	18.21	18.42
			Total plants 10	Avr= 214.80	Avr= 18.46	Aver= 18.48
		16(07-01) [382/20.94]	16(07-01)-01	70	24.60	18.87
			16(07-01)-02	75	20.00	18.47
			16(07-01)-03	77	22.10	18.56
			16(07-01)-04	170	20.25	19.87
			16(07-01)-05	65	22.06	18.42
			16(07-01)-06	70	20.24	18.57
			16(07-01)-07	89	20.16	18.78
			16(07-01)-08	59	20.60	18.45
			16(07-01)-09	85	20.18	18.47
			16(07-01)-10	130	19.08	19.20
			16(07-01)-11	58	17.60	18.97
			16(07-01)-12	58	17.80	18.78
			16(07-01)-13	74	21.50	18.58
			16(07-01)-14	97	18.78	18.48
			16(07-01)-15	88	19.20	18.45
			16(07-01)-16	66	19.80	18.59
			16(07-01)-17	126	21.31	19.56
			16(07-01)-18	154	18.51	19.47
			16(07-01)-19	201	17.99	19.78
			16(07-01)-20	216	18.50	19.48
			16(07-01)-21	93	19.30	18.87
			16(07-01)-22	83	20.82	18.65
			16(07-01)-23	100	18.30	18.63
			16(07-01)-24	168	23.47	19.20
			16(07-01)-25	168	19.79	19.46
			Total plants 25	Avr= 105.6	Avr= 20.15	Avr= 18.90
		16(04-11) [258/23.76]	16(04-11)6-1	32	26.96	18.97
			16(04-11)6-2	68	25.02	18.85
			16(04-11)6-3	31	25.16	18.59
			16(04-11)6-4	40	27.20	19.27
			16(04-11)6-5	45	23.34	18.98
			16(04-11)6-6	60	25.52	19.23
			16(04-11)6-7	74	26.98	21.52
			16(04-11)6-8	87	25.74	21.45
			16(04-11)6-9	91	24.52	21.42
			16(04-11)6-10	32	25.44	19.85
			16(04-11)6-11	48	26.18	19.54
			16(04-11)6-12	89	26.18	21.85
			16(04-11)6-13	48	23.12	18.45
			16(04-11)6-14	100	25.90	21.82
			16(04-11)6-15	67	22.89	18.59
			16(04-11)6-16	65	25.68	19.23
			16(04-11)6-17	45	26.84	20.17
			16(04-11)6-18	49	25.54	20.05
			16(04-11)6-19	39	26.40	21.42
			16(04-11)6-20	59	22.40	18.97

Variety	*Treatment/ Dose*	*M_2 plant no. (Seed plant^{-1}/ 100 Seed wt.*	*M_3 Plant no.*	*Seeds/ plant*	*100 Seed wt. (gm)*	*Protein content*
			Total plants=20	Avr= 60.80	Avr= 24.78	Avr= 19.91
		11(04-11) [258/23.76]	11(04-11)01-1	107	25.63	21.45
			11(04-11)01-2	72	28.60	21.83
			11(04-11)01-3	134	26.85	21.48
			11(04-11)01-4	145	27.40	21.89
			11(04-11)01-5	106	25.48	21.26
			11(04-11)01-6	52	29.10	22.82
			11(04-11)01-7	42	25.32	21.42
			11(04-11)01-8	43	26.00	21.30
			11(04-11)01-9	116	27.21	21.66
			11(04-11)01-10	36	28.00	22.28
			11(04-11)01-11	57	27.54	22.18
			11(04-11)01-12	20	24.50	20.88
			11(04-11)01-13	26	25.20	21.20
			11(04-11)01-14	37	25.20	20.85
			11(04-11)01-15	47	25.40	21.17
			11(04-11)01-16	111	24.40	21.55
			11(04-11)01-17	78	24.28	20.84
			11(04-11)01-18	73	27.12	21.08
			11(04-11)01-19	67	26.00	20.85
			11(04-11)01-20	123	27.94	21.46
			11(04-11)01-21	72	26.25	20.98
			11(04-11)01-22	121	27.45	21.58
			11(04-11)01-23	33	27.30	21.15
			11(04-11)01-24	34	27.20	21.10
			11(04-11)01-25	39	27.30	20.97
			11(04-11)01-26	68	23.48	20.85
			Total plants=26	Avr= 71.11	Avr=25.38	Avr= 21.38
		11(04-12) A [320/22.2]	11(04-12)02-1	66	21.72	20.17
			11(04-12)02-2	42	22.80	20.02
			11(04-12)02-3	26	20.30	19.18
			11(04-12)02-4	102	23.41	21.48
			11(04-12)02-5	38	26.38	21.25
			11(04-12)02-6	22	20.18	19.85
			11(04-12)02-7	110	27.20	22.02
			11(04-12)02-8	69	24.40	19.85
			11(04-12)02-9	147	25.60	21.98
			11(04-12)02-10	221	26.90	21.48
			Total plants=10	Avr=84.3	Avr= 23.88	Avr= 20.72
		11(04-12) B [320/22.2]	11(04-12)07-1	86	23.80	20.47
			11(04-12)07-2	70	27.00	20.85
			11(04-12)07-3	55	28.12	20.58
			11(04-12)07-4	66	25.20	20.15
			11(04-12)07-5	46	27.20	20.65
			11(04-12)07-6	42	25.75	20.27
			11(04-12)07-7	60	27.00	21.12
			11(04-12)07-8	50	25.10	20.17
			11(04-12)07-9	135	26.80	21.85
			11(04-12)07-10	38	26.40	21.25

Variety	*Treatment/ Dose*	*M_2 plant no. (Seed plant^{-1}/ 100 Seed wt.*	*M_3 Plant no.*	*Seeds/ plant*	*100 Seed wt. (gm)*	*Protein content*
			11(04-12)07-11	90	27.05	21.45
			11(04-12)07-12	37	27.10	21.62
			11(04-12)07-13	40	24.20	20.42
			11(04-12)07-14	40	27.00	21.72
			11(04-12)07-15	90	30.26	21.83
			11(04-12)07-16	108	24.58	21.48
			11(04-12)07-17	80	25.10	20.45
			11(04-12)07-18	50	25.00	20.45
			11(04-12)07-19	120	25.70	21.95
			11(04-12)07-20	40	24.50	20.48
			Total plants= 20	Avr= 65.85	Avr=26.15	Avr= 21.98
		11(04-12) C [320/22.20]	11(04-12)08-1	25	20.20	18.98
			11(04-12)08-2	34	25.60	20.85
			11(04-12)08-3	30	25.25	18.87
			11(04-12)08-4	17	25.00	18.96
			11(04-12)08-5	44	25.45	19.05
			11(04-12)08-6	41	27.20	19.45
			11(04-12)08-7	90	26.30	21.46
			11(04-12)08-8	25	23.40	18.87
			11(04-12)08-9	75	24.20	20.12
			11(04-12)08-10	40	23.80	19.86
			11(04-12)08-11	36	24.50	20.23
			11(04-12)08-12	45	25.25	20.27
			11(04-12)08-13	70	25.50	20.17
			11(04-12)08-14	60	28.20	20.22
			11(04-12)08-15	90	26.50	20.15
			11(04-12)08-16	115	26.29	22.05
			11(04-12)08-17	67	26.34	21.18
			11(04-12)08-18	40	25.40	20.27
			11(04-12)08-19	82	24.00	19.82
			11(04-12)08-20	97	25.46	20.15
			11(04-12)08-21	60	26.96	21.25
			11(04-12)08-22	60	26.40	20.26
			11(04-12)08-23	20	25.30	20.75
			11(04-12)08-24	62	24.48	20.02
			11(04-12)08-25	45	26.00	21.12
			11(04-12)08-26	48	25.30	20.47
			11(04-12)08-27	60	25.32	20.17
			11(04-12)08-28	45	25.20	20.32
			11(04-12)08-29	110	26.20	22.06
			11(04-12)08-30	33	23.00	19.85
			Total plants 30	Avr= 54.86	Avr= 25.26	Avr= 20.85
		16 (06-09) [301/21.43]	16(06-09)01-1	57	23.01	19.83
			16(06-09)01-2	51	24.72	20.12
			16(06-09)01-3	41	24.24	20.15
			16(06-09)01-4	--	--	--
			16(06-09)01-5	81	22.86	18.98
			16(06-09)01-6	52	23.52	19.35
			16(06-09)01-7	96	23.10	19.23
			16(06-09)01-8	87	26.28	19.85

Variety	*Treatment/ Dose*	*M_2 plant no. (Seed plant^{-1}/ 100 Seed wt.*	*M_3 Plant no.*	*Seeds/ plant*	*100 Seed wt. (gm)*	*Protein content*
			16(06-09)01-9	60	22.48	18.45
			16(06-09)01-10	26	24.12	20.25
			16(06-09)01-11	147	24.23	21.46
			16(06-09)01-12	--	--	--
			16(06-09)01-13	46	22.80	19.58
			16(06-09)01-14	32	25.20	20.46
			16(06-09)01-15	33	24.44	20.24
			16(06-09)01-16	25	27.20	21.23
			16(06-09)01-17	32	24.08	20.58
			16(06-09)01-18	122	24.17	21.45
			16(06-09)01-19	74	26.10	20.84
			Total plants=19	Avr= 60.36	Avr= 23.81	Avr= 20.11

Figure 1: High yielding bold seeded plant type in M_3

Figure 2: Early flowering mutants of Variety Vijay (M_3 Population)

Conflict of Interest

Authors have no Conflict of interest.

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RESEARCH ARTICLE

An update on role of salicylic acid (SA) in abiotic stress tolerance in crop plants: a review

Deepak Koche*, Ruchita Gandhi, Shubham Rathod, Rupali Shirsat

Koche D, Gandhi R, Rathod S, et al. An update on role of salicylic acid (SA) in abiotic stress tolerance in crop plants: a review. AGBIR. 2021;37(6):204-210.

Abiotic stresses have been recognized as the potential threat for agricultural production across the globe. Anthropogenic activities related to industrialization and urbanization also have aggravated the degradation of agricultural system as they are experiencing increasing impact of abiotic stresses. These stresses potentially induce various adverse effects on plants affecting their physiological, biochemical and molecular processes ultimately leading huge loss in crop productivity. Plant hormones are recognized amongst the handiest tools to mitigate the abiotic stress. Salicylic acid (SA) is one of most essential and multifaceted plant hormone that not only play vital role in plant defense but also have active participation in conferring abiotic stress tolerance. The present review deals with the illustrations of studies carried out by different workers on the role of SA in combating various types of abiotic stresses like metal stress, salinity stress, temperature stress and water stress in different crops.

Key Words: *Salicylic acid; Abiotic stress; Plant defense; Tolerance*

INTRODUCTION

Human beings are continuously exploiting natural resources to fulfill their needs without any check; this has huge negative impact on climatic conditions and agriculture. Though, there is improvement in agriculture production, but other natural resources are declining and when these coupled with increasing population, the overall situation appears alarming. Food and Agriculture organization (FAO) predicted that by 2050, we need to enhance agricultural food production by 70% (FAO, 2009). The effects of changing climate like global warming showed direct effect on the plant production and as per the report of IPCC (2007) there will be increase in global temperature of earth by 2-4oC and this will further affect the agricultural productivity [1,2].

Any negative change in the existing climate is the major cause of abiotic and biotic stress observed in a particular region. Several abiotic stresses coupled with developmental activities like urbanization and industrialization have been assessed as the potential threats to the agricultural productivity [3]. The major abiotic stresses includes salinity stress, water stress (flooding and scarcity) metal/ metalloid stress, temperature stress (extreme temperature), nutrient stress (deficiency and excess) are some major issues for world agriculture [4-7]. All these abiotic stresses potentially modulate physiological, biochemical and molecular mechanism in plants irrespective to their developmental stages and cause severe loss in the yield of crop plants [8,9].

MATERIALS AND METHODS

Salicylic acid (SA): brief history

The name of salicylic acid (SA) was derived from the Latin word Salix (willow tree). The bark and leaves of willow tree used by Americans, Indians and Greeks to cure aches and fever. It has been documented that Hippocrates for the first time administered a drug to relive pain of women during child birth and fever, it was salicylic acid. It was first isolated as glucoside of salicylic alcohol, salicin by a German scientist Johann Andreas Buchner. Later on it was reported from 36 other plants in addition to willow tree [10-13]. The phytohormone SA is a simple phenolic compound (C7H6O3) with an aromatic ring to which one carboxylic and one hydroxyl group are attached. The biosynthesis of this molecule takes place through shikimate pathway, which later branched as isochorimate pathway and phenylalanine pathway. The most common pathway in plants for SA synthesis is isochorismate pathway. About 90% of SA in plant is synthesized by this pathway. However, SA biosynthesis may also be accomplished by phenylalanine pathway [14-16]. The rout of synthesis of SA is schematically presented in (Figure1). Earlier, it was reported to be involved in various physiological processes like stimulation of root development, stomata closure, and reduced transpiration reversal of the effects of abscisic acid (ABA) (Davies, 2004) and regulation of gravitropism [17]. Yuan and Lin (2008) suggested that deficiency or very high concentration of SA increases the susceptibility of plants towards abiotic stress but moderate or optimal concentration (0.01 mM to 0.05 mM) of SA may be useful for abiotic stress tolerance.

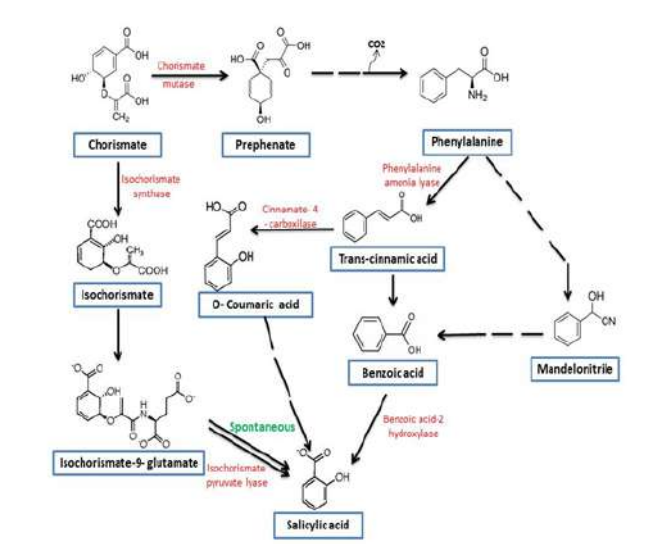

Figure 1) *Presentation of biosynthetic pathways of salicylic acid in plants*

METHODOLOGY

Salicylic acid (SA) in abiotic stress tolerance

LSA was reported to play a vital role in improving abiotic stress tolerance in several crop plants. Khan had taken an overview of historical background and biosynthesis of salicylic acid under both optimal and stressful environments in plants. They have also illustrated potential mechanisms governing salicylic acid-induced plant abiotic stress-tolerance. Li suggested that SA acts upstream of NO under high concentration of carbon dioxide (CO_2) to induce enhanced flavonoid biosynthesis in tea plants. This indicates that SA enhanced biosynthesis of secondary metabolites in tea plants under the abiotic stress conditions. Zaid reported that in watermelon plants, resistance against root-knot nematode by red light is regulated by the coordination of

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SA and Jasmonic acid (JA) signaling. This report indicates potential of SA in enhancing tolerance against biotic stress in watermelon. In general, it was noted to participate in several important plant processes and regarded as an important growth regulating and defense related molecules in plants [18-20]. The overall role of SA in managing/ combating different types of abiotic stress is been presented in (Figure 2).

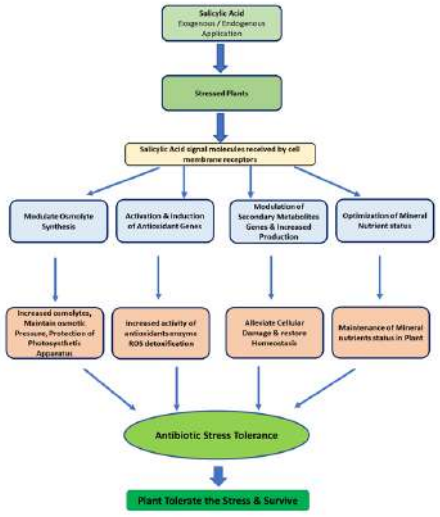

Figure 2) *Presentation of mechanism of salicylic acid in abiotic stress tolerance*

A in metal/ metalloid stress tolerance

Plant responds to metals and metalloid stress by generating reactive oxygen species (ROS). Overproduction of ROS can damage the nucleic acid, proteins, carbohydrates and lipid peroxidation [21,22]. To combat the uncontrolled oxidation, defense systems have to produce several enzymes (SOD, CAT, GR, GPX, GST etc.) and SA reportedly involved in this mechanism. SA increases plants tolerance to metal stresses by modulating various metabolites of antioxidant defense system, osmolytes, secondary metabolites and metal chelating compounds [23,24].

Some studies have reported that SA perform the role of an iron-chelation molecule or sometimes directly act as a scavenger of hydroxyl radicals and degrade metal-bioactivity by enhancing antioxidant enzyme activities [25]. Oxidative stress caused by ROS products such as H2O2 can be reduced by optimal concentrations of SA. In plants, when H2O2 is accumulated in high concentration, toxicity in plants caused by the production of reactive hydroxyl radicals can lead to oxidative stress and eventually disturb plant metabolism [26-30]. However, application of the low concentration of SA is reported to improve plant tolerance and increase plant defense by inducing antioxidant enzyme activities, leading to reduced oxidative stress [31]. Exogenous application of SA was reported to improve growth and photosynthetic traits in several crop plants including lead (Pb) exposed Oryza sativa, Cd exposed Zea mays (Krantev et al., 2008) and Cu -exposed Phaseolus vulgaris [18]. The efficacy of SA as foliar supplement on two mentha cultivars, namely, Kosi and Kushal grown under Cd (50 µM) stress conditions was tested by Zaid [32,34]. Out of three foliar applications of plant growth regulators, the application of SA at different growth stages proved best in alleviating Cd toxicity. Application of SA was also found to tolerate as toxicity in two varieties of Artemisia annua L. [35]. This study also suggested that the application of SA via leaf significantly increased the artemisinin content in both varieties. Es-sbihi studied the effects of SA on physiological traits, distribution of glandular hairs and essential oil (EO) composition in Salvia officinalis L., grown on Cu contaminated medium and noted that its foliar spray enhance the synthesis of essential oil. Thus, exogenous application of SA could enhance plants tolerance against metal stress. In general, SA is one of most essential phytohormone that regulates the plants tolerance to abiotic stress especially metal stress by stimulating genes associated with expression of defense system, modulating the cellular redox homeostasis and alteration of transcription element activities [36]. Some of the important reports of alleviation of metal and metalloid stress using SA are presented in (Table 1).

TABLE 1

Some representative report on salicylic acid (SA) mediated response towards abiotic stress impact in wild as well as crop plants (Adopted partially from Khan et al., 2015)

Plant Name	Conc. of salicylic acid used	Parameters studied	Response	References
Cd stress				
Ricinus communis	0.5 mM	Gas exchange, Chlorophyll content.	-	Liu et al., 2011
Brassica juncea	1.0 mM	Mineral nutrient content	+	Ahmad et al., 2011
Glycine max	120 mM	SOD activity, GSH content, heme- oxygenase-1 activity, and Chlorophyll content, relative protein content.	+	Noriega et al., 2012
Poa pratensis	0.5 mM	Nutrient element content	+	Guo et al., 2013
Poa pratensis	0.5 mM	Cd uptake	-	Guo et al., 2013
Cucumis melo	0.1 mM	Photosynthetic capacity, efficiency of PSII, Water use efficiency	+	Zhang et al., 2015
Zea mays	0.5 mM	Defense compounds	+	El Dakak and Hassan, 2020
Nickel Stress				
Thlaspi goesingense	0.5 mM	Induction of SAT/ increase in GSH	+	Freeman et al., 2015
Catharanthus roseus	10-5 M	Content of alkaloids vincristine and vinblastine	+	Idrees et al., 2013
Iron stress				
Arachis hypogaea	1.0 mM	Fe uptake and balance of mineral nutrients	+	Kong et al., 2014
Copper stress				
Phaseolus vulgaris	0.5 mM	Photosynthetic traits and growth	+	Zhengin, 2014
Manganese stress				
Cucumis sativus	100 µM	Oxidative stress in exposed leaves	-	Shi and Zhu, 2008
Mercury stress				
Vallisneria natans	100 µM	Pb uptake and Mn, Ca, and Fe content	-	Wang et al., 2011

Salinity stress				
Cucumis sativus	1.0 mM	uptake of N, P, K, Ca, and Mg	+	Yildirim et al., 2008
Zea mays	0.5 mM	K+/Na+ and Ca2+/Na+ ratios	+	Tufail et al., 2013
Vigna radiata	0.5mM	Glycinebetaine (GB) production, net photosynthesis, plant dry mass	+	Khan et al., 2014
Torreya grandis	0.5 mM	Chlorophyll content, net CO_2 assimilation rates, proline content	+	Shen et al., 2014
Glycine max	0.5 mM	Na+/K+ ratio	-	Ardebili et al., 2014
Glycine max	0.5 mM	SOD activity, ascorbate content	+	
Hardeum vulgare	0.05 mM	MDA content, Na+/K+ ratio	-	Fayez and Bazaid, 2014
Hardeum vulgare	10-4 mM	Content and activity of Rubisco, Rubisco activase	+	Lee et al., 2014
Brassica juncea	0.5 mM	S assimilation	+	Nazar et al., 2015
Gossypium barbadense	200 ppm	Growth and yield characters	+	El- Beltagi et al., 2017
Pennisetum glaucum	0.05mM	Physiological traits governing yield	+	Yadav et al., 2020
Zea mays	0.5 mM	Sugar contents, protein, proline, and activities of SOD, POD, CAT	+	Fahad and Bano, 2020
Cold, Chilling & Freezing stress				
Musa acuminata	0.5 mM	Ultrastructure of chloroplast of mesophyll cells, mitochondria of mesophyll cells	+	Kang et al., 2007
Hardeum vulgare	0.1 mM	Apoplastic antioxidative enzymes, ice nucleation activity, pattern of apoplastic proteins	+	Mutlu et al., 2013
Citrus limon	2.0 mM	Total phenolics, activity of phenylalanine ammonialyase (PAL)	+	Siboza et al., 2014
Spinacia oleracea	1.0 mM	Trehalose, proline, tocopherol, ascorbic acid, osmolytes and antioxidants	+	Min et al., 2019
Heat stress				
Brassica juncea	1.0 mM	Accumulation of essential elements	+	Ahmad et al., 2011
Triticum aestivum	0.5 mM	Proline content, glutamyl kinase activity, gas exchange, water potential	+	Khan et al., 2013
Triticum aestivum	0.5 mM	Antioxidants	+	Karpets et al., 2020
Water stress (Drought)				
Triticum aestivum	1,2,3 mM	Nitrogen assimilation	+	Singh and Usha, 2003
Triticum aestivum	1.0 mM	Ca, Mg, and K in shoot and roots	+	Al Tayeb and Ahmed, 2010
Zea mays	0.001 mM	Leaf rolling degree, water potential, dry weight	+	Saruhan et al., 2012
Simarouba glauca	0.05mM	Polyphenol, alkaloids, flavonoid content	+	Awate and Gaikwad, 2014
Portulaca oleracea	0.5 mM	growth, photosynthetic pigment contents, gas exchanges traits, fatty acid contents, compatible solutes, secondary metabolites	+	Saheri et al., 2020
Triticum aestivum	1.0 mM	Photosynthesis performance, membrane permeability, stress proteins and antioxidants	+	Khalvandi et al., 2021

Note: mM means Concentration in milimolar,µM means concentration in micro molar

RESULTS

SA in salinity stress tolerance

Increasing salt concentration in soil is a major issue causing salt or salinity stress in most part of the world. The major adverse effects of salinity stress include increased ion toxicity, osmotic stress, and nutrient acquisition, impaired stomatal conductance, reduction in leaf water potential, altered physiological/biochemical processes, and elevated ROS-causing oxidative stress [37,39]. The role of SA in strengthening salinity stress-tolerance mechanisms has been extensively evidenced in many crops including Brassica juncea and *V. radiata* [40-42].

Exogenous application of SA increases the proline content in wheat seedlings under salinity stress, thereby alleviating the deleterious effects of salinity [43]. The pre-treatment SA was found to improve the photosynthetic efficiency, enhanced ascorbate peroxidase (APX) and guaiacol peroxidase (GPX) activity in roots, and induces an accumulation of polyamines that could be correlated with increased tolerance to salinity [44,45]. The pre-soaking treatment of seeds with SA was reported that it positively affected the osmotic potential, shoot and root dry mass, K+ /Na+ ratio and contents of photosynthetic pigments in wheat seedlings, under saline and non - saline conditions [46]. Salicylic acid promotes germination under saline conditions by reducing NaCl induced oxidative stress [47]. Bastam reported that the external application of SA enhanced the tolerance of pistachio seedlings to NaCl stress. Exogenous application of SA (0.5 mM) minimizes the negative effects of salt stress with evidence of increasing the growth and productivity of tomato plants which could be correlated with increased photosynthetic pigments, soluble carbohydrate, protein content, total proline and phenol, electrolyte leakage percentage and leaf relative water content of plants [48,50]. Boukraa also demonstrated that SA treatment (exogenous or endogenous) potentially alleviate the negative results of chickpea under salt stress by increasing content and activity of antioxidant enzymes.

Salicylic acid (SA) mitigated salinity stress-injury in Solanum lycopersicum by causing characteristic changes in the expression pattern of GST gene family members [51,52]. SA was also reported to induce salinity tolerance and increased biomass in Torreya grandis as a result of increased chlorophyll content and the activity of antioxidant enzymes that eventually activated the process of photosynthesis and counter oxidative stress [53]. Foliar spraying of SA (0.5 mM) on mung been under salt stress condition induces accumulation of glycinebetaine due to increased methionine and suppressed ethylene formation under salt stress; this eventually enhances antioxidant system resulting in alleviation of adverse effects of salt stress on photosynthesis and growth [54].Some reports indicate that SA applications helped to combat salinity stress in various crops. Rajeshwari and Bhuvaneshwari had reviewed the role of salicylic acid in salinity stress tolerance in different crop plants.

In a hydroponic study exogenous SA was applied to alleviating salt stress in cucumber seedlings [55,56]. They noted that the exogenous application of SA alleviated the NaCl toxicity by enhancing photosynthesis and architecture of root system. Hussain et al. (2020) worked out the mechanism of SA and Sulfur (S) interplay under salt stress in mungbean plants. Salt-exposed plants showed an enhancement of reactive oxygen species (ROS), lipid peroxidase, glucose, antioxidant enzymes, reduced glutathione and proline but marked inhibitions in the nitrate reductase (NR), nitrite reductase (NiR) activities, Nitrogen content, photosynthesis rate, and growth traits. The supplementation of SA and S strengthened the antioxidant machinery, improved NR and NiR activities, Nitrogen content, antioxidant enzymes and also decrease accumulation of ROS and glucose (a photosynthesis repressor). This study suggested that proper application of SA with S scale down the negative impact of the NaCl-mediated changes in tested plants [57,58].

Fahad and Bano (2020) studied the effect of foliar spray of SA on a maize hybrid grown in saline soil conditions. The salinity treatment was found to significantly increased sugar contents, protein, proline, and activities of SOD, POD, and CAT but decreased the chlorophyll, carotenoid, osmotic potential and membrane stability index. The external application of SA to plants grown under salt-stressed conditions further increases the osmolytes, antioxidant enzymes, contents of endogenous abscisic acid (ABA), indole acetic acid (IAA), root length, and fresh and dry weights of roots [59]. This report indicates that foliar application of SA proved to be effective in combating ill effects of salinity stress on maize. Some of the important reports countering salinity stress in crop plants using SA are presented [60-62].

SA in temperature (extreme) stress tolerance

Present scenario of temperature extremes i.e. high temperature (heat) and low temperature (cold/ chilling/ freezing) represent potential threats to the crop plants as both type of stress conditions could affect many physiological and biochemical processes and molecular mechanism directly or indirectly [63]. SA was noted to help out plants to counter heat stress and chilling stress [64].

Khan had shown that treatment of SA can alleviate heat stress in T. aestivum. In yet another study Khan et al. exposed wheat plants to heat stress (40°C for 6 h) and studied the potential of 0.5 mM SA in alleviating the negative effects of heat stress on photosynthesis. Under heat stress, the net photosynthesis (Pn) and activity of ribulose 1,5-bisphosphate carboxylase (Rubisco) and photosynthetic nitrogen use efficiency (NUE) decreased, but metabolism of proline was found to be increased[65-68]. The results of this study suggested that SA supplementation alleviates heat stress effects by interacting with proline metabolism and ethylene formation to improve photosynthesis in wheat plants [69-72].

SA was also reported to protect ultra-structures in Musa acuminata seedlings under chilling stress [73-75]. Mutlu showed that external application of SA results in cold tolerance by enhancing antioxidant enzymes, ice nucleation activity, and the patterns of apoplastic proteins in H [76,77]. vulgare genotypes. SA mediated increased synthesis of total phenolics and the activity of PAL was reported to improve chilling tolerance in cold-stored lemon fruit [78-80]. In yet another related work, Kumar by using MALDI-TOF–TOF/MS showed that spraying 100 mM SA alleviates the heat-induced (38°C) oxidative stress damage in wheat plants via modulation of the expression of heat-stable genes and proteins.

Min studied the cellular mechanism of SA induced freezing tolerance in Spinach by metabolite profiling [81]. This study showed that the treated leaves showed presence of more trehalose, proline, tocopherol, ascorbic acid, higher amount of compatible solute (osmolytes) and antioxidants [82]. In a recent report, Pan worked out the involvement of hydrogen sulfide (H2S) in SA-induced chilling stress tolerance in cucumber seedlings by using specific scavenger. In this study, authors reported that SA acts as an up-streaming signaling molecule of cucumber plants by increasing antioxidant defense system and modulating the expression of chilling stress-responsive genes [83]. Few more studies indicating the role of SA in countering chilling, freezing or heat stress conditions are presented.

DISCUSSION

SA in water (flooding/ scarcity) stress tolerance

The effect of salicylic acid (SA) on water stress was reported more pronounced as compare to other stresses. Some early reports showed that the SA treatment improve the response to drought stress [84,86]. The improved drought response induced by SA is mostly associated with an increase or maintenance of plant growth, Rubisco activity, and the ant oxidative capacity [87]. Miura also reported that SA is important to tolerate drought stress as it induces the expression of drought related genes. It was suggested that that salicylic acid might be act as ROS scavenger [88]. Jesus demonstrated that salicylic acid could potentially modulate physiological and hormonal changes in Eucalyptus globules under water deficit environment [89].

Now it is believed that the expressions of dehydrins, chaperones, protein kinase genes and rubisco genes are involved in countering ROS production in photosynthetically active tissues [90]. Few studies have shown that external application of SA results in a positive effect by protecting plants against the oxidative damage caused by drought stress [91,93]. As SA is involved in induction of various genes related to antioxidant system, it was also noted to be directly involved in water stress tolerance [94].

Foliar application of Si, SA and especially the combination Si + SA, markedly improved grain yield and yield components of the two wheat cultivars under water-deficit. The results of the study highlight the role of Si and SA application in regulating water-stress response in wheat plant, suggesting that Si and SA are involved in physiological activities that could cope the negative impact of water deficit [95]. Saheri studied the effect of foliar application of salicylic acid under drought stress in *Portulaca oleracea* L. Usually, drought stress showed a decrease in the photosynthetic pigments, gas exchanges attributes, growth, biomass production, soluble sugars, total phenolic, flavonoids and unsaturated fatty acids like oleic, linoleic and linolenic acid, stearic and behenic acid but increased the contents of H2O2, MDA, and palmitic and arachidonic acid, respectively.

Application of SA improved the growth, photosynthetic pigment contents, gas exchanges traits, fatty acid contents, compatible solutes, secondary metabolites and observed the decrease in level of drought-induced oxidative stress compounds. Similar reports were made by Sohag et al. indicating the positive role of SA in drought tolerance of rice crops and Pourghasemian et al. (2020) in sesame crop [96].

Khalvandi et al. (2021) showed that SA treatments effectively ameliorated the negative effects of drought stress on wheat crop by improving the photosynthetic performance, keeping membrane permeability, induction of stress proteins, and enhancing the activity of antioxidant enzymes[97,98]. In the same year, with detailed morphological, physiological and biochemical alterations, Zafer et al. demonstrated that foliar application of SA improves water stress tolerance in *Conocarpus erectus* L. and Populus deltoides L. Some other reports on application of SA to tolerate water flooding conditions, water scarcity or drought conditions [99,100].

CONCLUSION

Abiotic stresses had been recognized as major threats to the agricultural production leading to huge loss in the productivity causing economic loss. To counter these, plants induce several physiological and molecular mechanisms. Investigations so far have shown that SA is a strong and potential tool in reducing and managing the adverse effects of most abiotic stresses on plants especially crop plants and their productivity. External application of SA has been shown to be beneficial for plants either in normal or stressful conditions. SA is reportedly regulating various plant metabolic processes and modulates the production of varied osmolytes, secondary metabolites and also maintains plant-nutrient status; and thus protect plants under abiotic stress conditions. Over last two decades, the work related to SA synthesis and its applications reaches to another level and revealed that a number of

SA signaling components involved in a variety of cellular processes. Recent SA -centered discoveries have significantly increased the capabilities of this natural compound beyond its previously identified functions in local and systemic defenses, development, stress management, cellular repair, growth, senescence and programmed cell death. In the recent years researches on SA and its applications has given new dimensions. Current researches on SA include SA-mediated signaling processes in growth, development and stress management which have been elucidated under various environmental conditions. It's important to investigate how SA induce and manage different types of abiotic stresses in various crop plants under different environmental conditions to improve the crop yield.

DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this review paper.

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AUTHORS CONTRIBUTION

DK has designed and developed the concept, RG and SR wrote primary manuscript, RS has reviewed it with inputs and all authors read final manuscript and approved for publication.

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Correlating medicarpin content of chickpea cultivars as a key defense compound against *Fusarium* wilt

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ABSTRACT

Fusarium wilt is one of the most important diseases on chickpea crop grown in Indian subcontinent, leading huge damage in crop productivity. A study was conducted during 2016 to 2019 at the field of Shri Shivaji College of Arts, Commerce and Science, Akola, Maharashtra, India to investigate the wilt resistance and role of phytoalexin medicarpin as a defense compound in the different cultivars of chickpea. Four Chickpea cultivars (Digvijay, Vijay, Jaki and JG-62) were analyzed *in vivo* and *in vitro* for natural and induced level of antimicrobial compound *i.e.,* phytoalexin medicarpin in their leaves to confirm their resistance status against fusarium wilt. It was observed that, medicarpin content in leaves of naturally grown chickpea cultivars increases gradually from 10th day after germination. However, the initial content and rate of increase differ in all four cultivars. In leaves of cultivar Digvijay and Vijay it was found to increase till fruiting stage and maturity with disease incidence of 7 and 12%, respectively. In cultivars Jaki and JG-62, it starts declining from flowering onwards with disease incidence of 34 and 38% respectively. The *in vitro* studies showed that, the medicarpin content in cotyledons and seedlings elicited with fusarium cell wall elicitor (FCWE) was highest on fourth day of elicitation but the content was significantly lesser in Jaki and JG-62 as compare to Digvijay and Vijay. This indicates that, medicarpin is an essential compound in chickpea which play vital role in defending fusarium wilt either solely or in synergistic action with other defense related compounds.

Key words : Chickpea, *Fusarium*, medicarpin, resistance, wilt

INTRODUCTION

The low molecular weight antimicrobial compounds that accumulate in plants as a result of infection or stress are known as phytoalexins. The rapidity of their accumulation is associated with resistance in plants to disease caused by pathogen (Anil *et al.*, 2014). These are inducible secondary metabolites possessing antimicrobial activity toward phytopathogens (Douglas, 2017). The phytoalexins either solely or in combination with other defense compounds could decide resistance of cultivars against specific pathogen or stress. Medicarpin is an isoflavonoid compound, reported for the first time by Barz and Welle (1992) in Chickpea upon infection with *Ascochyta rebiei*. Similar reports were made by several other workers in different plant species (Franzener *et al.*, 2018; Butt *et al.*, 2020).

Phytoalexins are restricted to compounds produced from remote precursors, through de novo synthesis of enzymes. This peculiarity makes deciphering their biosynthesis and regulation mechanisms very complex (Jeandet *et al.*, 2013). Some studies have attempted to determine the actual concentration and the nature of phytoalexins directly in plant tissues in response to invading microorganisms using spectroscopic methods (Becker *et al.*, 2014; Marti *et al.*, 2014; Valeriy *et al.*, 2019). But it observed difficult to analyze the events occurring under natural conditions between the plant and the pathogen. Singh and Chandrawat (2017) reviewed the role of phytoalexins in plant disease resistance in general. Pedras and Abdoli (2017) had given detail account of phytoalexins in family Cruciferae along with their role in pathogen defense. Some other important works accounted in this regard includes that of

Rashid and Chung (2017) and Zehra *et al.* (2017).

Being an important source of plant protein, chickpea is grown globally as a major pulse crop (Azizi *et al.*, 2017; Dhivya and Singaravel, 2018). However, biotic distracters like fungal pathogens cause huge damage to chickpea productivity. Wilt disease caused by *Fusarium oxysporium* is one of the most damaging pathogens and estimated to cause up to 100% yield loss (Jendoubi *et al*, 2017). Therefore, it is important to know the biochemistry of induction of defense related compounds in this crop plant that results into disease resistance. Therefore, present attempt was made to assess the resistance and to correlate the medicarpin content of four chickpea cultivars with their resistance against fusarium wilt caused by *Fusarium oxysporium.*

MATERIALS AND METHODS

The present investigation was carried out during 2016 to 2019 wherein germplasm of four cultivars were procured from Pulse Research Center, Dr. Panjabrao Deshmukh Krishi Vidyapith, Akola and Mahatma Phule Krishi Vidyapith, Rahuri, Maharashtra. Actual field experiments were carried out at the field of Shri Shivaji College of Arts, Commerce and Science, Akola, Maharashtra (20.7205° N, 77.2922° E). The experimental field soil was medium black type and climate was dry and typical subtropical type.

Seeds of all these cultivars were sown in the field for multiplication and the status of disease resistance was assessed under field conditions by analyzing different defense related compounds and medicarpin was one of them. Severity of symptoms on individual plants were rated on a scale from 01-09 rating scale (Iqbal *et al.*, 2005); where 1=highly resistant (0- 10% plants wilted), 3=resistant (11-20% plants mortality), 5=moderately resistance (21-30% mortality), 7=susceptible (31-50% mortality) and 9= highly susceptible (more than 50% mortality).

The accumulation of phytoalexin medicarpin, in response to natural infection by *Fusarium oxysporium,* was analyzed by high performance liquid chromatography (HPLC) following the method adopted by Edward and Strange (1991). It was also analyzed in cotyledons and seedlings elicited with *Fusarium* cell wall elicitor (FCWE), prepared as per Chavan *et al.*, (2010). One gram of sample was extracted with 5 mL of 80 % methanol. The methanol extract was reduced to $1/4^{th}$ of initial volume, under vacuum and extracted (3x) with ethyl acetate. The pooled ethyl acetate extract was reduced to dryness and contents were dissolved in one-ml acetonitrile. The 20 mL acetonitrile extract was injected for quantitative analysis. The samples were chromatographed on Shimadzu HPLC system with ODS C_{18} (Spherosphere) column (4 x 250 size) maintained at 35°C temperature. The flow rate of mobile phase (50 % aqueous acetonitrile) was 1.5mL/minute. Medicarpin was detected at 290 nm using a PDA detector with retention time of 23 minutes. The retention time was determined by co-chromatography of standard obtained from Sigma.

RESULTS AND DISCUSSION

The field experiment reveals that chickpea cultivar Digvijay showed only 7% disease incidence. The disease incidence percentage of cultivar Vijay and Jaki was found to be 12 and 34%, respectively and, the cultivar JG-62 was with 38% disease incidence (Table 1). Thus, in growing field experiments Digvijay and Vijay appeared highly resistant and resistant to wilt, respectively while Jaki and JG-62 were susceptible as per disease incidence scale.

Table 1. Disease incidence and disease severity of *Fusarium* wilt 40 days after germination in four naturally grown chickpea cultivars

Cultivars	Progeny size (No. of plants)	Disease incidence (%)	Disease incidence rating (1- 9 scale)
Digvijay	480	07	1 (Highly Resistant)
Vijay	460	12	3 (Resistant)
Jaki	430	34	7 (Susceptible)
JG-62	468	38	7 (Susceptible)

The HPLC analysis of chickpea cultivars showed specific trend in the accumulation of phytoalexin. Phytoalexin medicarpin in leaves of naturally grown chickpea cultivar was analyzed periodically. The time course analysis showed that, the content of medicarpin in leaves increases from 10^{th} day after germination upto 60 day and then

start to decline. The highest accumulation of medicarpin is showed by the cultivar Digvijay after 60 days of germination (81.5 mg/g fresh leaf tissue) followed by in cultivar Vijay and Jaki. The least content was observed in JG-62 where the peak accumulation was 22.9 mg/g fresh leaf tissue after 40 days of germination. Further, it could be stated that the peak content of phytoalexin medicarpin of Jaki and JG-62 was achieved nearly 40 days *i.e.*, 20 days before that of Digvigajy and Vijay. However, the content is very less and also not persisted steadily towards the maturity in Jaki and JG-62 (Fig. 1).

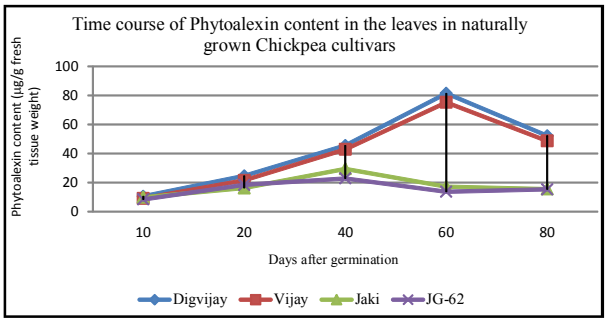

Fig. 1. Phytoalexin medicarpin content (µg/g fresh tissue weight) in naturally grown chickpea cultivars (values are mean of triplicate analysis).

It was noted that induction of medicarpin in cotyledons was more expressive than in seedlings. In cultivar Digvijay FCWE induced about 7 folds more medicarpin in cotyledons as compare to control, while this induction in seedling was found to be about 3 folds (Table 2). From these results it could be interpreted that cultivars Digvijay and Vijay showing resistant interaction due to strong inbuilt biochemical defense mechanism against fusarium wilt while Jaki and JG-62 are probably lacking it and showed susceptibility to fusarium wilt.

These observations indicate that resistance status of chickpea cultivars can be correlated with the rapid accumulation of phytoalexin medicarpin. Our field results (Table 1) on percentage of *Fusarium* wilt incidence also support this analysis.

Phytoalexins are the diverse group of phytochemicals synthesized by plants in response to different adverse stimuli (Dixon and Paiva, 1995; Mazid *et al.*, 2011; Lev-Yadam, 2016; Yaguchi *et al.*, 2017). Phytoalexins are reportedly synthesized by plants as secondary

Table 2. Peak medicarpin content (µg/g fresh leaf tissue) on 4th day after elicitation with FCWE in cotyledons and seedling tissues

Cultivars	Medicarpin content (µg/g fresh leaf tissue) ± SD		
	Control	In Cotyledons	In Seedlings
Digvijay	10.5 ± 0.22	75.6 ± 0.18	35.6 ± 1.05
Vijay	8.7 ± 0.15	72.8 ± 0.25	52.9 ± 0.86
Jaki	8.4 ± 0.21	27.8 ± 0.66	26.5 ± 0.59
JG-62	8.4 ± 0.25	19.5 ± 0.35	16.5 ± 0.83

metabolites in a wide range of plant families in response to natural or induced biotic stress (Ahuja *et al.*, 2012; Lev-Yadam, 2016; Shirakawa and Hara-Nishimura, 2018; Jessica *et al.*, 2020) and this group largely acts as antimicrobial compounds. Medicarpin is an isoflavonoid phytoalexin synthesized by most legume plants. In present study, we have analyzed the medicarpin content in naturally grown four cultivars of chickpea and also in cotyledons and seedlings elicited with FCWE. The results showed that the content of medicarpin is directly related to the resistant status of the respective cultivars. Some other reports especially of Kale and Choudhary (2001) who extensively studied the *Arachis* - *Cercospora* interaction and showed the positive relation between increasing level of medicarpin and resistance in groundnut (*Arachis hypogaea* L.). In Columbian beans study of accumulation of several phytoalexins and its correlation with crops resistance against *Colletotrichum lindmuthianum* was reported earlier (Duranga *et al.*, 2002). Similar kind of positive correlation in phytoalexin accumulation and higher activity of PR proteins was observed in mungbean cultivars (Badere *et al.*, 2007). Singh and Chandrawat (2017) had summarized the different phytochemical groups of phytoalexins found in seventeen plant families with their impact on plant resistance against pathogens or any stress conditions. Most of the workers reported that there is positive correlation between level of phytoalexin and disease resistance status of the plant.

Different phytoalexins either singly or in combination with other defense compounds was reported to have role in basal defense of different crop plants (Li *et al.*, 2015; Arruda *et al.*, 2016; Deice *et al.*, 2019). In several crop plants the phytoalexin content was reported to boost the resistant status of respect plant

species. Similar results were reported by Tian *et al.* (2016), Christensen *et al.* (2018) and Reim *et al.* (2020) in Cotton, Maize and *Malus* species, respectively. The results of present study are in accordance with above discussed earlier studies.

CONCLUSION

The present study includes *in vitro* analysis of medicarpin content in the cotyledons and seedlings of four chickpea cultivars and, also in the leaves of their field grown plants. When this was compared with field data of fusarium wilt incidence on naturally grown chickpea cultivars revealed positive correlation. It showed more and rapid accumulation of medicarpin in cotyledons, seedlings and leaves of cultivars Digvijay and Vijay directly relates their resistance to wilt (lesser disease incidence). The phytoalexin content in Jaki and JG-62 was less and these cultivars showed comparatively more disease incidence, hence could be regarded as susceptible. However, it is unclear that, whether phytoalexin medicarpin alone or in combination with other defense related compounds confers resistance to these cultivars. But its rapid accumulation upon elicitation indicates a vital role of phytoalexin medicarpin in assigning resistance to chickpea cultivars.

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Nutritional profiling of wild areal tubers of *Dioscorea bulbifera* L. from Maharashtra, India

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Abstract
Dioscorea bulbifera is a wild twiner from family Dioscoreaceae with edible areal tubers. The forest dwellers and tribals were found to use these tubers as food during food crises, especially in Asian and African countries. Present study is an attempt to analyze nutritional profile (the physic-chemical, proximate content, amino acid profile, mineral and vitamin content) and phytochemicals in the edible areal tubers of *D. bulbifera* collected from three different forest areas of Maharashtra (India). It was found that, the tubers contains significant amount of proximate content, minerals and vitamins with good amino acid profile, but also noted to have some anti-nutrient factors like phytic acid. Hence, it is suggested that aerial tubers of this plant could be effectively use as supplementary food material during food scarcity.

Keywords: amino acids, *Dioscorea bulbifera*, minerals, proximate content, vitamins

Introduction
Dioscorea bulbifera is a wild edible tuber plant species from family Dioscoreaceae (Yam family). The genus *Dioscorea* comprises over 600 species worldwide (Amanze *et al*., 2011) [1] and reported as native of South Africa. The areal as well as underground tubers of most of the species were found to be utilized by the local and tribal communities across the world as a source of food especially in food crises. Out of these, 10 species of *Dioscorea* were reportedly cultivated, mostly in African countries like Nigeria and Ghana (Obidiegwu, *et al*., 2020) [33].
About 26 species of *Dioscorea* were reported from Indian subcontinent (Kumar *et al*., 2012) [27]. Major *Dioscorea* species includes *D. alata, D. belophylla, D. bulbifera, D. esculenta, D. hispida, D. pentaphylla, D. wallichi* and *D. spinosa*. Off these, *D. bulbifera* is the most common species in Central India including Maharashtra.
The tubers of *D. bulbifera* were used by different tribal communities for intestinal colic problem, relieving dysmenorrhoea, reducing acidity, against rheumatoid arthritis, to relieve intense inflammation, in spasmodic asthma, for menopausal problems, for labor pain and the prevention of early miscarriage and to check diarrhea (Nayak *et al*., 2004; Bhogaonkar and Kadam, 2006; Mehta and Bhatt, 2007: Kamble *et al*., 2010; Jadhav *et al*., 2011 and Datta, 2015) [31, 5, 29, 21, 18, 10]. Apart from this the most important is nearly all local and tribal communities use the areal tubers as source of nutrition, especially in food crises and as nutritional aid to regular diet. These tubers are also found in the local India markets for sale during early summer season.
The present study is focused on nutritional profiling of *D. bulbifera* aerial tubers collected from three different forest ranges from Maharashtra India. It include physic-chemical, proximate analysis, mineral and vitamin analysis and phytochemical study to identify major medicinally important as well as anti-nutrient factors present in the tubers of *D. bulbifera*.

Material and Methods
Collection of tubers and Preparation of samples
The tubers of *Dioscorea bulbifera* were collected from three different forests zones of Maharashtra, India i.e. Katepurna Wildlife Sanctuary, District Akola (Sample- A), Nagzira Wildlife Sanctuary, District Gondia (Sample- B) and Tadoba Wildlife Sanctuary, District Chandrapur (Sample- C) during February 2017. The plants were identified using flora of Marathwada (Naik, 1998) [30] and flora of Maharashtra (Singh and Karthikeyan, 2000) [44]. Medium sized tubers were selected for experimentation. About 15 tubers were collected from each selected forest range for study. Each tuber is washed thoroughly, cleaned, peeled and cut into thin slices. These slices were oven dried (at 60ºC for 48 Hrs) and packed into airtight polybags until use. Before analysis, the dried slices were ground into fine powder, that was sieved through mesh of 200 □m and dried further at 100ºC until achieve constant weight.

Physic-chemical and Proximate analysis
The moisture content of tuber and ash value were determined using standard protocols (AOAC, 1990) [3]. For crude protein content, the samples were digested using Kjeldahl and nitrogen content was detected by the method of Devani (1989) [8] and then the crude protein was calculated by multiplying the nitrogen content by conversion factor 6.25. The carbohydrate content was determined by anthrone method (Sadasivam and Manikam, 2005) [37]. Other proximate contents were determined by using protocols and guidelines of AOAC (1990) [3].

Amino acid profiling
The extraction of the samples to analyze amino acid content was done as per AOAC (2010) [2]. 5g sample was taken in 250 mL flask and defatted by extracting the fat content of the sample with 30 mL of petroleum ether. The sample was hydrolyzed, evaporated and then loaded into biochemical amino acid analyzer (Sykam S430).

Minerals and Vitamin analysis

The mineral analysis of the powdered tuber samples was done using Atomic absorption spectroscopy. For mineral analysis, the method of Karpiuk *et al*., (2016) [22] was followed. The standards stock solutions of each metal element (1000mg/L) were used to prepare the requisite concentrations of dilutions using nitric acid solution (1% v/v). All the standards and reagents required (AR grade) were procured from Sigma- Aldrich and ultrapure deionized water for preparing solutions. The instrument (Perkin Elmer AAnalyst 8000 model) with deuterium corrector was sued for mineral analysis. The operating parameters were as per the recommendations of manufacturer. For the analysis of Vitamin A, and Vitamin E was done by method of Kirk and Sawyar (1998) [23] and other vitamins in powdered samples were analyzed as per modified method of Koche (2011) [24].

Phytochemical analysis

The quantitative phytochemical analysis of powder of *D. bulbifera* tubers was done using the method of Ezeonu and Ejikeme (2016) [11]. For the present study alkaloids, phenolic compounds, tannins, saponins and phytic acid was quantified.

Result and Discussion

Food and nutritional security is one the major challenges of this era. To meet the demand of food for all, we have to identify some alternative sources of food and nutrition or at least some supplements. The present study is an attempt to present a wild tuber plant *Dioscorea bulbifera* as an alternative source of food or supplementary food.

Physic-chemical and Proximate content

Moisture content of tubers in the form of water content in fresh material was found in the range of 57.25 ± 0.32 to 62.25 ± 0.21 % with highest content in sample-C. The ash value of analyzed samples were found in the range of 1.65 ± 0.01 to 1.85 ± 0.11 % and highest ash value was noted for the sample-A. The crude protein content was highest in sample- A (12.68 ± 0.03 g/100 g DM) and lowest in sample-C (10.08 ± 0.01 g/100 g DM). The carbohydrate content was found highest in sample- B (78.20 ± 0.02 g/100g DM) and least in sample- C (72.50 ± 0.05 g/100g DM). Crude fiber content in three samples was in the range of 1.95 ± 0.11 to 2.25 ± 0.03 g/100g DM and crude fat content was noted in the range of 0.65 ± 0.02 to 0.78 ± 0.05 g/100g DM. The Soluble sugar was noted highest in the sample – A and least in the sample-C. The energy calculated per 100 g dry matter was highest in the sample-B (382 ± 0.20 Kcal/100 g DM) followed by in sample- A and sample- C respectively (table-1). The difference in proximate content of three samples of tubers might be due to bioavailability, physical properties of soil, soil pH and soil composition (Jung, 2008 and Soetan *et al*., 2010) [20, 45]. Our results are in analogy with the report of Zelalem and Shisho (2019) [47].

Table 1: Comparative Proximate composition of *Dioscorea bulbifera* areal tuber samples collected from different forests of MS India

Composition	Content		
	Sample- A	**Sample- B**	**Sample- C**
Water content (% fresh wt.)	57.25 ± 0.32	60.55 ± 0.25	62.25 ± 0.21
Ash values (%)	1.85 ± 0.11	1.65 ± 0.01	1.72 ± 0.03
Crude Protein (g/100g DM)	12.68 ± 0.03	11.28 ± 0.03	10.08 ± 0.01
Carbohydrate (g/100g DM)	73.50 ± 0.05	78.20 ± 0.02	72.50 ± 0.05
Crude fiber (g/100g DM)	2.25 ± 0.03	1.95 ± 0.11	2.10 ± 0.02
Fats (g/100g DM)	0.78 ± 0.05	0.65 ± 0.02	0.68 ± 0.02
Soluble sugars (g/100g DM)	0.25 ± 0.02	0.22 ± 0.02	0.20 ± 0.00
Energy (Kcal/ 100 g DM)	375 ± 0.80	382 ± 0.20	377 ± 0.85

Values are means ± SE of replicates (n = 3)

Amino acid analysis

Total eleven amino acids were analyzed and quantified. The analyzed amino acids include alanine, aspartic acid, Cysteine, glycine, glutamic acid, isoleucine, leucine, methionine, phenylalanine, proline and tryptophan. Amongst all the analyzed amino acids, all three samples showed highest amount of leucine (5.77 ± 0.03 to 5.97 ± 0.28 mg/g DM) followed by glutamic acid (5.66 ± 0.11 to 5.86 ± 0.15 mg/g DM) and aspartic acid (5.20± 0.15 to 5.30 ± 0.33 mg/g DM) respectively. The amino acid which showed the least amount amongst all analyzed amino acids was cysteine (0.60 ± 0.10 to 0.65 ± 0.11mg/ g DM). Table-2 showed the amount of different amino acids analyzed in tuber powder of *D. bulbifera*. It was found that all three samples analyzed showed insignificant difference in the level of amino acids. Doss *et al*., (2019) [9] have studied amino acid in nine *Dioscorea* species including *D. bulbifera* and suggested that the tubers are good source of amino acids. Thus our results are in line to demonstrate that the tubers are with significant level of amino acids and could be utilize as their natural source as supplementary diet.

Table 2: Comparative Amino acid composition of *Dioscorea bulbifera* areal tuber samples collected from different forests of MS India

Amino acid	Content		
	Sample- A	**Sample- B**	**Sample- C**
Alanine (mg/g DM)	3.22 ± 0.33	3.02 ± 0.12	3.15 ± 0.03
Aspartic acid (mg/g DM)	5.25± 0.45	5.30 ± 0.33	5.20± 0.15
Cysteine (mg/g DM)	0.65 ± 0.11	0.60 ± 0.10	0.60 ± 0.15
Glycine (mg/g DM)	3.15 ± 0.25	3.12 ± 0.02	3.18 ± 0.22
Glutamic acid (mg/g DM)	5.86 ± 0.15	5.85 ± 0.11	5.66 ± 0.11
Isoleucine (mg/g DM)	2.26 ± 0.18	2.22 ± 0.10	2.20 ± 0.10
Leucine (mg/g DM)	5.97 ± 0.28	5.90 ± 0.18	5.77 ± 0.03
Methionine (mg/g DM)	0.85 ± 0.11	1.15 ± 0.09	0.80 ± 0.11
Phenylalanine (mg/g DM)	3.95 ± 0.25	3.92 ± 0.22	3.85 ± 0.05
Proline (mg/g DM)	2.58 ± 0.29	2.51 ± 0.11	2.45 ± 0.09
Tryptophan (mg/g DM)	0.78 ± 0.11	0.75 ± 0.01	0.79 ± 0.03

Values are means ± SE of replicates (n = 3)

Mineral content

Eight mineral elements (Ca, Cu, Fe, K, Mg, Mn, Na and Zn) were analyzed for their availability in tubers of *D. bulbifera*. In three analyzed samples, Calcium (Ca) was recorded in the range of 72.10 to 78.60 µg/100g with highest in sample

A. Copper (Cu) content of the analyzed samples was found in the range of 11.33 to 12.59 µg/100g DM with highest in sample-B. Iron (Fe) content of the three samples of tubers of *D. bulbifera* was noted in the range of 13.12 to 13.25 µg/100g DM. There is not much difference in the level of Iron in analyzed samples (table-3). Potassium (K) content was found in the rage of 33.12 to 33.42 µg/100g DM in three analyzed tuber samples of *D. bulbifera*, with highest in sample-A. The magnesium (Mg) content of the three samples of *D. bulbifera* was noted in the range of 21.12 to 22.48 µg/100g DM and Manganese (Mn) content in the dry mater of tuber was noted in the range of 0.60 to 0.69 µg/100g DM. In the analyzed samples Sodium (Na) content was found to be in the range of 43.25 and 44.12 µg/100g DM and The zinc (Zn) content of the tubers of *D. bulbifera* was noted in the range of 2.21 to 2.84 µg/100g DM. Calcium is necessary for the blood coagulation and bone health and also to regulate acidity (Garcia-Chuit and Boella, 1993 and Jacques *et al*., 2016) [14, 19]. Several reports indicated that copper is necessary for boosting immunity, host defense, as iron career and in brain development (Uauy *et al*., 1998; Olivares *et al*., 2000 and Seal *et al*., 2020) [40]. Further, the iron content play vital role in improving general health and oxygen carrying capacity of RBCs, further its proper intake is essential to women during pregnancy (Kordas and Stoolzfus, 2004 and Saikia *et al*., 2013). Similarly, Potash is one of the important elements related to heart activities and also regulation of the blood pressure and body water content (Jacques *et al*., 2016 and Seal *et al*., 2020) [19, 40]. Magnesium is essential for synthesis of proteins and nucleic acids and also for proper vascular functioning. It is also a co-factor for over 350 enzyme catalyzed metabolic cellular reactions. Further, Sodium is important for Na/ K and promote health at risk for chronic diseases (Jacques *et al*., 2016) [19] and Zinc in one of the most essential mineral boosting the general health, improve cellular immunity and growth (Seal *et al*., 2020) [40]. The mineral content in three different tuber samples of *D. bulbifera* is presented in table-3. The values represent the mean of triplicate analysis. Jacques *et al*., (2016) [19] reported higher level of Ca, Cu, Fe, Mg and Zn in the tubers of *D. bulbilis* from African forest. Similar report was presented by Mansfria *et al*., (2019) [32] on mineral analysis of *D. hispida*. Our study results are in analogy of these reports indicating that the aerial tubers of *D. bulbifera* contain significant amount of major mineral elements.

Table 3: Comparative Mineral composition of *Dioscorea bulbifera* areal tuber samples collected from different forests of MS India

Mineral	Content (µg /100g DM)			Mineral	Content (µg/100g DM)		
	Sample- A	Sample- B	Sample- C		Sample- A	Sample- B	Sample- C
Ca	78.60 ±0.05	75.00 ±0.00	72.10 ±0.01	Mg	22.48± 0.05	22.28± 0.05	21.12± 0.03
Cu	11.38 ± 0.03	12.59 ± 0.03	11.33 ±0.01	Mn	0.69± 0.03	0.60± 0.03	0.65± 0.01
Fe	13.25 ± 0.05	13.12 ± 0.02	13.18 ±0.02	Na	43.25 ± 0.05	44.12 ± 0.11	43.40 ± 0.03
K	33.42± 0.09	31.12± 0.05	31.18± 0.05	Zn	2.85± 0.15	2.54± 0.09	2.21± 0.05

Values are means ± SE of replicates (n = 3)

Vitamin content

The details of vitamin content of three samples to powdered tubers of *D. bulbifera* are presented in table-4. The results indicate that all three samples have highest amount of vitamin C as compare to other vitamins and least content of thiamin. Moreover, it showed that the tuber contain significant amount of vitamin A, vitamin C, vitamin E, niacin, riboflavin and thiamin. The high content of vitamin C indicates that the tuber might have high antioxidant potential and could help in higher absorption of Iron (Roger, 1999). The plants with significant amount of vitamin C could be used to decrease atherosclerosis and few types of cancers (Rekha *et al*., 2012). Availability all tested vitamins in the tubers indicates its usefulness as supplementary food. The plants with natural vitamins availability could be used in dietary system (Seal *et al*., 2020) [40].

Table 4: Comparative Vitamin composition of *Dioscorea bulbifera* areal tuber samples collected from different forests of MS India

Vitamin	Content		
	Sample- A	Sample- B	Sample- C
Vitamin A (mg/g DM)	0.35 ± 0.01	0.41 ± 0.11	0.38 ± 0.03
Vitamin C (mg/g DM)	1.25± 0.05	1.28± 0.03	1.28 ± 0.05
Vitamin E (mg/g DM)	0.42 ± 0.11	0.41 ± 0.11	0.38 ± 0.15
Niacin (mg/g DM)	0.15 ± 0.00	0.17 ± 0.01	0.17 ± 0.01
Riboflavin (mg/g DM)	0.06 ± 0.01	0.06 ± 0.01	0.05 ± 0.01
Thiamin (mg/g DM)	0.04 ± 0.00	0.03± 0.01	0.04 ± 0.02

Values are means ± SE of replicates (n = 3)

Phytochemical analysis

The major phytochemicals analyzed for the present study includes alkaloids, phenolics, flavonoids, phytic acid, saponins and tannin. The analyzed phytochemicals in *D. bulbifera* tuber is presented in table-5. It showed no significant difference in the amount of phytochemicals in all three samples. All samples showed highest amount of saponins followed by tannins, phytic acid, phenolics, flavonoids and alkaloids respectively. The availability of significant amount of phenolics and flavonoids at one side play role in plant defense and also can contribute as nutrient. However, the amount of phytic acid is cause of concern as its higher level reduces the availability of proteins and minerals at consumer end. Subhas *et al*., (2012) [46] reported the phytochemical analysis of *D. bulbifera* tubers and earlier Santhakumar (2008) [42] and Shajila *et al*., (2011) [41] and Ifeanacho *et al*., (2017) [16] reported the nutritional and toxic properties of *Dioscorea* species. Our report is analogous with these reports. However, the tubers has potential to be used as supplementary food item.

Table 5: Comparative Phytochemical analysis of *Dioscorea bulbifera* areal tuber samples collected from different forests of MS India

Phytochemical	Content		
	Sample- A	Sample- B	Sample- C
Alkaloids (mg/100g DM)	0.75 ± 0.03	0.78 ± 0.10	0.72 ± 0.02
Flavonoids (mg/100g DM)	1.62 ± 0.11	1.58 ± 0.01	1.61 ± 0.15
Phenolics (mg/100g DM)	1.85 ± 0.05	1.81 ± 0.03	1.80 ± 0.05
Phytic acid (mg/100g DM)	1.78 ± 0.15	1.75 ± 0.05	1.73 ± 0.03
Saponins (mg/100g DM)	3.52 ± 0.15	3.45 ± 0.05	3.50 ± 0.15
Tannins (mg/100g DM)	2.25± 0.05	2.28 ± 0.02	2.27± 0.03

Values are means ± SE of replicates (n = 3)

Conclusion

The results indicate that the areal tuber of *D. bulbifera* has significant proximate content with good amino acid profile, significant amount of minerals and vitamins and also have richness in phytoconstituents. However, the calculated proximate, mineral and vitamin content is comparatively less as per Dietary Reference Index (DRI). Further, it also possesses some antinutruents like phytic acid which reduces the availability of proteins and minerals at consumer level. Therefore, it is stated that this tuber should not be used as main diet solely; however, could be effectively use as supplementary food item at least during the time of food scarcity.

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Physico-chemical, Fluorescent and Phytochemical analysis of *Anisochilus carnosus* (L.f.) Wall: a Lamiaceae herb from Maharashtra, India

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Abstract

Anisochilus carnosus (L. f.) Wall is one of the wild and aromatic lamiaceae members with significant medicinal potential. It is being used by Bhilla and Paliyar tribals from Maharashtra and Tamil Nadu states as indigenous traditional medicine. Present work is focused on the physico-chemical and fluorescent analysis of powdered drug material of the leaves of the plant and its phytochemical analysis. The study showed that the plant is rich in phytoconstituents like alkaloids, phenolics, flavonoids, terpenes and steroids. Further, HPLC analysis reveals the availability of caffeic acid, luteolin -7 glucoside, nepetin-7 glucoside, homoplantagenin, luteolin and ursolic acid with the highest content of homoplantagenin (4.20µg/g dry drug sample) followed by nepetin-7 glucoside (3.80 µg/g dry drug sample). The plant sample has rich diversity of phytoconstituents. The identified phytoconstituents are correlated with bioactivities of the plant to validate traditional medicinal claims of the plant.

Natural products and plant derived herbal remedies are getting increased attention since last two decades. Throughout the human history, many infectious diseases have been treated with herbal medicines. A number of scientific investigations have highlighted the importance and the contribution of several thousand medicinal plants. The wealth of Indian medicinal plants is well documented with their active principles and properties[9,23]. The medicinal plants play vital role in routine healthcare, holistic growth, health and well beings, especially in rural areas of India[29].

The use of all botanicals is well rooted in medical practice. Since ancient times, herbal healers collected information about herbs and developed well-defined pharmacopoeias to treat a variety of diseases and disorders. More than a quarter of all drugs used today contain

active ingredients derived from plants or plant products[18].

It's estimated that nearly 80 percent of the world's population use herbs as reliable solution for their primary health care. All over the world several botanicals are sold as dietary supplements because of their high efficacy and safety. It indicates that medicinal plants play a vital role for the development of new drugs[40]. Medicinal plants play a central role not only as traditional medicines but also as trade commodities, meeting the demand of distant markets. India has a very small share (less than 2%) in medicinal plants trade commodities of global market[8,51]. To compete with the growing market, there is urgency to expeditiously utilize and scientifically validate more medicinally useful plants. Keeping this view, present study was focused on physico-chemical, fluorescent and phytochemical analysis of *Anisochilus carnosus* a wild member of family lamiaceae.

Anisochilus carnosus is an annual, erect herb of mint family- lamiaceae, commonly called as *Kapuri* (in Marathi), *Karpoorada* gidda (in Kannada) and *Karpurvali* (in Telgu), a common inhabitant of higher altitudes[19,42]. Usually, the plant appears as a beautiful herb with height ranging from 0.3 to 0.6m. It was so far reported from Karnataka, Maharashtra, Rajasthan and Tamil Nadu as traditional medicine by tribal communities of respective states for different ailments[32]. The whole plant is used as diaphoretic, stimulant and expectorant; it was also use to cure liver disorders, cough, cold and skin diseases[2,20,41,48]. Leaves are used for cough, dropsy, indigestion and sores in the leg fingers[6,13,44].

Collection of plant, identification and powder preparation :

The plant material of *Anisochilus carnosus* (L. f.) Wall was collected form the Chikhaldara forest ranges of Amravati Division, Maharashtra State (India). After collection, the plant was identified taxonomically (fig. 1) using flora of Marathwada[39] and flora of Maharashtra state[49]. A voucher specimen (No. D- 1058) was submitted to Department of Botany, Shri Shivaji College of Arts, Commerce and Science, Akola (MS). The collected plant material was then shade dried for about 10 days and powdered using mortar and pestle. The fine powder was kept in air tight polythene bags until use.

Physico-chemical, fluorescent and preliminary phytochemistry :

The physico-chemical and fluorescence analysis was done as per standard methods[12,15,37]. To analyze preliminary phytochemistry, standard protocols were followed[11,17,27,50]. The powdered material was extracted in distilled water (AQ), methanol (ME) and Chloroform (ChE) and qualitative tests were done to check the presence of alkaloids, phenolics, flavonoids, terpenes, tannins, saponins, glycosides, volatile oils, carbohydrates, proteins and amino acids.

Crude quantification of the major phytochemicals :

Only alkaloids, Phenolics, Tannins and flavonoids compounds were quantified in powdered material of *A. carnosus*. The methods applied for the same are discussed below-

Alkaloids : Powdered sample (5 ml) was mixed in 200 ml of 10% CH_3COOH in C_2H_5OH (ethanol) the flask was covered and mixed well and allowed to stand for 4 hrs. Then filtered the mix and the filtrate is heated in a water bath until reaches ¼ of the original value. To this, concentrated NH_4OH was added till the complete precipitation and the precipitate was collected and washed with dilute NH4OH. Then the solution was filtered and the residue was weighed as crude alkaloid content[11].

Phenolics: The total phenolics in the extract were determined using modified Folin-ciocalteu method[28]. To each sample solution (1.0 ml) and standard (Gallic acid) was added 5 ml of Folin-ciocalteu and 4 ml sodium carbonate (7 % w/v). The mixture were shaken and allowed to stand for 30 min in the dark at room temperature; after which absorbance was measured at 765 nm using a spectrophotometer. The amount of total phenolics was expressed as Gallic acid equivalent (GAE) in milligram per gram dry plant extract using the expression; C = c x (V/m); (where C= Total phenolics content of plant extract in mg/g GAE, c= concentration of Gallic acid established from calibration curve mg/g, V= volume of the extract (ml) and m= weight of pure plant extract (g).

Tannins: Take 0.5 gm sample in 50 ml of distilled water; stir the solution for 1 hr. filter the mixture and take 5 ml of filtered sample in test-tube. To this add 2 ml of 0.1 M $FeCl_3$ in 0.1 M HCl and 0.008 M $K_4Fe(CN)6 .3H_2O$. Take the absorbance at 395nm wavelength and record changes within 10 minutes[1].

Flavonoids : Take 10 gm of powdered sample and repeatedly extract it with 100 ml of 80% aqueous Methanol. Filter the solution and filter is then transferred into a water bath for evaporation into dryness. The residue is weighed as flavonoid content[7].

Spectral and Chromatographic analysis :

For the spectrophotometric analysis of *Anisochilus carnosus* leaf powder, eleven different standards were selected. These were- Caffeic acid, Rosmarinic acid, Luteolin, Luteolin-7- glycoside, Nepetin, Nepatine-7 glycoside, Homoplantagenin, Hispidulin, Salvigenin, Ursolic acid and Carnosic acid. These standards were procured from Sigma –Aldrich India ltd. The UV-spectra of each of these standards were recorded along with their retention time.

Chromatographic analysis was performed on Shimadzu make high performance liquid chromatography system, equipped with a diode array detector working in the range of 190–400 nm, a quaternary solvent delivery system, a column temperature controller and an autosampler. Analysis was carried out at 30°C on a C18 column (250mm×4.6mm, 5 μm). A linear gradient elution of eluents A (0.5%, v/v aqueous glacial acetic acid) and B (methanol) was used for the separation. The elution programme was optimized and conducted as follows: a linear gradient of 38–42% B with the range of 0.0–14.0 min, a linear gradient of 42–45% B with the range of 14.0–17.0 min, a linear gradient of 45– 48% B with the range of 17.0–17.1 min, a linear gradient of 48–50% B with the range of 17.1–32.0 min and a linear gradient of 50–85% B with the range of 32.0–

45.0 min. This was followed by a 10min equilibration period prior to the injection of each sample.

All the samples were milled into powder and oven-dried at 50°C until constant weight was reached. 1.0 g powder of each dried sample was extracted with 20 ml 70% (v/v) aqueous methanol in an ultrasonic bath for 2 h and then cooled at room temperature. The extract was filtered through glass wool for sample, cleaned up and diluted to 25 ml with 70% methanol. The sample solution was filtered through a 0.45µm membrane filter prior to HPLC analysis and the injection volume was 5µl [35-36].

Physico-chemical and Fluorescent analysis:

The physico-chemical study of *Anisochilus carnosus* was done, the results are presented in the table-1. The Moisture content of the plant recorded as 16.20%. The extractive values of the water, alcohol and chloroform extracts were 6.8% (fairly green), 8.5% (yellowish green) and 4.1% (grayish green) respectively. The ash values calculated as total ash (8.4%), acid insoluble ash (4.2%) and water soluble ash (6.5%).

The reaction of powdered drug with the routine laboratory chemicals was also analyzed. The results of reactions of different laboratory chemicals are presented in the table 2. This is one of the unique criteria to identify adulteration in the *Anisochilus* drug powder available in the market.

The original leaf powder color of the plant as such was pale yellow. When treated with iodine the color changes to light green. The treatment of 5% ferric chloride gives yellow color. With 1N NaOH, the powder color changes to green while with acetic acid it gives light brown color. With strong acids, the color becomes green. The powder extract with liquid ammonia and lead acetate gives brown and cream color respectively (table-2). However, when the same treated samples were visualized under UV-light, it appeared to have different colours. This could be used as standard marker to analyze market available powdered drug materials.

Preliminary Phytochemical Analysis :

For the qualitative phytochemical analysis, three different solvents (aqueous, methanolic and chloroform) were used for extract preparation. These extracts were analyzed for the presence of 10 different parameters according to the methods described elsewhere. Of all the extracts, methanolic extracts showed presence of all tested phytocompounds except alkaloids. The water extracts showed presence of phenolics, tannins, flavonoids, saponins, proteins and amino acids whereas the chloroform extract showed positive tests of alkaloids, phenolics and terpenes (table-3).

Crude quantification of major phytochemicals of Anisochilus carnosus :

The crude content of major phytochemical compounds in *Anisochilus carnosus* was determined using different methods[17,27]. The quantitative analysis of alkaloids, Phenolics, tannins and flavonoids was done. The content of alkaloids was found 0.85± 0.31 µg/g of dry sample, that of phenolics

1.47± 0.11 µg/g of dry sample, tannins 0.11± 0.10 µg/g of dry sample and flavonoids 1.20± 0.81 µg/g of dry sample. The extract showed presence of highest amount of phenolics and lowest amount of tannins (Table-4 and Fig. 2).

HPLC analysis of Methanolic extract of A. carnosus :

Spectrophotometric and chromatographic analysis of *A. carnosus* leaf powder extract was done. For the analysis aqueous methanolic extracts were prepared and the data was compared with the reference standards. Eleven reference standards were used for the analysis which was chosen on the basis of previous work done on different species of lamiaceae members. For spectrophotometric analysis in current study, eleven standard compounds were selected as reference standards (table-5).

The preparation of standard references and their UV and HPLC analysis method was described in the previous chapter. The retention time of these standards for HPLC analysis is given in the table 5. The content of each phytoconstituent in the sample of *A. carnosus* leaf powder drug is presented in the table-6. For the analysis of the phytoconstituents present in the experimental sample the author had used the similarity index, of retention time and absorption (λ-max). The content of the sample is presented in µ g/g of sample.

Total nine prominent peaks were observed in HPLC chromatogram of *A. carnosus* methanol leaf extract (fig. 3). Out of nine peaks, peak number 5 and 8 were remained unidentified. The other peaks showed presence of caffeic acid, luteolin-7-glucoside, nepetin-7 glucoside, homoplantagenin, luteolin and ursolic acid. The peaks with respective peak numbers, retention time and content of compounds on the basis of peak area are presented in the table -6. The highest content was noted that of homoplantagenin (4.20µg/g dry drug sample) followed by nepetin-7 glucoside (3.80 µg/g dry drug sample).

Simple plant extracts or decoctions are probably the crude forms of plant drugs of earlier generation[22,34]. In the beginning of the 21st century, several workers have estimated that plant materials are present in nearly 50 % of western medicines[34,43]. The primary benefits of using plant derived medicines are that they are relatively safer than synthetic alternatives, offering profound therapeutic benefits and more affordable treatment[2,14]. The present work is focused on the physico-chemical, fluorescent and phytochemical analysis of a lamiaceae member *Anisochilus carnosus* to correlate its phytoconstituents with medicinal potential.

Moisture content, extractive values and ash values are significant in determining the purity and authenticity of the crude material and decide its applicability as drug material[15,31]. These physico-chemical values for *A. carnosus* indicate suitability of this plant as drug source. Further, the interaction of leaf powder with different lab chemicals visualized under normal sunlight and under UV- light could act as baseline marker to authenticate the powder available in the market and its purity[37]. Certainly, the powder with adulterants will not match physico-chemical and fluorescent properties presented in this study.

Fig. 1: Habit of *Anisochilus carnosus* (L.f.) Wall.

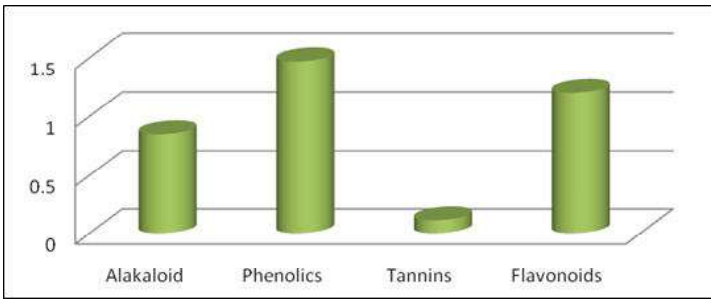

Fig. 2: Content of major phytochemicals in *Anisochilus carnosus* extract (µg/g dry wt.)

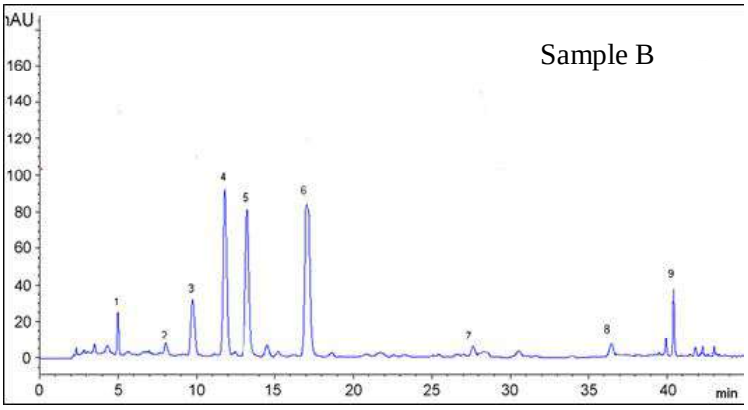

Fig. 3: HPLC Chromatogram of *Anisochilus carnosus* powder extract.

Table-1. Physico-chemical characterization of *Anisochilus carnosus*

Moisture content	Extractive values	In %	Ash value	In %
16.20%	Water	6.8% (Fairly Green)	Total ash	9.7%
	Alcohol	8.5%(Yellowish green)	Acid insoluble ash	4.2%
	Chloroform	4.1%(Gray)	Water soluble ash	6.5%

Table-2. Effects of various chemicals on powder drug of *A. carnosus* and fluorescence analysis

Sr. No.	Colour test	Visual observations	
		Under normal Sunlight	Under UV light
1	Powder As Original	Pale yellow	Yellow green
2	Powder + Iodine	Light green	Green
3	Powder + 5% Ferric Chloride	Yellow	Pale yellow
4	Powder + 1 N NaOH	Green	Dark green
5	Powder + Acetic acid	Light brown	Green
6	Powder + 50% H_2SO_4	Green	Dark green
7	Powder + 50% Conc. HCl	Green	Dark green
8	Powder + Liquid Ammonia.	Brown	Light brown
9	Powder + NaOH + Lead acetate	Creamy	Brown

Table-3. Preliminary phytochemical analysis of various extracts of *A. carnosus* leaf powder (n=3)

Parameters tested	*Anisochilus* extracts		
	AQE	ME	ChE
Alkaloids	—	-	+
Phenolics	+	+	+
Tannins	+	+	-
Flavonoids	+	+	-
Saponins	+	+	-
Glycosides	-	+	-
Terpenes	-	+	+
Proteins and amino acids	+	+	-
Carbohydrates	-	+	-
Volatile oil	-	+	-

Note: AQE = Aqueous extract, ME = Methanol extract and ChE= Chloroform extract

Table-4. Quantitative phytochmical analysis (crude content in µg/g of dry sample) (n=3)

Sr. No.	Phytochemicals	crude content in µg/g of dry sample
1	Alkaloids	0.85 ± 0.31
2	Phenolics	1.47 ± 0.11
3	Tannins	0.11 ± 0.10
4	Flavonoids	1.20 ± 0.81

Table-5. Spectral and HPLC analysis of standards used during experimentation

Sr. No.	Standard used	Retention time RT (min)	Peak wavelength (µ-max) nm
1	Caffeic acid	5.18	217, 239, 328
2	Rosmarinic acid	5.57	328
3	Luteolin -7 glycoside	11.2	269, 340
4	Nepetin-7 glycoside	13.5	239, 322
5	Homoplantagenin	17.5	276, 332
6	Luteolin	27.4	258, 346
7	Nepetin	28.30	270
8	Salvigenin	34.6	277, 358
9	Hispidulin	37.5	274
10	Carnosic acid	37.7	282, 363
11	Ursolic acid	41.9	257

Table-6. HPLC analysis of methanolic extract of *Anisochilus carnosus*

Sr. No.	Compounds identified in sample	Retention time RT (min)	Content (µg/g dry wt. of sample)
1	Caffeic acid	5.18	0.65
2	Unidentified	7.60	0.22
3	Luteolin -7 glucoside	11.2	1.20
4	Nepetin-7 glucoside	13.5	3.80
5	Unidentified	15.62	ND
6	Homoplantagenin	17.5	4.20
7	Luteolin	27.4	0.20
8	Unidentified	36.6	ND
9	Ursolic acid	41.9	1.25

The preliminary phytochemistry showed that the plant is rich is phytoconstituents like alkaloids, phenolics, flavonoids, tannins, terpenes, saponin, steroids and glycosides. These secondary metabolites as per their availability in the plant, gives diverse medicinal properties to that plant. Due to its phyto-chemical richness, the plant is being used to treat cough, cold, liver disorder, skin diseases and certain gastric problems by different tribal communities across India[2,6,13,20,41,44].

In the present study, authors quantified the alkaloids, phenolics, flavonoids and tannins (table 4 and fig.2). further, the HPLC analysis of methanol leaf extract of *A. carnosus* showed presence of caffeic acid, luteolin -7 glucoside, nepetin-7 glucoside, homoplantagenin, luteolin and ursolic acid with the highest content of homoplantagenin (4.20µg/g dry drug sample) followed by nepetin-7 glucoside (3.80 mg/g dry drug sample) (table-6 and fig. 4). Earlier few workers have reported identification and isolation of bioactive compounds from this plant [10,24]. Availability of these phytochemicals in the powdered drug material is rightly correlated with the medicinal potential. The level of phenolics and flavonoids in the plant extract is directly correlated with the antioxidant and anticancer potential of the plant[25-26,33,38].

Cytotoxicity of ethanolic extract of *A. carnosus* was opined to have potential anticancer activity due to availability of luteolin[5] and the anticancer activity of ethanolic leaf extract of *A. carnosus* might be due to presence of phytosterols, terpenes and flavonoids[16]. Ethanolic extract of leaves of this plant was reportedly have hepatoprotective and antioxidant potential[52] and that alcoholic extract of *A. carnosus* showed antimicrobial activity against human pathogen Helicobacter pylori and other bacterial strains[45,47]. In 2020, this plant was reported to have significant antimicrobial activity and proposed this plant as a novel candidate with therapeutic potential against multi-drug resistant *Staphylococcus aureus*[21]. However, still there are some compounds identified in the methanol extract of *A. carnosus* like caffeic acid, nepetin-7- glucoside, luteolin-7- glucoside, ursolic acid which are not explored for their medicinal values. These compounds have been reported from other plants of this family having antiviral[4], anti-inflammatory[30] properties and could be use to reduced apoptosis and cure cardiovascular disorders[46]. Thus, *A. cornosus* appears to have rich chemical diversity which is responsible for its varied medicinal properties.

From the above discussion it is clear that, *A. carnosus* is an aromatic plant with tremendous medicinal potential. The physico-chemical and fluorescent analysis of crude drug material of the plant could be the standard to check the adulteration in market available drug powder. It has diverse range of phytoconstitues and therefore responsible to cure diverse ailments starting with cough cold to cancer. However, still there are few compounds isolated from this plant which should be properly evaluated for their bioactivities and drug candidacy which might help further to develop new drug molecules.

Authors contribution:

DK developed the concept, monitored

the work and edited the manuscript. RG and NK designed the experiments and conducted the analysis. RS and SR helped in plant collection, phytochemical analysis and writing the first draft of this manuscript.

Declaration of Competing Interest:

The authors declare no conflict of interest with respect to research, authorship and publication.

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Antimicrobial Activities of 3-aryl-4-*S*-benzyl-6-phenylimino-2-hepta-*O*-acetyl-β-D-maltosylimino-2,3-dihydro-1,3,5-thiadiazines (hydrochloride)

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ABSTRACT

Several 3-aryl-4-S-benzyl-6-phenylimino-2-hepta-O-acetyl-β-D-maltosylimino- 2,3-dihydro-1,3,5-thiadiazines (hydrochloride) were synthesized by the interaction of N-hepta-O-acetyl-β-D-maltosyl isocyanodichloride with 1-aryl-5-phenyl-2-S-benzyl-2,4-isodithiobiurets. N-hepta-O-acetyl-β-D-maltosyl isocyanodichloride was prepared for the first time by the excess chlorination of hepta-O-acetyl-β-D-maltosyl isothiocyanate. The identities of these newly synthesized N-maltosides have been established on the basis of usual chemical transformations and IR, ^{1}H NMR and Mass spectral studies. The title compounds have been assayed for their antimicrobial activity against gram-positive microorganisms as well as gram-negative microorganisms.

Keywords: N-maltosides, Thiadiazines, Antibacterial, Antifungal

INTRODUCTION

The chemistry of heterocyclic compounds continues to be an explore field in the carbohydrate chemistry. One of the most common and popular methods for preparing heterocyclic compounds is the cyclization of suitable compounds. Thiadiazines and their derivatives act as antifibrinolytic (Ozcelik *et al.,* 2007), antimicrobial (Chande *et al.,* 1988) cardiotonic (Ravens *et al.,* 1997), anesthetic, cardiovascular and hypometabolic agents (Chupakhin *et al.,* 1997). Also it may be used in agriculture as insecticides (Coburn *et al.,* 1982) and fungicides (Vicentini *et al.,* 2002). Literature survey also revealed that the heterocyclic derivatives of sugar possess antimicrobial (Bhagat and Deshmukh, 2005, Mahalle *et al.,* 2008, Agrawal and Deshmukh, 2010) and antitumor activity (Shusheng *et al.,* 2008). In view of the applications of *N*-maltosides in medicinal chemistry and many other ways, it appeared interesting to synthesize some *N*-maltosylated thiadiazines (hydrochloride).

The antimicrobial activities of all the target compounds against *Escherichia coli, Proteus vulgaris, Pseudomonas aeruginosa, Bacillus subtilis, Klebsiella pneumoniae, Staphylococcus aureus, Salmonella typhimurium, Aspergillus niger* and *Candida albicans* were evaluated. The antimicrobial bioassays indicated that some title compounds exhibited noteworthy antimicrobial effects against the above strains.

MATERIAL AND METHODS

The media was prepared by dissolving weighed ingredients and was sterilized at 121°C and 15 lbs/inch^2 pressure for 15 min. After sterilization it was cooled down at about 50° C and poured into sterile Petri plates and allowed to solidify. The plates were seeded with 24 hrs. Old active nutrient broth culture of the test organism in order to obtain lawn culture. A stainless-steel cork borer of 5 mm diameter was used to bore in the agar palates.

The compounds were taken at a concentration of 1mg/ml using dimethyl sulphoxide (DMSO) as a solvent. The drug solution was allowed to diffuse for about an hour into the medium. The plates were incubated at 37°C for 24 hr. for antibacterial activity and at 30°C for 48 hr for antifungal activity. The zone of inhibition observed around the wells after respective incubation was measured and interpreted by using antibiotic zone reader. The results were cited in Table 1.

RESULTS & DISCUSSION

Co-trimazine (100 µg/ml) was used as a standard for antibacterial activity and Fluconazole (100 µg/ml) was used as a standard for antifungal activity. The compounds 3-phenyl-4-*S*-benzyl-6-phenylimino-2-hepta-*O*-acetyl-β-D-maltosylimino-2,3-dihydro-1,3,5-thiadiazine (hydrochlorides) **(4a)** and 3-*p*-tolyl-4-*S*-benzyl-6-phenylimino-2-hepta-*O*-acetyl-β-D-maltosylimino-2,3-dihydro-1,3,5-thiadiazine (hydrochlorides) **(4d)** against *B. subtilis* and the compound 3-*m*-tolyl-4-*S*-benzyl-6-phenylimino-2-hepta-*O*-acetyl-β-D-maltosylimino-2,3-dihydro-1,3,5-thiadiazine (hydrochlorides) **(4c)** against *C. albicans* exhibit promising activity. The compounds 3-*o*-tolyl-4-*S*-benzyl-6-phenylimino-2-hepta-*O*-acetyl-β-D-maltosylimino-2,3-dihydro-1,3,5-thiadiazine (hydrochlorides) **(4b)** and 3-*m*-chloro-phenyl-4-*S*-benzyl-6-phenylimino-2-hepta-*O*-acetyl-β-D-maltosylimino-2,3-dihydro-1,3,5-thiadiazine (hydrochlorides) **(4f)** showed moderate to weak activity against fungi and no activity against all bacteria.

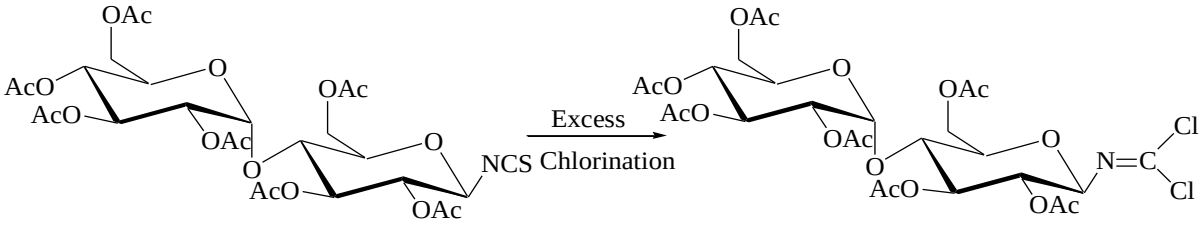
Table 1: Antimicrobial activities of some newly synthesized 3-aryl-4-*S*-benzyl-6-phenylimino-2-hepta-*O*-acetyl-β- D-maltosylimino-2,3-dihydro-1,3,5-thiadiazines (hydrochloride) (4a-g) (given in mm)

Compounds	*E. coli*	*P. vulgaris*	*Ps. aeruginosa*	*B. subtilis*	*K. pneumoniae*	*S. aureus*	*S. typhi*	*A. niger*	*C. albicans*
4a	+++	++	--	++++	+++	--	--	+++	+++
4b	--	--	--	--	--	--	--	++	+++
4c	--	--	--	--	--	--	--	--	++++
4d	++	--	--	++++	--	--	--	++	+++
4e	--	++	--	--	--	--	--	++	++
4f	--	--	--	--	--	--	--	+++	++
4g	++	--	++	+++	--	--	--	+++	+++

++++ Strong activity (above 18 mm)
+++ Moderate activity (above 14 to 18 mm)
++ Weak activity (above 8 – 14 mm)
- - Inactive (below 8 mm)
Bore size = 5 mm

Reaction Scheme

Scheme I



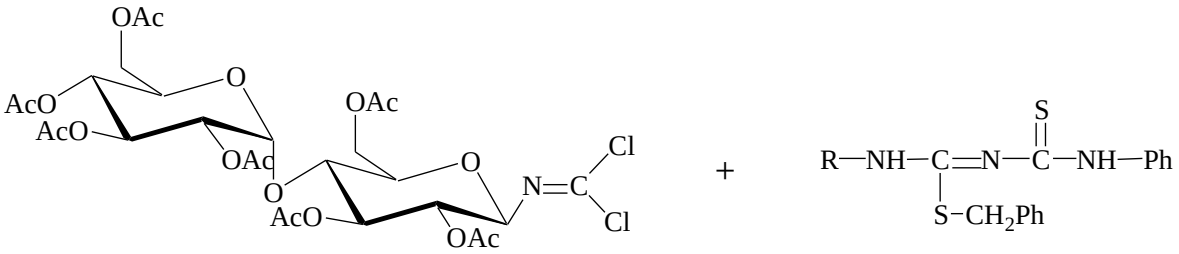
Hepta-*O*-acetyl-β–D-maltosyl isothiocyanate

(1)

N-hepta-*O*-acetyl-β–D-maltosyl isocyanodichloride

(2)

Scheme II



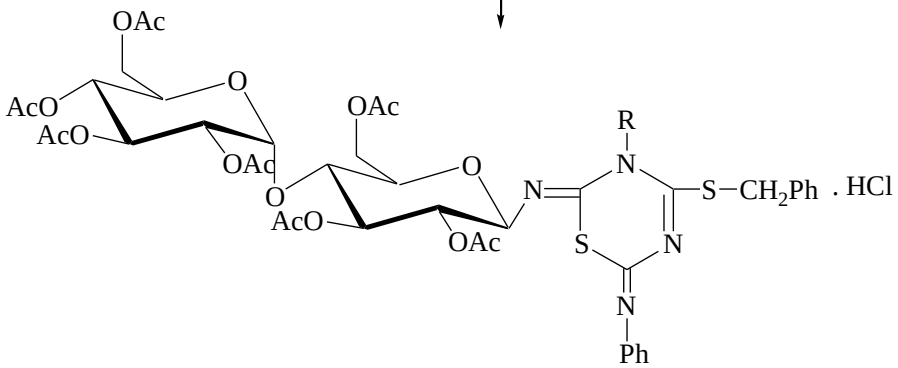
N-hepta-*O*-acetyl-β–D-maltosyl isocyanodichloride

(2)

1-aryl-5-phenyl-2-*S*-benzyl-2,4-isodithiobiurets

(3a-g)

Reflux, 2h | Chloroform



3-aryl-4-*S*-benzyl-6-phenylimino-2-hepta-*O*-acetyl-β-D-maltosylimino-2,3-dihydro-1,3,5-thiadiazines (hydrochloride) **(4a-g)**

Where, R = a) phenyl, b) *o*-tolyl, c) *m*-tolyl, d) *p*-tolyl, e) *o*-Cl-phenyl, f) *m*-Cl-phenyl, g) *p*-Cl-phenyl

CONCLUSION

From the results, it can be concluded that some of *N*-maltosylated thiadiazines (hydrochlorides) were synthesized and evaluated as antibacterial and antifungal agents. Almost many of them displayed strong to moderate activity against the tested strains of bacteria and fungi. Synthesized compounds were found to be sensitive towards *B. subtilis* and *C. albicans*.

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Synthesis of 1,3,4-Thiadiazole Lactosylamino Derivatives as Antimicrobials

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ABSTRACT A series of new 2'-(substituted) benzylidene hydrazino-5-hepta-*O*-acetyl-β-D-lactosylamino-1,3,4-thiadiazoles **(5a-e)** has been synthesized by the condensation of 1-hepta-*O*-acetyl-β-D-lactosyl thioamido thiocarbohydrazide **(3)** with different aromatic aldehydes in benzene, followed by intramolecular cyclization of compounds **(4a-e)** in refluxing ethanol. The identities of the synthesized compounds were established by spectral analysis. The compounds were assayed for their antimicrobial activity against Gram-positive and Gram-negative microorganisms-bacteria and fungi.

KEYWORDS Antimicrobial activity, Lactosyl isothiocyanate, Thiocarbohydrazide, 1,3,4-Thiadiazoles.

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INTRODUCTION

1,3,4-Thiadiazoles belong to the class of nitrogen–sulfur-containing heterocycles with the extensive application as structural units of biologically active molecules and as useful intermediates in medicinal chemistry. During the past years, substituted 1,3,4-thiadiazole derivatives have received significant attention and have been increasingly investigated due to their broad spectrum of pharmacological properties. They are used as dyes, lubricant additives, vulcanization, accelerators, and a large number of these have been reported as fungicides, antimicrobial,[1,2] anticonvulsant,[3] antitubercular,[4,5] and anti-inflammatory agents. It is supposed that 1,3,4-thiadiazole derivatives exhibit various biological activities due to the presence of =N−C−S− moiety.[6] There is also an assumption that the biological activities of 1,3,4-thiadiazole derivatives are due to the strong aromaticity of the ring, which also provides great *in vivo* stability to this five-membered ring system and low toxicity for higher vertebrates, including human beings.[7] As we know, amino sugars are chemical compounds that have a sugar backbone, in which one of the hydroxyl groups is replaced by an amine group. Likewise, derivatives of amine-containing sugars are also considered as amine sugars and can be incorporated into protein-linked sugar chains, amino sugars regulate protein function and, combined with other compounds, form antibiotics. Hence, an attempt to prepare active compounds of the thiadiazole derivatives combining the lactosyl moiety has been made. Literature survey also revealed that sugar with a heterocyclic nucleus is known to have pharmacological properties[8,9] and many of them function as therapeutic agents.[10] By keeping these aspects in view and in continuation of our research on heterocyclic sugar chemistry.[11-14] the present study focuses on the synthesis and antimicrobial study of 2'-(substituted) benzylidene hydrazino-5-hepta-*O*-acetyl-β-D-lactosylamino-1,3,4-thiadiazoles.

RESULTS AND DISCUSSION

The reaction sequence leading to the formation of the desired heterocyclic compounds is outlined in **Scheme 1.** The synthesis of 2'-(substituted) benzylidene hydrazino-5-hepta-O-acetyl-β-D-lactosylamino-1,3,4-thiadiazoles (**5a-e**) was achieved by reacting 1-hepta-O-acetyl-β-D-lactosyl thioamido thiocarbohydrazide (**3**) with different aromatic aldehydes in benzene and subsequent intramolecular cyclization of resulting derivatives **4a-e** in ethanol. The required 1-hepta-*O*-acetyl-β-D-lactosyl thioamido thiocarbohydrazide (**3**) was prepared by the interaction of 1-hepta-*O*-acetyl-β-D-lactosyl isothiocyanate (**2**) with thiocarbohydrazide (**1**).

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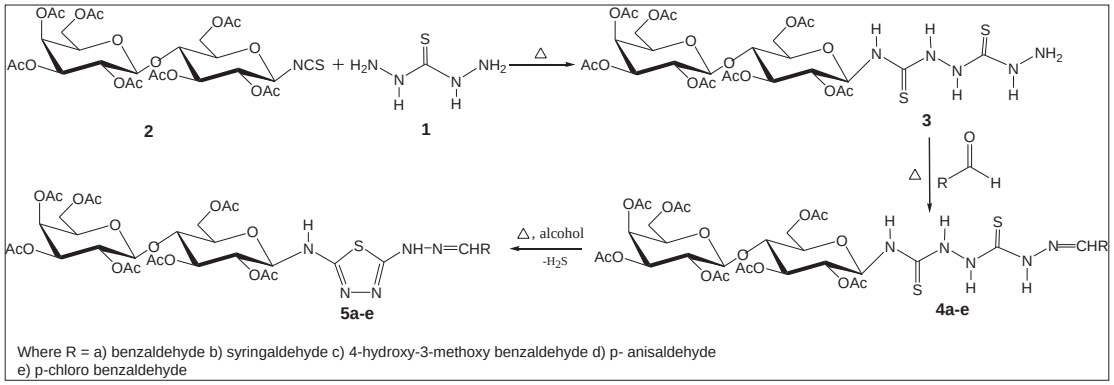
The products were found non-desulphurisable when boiled with alkaline plumbite solution. On boiling with conc. sulfuric acid it charred, indicating the presence of lactosyl group. The products were found to be optically active. The chemical structures of the title compounds were deduced by IR, ^{1}H NMR, mass spectral analysis, and elemental analysis. The characterization and elemental analytical data are summarized in **Table 1.**

ANTIMICROBIAL ACTIVITY

The title compounds **(5a-e)** were screened for both antibacterial and antifungal activities using the cup-plate agar diffusion method[15,16] by measuring the inhibition zone in mm. Amikacin (100 µg/ml) was used as a standard drug for antibacterial activity and fluconazole (100 µg/ml) as a standard drug for antifungal activity. The compounds were screened for antibacterial activity against *Escherichia coli*, *Staphylococcus aureus*, *Proteus vulgaris*, and *Pseudomonas aeruginosa* in nutrient agar medium and for antifungal activity against *Aspergillus niger* and *Candida albicans* in potato dextrose agar medium. These sterilized agar media were poured into Petri-dishes and allowed to solidify. On the surface of the media, microbial suspensions were spread with the help of a sterilized triangular loop. A stainless-steel cylinder of 8 mm diameter (pre-sterilized) was used to bore cavities. All the synthesized compounds (100 µg/ml) were placed serially in the cavities with the help of a micropipette and allowed to diffuse for 1.0 h. DMSO was used as a solvent for all the compounds and as a control. These plates were incubated at 37°C for 24 h and 28°C for 48 h for antibacterial and antifungal activities, respectively. The zone of inhibition observed around the cups after the respective incubation was measured.

The results are presented in **Table 2**.



Scheme 1: Synthesis of 2'-(substituted) benzylidenehydrazino-5-hepta-*O*-acetyl-β-D-lactosylamino-1,3,4-thiadiazoles (5a-e)

Table 1: 2'-(Substituted) benzylidenehydrazino-5-hepta-*O*-acetyl-β-D-lactosylamino-1,3,4-thiadiazoles (5a-e)

Product	m.p. (°C)	Yield (%)	R_f	Reaction time	$[\alpha]^{31}_D$ (*c*, in $CHCl_3$)	Elemental analysis (%) Found (Required)	
						N	S
5a	97	93	0.70	4 h	−124.30°	8.33 (8.36)	3.99 (3.82)
5b	148	89	0.71	4 h	−119.31°	7.60 (7.66)	3.59 (3.50)
5c	138	85	0.74	4 h	−156.36°	7.89 (7.92)	3.66 (3.62)
5d	123	81	0.76	4 h	−112.30°	8.01 (8.07)	3.72 (3.69)
5e	143	84	0.72	4 h	−118.12°	8.00 (8.03)	3.69 (3.67)

Table 2: Antimicrobial activity of novel 2'-(substituted) benzylidene hydrazino-5-hepta-*O*-acetyl-β-D-lactosylamino-1,3,4-thiadiazoles (5a-e)

Compounds	Antibacterial**				Antifungal**	
	Escherichia coli	*Staphylococcus aureus*	*Proteus vulgaris*	*Pseudomonas aeruginosa*	*Candida albicans*	*Aspergillus niger*
5a	11	19	19	20	21	20
5b	15	16	17	17	20	22
5c	14	15	19	19	20	19
5d	13	17	20	20	19	20
5e	11	17	14	15	15	16
Amikacin	24	23	25	25	--	--
Fluconazole	--	--	--	--	25	25

** Zone of inhibition in mm (12 mm or less) resistance, (13–15 mm) weak, (16–18 mm) moderate, and (more than 19 mm) sensitive

ANTIBACTERIAL ACTIVITY

Compounds **5a** and **5d** exhibited significant activity against *S. aureus*, *P. vulgaris*, and *P. aeruginosa*. Compound **5b** showed moderate activity, whereas compound **3e** exhibited low activity toward the microorganisms. All the compounds showed weak activity toward *E. coli*.

ANTIFUNGAL ACTIVITY

All the compounds **5a**, **5b**, **5c,** and **5d** showed significant activity toward *C. albicans* and *A. niger*. Compound **5e** showed moderate activity toward *C. albicans* and *A. niger.*

EXPERIMENTAL

Melting points were taken in open capillary tubes on Mac digital melting point apparatus and are uncorrected. IR spectra were recorded on a PerkinElmer Spectrum RXI FTIR spectrometer 4000–450 cm^{-1}. The ^1H NMR spectra were recorded in $CDCl_3$ at 300 MHz on a Bruker DRX300 NMR Spectrometer. The FAB mass spectra were recorded on a Jeol SX-102/Da-600 mass spectrometer/data system using argon/xenon (6 KV, 10 mA) as the FAB gas. The accelerating voltage was 10 KV and the spectra were recorded at room temperature. Optical rotations $[\alpha]_D^{31}$ were measured on Equiptronics EQ-800 Digital polarimeter at 31° in chloroform. Thin-layer chromatography was performed on E Merck pre-coated silica gel plates.

The chemical structures of the title compounds were deduced by IR, ^1H NMR, mass spectral analysis,[17-19] and elemental analysis, the results of which are given herein.

Synthesis of 2'-(substituted) benzylidene hydrazino-5-hepta-*O*-acetyl-β-D-lactosylamino-1,3,4-thiadiazoles (5a-e)

A mixture of thiocarbohydrazide **(1)** (0.01 M) and 1-hepta-*O*-acetyl-β-D-lactosyl isothiocyanate **(2)** (0.01 M) was refluxed in benzene (15ml) to give 1-(*N*-hepta-*O*-acetyl-β-D-lactosyl) thiocarbohyrazide **(3)** m.pt. 130°C yield 95.6%.

The reaction mixture was refluxed for 3 hrs. After heating, the solvent was distilled off and the sticky mass obtained as residue was triturated with petroleum ether (60–80°C), a white product separated out. It was crystallized from ethanol.

4a: IR (KBr) cm^{-1}: υ 3352 (N-H), 3040.5 (Ar. C-H), 2849.27 (ali. C-H), 1740.33 (C=O), 1570 (C=N), 1316 (C-N), 1215 (N-N), 1210.18 (C-O), 1039.38 and 934.44 (characteristic of lactose) ,755 (C=S). **^1H NMR** (δ in ppm, CDCl3): δ 9.97 (s, 2H, 2N-H), δ 9.30 (s, 2H, 2N-H), 7.29 (s, 5H, Ar-H), 5.16 -3.834 (m, 14H, lactose unit), 2.52 -1.11 (m, 22H, $7COCH_3$) Anal. Calcd for $C_{35}H_{45}O_{17}N_5S_2$, Requires: C, 48.22; H, 5.16; N, 8.03; S, 7.34; Found: C, 48.88; H, 5.12; N, 7.99; S, 7.69 %. Similarly compounds **(4b-e)** were prepared in the same manner and physical characterization results are as follows 4b: m.pt. 133°C, yield 81.30%, **4c:** m.pt. 160°C, yield 85.11%, **4d:** m.pt. 155°C, yield 91.09 %, **4e:** m.pt. 170°C , yield 89.40%.

Compound **(3)** (0.01 M) was refluxed with benzaldehyde (0.01M) in benzene (15ml) for 3 hrs. On completion of reaction and distilling of solvent, a white solid powder of 1-hepta-O-acetyl-β-D-lactosylthioamido-5-benzylidene thiocarbohydrazide **(4a)** was isolated. It was crystallized from acetone. m.pt. 145°C, yield 88.45%.

Refluxing alone **(4a-e)** in ethanol afforded cyclized products **5a-e** with evolution of H_2S gas (tested with lead acetate paper). The reactions were completed within 4 h. On pouring the reaction mixture in H_2O, 2`-(substituted) benzylidenehydrazino-5-hepta-*O*-acetyl-β-D-lactosylamino-1,3,4-thiadiazoles **(5a-e)** were isolated as white crystalline solids. The products were crystallized from aqueous ethanol (70%). These were found non-desulphurizable with hot alkaline plumbite solution indicating the absence of >C=S group. The physical characterization results are presented in **Table 1** and spectral characterization results are summarized**.**

5a: 2'-(benzaldehyde) benzylidenehydrazino-5-hepta-*O*-acetyl-β-D-lactosylamino-1,3,4-thiadiazole

IR (KBr) cm^{-1}: υ 3341.58 (N-H), 3022.2 (Ar. C-H), 2953.92 (Ali. C-H), 1749.33 (C=O), 1555 (C=N), 1218.38 (C-O), 1041.35 and 930.42 (characteristic of lactose), 755 (C-S).

^1H NMR (δ in ppm, $CDCl_3$): δ 7.262 (s, 5H, Ar-H), 6.25 (s, 1H, N-H), 5.36 -3.844 (m, 14H, lactose unit), 5.10–4.97 (d, 1H, N-H), 2.62-1.258 (m, 22H, $7COCH_3$).

Mass (m/z): M^+ 837, 619, 560.

5b: 2'-(4-hydroxy-3,5-dimethoxy) benzylidene hydrazino-5-hepta-*O*-acetyl-β-D-lactosylamino-1,3,4-thiadiazole

IR (KBr) cm^{-1}: υ 3400 (N-H), 3050 (Ar. C-H), 2954.95 (Ali. C-H), 1745.58 (C=O), 1577.17 (C=N), 1371.39 (C-N), 1236.37 (C-O), 1053.13 and 908.47 (characteristic of lactose), 754 (C-S).

^1H NMR (δ in ppm, $CDCl_3$): δ 7.283 (s, 2H, Ar-H), 6.28 (s, 1H, N-H proton), 5.38-3.80 (m, 14H, -lactose unit), 5.31 (s, 1H, OH proton), 5.12-4.99 (d, 1H, N-H proton), 3.89 (s, 6H, $2\text{-}OCH_3$), 2.39 -1.27 (m, 22H, $7COCH_3$).

Mass (m/z): M^+ 913, 619, 560.

5c: 2'-(4-hydroxy-3-methoxy) benzylidene hydrazino-5-hepta-*O*-acetyl-β-D-lactosylamino-1,3,4-thiadiazole

IR (KBr) cm^{-1}: υ 3350.35 (N-H), 3153.61 (Ar C-H), 2918.30 (C-H), 1743.65 (C=O), 1555.70 (C=N), 1369.46 (C-N), 1236.37 (C-O), 755 (C-S),1055.06 and 902.69 (characteristic of lactose), 755 (C-S).

^1H NMR (δ in ppm, $CDCl_3$): δ 7.285 (s, 3H, Ar-H), 6.27 (s, 1H, N-H proton), 5.48-3.80 (m, 14H, lactose unit), 5.31 (d, 1H, O-H proton), 5.13-4.11 (d, 1H, N-H proton), 3.89 (s, 3H, $-OCH_3$), 2.18 - 1.27 (m, 22H, $7COCH_3$).

Mass (m/z): M^+ 883, 719, 619, 560.

5d: 2'-(4-methoxy) benzylidene hydrazino-5-hepta-*O*-acetyl-β-D-lactosylamino-1,3,4-thiadiazole

IR (KBr) cm^{-1}: υ 3401.18 (N-H), 3011.8 (Ar. C-H), 2933.71 (ali. C-H), 1743.48 (C=O), 1561 (C=N), 1209.18 (C-O), 1055.31 and 931.48 (characteristic of lactose) ,755 (C-S).

^{1}H NMR (δ in ppm, $CDCl_3$): δ 7.262 (s, 4H, Ar-H), 6.25 (s, 1H, N-H), 5.36 -3.844 (m, 14H, lactose unit), 5.10 – 4.97 (d, 1H, N-H), 3.33 (s, 3H, $-OCH_3$),2.62 -1.258 (m, 22H, $7COCH_3$)

Mass (m/z) : M^+ 867, 619, 560

Anal. Calcd for $C_{36}H_{45}O_{18}N_5S$, Requires : C, 49.82; H, 5.19; N, 8.07; S, 3.69; Found : C, 49.78; H, 5.17; N, 8.01; S, 3.72 %.

5e: 2'-(4-chloro) benzylidene hydrazino-5-hepta-*O*-acetyl-β-D-lactosylamino-1,3,4-thiadiazole

IR (KBr) cm^{-1}: υ 3348.68 (N-H), 3050.3 (Ar. C-H), 2949.77 (ali. C-H), 1748.43 (C=O), 1566 (C=N), 1216.16 (C-O), 1040.35 and 934.44 (characteristic of lactose) ,755 (C-S).

^{1}H NMR (δ in ppm, $CDCl_3$): δ 7.288 (s, 4H, Ar-H), 6.28 (s, 1H, N-H), 5.16 -3.834 (m, 14H, lactose unit), 5.09 – 3.97 (d, 1H, N-H), 2.58 -1.243 (m, 22H, $7COCH_3$)

Mass (m/z) : M^+ 871, 619, 560

Anal. Calcd for $C_{35}H_{42}O_{17}N_5SCl$, Requires : C, 48.22; H, 4.82; N, 8.03; S, 3.67; Found : C, 49.78; H, 5.17; N, 8.00; S, 3.69 %.

CONCLUSION

The present study reports the synthesis of new 2'-(substituted) benzylidene hydrazino-5-hepta-*O*-acetyl-β-D-lactosylamino-1,3,4-thiadiazoles **(5a-e)** from the precursors lactosyl thioamido thiocarbohydrazide and various aromatic aldehydes. The newly synthesized compounds exhibited antibacterial and antifungal activities against the organisms tested.

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INVESTIGATION OF PHYSICOCHEMICAL AND MEDICINAL PROPERTIES OF OIL SEED OF CERTAIN WILD PLANT SPECIES OF GADCHIROLI DISTRICT OF MAHARASHTRA

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1.0 Introduction

Plants are the sources of a variety of classes of organic compounds such as terpenoids, alkaloids, saponins, and fats and oils etc. Most of these contents have certain applications and notable amongst them is the medicinal properties exhibited by these plants. It has been reported that the crude extracts of some plants have shown remarkable physiological effects on biological systems which is a function of some chemical constituents that are present in plants. These constituents are often considered as the active principles for various reactions. Amongst the various parts of the plants, the seeds occupy an important place as they are the energy stores and are agents for propagation in wild as well as cultured conditions. Seeds also find a lot of uses in various industrial and agricultural set ups. There is variety of types of seeds and their occurrence depends upon the particular type of seed under consideration; for example, oilseeds are among the important cash crops of India and offer a means to generate good revenue.

Although knowledge related to the regularly cultivated seeds in terms of its chemical composition and uses, same is not true with the less utilized oil seeds, which are generally found in the wild. Information on the seeds of under studied plant species is also important as it holds information that can have huge potential in, which can be widely used. Although the search for new sources as industrial raw materials is gradually providing more and more information about seeds of wild plants, the knowledge pertaining to their potential use as a medicinal plant or plant derived substance for that matter is still scanty. Hence, seed chemistry appears to be an interesting subject that has good prospects for offering new avenues to the scientific community. In the backdrop of above information, this study was performed to unearth the physicochemical and medicinal properties of oil seeds of certain wild plants obtained from the forest area of Gadchiroli District of Maharashtra.

2.0 Materials and Method

2.1 Selection of Plants and Collection of Seeds – Study Area Gadchiroli

The plants situated in the wild were selected from the forest areas of Gadchiroli District of Maharashtra. Majority of geographical portion of Gadchiroli District is covered with dense forest. The climatic conditions are extreme with temperature reaching 47.3°C in Summer & 9.4°C in winter. Based on the reconnaissance survey of the study area and interaction with subject experts of Gadchiroli District; two wild plants such as *Alangium salviifolium* (L.f.) Wangerin and *Trichosanthes bracteolata* were selected for the study.

- ***Alangium salviifolium* (L.f.) Wangerin seeds:** *Alangium salviifolium* (L.f.) Wangerin collected from the Gadchiroli District in the month of March 2018.
- ***Trichosanthes bracteolata* seeds:** *Trichosanthes bracteolata* seeds collected from Gadchiroli District, in the month of August 2018.

Dried fruits collected in the polythene bags and brought to the laboratory. Seeds separated from the fruit pod and stored in airtight glass bottles and kept in a refrigerator prior to analysis. The seeds were cleaned and washed with running water and dried in air. Powder of these seeds was made by grinding. This powder was stored under -20º C refrigerator. Oil of this powdered sample was extracted by using various solvents methods. Physiochemical and medicinal values of this extract oil was estimated by various techniques.

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2.2 Proximate analysis of seeds

Proximate constituents of the seeds of *Alangium salviifolium* (L.f.) Wangerin and *Trichosanthes bracteolata* were evaluated as described by the Association of Official Analytical Chemist (AOAC, 1990). These components were studied as they determine the properties of the oil and vary from source to source and widely with plant variety and growing conditions.

2.3 Physico-chemical properties of seed oil

Empty weight of cleaned and dried pycnometer taken (W), then filled with water stoppered, wiped and again weighed (w1), the same procedure repeated with sample and weight taken (w2) again. The specific gravity was calculated as per following equation.

Specific gravity gm/ml = w2-W /w1-W

Acid value (mg KOH/gm)

Acid value is the number of mg of potassium hydroxide required to neutralize free acids in 1 gm of the oil sample. The acid value was determined by titration method.

Unsaponifiable and Saponifiable matter

Unsaponifiable matter indicates impurities percentage in oil, which are not saponified by alkali and extracted by organic solvent. Total Solution extracted three times with 100 ml of ether.

Unsaponifiable matter% w/w = 100 x W1 /W

W1-residue in gm, W-sample weight (gm)

Saponification value gives the number of mg of potassium hydroxide required to neutralize free fatty acids, obtained from the hydrolysis of 1gm of oil or fat sample. Saponification value of the oil is calculated as under mentioned formula.

Saponification value = (S-B) x M x 56.1/sample weight (g)

S= Sample titre value, B = Blank titre value, M = Molarity of HCl,

Molecular weight of KOH = 56.1

2.4 Determination of antibacterial and antifungal activity

The agar-well diffusion assay as described by Vollekova *et al*. (2001) was used to determine the growth inhibition of bacteria by the seed oil. The tests were carried out by using a stock concentration of 100 mg mL^{-1} prepared by dissolving 1 g of the ethanol extract into 10 mL of distilled water. Nutrient agar was prepared and 25 mL each was poured into sterile petri dish and a lawn culture of test organisms was prepared on it. Using a sterile cock-borer of 4 mm diameter three equidistant holes per plate were made in the set agar. Thereafter, the wells (holes) were filled with 0.2 mL of the extract solution. The plates were incubated at 37°C for 24 h. The resultant zone of inhibition (3 replicates) of the different plant extracts were observed and measured using a transparent meter rule. The test organisms were as follows

Gram-negative bacteria

- *Escherichia coli, Salmonella typhi, Pseudomonas aeruginosa*

Gram – positive bacteria

- *Staphylococcus aureus* and *Bacillus subtilis*

Fungal strains

- *Candida tropicalis* and *Candida albicans*

3.0 Results and Discussion

3.1 Proximate analysis of seeds

Table 1: Proximate analysis of seeds of various plants

Content (%)	*Alangium salviifolium* (L.f.) Wangerin	*Trichosanthes bracteolata*
Moisture	5.51	6.51
Ash content	5.14	2.31
Carbohydrate	45.15	14.30
Protein	18.56	25.10
Oil Yield	16.35	40.20

Crude Fibre	7.30	2.36

Above table 1 shows the proximate analysis of seeds of various plants (*Alangium salviifolium* (L.f.) Wangerin and *Trichosanthes bracteolate).*

- **Moisture content:** The study results obtained shows that moisture content in *Trichosanthes bracteolate* was 6.51%. In addition to this *Alangium salviofolium (L.f.) Wangerin* have 5.51% moisture content
- **Ash content:** The study results shows that ash content of *Alangium Salvifolium (L.f.) Wangerin* seeds was 5.14% while ash content occurred in the seeds of *Trichosanthes bracteolata* was 2.31%.
- **Carbohydrate:** The study results shows that content of carbohydrate among *Alangium Salvifolium (L.f.) Wangerin* was 45.15% while carbohydrate content in *Trichosanthes bracteolata* seeds was 14.3%. From the study results it is evident that *Alangium Salvifolium (L.f.) Wangerin* seeds have highest carbohydrate content.
- **Protein**: The study results shows that content of protein among *Trichosanthes bracteolata* seeds was 25.10% while *Alangium Salvifolium (L.f.) Wangerin* seeds have 18.56% protein content.
- **Crude Fibre**: The study results show that *Alangium Salvifolium (L.f.) Wangerin* seeds have 7.30% while *Trichosanthes bracteolata* seeds have 2.36% crude fibre content.
- **Oil Yield**: The study results shows that *Trichosanthes bracteolata* seeds had highest content of oil i.e 40.20% followed by *Alangium Salvifolium (L.f.) Wangerin* seeds have 16.35%. From the study results it is evident that *Trichosanthes bracteolata* seeds have highest oil content.

3.2 Physico-chemical properties of seed oil

Table 2: Physico-chemical properties of seed oil

Chemical properties	***Alangium salviifolium* (L.f.) Wangerin**	***Trichosanthes bracteolata***
State at room temperature	liquid	liquid
Colour	Yellow	Pale yellow
Odour	Odourless	Odourless
Refractive index (at 40°C)	1.4509	1.4632
Specific gravity (at 25°C)	0.8905	0.9167
Acid value (mg KOH/gm)	4.14	4.01
Iodine Value	108.0	97.0
Unsaponifiable matter% w/w	0.43	0.67
Saponification Value (mg KOH/gm)	214.1	187

Above Table 2 shows the physico-chemical properties of the seeds oil of various plants (*Alangium salviifolium* (L.f.) Wangerin and *Trichosanthes bracteolate).* The study results obtained shows that:

- **Refractive Index:** The refractive index of *Alangium salviifolium* (L.f.) Wangerin and *Trichosanthes bracteolata was* 1.4509 and 1.4632 respectively.
- **Specific gravity:** The specific gravity of *Alangium salviifolium* (L.f.) Wangerin and *Trichosanthes bracteolata was* 0.8905 and 0.9167 respectively. It has been reported that the specific gravity (density) of plant based oils is usually about 0.920 at 25°C (Elert, 2001). Moreover, there are 22 common edible oils, whose specific gravity lies in the range of 0.88 to 0.94 (Tool Box, 2005). For example, Biswas (2001) determined specific gravity of 0.921 in sesame oil, 0.924-0.926 in sunflower oil, 0.915-0.919 in olive oil, 0.921-0.945 in cotton seed oil and 0.922-0.928 for specific gravity in soybean oil. Thus, our results are similar to those reported for other edible oils vis-à-vis specific gravity of oils.
- **Acid value:** The acid value of *Alangium salviifolium* (L.f.) Wangerin and *Trichosanthes bracteolata was* 4.14 and 4.01 respectively.

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- Often, the purity of vegetable oil indicated by acidity of oil (Perez-Camino, 2000). Acid value of oils are an important criteria for edibility of oil and should lie in the range of 4.05 to 6.59 (Dawodu, 2009).
- **Iodine value:** The iodine value of *Alangium salviifolium* (L.f.) Wangerin and *Trichosanthes bracteolata was* 108.0 and 97.0 respectively. From the study results it is evident that Iodine value of oils is related with unsaturation of carbon chain fatty acids. Iodine value of *Alangium salviifolium (L.f.) Wangerin* and *Trichosanthes bracteolata* (ranged between 102.0 and 115.8) lies in the non drying category and comparable to other seed oils like cotton seed (108), mustard (108) mentioned in Nutritive value of Indian food.
- **Unsaponifiable matter:** The unsaponifiable matter value of *Alangium salviifolium* (L.f.) Wangerin and *Trichosanthes bracteolate* 0.43% and 0.67% respectively. The Unsaponifiable matter of oil contains minor compounds comprising sterols and fat-soluble vitamins and our results show that it (unsaponifiable matter) lies in the range of edible oils.
- **Saponification Value:** The saponification value of seed oil ranged from 172-286.1 mg KOH/gm. Saponification value of *Alangium salviifolium* (L.f.) Wangerin and *Trichosanthes bracteolata was* 214.1 mg KOH/gm and 187 mg KOH/gm respectively. Thus, on the basis of results, it is clear that the seed oils of plant species studied lie in the range of edible oils, means these oils can be utilized for edible, but refining must necessary before use.

3.3 Antimicrobial activity of seed oils

The antibacterial and fungal strains used for testing the antimicrobial activity are as follows

Table 3: Inhibition zones (mm) of *Alangium salviifolium (L.f.) Wangerin* seed oil

Name of Microorganisms	Inhibition zone (mm) Concentration of sample (mg/ml)			+ control (mg/ml) Ciprofloxacin
Gram -ve bacteria	**4.0**	**2.0**	**1.0**	**0.01**
Escherichia coli.	9.98 ± 0.14	17.5 ± 0.11	*	17.5 ± 0.11
Salmonella typhi	*	*	*	16.81 ± 0.08
Pseudomonas aeruginosa	16.26±0.09	16.58±0.12	*	16.58 ± 0.12
Gram +ve bacteria				
S. aureus	14.12±0.08	12.16±0.11	10.16 ± 0.11	14.98 ± 0.11
Bacillus subtilis	*	*	*	15.88 ± 0.09
Fungal strains				Fluconazole
Candida tropicalis	11.58±0.08	9.72 ± 0.08	*	13.65±0.14
Candida albicans	*	*	*	14.23±0.11

* No zone of inhibition observed

Above Table 3 shows the results of antimicrobial activity of oil obtained from *Alangium salviifolium (L.f.) Wangerin* seeds. It is evident from the results that *S. aureus* are susceptible to this oil while, *E coli*, *S. typhi*, *P. aeruginosa*, *B. subtilis*, *C tropicalis* and *C. albicans* are resistant to the oil (as there was no inhibition zone).

Table 4: Inhibition zones (mm) of *Trichosanthes bracteolata* seed oil

Name of Microorganisms	Inhibition zone (mm) Concentration of sample (mg/ml)			+ control (mg/ml) Ciprofloxacin
Gram -ve bacteria	**4.0**	**2.0**	**1.0**	**0.01**
Escherichia coli.	12.86±0.08	10.08±0.08	*	17.5±0.11
Salmonella typhi	14.31±0.08	13.63±0.08	12.2± 0.08	16.81±0.08
Pseudomonas aeruginosa	*	*	*	16.58±0.12

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Gram +ve bacteria				
S. aureus	10.12±0.08	9.16 ± 0.08	8.16± 0.08	14.98±0.11
Bacillus subtilis	*	*	*	15.88±0.09
Fungal strains				Fluconazole
Candida tropicalis	*	*	*	13.65±0.14
Candida albicans	*	*	*	14.23±0.11

* No zone of inhibition observed

Above Table 4 shows the results of antimicrobial activity of oil obtained from *Trichosanthes bracteolata* seeds. It is evident from the results that *S. typhi* and *S. aureus* are susceptible to this oil while, *E coli*, *P. aeruginosa*, *B. subtilis*, *C tropicalis* and *C. albicans* are resistant to the oil (as there was no inhibition zone).

4.0 Conclusion

The study results showed that the basic components of the oils obtained from the seeds of *Alangium salviifolium* (L.f.) Wangerin and *Trichosanthes bracteolate* showed that the pharmacognostic properties (of seeds), related to moisture, ash, fat, protein, carbohydrate are more or less similar to the presently used edible oils. In addition to this the data shows that these seeds obtained from the wild varieties of *Alangium salviifolium* (L.f.) Wangerin and *Trichosanthes bracteolata* contain noticeable quantity of nutrients. The proximate analysis results shows that these oil seeds are quite similar to other oil seeds that are widely used on commercial basis thereby indicating a potential for use of these oil seeds. In addition to above, the seed oils obtained from *Alangium salviifolium* (L.f.) Wangerin and *Trichosanthes bracteolata* showed specific antibacterial and antifungal activity, which shows promising potential of these seed oils as antimicrobial agents, which can be used in gels and lotions.

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Green Multicomponent method for synthesis of substituted derivatives 2-amino Chromenes by using Na_2CO_3 as a catalyst

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ABSTRACT

2-amino- 4H-chromenes represent an important class of compounds being the main component of many naturally occurring products. The basic structural frameworks of chromene for example is a common feature of many tannins and polyphenols found in tea, fruits vegetables and red wine. Derivatives of chromene are an important group of compounds found in plants including fruit and vegetables. chromene are biologically active with wide range of activities such as antimicrobial, mutagenicity, antiviral, antiproliferative and central nervous system activities. In this research work substituted 2-amino 4H-chromenes were synthesized by one pot synthesis method by interaction with substituted benzaldehyde, β-naphthol, and malononitrile by using sodium bicarbonate as catalyst. The yield of product is found to be very good. The synthesized compounds were recognized by IR, NMR and mass spectroscopic technique.

Keywords :2-amino 4H-chromene, benzaldehyde, B-naphthaol, malononitrile, Na_2CO_3

INTRODUCTION

Multicomponent reactions are of increasing importance in organic and medicinal chemistry. In times where a premium is put on speed , diversity and efficiency in the drugs discovery process MCRs strategies offer significant advantage over conventional linear type synthesis. In such reactions three or more reactant comes together in a single reaction vessel to form new product that contain portion of all the components. MCRs providing product with the diversity needed for the discovery of new lead compound. Over The last decade industrial and academic researchers have made such powerful MCR strategies into one of the most efficient and co-effective tools for combinatorial and parallel synthesis (Weber, 2002, Jankun *et al*., 1997).

Multi-component reactions (MCRs) are one step reaction that combines two or more reagents to form an end product (Mirjalili *et al*., 2012).

Since an MCR forms product in one step it generates considerably less waste than a multistep synthesis. Multi-component reactions (MCRs) important for the achievement of high level of brevity and diversity. They allow more than two simple and flexible building blocks to be combine in practical, time saving one pot operation, giving rise to complex structure by simultaneous formation of two or more bond, according to domino principle (Zhu and Bienayme, 2005). Consequently, from the point of green chemistry, MCRs constitute a very useful class of tools for the synthesis of new chemicals. MCRs contribute to the requirements of an environmental friendly process by reducing the number of synthetic steps energy consumption and waste production. Researcher have transformed this poewrfull technology into one of the most efficient and economic tools for combinatorial and parallel synthesis (Zhu and Bienayme, 2005, Beck, *et al*., 2000). Due to their inherent simple experimental procedure and their one pot character, they are perfectly suited for Automated synthesis. thus MCRs attracted considerable interwst owing to their exceptional synthetic efficiency (Nishiyama *et al*., 2004, Bienayme, Hulme *et al*., 2000).

Several protocols have been reported for the synthesis of 2-amino-4H-chromenes and their derivatives using malononitrile, resorcinol and aldehyde. Various catalysts such as piperidine,9 triethyl amine,10 aqueous K2CO3,11 cetyltrimethylammonium bromide (CTABr),12 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU),13 Ca(OH)2,14 HT/MW 15 and basic ionic liquids16 have been used for these reactions. In current work mild reaction condition (Ethanol and water) and sodium bicarbonate is used as catalyst as it is easily available

MATERIALS AND METHOD

All melting points were taken in open capillaries and are uncorrected Infrared (IR) spectra were recorded with a Shimadzu 8400s FT-IR spectrometer using potassium bromide pellets. 500MHz ^{1}HNMR spectra were recorded on a DRX-500 Avance Bruker spectrometer. The chemical shifts are reported in ppm (δ-scale) relative to internal TMS Reagents are obtained from commercial resource. Commercially available regents were used without further purification. Products are all known compounds and were identified by comparing of their physical and spectra data with those reported in the literature.

General procedure for 2-Amino-4H-Chromenes

A mixture of resorcinol (5mmol), malononitrile (5mmol), and aromatic aldehyde (5mmol) was taken round bottom flask containing 5 mL of water and 5 ml ethanol. (10wt%) catalyst Na_2CO_3 with respect to resorcinol was then added to the reaction flask and the contents were stirred. The reaction mixture was refluxed. The progress of the reaction was monitored by thin layer chromatography (ethyl acetate/pet ether: 30%). After reaction was completed, the reaction mixture was allowed to cool at room temperature. The crude product was extracted with ethyl acetate. The organic layer was washed with water (25 mL), dried with anhydrous Na2SO4, the solvent evaporated under vacuum and the crude product recrystallized from ethanol. Characterization data for selected compounds are provided below:

Selected characterization data

4a: IR (KBr), ν (cm^{-1}): 3400, 3316 ,2180,1645,1590; ^{1}H NMR (DMSO-d_6 500 MHz), δ (ppm): 5.34 (s, 1H, CH), 7.12 (s, 2H, NH_2)7.12-7.22 (d, 2H, J=8.2, ArH), 7.30-7.37 (m, 3H, ArH), 7.40-7. 47 (m, 2H, ArH), 7.81-7.82 (d, 1H, J=8.02, ArH),7.91-7.96 (m, 2H, ArH).

RESULTS & DISCUSSION

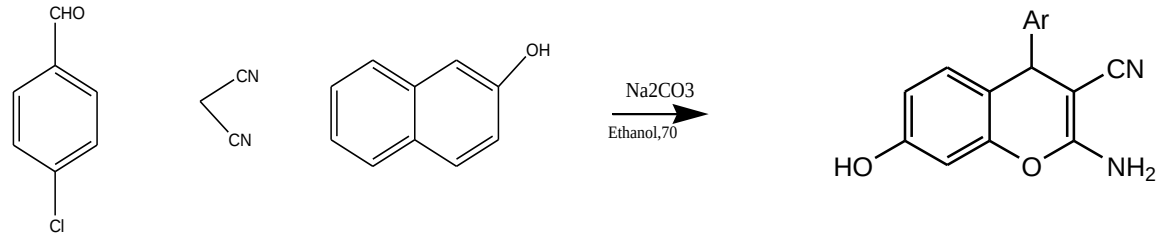
Initially, multicomponent reaction of benzaldehyde, resorcinol and malononitrile were chosen as the model reaction. Effects of various reaction parameters such as the effect of the solvents, the effect of catalyst concentration and the effect of temperature were studied to optimize the reaction conditions

It was observed that sodium bicarbonate (Na_2CO_3) with 10 mol% found to be more influencing catalyst in the synthesis of 2-amino4-H chromene by three component reaction of benzaldehyde, resorcinol and malononitrile resulting into a very good yield of the desired products.
It is reported that in the absence of catalyst no formation of product was observed even in same reaction condition (Table 1, entry 1).

Table 1: Optimization of reaction conditions [a]

Entry	Reaction condition	Catalyst (mol%) [b]	Time (min)	Yield (%)[c]
1	H2O, 70 ^{0}C	No catalyst	24 h	0
2	EtOH, 70 ^{0}C	Na_2CO_3 (5)	5 h	80
3	MeCN 7 0 ^{0}C,	Na_2CO_3 (5)	5 h	35
4	DMF 70 ^{0}C,	Na_2CO_3 (5)	5 h	55
5	Toluene 70 ^{0}C,	Na_2CO_3 (5)	5 h	0
6	EtOH,: H2O(1:1), 70 ^{0}C	Na_2CO_3 (5)	5 h	85
7	Solvent free ,70 ^{0}C	Na_2CO_3 (5)	5 h	0
8	EtOH, 70 ^{0}C,	Na_2CO_3 (10)	5 h	81
9	MeCN 70 ^{0}C,	Na_2CO_3 (10)	5 h	44
10	DMF 70 ^{0}C	Na_2CO_3 (10)	5 h	46
11	Toluene 70 ^{0}C	Na_2CO_3 (10)	5 h	0
12	EtOH,: H2O(1:1), 70 ^{0}C	Na_2CO_3 (10)	5 h	94

[a] Reaction condition: benzaldehyde (5 mmol), resorcinol (5 mmol), malononitrile (5 mmol). [b]Weight percentage of the catalyst with respect to resorcinol. [c] Isolated yield



1 2 3

Table 2 : 2-Amino-4H-chromene synthesis in Ethanol: Aqueous (1:2) medium

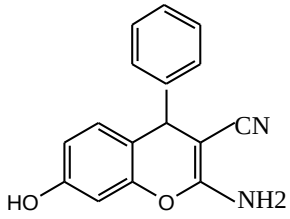
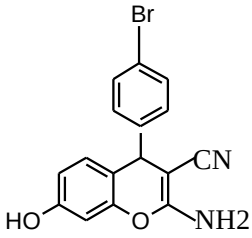
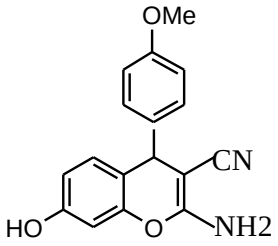
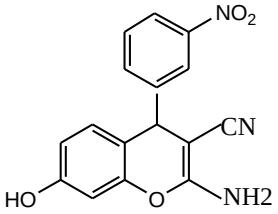
Entry	Aldehyde	Product	Code	Time	Yield	M. P. (1C)	
	R	Structure				Found	Reported
1	-H		4a	5 h	85	233–236	234-236[17]
2	-Br		4b	6h	84	224–226	225–227[18]

Table 2 : Continued...

Entry	Aldehyde R	Product Structure	Code	Time	Yield	M. P. (1C) Found	M. P. (1C) Reported
3	-oMe		4c	7 h	80	112–114	112–114[18]
4	-NO2		4d	5.5h	89	187–189	188–190

Use of catalyst in different mole percent found to be more effective. With 5 mol% (entry 2-7, table 1) yield of desir product was found to be less but with increase in loading of catalyst upto 10 mol% yield goes on increasing (entry 7-11, Table 1)

CONCLUSION

In conclusion, the MCR methodology was used to prepare 2-amino-4H-chromenes. The procedure is very simple, efficient and environmentally friendly as it does not use any auxiliary and reasonable catalyst.

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Conflicts of interest: The authors stated that no conflicts of interest.

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N-Tosylhydrazone as an oxidizing directing group for the redox-neutral access to isoquinolines *via* Cp*Co(III)-Catalyzed C–H/N–N activation

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ABSTRACT

Herein, an efficient and economic access has been revealed for the synthesis of isoquinolines *via* C–H bond activation strategy by using comparatively inexpensive and versatile cobalt catalyst. A hardly investigated directing group, *N*-tosylhydrazone has been effectively applied as an internal oxidant for an annulation reaction with internal alkynes *via* C–H/N–N bond functionalization. This catalytic protocol works for the extensive variety of substrates in moderate to excellent yields under external oxidant-free conditions. Additionally, the proposed protocol has advantages such as broad substrate coverage with significant product yields, readily synthesized substrates as well as scalability up to the gram quantity which further improves the competency of the methodology.

1. Introduction

Isoquinoline and its derivatives represents the important class of organic molecules which possess different biological activities such as anti-tumour, anti-malarial, cardiovascular, anti-inflammatory, anti-HIV, etc. [1] They are also utilized for the development of numerous inhibitors, alkaloids chiral ligands and organic light-emitting diodes [2]. Thus, this moiety has achieved a great deal of attention in the field of medicinal and pharmaceutical chemistry (see Schemes 1 and 2).

Straight C–H bond activation has appeared to be an influential tactic in synthetic chemistry by creating new opportunities in the retrosynthetic strategies as well as enhancing the entire capability of the anticipated conversions [3]. Being atom economic, transition-metal assisted coupling transformations by direct C–H bond activation would streamline the synthetic processes and reduce the formation of unwanted by products. Various prior approaches on C–H bond activations are mainly centered around complexes of transition-metals such as Pd, Rh, Ir and Ru for the efficient synthesis of important organic scaffolds [4]. Due to the shortcomings of cost efficiency, sustainability, plenitude and poisonous nature, the second-row transition-metals possess limitations for the wide application in drug discovery as well as large-scale manufacturing of active pharmaceutical ingredients (API) and natural products which would be the final aim of synthetic chemistry research. Therefore, taking into consideration the economic practicability of organic synthesis, there is a growing interest in developing catalysts in accordance with the economical first-row transition metals for C–H bond functionalization which represents an attractive alternative [5]. Among them, cobalt is having an extensive application of functionalizing the inactive C–H bonds [6]. Being fairly reactive, low-cost, abundant and comparatively less harmful by character in contrast to noble metals, it has turn into the centre of interest in the area of C–H activations. The initial Cp*Co(III)-catalyzed C–H activation reaction was reported by Matsunaga, Kanai, and co-workers in 2013 [7]. These Cp*Co(III) catalysts were proved to be suitable replacements to Cp*Rh(III) catalysts for C–H activations. A prevailing catalytic system utilizing Cp*Co(CO)I2 [8] for C-2 selective C– H amidation of indoles with sulfonyl azides was testified by the same group [9]. Recently, new class of Cp*Co(III)-*p*NHC templates was utilized in catalytic annulation of azoles with internal alkynes [10].

Earlier, almost transition-metal-catalyzed C–H activation strategies required stoichiometric or super-stoichiometric amount of oxidizing agent in order to maintain the catalytic cycle. These are mostly toxic metal salts, which certainly gives rise to reduced atom-economy by generating off-cycle lateral transformations and unwanted waste. The constraint of the necessity of an oxidizing agent has been resolved by fixing a multifunctional group in substrate which plays the role of directing group and oxidizing agent both [11]. In this strategy, the

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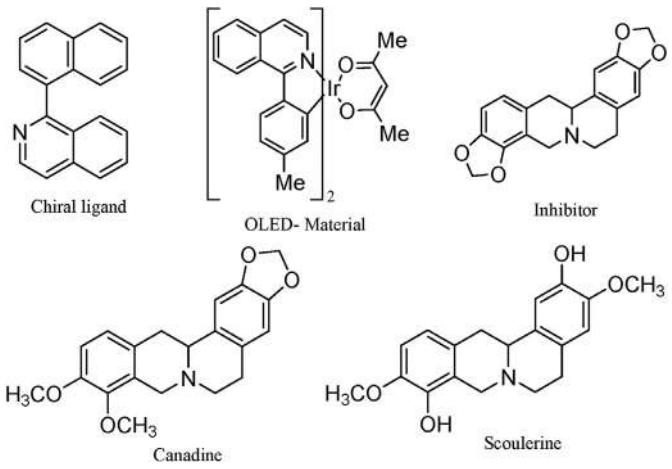
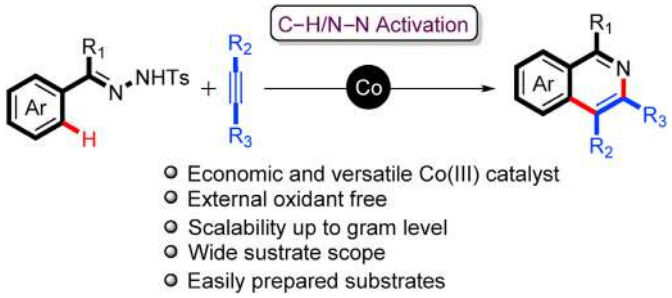


Scheme 1. Demonstrative biologically active and other vital molecules containing isoquinoline skeleton.



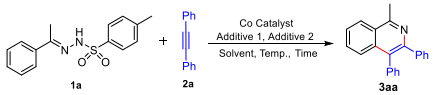
Scheme 2. *N*-Tosylhydrazone directed redox-neutral synthesis of isoquinolines *via* Cp*Co(III)-catalyzed C–H activation.

cleavage of N–N, N–O or O–O bonds for the redox-neutral methods were employed as an essential tool. The technique has potential for the enhanced reactivity as well as has obvious merits of selectivity, better yields and substrate coverage.

Due to the wealth of isoquinoline skeletons, many synthetic routes have been given for their synthesis that are established by Pomeranz–Fritsch, Pictet–Spengler, and Bischler–Napieralski reactions [12]. However, such approaches are suffered by some drawbacks like poor yield, low regioselectivity, limited substrate scope, longer reaction duration and tedious as well as harsh reaction conditions in some cases. To overcome these shortcomings, potent alternate routes were given by cyclization kind of transformations with alkynes through C–H bond activation [13]. Further, the 'external-oxidant-free' ideal strategy which is modest, secured, and ecologically benign also contributed in the rationalized access of isoquinolines *via* transition-metal-catalyzed C–H bond activations. Transition metals such as Pd [14], Ru [15] and Rh [13c, 16] were employed significantly for the streamlined synthesis of isoquinolines using "external-oxidant-free" approach. These catalysts showed effective catalytic activity, a wide substrate scope, and high functional group compatibility. However, comparatively low cost and abundant cobalt catalyst attracted scientists to give alternate inexpensive and efficient external oxidant free methodologies for the synthesis of isoquinolines. In these strategies, the N–O and N–N bonds have been employed as a significant handle for both C–N cyclization and catalyst turnover. Considering the N–O bond as an internal oxidant, in 2015, Ackermann [17], Sundararaju [18] and Matsunaga [19] groups, independently reported cobalt-catalyzed C–H/N–O activations for the synthesis of isoquinolines using different oxidizing directing groups. Subsequently, in 2016, Cheng [20] and Jeganmohan [21] research groups reported Co catalyzed annulation reactions for the access of isoquinolines using similar strategy. Recently, in 2019, Song and co-workers mentioned Cp*-free cobalt-catalyzed C–H activation using N,O-bidentate directing group in order to synthesize isoquinolines [22]. On the other hand, N–N bond was also recruited as an internal oxidant for the redox-neutral synthesis of isoquinolines. Zhu group [23] and Lade group [24], in 2016, reported C–H/N–N functionalization reactions for the synthesis of isoquinolines under external oxidant free conditions.

Our research group has also paid substantial attention for various protocols in order to access isoquinolines using different directing groups and transition-metals as catalysts [25]. In 2019, *N*-Cbz hydrazone was utilized as a directing group for the synthesis of isoquinolines using Cp*Co(III)-catalyst through C–H and N–N bond functionalization [25e].

Table 1
Optimization of reaction parameters.[a].



Entry	Co Catalyst	Additive 1	Additive 2	Solvent	Temp (°C)	Time (h)	Yield[b] (%)
1	$Co(OAc)_2.4H_2O$	$AgSbF_6$	NaOAc	TFE	110 °C	24	–
2	$[Cp^*CoI_2]_2$	$AgSbF_6$	NaOAc	TFE	110 °C	24	18
3	$[Cp^*Co(CO)I_2]$	$AgSbF_6$	NaOAc	TFE	110 °C	24	34
4[c]	$[Cp^*Co(CO)I_2]$	$AgSbF_6$	NaOAc	TFE	110 °C	24	35
5[d]	$[Cp^*Co(CO)I_2]$	$AgSbF_6$	NaOAc	TFE	110 °C	24	21
6	$[Cp^*Co(CO)I_2]$	$AgSbF_6$	NaOAc	1,2-DCE	110 °C	24	Trace
7	$[Cp^*Co(CO)I_2]$	$AgSbF_6$	NaOAc	MeOH	110 °C	24	–
8	$[Cp^*Co(CO)I_2]$	$AgSbF_6$	NaOAc	TAA	110 °C	24	–
9	$[Cp^*Co(CO)I_2]$	$AgSbF_6$	NaOAc	HFIP	110 °C	24	54
10	$[Cp^*Co(CO)I_2]$	$AgSbF_6$	KOAc	HFIP	110 °C	24	59
11	$[Cp^*Co(CO)I_2]$	$AgSbF_6$	CsOAc	HFIP	110 °C	24	66
12	$[Cp^*Co(CO)I_2]$	$AgSbF_6$	AcOH	HFIP	110 °C	24	84
13	$[Cp^*Co(CO)I_2]$	KPF_6	AcOH	HFIP	110 °C	24	49
14	$[Cp^*Co(CO)I_2]$	$AgSbF_6$	AcOH	HFIP	100 °C	24	83
15	$[Cp^*Co(CO)I_2]$	$AgSbF_6$	AcOH	HFIP	90 °C	24	63
16	$[Cp^*Co(CO)I_2]$	$AgSbF_6$	AcOH	HFIP	100 °C	12	81
17	$[Cp^*Co(CO)I_2]$	$AgSbF_6$	AcOH	HFIP	100 °C	10	69

[a] reaction conditions: ketazine **1a** (0.2 mmol), diphenylacetylene **2a** (0.4 mmol), Co catalyst 10 mol%, Additive **1** (20 mol %), Additive **2** (20 mol%), Solvent 2 mL.
[b] GC yield.
[c] 15 mol% Co catalyst was used.
[d] 5 mol% Co catalyst was used. TFE: 2,2,2-Trifluoroethanol; 1,2-DCE: 1,2-Dichloroethane; MeOH: Methanol; TAA: *tert*-Amyl alcohol; HFIP: Hexafluoro-2-propanol.

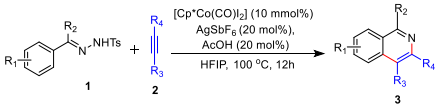
In 2018, we reported *N*-tosylhydrazone directing group in order to generate isoquinoline derivatives utilizing ruthenium as a catalyst [25a]. Although, the protocol is highly efficient, it required external oxidant and comparatively expensive ruthenium catalyst. On the other hand, to the best of our knowledge, a directing group, *N*-tosylhydrazone was not reported for C–H functionalization reactions under external oxidant free conditions and using comparatively economic first row transition-metal catalyst. In this context, it is highly desired to develop a protocol for the activation of C–H/N–H bonds of *N*-tosylhydrazones which fulfils these shortcomings. With the concern for the effective synthesis of heterocyclic moieties, here, we provide a potential method for the access of isoquinoline derivatives by C–H/N–H bond activation policy employing *N*-tosylhydrazone directing group and [Cp*Co(CO)I_2] as a catalyst using external oxidant free circumstances.

2. Results and discussion

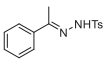
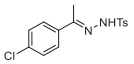
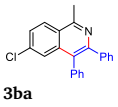
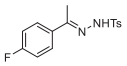
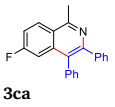
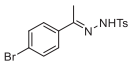
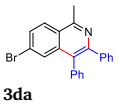
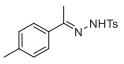
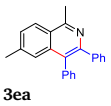
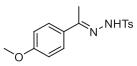
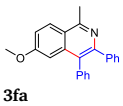
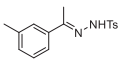
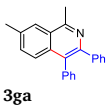
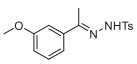
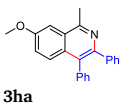
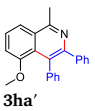
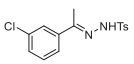
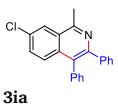
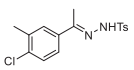
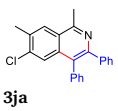
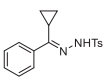
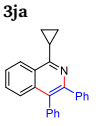
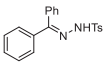
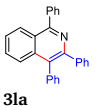
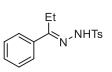
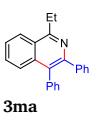
Our initial study was performed with the annulation reaction of *N*-tosylhydrazone **1a** (0.2 mmol) with diphenylacetylene **2a** (0.4 mmol) in presence of Co catalyst and $AgSbF_6$ & NaOAc as additives in order to generate isoquinolines **3aa** as model reaction (Table 1). The introduction of $AgSbF_6$ and acetate source was determined by previous studies which are required for the generation of active cationic Cp*Co(III) species in order to complete the desired transformation [17,19,23]. To examine the catalytic efficiency, three cobalt catalysts i.e. $Co(OAc)_2{\cdot}4H_2O$, $[Cp^*CoI_2]_2$ and [Cp*Co(CO)I_2] were screened for a standard transformation at 110 °C for 24 h in 2,2,2-trifluoroethanol as solvent (Table 1, entries 1–3). Out of these catalysts, [Cp*Co(CO)I_2] exhibited the highest catalytic activity with 34% yield (Table 1, entry 3), whereas $Co(OAc)_2{\cdot}4H_2O$ was inefficient for the proposed transformation (Table 1, entry 1). Further, optimization studies to determine the exact requirement of amount of catalyst were performed. With 15 mol% [Cp*Co(CO)I_2], no significant impact on the yield of product was detected, whereas on lowering the catalyst concentration to 5 mol%, the yield of the desired product was decreased to 21%. (Table 1, entries 4 and 5). Screening various solvents for the proposed methodology, trace amount of isoquinoline **3aa** was obtained when 1,2-dichloroethane was used (Table 1, entry 6). While, two other solvents such as methanol and *tert*-amyl alcohol were non-efficient for the suggested transformation (Table 1, entry 7 and 8). On the other hand, attempting the reaction in HFIP, we found that the reaction worked efficiently to produce 54% product yield (Table 1, entry 9). This indicates that HFIP found to be the most suitable among various solvents for the stated methodology. Next, different additives like KOAc, CsOAc and HOAc were also screened for the given reaction. Out of those, HOAc proved to be superior in order to produce the anticipated product with 84% yield (Table 1, entries 10–12). Consequently, an attempt was made to replace $AgSbF_6$ with KPF_6 as an additive, however, unfortunately, the reaction efficiency deteriorated giving product **3aa** with 49% yield (Table 1, entry 13). Next, to visualize the effect of temperature on the reaction efficiency, the reactions were attempted at different temperatures. Performing the reaction at 100 °C, no considerable consequence on the yield of product **3aa** was detected, although further decrease in temperature results in lowering of the product yield (Table 1, entries 14 and 15). At the end, optimum time study was performed. By reducing the reaction time to 12 h, the reaction worked with similar efficiency, while further decrease in time to 10 h lowered the product yield (Table 1, entries 16 and 17). So, the optimum reaction parameters are *N*-tosylhydrazone **1a** (0.2 mmol), diphenylacetylene **2a** (0.4 mmol), [Cp*Co(CO)I_2] (10 mol%), $AgSbF_6$ (20 mol %), AcOH (20 mol%), HFIP (2 mL), 100 °C, 12 h.

With the optimum reaction parameters, the extent of the annulation reaction of substituted *N*-tosylhydrazones (**1a-p**) with diphenylacetylene (**2a**) was analysed. A wide range of *N*-tosylhydrazones (**1a-p**) bearing various electron withdrawing and donating groups (e.g. Me, OMe, Ph, F, Cl, Br, I) were employed for annulation reaction with diphenylacetylene (**2a**) which could lead to successful formation of anticipated products. *N*-

Table 2
Co(III) catalyzed annulation of *N*-tosylhydrazones for the synthesis of isoquinolines.[a]

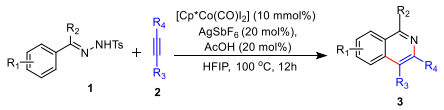


1 2 3

Entry	Azine (1)	Alkyne (2)	Product (3)	Yield[b] (%)
1	 **1a**	 **2a**	 **3aa**	81
2	 **1b**	**2a**	 **3ba**	76
3	 **1c**	**2a**	 **3ca**	73
4	 **1d**	**2a**	 **3da**	78
5	 **1e**	**2a**	 **3ea**	83
6	 **1f**	**2a**	 **3fa**	87
7	 **1g**	**2a**	 **3ga**	80
8	 **1h**	**2a**	 **3ha**  **3ha′**	49 33
9	 **1i**	**2a**	 **3ia**	71
10	 **1j**	**2a**	 **3ja**	74
11	 **1k**	**2a**	 **3ka**	78
12	 **1l**	**2a**	 **3la**	89
13	 **1m**	**2a**	 **3ma**	84

(*continued on next page*)

Table 2 (*continued*)



1 2 3

Entry	Azine (1)	Alkyne (2)	Product (3)	Yield[b] (%)
14	**1n**	**2a**	**3na**	76
15	**1o**	**2a**	**3oa**	nd
16	**1p**	**2a**	**3pa**	73
17	**1a**	**2b**	**3ab**	71
18	**1a**	**2c**	**3ac**	74
19	**1a**	2d	**3ad**	83
20	**1a**	**2e**	**3ae**	nd

[a] reaction conditions: azine **1** (0.2 mmol), alkyne **2** (0.4 mmol), [Cp*Co(CO)I_2] catalyst (10 mol%), $AgSbF_6$ (20 mol %), HOAc (20 mol%), HFIP (2 mL), 100 °C, 12 h.

[b] isolated yields.

tosylhydrazone with no substitution on the phenyl ring could generate corresponding product **3aa** with 81% yield (Table 2, entry 1). Electron-withdrawing substituents like Cl, F and Br at *para*-position of the aromatic ring of hydrazones afforded the respective target molecules **3ba**, **3ca** and **3da** in 76%, 73% and 78% yields respectively (Table 2, entries 2–4). The presence of electron-donating substituents such as –Me and –OMe at the *para* position of the benzene ring of the *N*-tosylhydrazone improved the yields of respective target moieties to 83% and 87% respectively (Table 2, entries 5 and 6). Substituents such as –Me and –Cl at the *meta* position of the benzene of *N*-tosylhydrazone provided anticipated moieties **3ga** and **3ia** solely with 80% and 71% yields correspondingly, whereas, –OMe at the *meta* position of the hydrazone produced moieties **3ha** and **3ha′** with 49% and 33% yields correspondingly (Table 2, entries 7–9). Furthermore, the proposed methodology is appropriate for various disubstituted *N*-tosylhydrazones also and the desired product **3ja** was detected in good yields and particular regioselectivity (Table 2, entry 10). Consequently, cyclopropyl phenyl ketone, benzophenone and propiophenone was also utilized as substrates *for N*-tosylhydrazones preparation which could generate the desired substituted isoquinolines **3ka**, **3la** and **3ma** with 78%, 89% and 84% product yields correspondingly (Table 2, entries 11–13). Satisfyingly, even hydrazone derived from 1-acetylnaphthalene functioned for the projected transformation, generating anticipated molecule **3na** with 76% yield (Table 2, entry 14). In addition, the ability of *N*-tosylhydrazone prepared from heterocyclic ketones (e.g. 4-acetylpyridine and 2-acetylthiophene) was also evaluated for the proposed protocol. Out of those, hydrazones derived from 4-acetylpyridine couldn't produce an anticipated product, while, hydrazone from 2-acetylthiophene gave desired isoquinoline product **3pa** with 73% yield (Table 2, entries 15–16).

Finally, we briefly investigated the scope of the symmetrical, unsymmetrical as well as substituted internal alkynes for the proposed transformation. To the gratification, 3-hexyne and 1-phenyl-1-propyne worked effectively for the annulation with hydrazone **1a** to generate corresponding isoquinolines **3ab** and **3ac** with 71% and 74% yields respectively (Table 2, entries 17–18). Also, diphenylacetylene with methyl substituents at *para* position provided desired product **3ad** with 83% yield (Table 2, entry 19). However, terminal alkyne was ineffective under a projected methodology (Table 2, entry 20).

3. Conclusion

In summary, Cp*Co(III) catalyzed annulation reaction of *N*-tosylhydrazones with alkynes has been established *via* C–H/N–N bond activation in order to synthesize isoquinoline derivatives. In the proposed protocol, *N*-tosylhydrazone played a dual role, i.e. directing group as well as internal oxidant efficiently. This protocol is applicable to an extensive series of *N*-tosylhydrazones possessing electron withdrawing and donating groups without using any external oxidizing agent. The developed methodology proved to be efficient as an air stable catalytic system Cp*Co(III) worked effectively for this transformation and the reported methodology could also work for the gram level synthesis with slight reduction in the yield of product. Furthermore, a wide range of isoquinoline derivatives could be fruitfully obtained with moderate to excellent yields under a proposed protocol.

Declaration of competing interest

There are no conflicts to declare.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jics.2021.100001.

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An efficient and cost effective synthesis of acetamides catalyzed by calcium chloride

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$CaCl_2$ has been found to be an efficient and cost effective catalyst for the rapid synthesis of acetamides in high yields. The use of stoichiometric quantities of acetic anhydride under solvent free conditions without any additional chromatographic purifications makes this protocol a safe alternative to the existing methods.

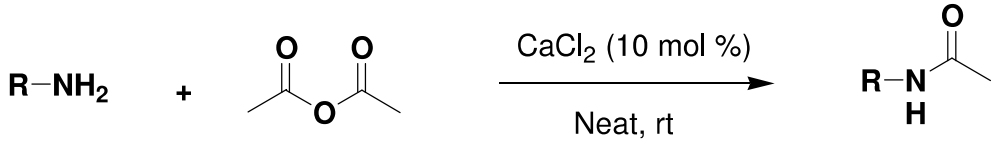
Keywords: Acetamide, acylation, acetylation, amine, $CaCl_2$

Protection and deprotection techniques are the frequently encountered exercise for the synthesis of complex organic materials. Hence, the protection of various functional groups *via* environmentally benign procedures is highly desirable. Amine functionality is one of the most important functional group present in plethora of biologically relevant molecules. Many protective groups are available for the protection of amine functionality. Out of these acetyl group is the most common, as it is stable in acidic conditions and can be removed easily under alkaline conditions[1]. Different reagents used for the acetyl protection of amines are acetic anhydride[2], acetyl chloride[3], acetyl acetone[4], acetic acid[5], zinc acetate[6] and thioacid[7]. Among these, acetic anhydride is the most commonly used reagent as it is cheap, easy to handle and readily available. Besides their use as a protecting group, acetamides are present in various important natural products and pharmaceuticals such as paracetamol, zonisamide, lacosamide, *etc*. that are required in bulk quantities. Various methods are available for the acetamide synthesis under basic as well as acidic conditions using acetic anhydride[8].

However, most of the methods suffer from one or more drawbacks such as harsh conditions, expensive reagents and catalysts, elevated temperatures, long reaction times and high toxicity. Very recently, Kim *et al.*[9] reported the synthesis of acetamides using sulfated choline ionic liquid as a catalyst using grindstone method, though this method is quite efficient in terms of yield and reaction times, however the catalyst is not commercially available, and require preparation. To overcome these drawbacks still there is an avenue to develop a new catalyst system that can minimize these limitations. Therefore, efficient catalysts that are environmentally friendly, more economical and use stoichiometric amount of reagent in absence of volatile organic solvents (VOSs) are desirable. Calcium chloride ($CaCl_2$) is a readily available, inexpensive reagent used for dehydration and recently gaining momentum as a green catalyst in various organic transformations. To exemplify, $CaCl_2$ has been used in Mannich reaction[10], Kabachnik-Fields three component reaction[11] Biginelli and aldol transformations[12,13]. Recently, it has been utilized as an efficient Lewis acid catalyst for the synthesis of 9-aryl-1,8-dioxooctahydroxanthene[14].

Results and Discussion

These findings motivated us to extend the utility of $CaCl_2$ in facile organic transformations, herein we report for the first time an efficient, environmentally benign, low cost and clean protocol for acetamide synthesis using $CaCl_2$. Initially, we carried out the reaction with equimolar quantities of aniline and acetic anhydride in presence of 10 mol% $CaCl_2$ using acetonitrile as a solvent and to our delight, the reaction was completed in 20 min with 94% yield (Scheme I). Next, we evaluated different solvents like acetone, chloroform and they



Scheme I — $CaCl_2$ catalyzed synthesis of acetamides

also produced excellent results in short reaction time (Table I).

Polar solvents (Table I, entry 3,5) shows slight decrease in yields as compared to other less polar solvents. But the best results were obtained when the reaction was carried out in solvent free conditions, the desired product was obtained in 97% yield in 10 min. Comparison of our result with few of the reported procedures is presented in Table II which clearly indicates the efficiency of $CaCl_2$ in the synthesis of acetamides.

With the optimized reaction conditions in hand, we evaluated the scope of the reaction with various aromatic, heteroaromatic and aliphatic amines. Several amines were treated with 1 eq. of freshly distilled acetic anhydride in presence of 10 mol% of $CaCl_2$ under solvent free conditions to obtain pure products without any column purification (Table III). Anilines possessing electron withdrawing groups on the phenyl ring (such as chloro or nitro group) shows decrease in product yields with slight longer reaction time. In contrast, aniline having electron donating groups on the phenyl ring (methyl or methoxy) results in higher yields with rapid product formation. Position of substituents on aniline does not affect much on the yields of the product but, the effect can be seen on the reaction time. For example, substituent on *ortho* position of aniline requires more time for the completion of reaction as compared to *meta* and *para* positions due to the *ortho* effect. Sterically hindered amine (entry 19, 20, 21) was conveniently transformed into its corresponding product with moderate to good yield. Excellent chemoselectivity was observed in case of amino alcohols (entry 23-26) and phenylene diamine (entry 9) to provide the required product without formation of any side products. Heterocyclic (entry 15-17) and aliphatic amines (entry 27-30) also worked well using this protocol in high yields and shorter reaction times. Moreover, chiral amine (entry 31) was easily converted to the desired product without any detriment decrease in optical purity.

Table I — Effect of various solvents on the yield of the model reaction[a]

Entry	Solvent	Time	Yield (%)
1	Acetone	15 min	95
2	Acetonitrile	20 min	94
3	$CHCl_3$	20 min	90
4	Ethanol	25 min	90
5	Ethyl acetate	25 min	92
6	Methanol	30 min	88
7	THF	15 min	92
8	Solvent free	10 min	97

[a] Aniline (1mmol), $(Ac)_2O$ (1 mmol), $CaCl_2$ (0.1mmol), Solvent (1mL), RT.

Experimental Section

All commercially available reagents were used without purification unless otherwise noted. Acetic anhydride was distilled prior to use. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-200 NMR spectrometer. Spectra were obtained in $CDCl_3$. Chemical shifts are reported in δ (ppm) and coupling constants are reported in Hertz (Hz). Monitoring of reactions was carried out using TLC plates (Merck Silica Gel 60 F254) and visualization with UV light (254 and 365 nm), I_2 and anisaldehyde in ethanol as development reagents. Mass spectra were recorded on LC-MS. Optical rotations were measured with a JASCO P 1020 digital polarimeter.

General procedure for the synthesis of acetamides

To a mixture of amine (0.1 mol) and acetic anhydride (0.1 mol) was added $CaCl_2$ (0.01 mol) and stirred at room temperature for appropriate time as shown in Table III. The progress of reaction was monitored by TLC. After completion, the reaction mixture was washed with saturated aq. $NaHCO_3$ solution (15 mL) and extracted with ethyl acetate (3 × 15 mL). The combined organic layer was dried over anhydrous sodium sulfate and concentrated *in vacuo* to afford pure product.

Spectral characterization of the compounds

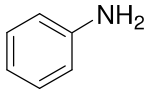
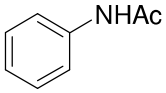
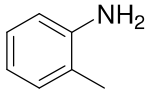
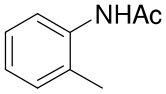
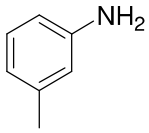
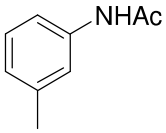
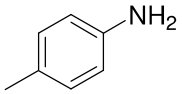
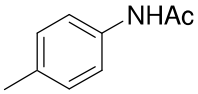
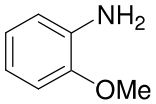
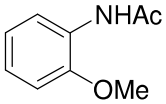
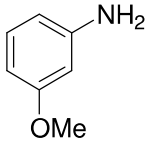
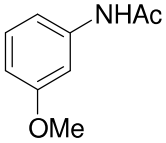
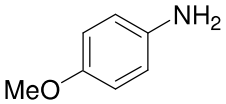
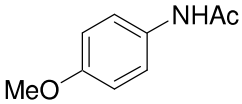
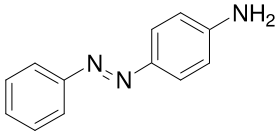
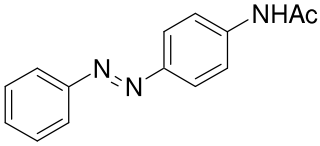
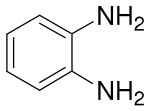
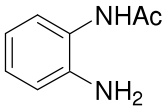
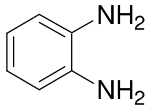
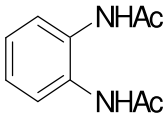
***N*-(4-Phenylazo-phenyl)-acetamide (Entry 8,** Table III): ^1H NMR (200 MHz, $CDCl_3$): δ_H 1.78 (s, 1H), 2.22 (s, 3H), 7.39-7.60 (m, 3H), 7.65-7.76 (m,

Table II — Comparision of various catalysts employed for the synthesis of phenylacetamide[#]

Entry	Catalyst	Solvent	Time (min)	Yield (%)	Ref.
1	Ag(OTf) (1 mol%)	Neat, 80°C	3	99	8b
2	Nano-CdO (10 wt%)	Neat (MW, 80°C)	5	98	8c
3	Sodium dodecyl sulfate (SDS)	H_2O	5-10	83	8e
4	LiCl (5 mol%)	Neat	120	95	8i
5	SCIL (3.5 mol%)	Neat	10	98	9
6	$CaCl_2$ (10 mol%)	Neat	10	97	This work

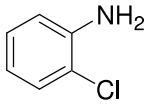
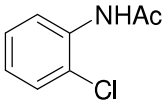
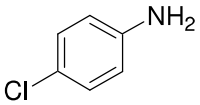
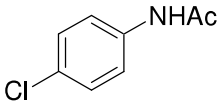
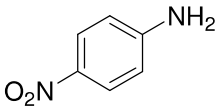
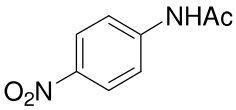
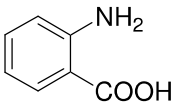
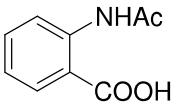
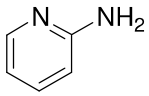
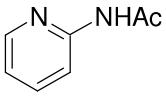
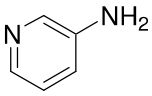
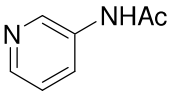
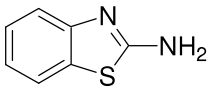
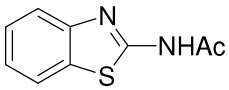
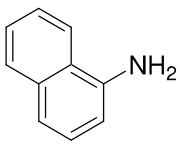
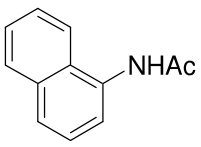
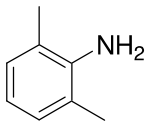
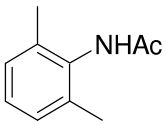
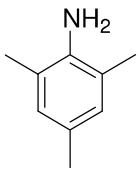
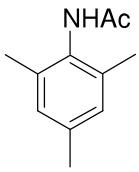
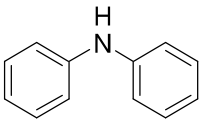
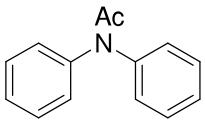
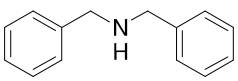
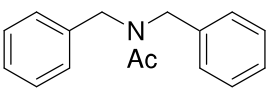
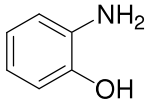
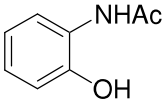
[#]Reaction conditions: Aniline: $(Ac)_2O$ (1:1), RT. MW-microwave

Table III — Synthesis of various acetamides catalyzed by $CaCl_2$

Entry	Amine	Time	Product	Yield (%)	m.p. (°C)
1		10 min		97	113-14 (114)[8i]
2		30 min		92	109-10 (112)[6]
3		20 min		95	65 (65-67)[9]
4		20 min		92	152-54 (152-53)[6]
5		25 min		92	86 (86-87)[6]
6		15 min		94	77-80
7		15 min		95	128-29 (128-30)[6]
8[#]		45 min		82	138-40
9		25 min		72	oil
10[#]		30 min		84	185-187 (186)[8i]

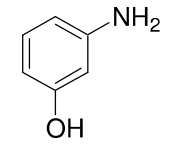
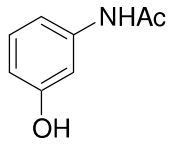
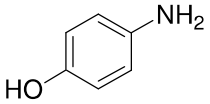
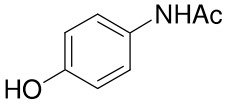
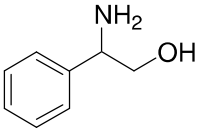
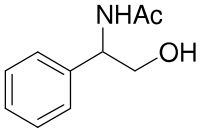
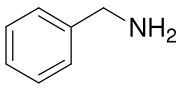
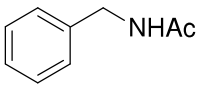
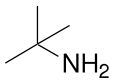
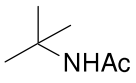
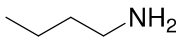
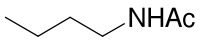
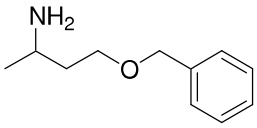
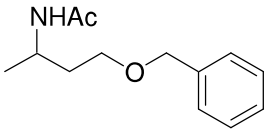
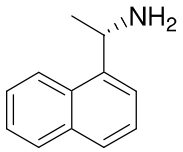
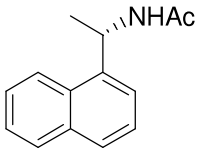
(*contd.*)

Table III — Synthesis of various acetamides catalyzed by $CaCl_2$ (*contd.*)

Entry	Amine	Time	Product	Yield (%)	m.p. (°C)
11		30 min		80	86-87 (88)[6]
12		30 min		70	177-79 (178)[6]
13		30 min		65	214 (215-16)[6]
14		45 min		80	183 (184)[6]
15		20 min		84	64-65
16		30 min		68	128-30
17		30 min		94	179-80
18		25 min		92	159-60 (158-60)[6]
19[#]		120 min		91	179-81 (181-83)[9]
20[#]		150 min		90	213-14 (211-12)[9]
21		60 min		70	101-03 (100-02)[6]
22		15 min		95	oil
23		30 min		80	207-09 (207-09)[6]

(*contd.*)

Table III — Synthesis of various acetamides catalyzed by $CaCl_2$ (*contd.*)

Entry	Amine	Time	Product	Yield (%)	m.p. (°C)
24		30 min		74	144-46 (146-48)[6]
25		30 min		72	168 (166-67)[6]
26[#]		40 min		85	oil
27		10 min		94	58-60 (60-62)[9]
28		30 min		72	oil
29		20 min		68	110-12 (111-13)[9]
30		25 min		90	oil
31		5 min		98	151-52

#2 equivalent of $(Ac)_2O$ was used

#1 mL ethyl acetate was added for 1 mmol.

3H), 7.78-8.05 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$): δ_C 168.6, 152.6, 149.0, 140.5, 130.7, 129.0, 123.9, 122.7, 122.2, 120.0, 119.8, 24.7; MS: *m/z* 240 $[M+H]^+$.

***N*-Benzothiazol-2-yl-acetamide (Entry 17,** Table III): ^{1}H NMR (200 MHz, $CDCl_3$): δ_H 2.22 (s, 3H), 7.07-7.52 (m, 2H), 7.55-7.98 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ_C 169.0, 160.1, 147.5, 131.7, 126.4, 124.0, 121.7, 120.2, 23.5; MS: *m/z* 193 $[M+H]^+$.

***N*,*N*-Dibenzyl-acetamide (Entry 22,** Table III): ^{1}H NMR (200 MHz, $CDCl_3$): δ_H 2.25 (s, 3H), 4.47 (s, 2H), 4.64 (s, 2H), 7.07-7.65 (m, 11H); ^{13}C NMR (50 MHz, $CDCl_3$): δ_C 171.1, 137.2, 136.3, 128.9, 128.5, 128.2, 127.6, 127.3, 126.3, 50.7, 47.9, 21.6; MS: *m/z* 240 $[M+H]^+$.

***N*-(2-Hydroxy-1-phenyl-ethyl)-acetamide (Entry 26,** Table III): ^{1}H NMR (200 MHz, $CDCl_3$): δ_H 2.02-2.08 (m, 3H), 3.88 (d, *J* = 4.9 Hz, 2H), 5.07 (dt, *J* = 7.1, 5.0 Hz, 1H), 6.28 (brs, 1H), 7.30-7.39 (m, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): δ_C 170.8, 138.9, 128.9, 127.9, 126.7, 66.5, 56.0, 23.3; MS: *m/z* 180 $[M+H]^+$.

***N*-Benzyl-acetamide (Entry 27,** Table III): ^{1}H NMR (200 MHz, $CDCl_3$): δ_H 1.97 (s, 3H), 4.38 (d, *J* = 5.7 Hz, 2H), 6.14 (brs, 1H), 7.08-7.46 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$): δ_C 170.0, 138.2, 128.6, 127.7, 127.4, 43.6, 23.1; MS: *m/z* 150 $[M+H]^+$.

***N*-(3-Benzyloxy-1-methyl-propyl)-acetamide (Entry 30,** Table III): ^{1}H NMR (200 MHz, $CDCl_3$): δ_H 1.08 (d, *J* = 6.7 Hz, 3H), 1.51-1.77 (m, 2H), 1.79

(s, 3H), 2.02 (brs, 1H), 3.41-3.64 (m, 3H), 3.93-4.15 (m, 1H), 4.36-4.45 (m, 2H), 6.01 (brs, 1H), 7.21-7.29 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$): δ_C 169.3, 138.1, 132.1, 131.9, 128.6, 128.4, 127.7, 127.6, 73.2, 67.6, 43.9, 35.5, 23.4, 20.2; MS: *m/z* 222 $[M+H]^+$.

(*S*)-*N*-(1-Naphthalen-1-yl-ethyl)-acetamide (Entry 31, Table III): $[\alpha]^{21}_D$ = −126.5° (*c* 1.0, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ_H 1.56-1.72 (m, 3H), 1.94 (s, 3H), 5.74-6.06 (m, 2H), 7.39-7.61 (m, 4H), 7.70-7.95 (m, 2H), 7.98-8.19 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ_C 168.9, 138.2, 133.8, 131.0, 128.7, 128.3, 126.5, 125.8, 125.1, 123.4, 122.5, 44.5, 23.2, 20.6; MS: *m/z* 214 $[M+H]^+$.

Conclusion

In conclusion, we described here a simple, convenient and environment-friendly protocol for the acetamide synthesis using $CaCl_2$ as a mild and cheap catalyst under solvent free conditions. The present protocol shows several advantages such as high yields, shorter reaction times in minutes, safe handling, clean reactions, excellent selectivity and low cost. We envisage that this new method would be used as an alternative to other existing methods for the acetamide synthesis.

Supplementary Information

Supplementary information is available in the website http://nopr.niscair.res.in/handle/123456789/60.

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A STUDY OF ROUTING PROTOCOL IN WIRELESS SENSOR NETWORK

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Abstract*:* Wireless sensor network is emerging field because of its wide applications. It is a wireless network which subsist a group of small sensor nodes which communicate through radio interface. The four basic elements of these sensor nodes are sensing, computation, communication, and control. With the notion that there will be cases for energy awareness, many routing, power management, and data dissemination protocols have been explicitly developed for wireless sensor networks. However, the key resource constraints are limited energy, communication capability, storage, and bandwidth. The flexibility, fault tolerance, high sensing fidelity, low cost, and rapid deployment characteristics of sensor networks create many new and exciting application areas for remote sensing. Our survey is based on various aspects of routing protocols in wireless sensor networks.
Keywords: WSN, Sensor nodes, Routing, Ad hoc networks

I INTRODUCTION OF WSN

Wireless Sensor Networks (WSNs) have begun to draw the attention of researchers with the fast technical advancement of wireless technologies and embedded electronics. A standard WSN consists of small devices that are known as nodes. New technologies and standards are used for wireless sensor networks. They include lightweight, energy-efficient machines, co-design of hardware/software, and support for networking. Wireless sensor networks are now an integral part of everyday, technological and military systems of everyday life. As new technologies are evolving and new applications are being created, this is a fast-growing field. These nodes have a built-in CPU, some intelligent sensors and minimal processing power. Nodes are used with these sensors to track environmental conditions such as heat, humidity, vibration and noise surrounding them. In every WSN, a node usually includes a transceiver unit, a sensor controller, a computer unit, and a control unit. By having nodes capable of communicating with each other to relay data collected by their sensors, these units perform critical tasks. To have a centralised structure, coordination between the nodes is essential. The need for this device contributes to the growth of the notion of the internet of things (IoT).

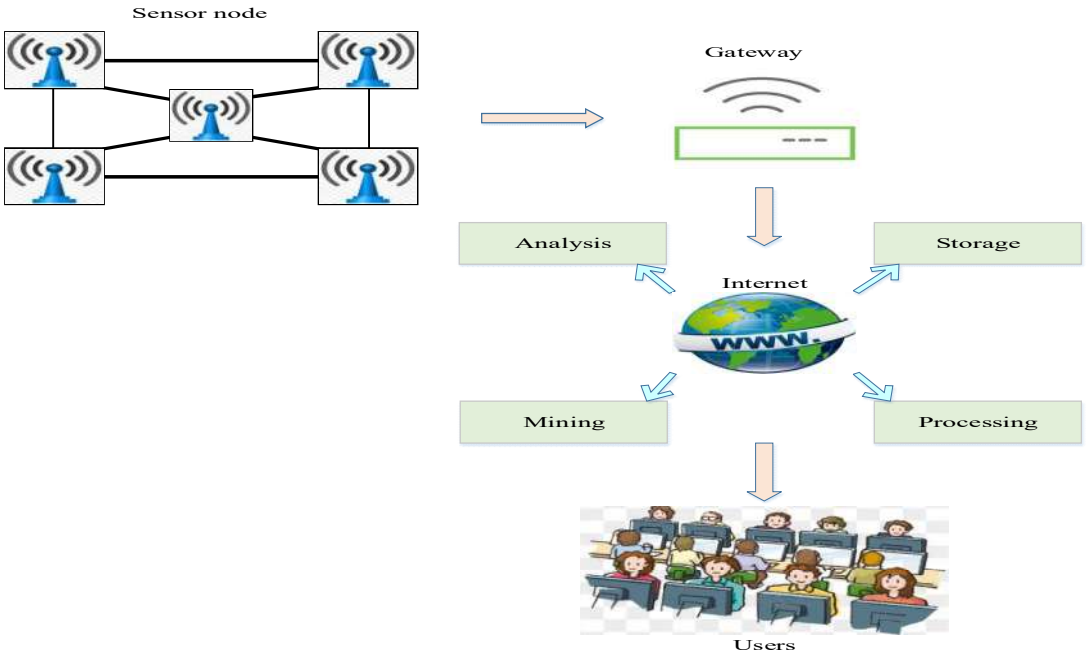

Figure 1: Architecture of WSN.

A WSN may usually be described as a network of nodes that act in a cohesive way to sense and regulate the world around them. Through wireless networks, these nodes are linked. This relation is used by nodes to communicate with each other. There are 3 elements in the structure of a standard WSN such as sensor nodes, internet and user nodes. The sensor area constitutes sensor nodes and gateways. Gateways and observers are linked by special networks or, most often, through the internet

II. COMPONENTS OF WSN

A WSN consists of multiple sensor numbers and a gateway to offer an Internet connection. The components of WSNs are sketched in figure 9.

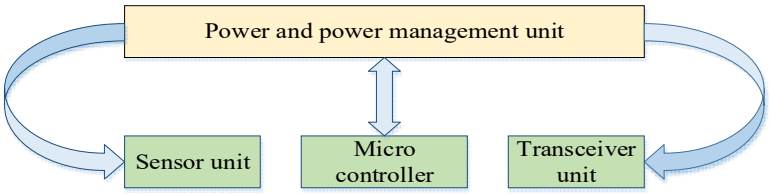

Figure 2: Components of WSN

Sensor Unit

A sensor node is a compact computer with a low power supply. While it has small energy capacity, it has a simultaneous processing role and has a low price as well. Individual units of a sensor node accomplish data collection and data transfer steps. The power source is located at the base of the sensor node. It provides power for different sensor node devices, such as sensor units, radio and CPU.

Microcontroller

Usually, a microprocessor and a flash memory are made of the CPU of a sensor. It provides connectors for most sensor nodes that can easily add external processing units and sensors to the main device. For the critical functions of the CPU, decision-making and coping with collected data can be identified as examples.

Transceiver

It's responsible for a sensor node's wireless communications. The transceiver primarily has four working conditions such as receive, transmit, idle and sleep. Radio Frequency (RF) and Infrared Laser can be selected as wireless networks in the transceiver. For WSNs, RF is commonly favoured among these wireless communication technologies. The standard RF range of operation is 10s of indoor meters and 100s of outdoor meters.

III. ROUTING PROTOCOLS IN WSNS

Depending on the network layout, routing in WSNs can in general be divided into flat-based routing, hierarchical-based routing, and location-based routing. All nodes are usually allocated equivalent roles or features in flat-based routing. Nonetheless, in hierarchical-based routing, nodes can perform various network functions. In location-based routing, the locations of the sensor nodes are exploited to route network data. In order to adjust to current network conditions and available energy levels, a routing protocol is called adaptive if certain device parameters can be managed. In fact, these protocols can, depending on the protocol operation, be divided into query-based, negotiation-based, multipath-based, QoS-based, or coherent-based routing techniques. In addition to above, based on how well the source flows a path to the destination, routing protocols can be divided into three sets, namely proactive, reactive, and hybrid protocols. In proactive protocols, all routes are calculated before they can be really required, whereas routes are computed on demand in reactive protocols. A mixture of these two thoughts is used by hybrid protocols. If sensor nodes are fixed, instead of using reactive protocols, it is preferable to have table guided routing protocols. In the route discovery and configuration of reactive protocols, a significant amount of energy is used. Cooperative routing protocols are called another class of routing protocols. Nodes send data to a central node in cooperative routing, whereby data could be aggregated and further processed, thus reducing path costs in terms of energy usage. Many other protocols are based on timing and information.

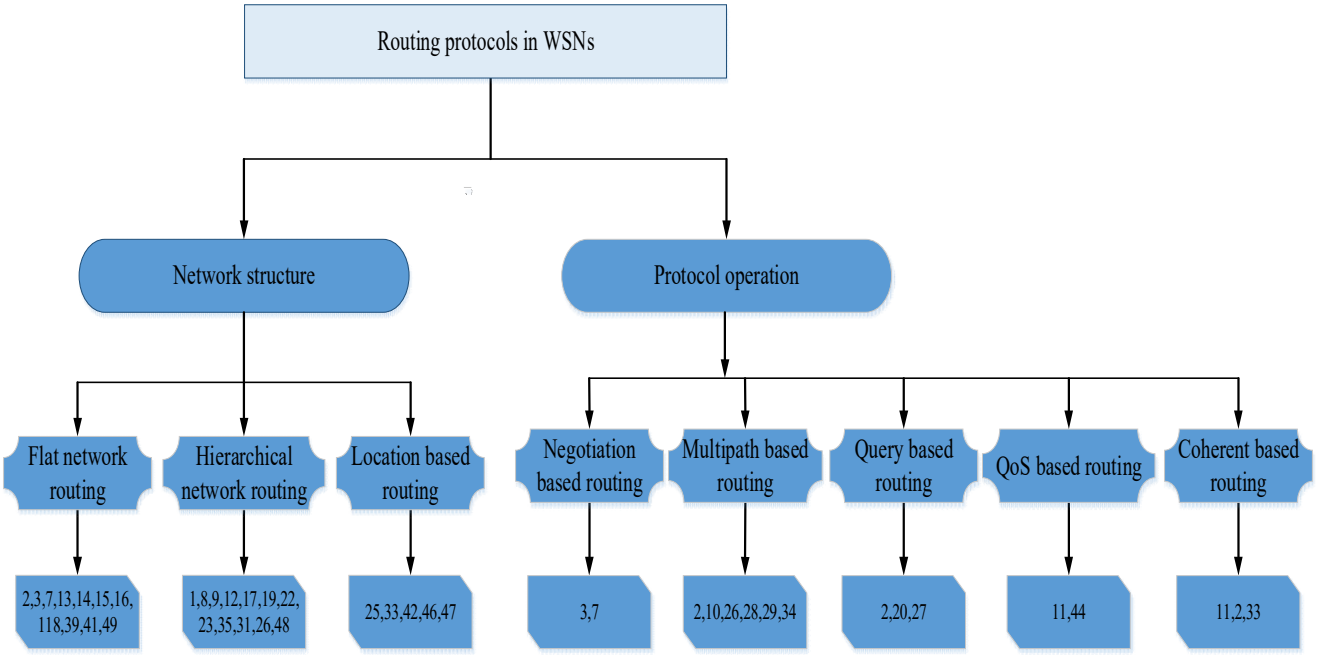

Figure 3: Routing protocols in WSNs

(i) Network Structure Based Routing Protocols

In the application of the routing protocol within WSNs, the underlying network structure may play a significant role. In this chapter, we discuss most of the protocols that come under this category in detail.

A. FLAT NETWORK ROUTING

Multi-hop flat routing protocols are the first type of routing protocols. Each node usually plays the same function in flat networks and sensor nodes cooperate to conduct the sensing task collectively. This is not feasible to allocate each node a global identifier due to the large number of such nodes. . Such factor has resulted in data centred routing, where the BS sends queries to some regions and waits for sensor data located in the regions selected.

Sensor Protocols for Information via Negotiation (SPIN):

About Heinzelman et.al. A family of adaptive protocols called Sensor Protocols for Information through Negotiation (SPIN) was proposed to disseminate all the information at each node in a network, suggesting that all nodes in the network are possible access points. This allows any node to be queried by a user and get the necessary details instantly [45]. Such protocols make the use of premise that identical data is available to nodes in close proximity, so it is only necessary to transmit the information which other networks do not have.

Directed Diffusion:

Directed diffusion is a common data aggregation model for WSNs that has been proposed. Directed diffusion is a data-centric (DC) and application-aware paradigm in the sense that all data provided by sensor nodes is called by attribute-value pairs. The key concept behind the DC model is to integrate data from different sources en route by removing redundancy and reducing the number of transmissions, saving network resources and extending its lifespan. Unlike conventional end-to-end routing, DC routing searches for routes from different sources to a single destination, enabling redundant data to be consolidated within the network. In Directed diffusion, sensors quantify events and establish information gradients in their immediate surroundings.

Rumour Routing:

Rumour routing is a form of guided diffusion that is used in situations where geographic routing is not possible. When there is no regional requirement to diffuse activities, guided diffusion uses flooding to inject the query through the entire network. However, in some situations, the amount of data required from the nodes is insignificant, and flooding is therefore unnecessary. If the number of events is small but the number of queries is high, flooding the events is an alternative.

Minimum Cost Forwarding Algorithm (MCFA):

The MCFA algorithm takes advantage of the fact that the routing path, that is, towards the fixed external base-station, is always known. As a result, a sensor node does not need a unique ID or the maintenance of a routing table. Instead, each node keeps track of the cheapest route from itself to the base station. Each message that the sensor node needs to forward is broadcast to its neighbours.

Gradient-Based Routing:

Gradient-Based Routing is a variant of guided diffusion suggested by Schurgers (GBR). When the interest is dispersed throughout the entire network, the main concept in GBR is to memorise the number of hops. As a result, each node can measure a parameter known as the node's height, which is the minimum number of hops required to reach the BS. The gradient on a connection is defined as the

difference in height between a node and its neighbour. The highest gradient connection is used to forward a packet.

Information-driven sensor querying (IDSQ) and Constrained anisotropic diffusion routing (CADR):

Information-driven sensor querying (IDSQ) and constrained anisotropic diffusion routing (CADR) are two routing techniques proposed in. CADR aspires to be a broad definition of guided diffusion. The main concept is to query sensors and route data through the network in such a way that information gain is maximised while latency and bandwidth are reduced. CADR diffuses queries by selecting which sensors should receive data based on a set of information parameters. This is accomplished by only triggering sensors that are in close proximity to a specific event and dynamically changing data routes.

COUGAR:

COUGAR, a data-centric protocol, sees the network as a massive distributed database system. The main concept is to use declarative queries to separate query processing from network layer functions such as sensor selection and so on. To save even more resources, COUGAR uses in-network data aggregation. An additional query layer sits between the network and application layers to facilitate the abstraction. COUGAR includes a sensor database system architecture in which sensor nodes choose a leader node to conduct data aggregation and transmission to the BS.

ACQUIRE:

Sadagopan proposed the Active Query Forwarding In Sensor Networks (ACQUIRE) technique for querying sensor networks. ACQUIRE, like COUGAR, sees the network as a distributed database where complex queries can be broken down into several sub questions. The following is a summary of how ACQUIRE works. The BS node sends out a query, which is forwarded to each node that receives it. During this time, each sensor node tries to partially respond to the query by using pre-cached information before passing it on to another sensor node. If the pre-cached information is out of date, the nodes look up information from their neighbours within d hops. Once the question has been fully resolved, it is sent back to the BS via the reverse or shortest direction.

Energy Aware Routing:

The aim of the energy-aware routing protocol, which is a destination initiated reactive protocol, is to extend the lifetime of the network. While similar to guided diffusion, this protocol differs in that it maintains a number of paths rather than maintaining or implementing one optimal path at higher rates. These paths are held and chosen based on a collection of probabilities. The value of this probability is determined by how low each path's energy consumption can be reduced. The energy of any single path would not deplete quickly because the paths were chosen at different times. As energy is dissipated more evenly over all nodes, this can result in a longer network lifetime. The protocol's key metric is network survivability.

Routing Protocols with Random Walks:

The aim of the random walks-based routing technique is to achieve load balancing in WSNs using multi-path routing in a statistical sense. Only large-scale networks with very restricted mobility are included in this technique. Sensor nodes are assumed to be switched on and off at random times in this protocol. Furthermore, each node has its own unique identifier, but no information about its location

is needed. The topology may be irregular, but nodes were arranged so that each node falls exactly on one crossing point of a normal grid on a plane.

B. HIERARCHICAL ROUTING

Hierarchical or cluster-based routing, originally proposed in wire line networks, are well-known techniques with special advantages related to scalability and efficient communication. As such, the concept of hierarchical routing is also utilized to perform energy efficient routing in WSNs. In a hierarchical architecture, higher energy nodes can be used to process and send the information while low energy nodes can be used to perform the sensing in the proximity of the target.

LEACH protocol

Low Energy Adaptive Clustering Hierarchy was introduced by Heinzelman as a hierarchical clustering algorithm for sensor networks (LEACH). LEACH is a cluster-based protocol that involves the creation of distributed clusters. LEACH selects a few sensor nodes at random as cluster heads (CHs) and rotates them to spread the energy load equally across the network's sensors. To minimise the amount of data that must be transmitted to the base station, the cluster head (CH) nodes compress data arriving from nodes belonging to the respective cluster and send an aggregated packet to the base station. To minimise inter-cluster and intra-cluster collisions, LEACH employs a TDMA/CDMA MAC.

Power Efficient Gathering in Sensor Information Systems (PEGASIS):

It was suggested that the LEACH protocol be improved. PEGASIS (Power Efficient Gathering in Sensor Information Systems) is a chain-based protocol that is near optimal. The protocol's basic concept is that nodes only need to connect with their nearest neighbours in order to expand network lifetime, and they take turns communicating with the base station. A new round will begin when the round with all nodes interacting with the base-station ends, and so on. Since the power draining is distributed evenly over all nodes, the power needed to transfer data per round is reduced. As a result, PEGASIS has two primary goals. To begin, use collective techniques to extend the lifetime of each node, resulting in a longer network lifetime. Second, only allow local collaboration between nodes that are close together to minimise communication bandwidth use. Unlike LEACH, PEGASIS does not form clusters and instead sends data to the BS through a single node in a chain rather than multiple nodes.

Threshold-sensitive Energy Efficient Protocols (TEEN and APTEEN):

TEEN (Threshold-sensitive Energy E–cient sensor Network protocol) and APTEEN (Adaptive Periodic Threshold-sensitive Energy E–cient sensor Network protocol) are two hierarchical routing protocols proposed for time-critical applications [51]. Sensor nodes continuously sense the medium in TEEN, but data transmission is done less frequently. A cluster head sensor gives its members a hard threshold, which is the sensed attribute's threshold value, and a soft threshold, which is a minor shift in the sensed attribute's value that causes the node to turn on its transmitter and transmit. As a result, the hard threshold attempts to minimise transmissions by allowing nodes to transmit only when the sensed attribute is within the range of interest. If there is little to no shift in the sensed attribute, the soft threshold decreases the number of transmissions that would otherwise occur.

Small Minimum Energy Communication Network (MECN):

By using low power GPS, a protocol is proposed that computes an energy efficient sub network, namely the minimum energy communication network (MECN), for a specific sensor network. Every node in MECN is assigned to a relay area. The relay region is made up of nodes in the immediate vicinity where transmitting through those nodes saves energy over direct transmission. The union of all relay regions that node I can access is then used to establish the enclosure of node i. MECN's main goal is to find a sub-network with a smaller number of nodes and lower power requirements for transmission between any two nodes.

Self-Organizing Protocol (SOP):

Subramanian et al. define a self-organizing protocol and an application taxonomy that were used to create heterogeneous sensor architecture. These sensors may also be mobile or stationary. Some sensors collect data from the atmosphere and send it to a group of nodes that serve as routers. The backbone of communication is formed by router nodes, which are stationary. The collected data is forwarded to the more powerful BS nodes via routers.

Sensor Aggregates Routing:

The authors proposed a series of algorithms for constructing and preserving sensor aggregates. The aim is to control target behaviour in a specific setting as a group (target tracking applications). A sensor aggregate is made up of nodes in a network that meet a predicate for grouping in a collaborative processing activity. The predicate's parameters are determined by the mission and its resource requirements. In terms of allocating resources to sensing and communication tasks, the creation of suitable sensor aggregates was addressed. Sensors in a sensor area are grouped into clusters based on the frequency of their sensed signal, with only one peak per cluster.

Virtual Grid Architecture routing (VGA):

An energy efficient routing paradigm is proposed that utilizes data aggregation and in-network processing to maximize the network lifetime. Due to the node stationarity and extremely low mobility in many applications in WSNs. A GPS-free approach is used to build clusters that are fixed, equal, adjacent, and non-overlapping with symmetric shapes. Square clusters were used to obtain a fixed rectilinear virtual topology. Inside each zone, a node is optimally selected to act as cluster head. Data aggregation is performed at two levels: local and then global.

Hierarchical Power-aware Routing (HPAR):

A power-aware hierarchical routing was suggested. The protocol divides the sensor network into classes. Each zone is made up of a group of sensors in close proximity, and each zone is regarded as a separate entity. To perform routing, each zone is given the freedom to choose how a message will be routed hierarchically through the other zones, maximising the battery life of the system's nodes. The max-min course, which has the maximum over all the minimum of the remaining capacity, is used to route messages. The reason for this is that using nodes with high residual power can be more costly than taking the path with the least amount of power consumption. The max-min zPmin algorithm is an approximation algorithm.

C. LOCATION BASED ROUTING PROTOCOLS

Sensor nodes are addressed by their positions in this form of routing. On the basis of incoming signal strengths, the distance between neighbouring nodes can be calculated. By sharing such information between neighbours, relative coordinates of neighbouring nodes can be obtained. If nodes are fitted

with a small low-power GPS receiver, the location of nodes can also be obtained directly by communicating with a satellite via GPS (Global Positioning System).

Geographic Adaptive Fidelity (GAF):

GAF is an energy-aware location-based routing algorithm designed primarily for mobile ad hoc networks, but may be applicable to sensor networks as well. The network area is flrst divided into fixed zones and form a virtual grid. Inside each zone, nodes collaborate with each other to play different roles.

MFR, DIR, and GEDIR:

Simple distance, development, and direction-based approaches are covered in these protocols. The most important topics are forward and backward movement. Any intermediate node or source node will choose one of its neighbours based on a set of criteria. MFR (Most Forward inside Radius), GEDIR (The Geographic Distance Routing), a variation of greedy algorithms, 2-hop greedy method, alternative greedy method, and DIR are all routing methods that fall into this group (compass routing method).

IV. CONCLUSION

One of the newest areas of study is wireless sensor networks. Sensor networks' versatility, fault tolerance, high sensing fidelity, low cost, and fast deployment characteristics open up a slew of new and exciting remote sensing applications. Sensor networks will become an important part of our lives in the future as a result of this broad variety of application areas. The ability to track environmental and physical conditions is a unique advantage of wireless sensor networks. We addressed different types of routing protocols for wireless sensor networks in this paper. Sensor networks will become an integral part of our lives in the future due to their wide range of applications. One of the most promising areas for future research is the energy efficiency of wireless sensor networks. Due to the limited energy resources of sensors, one of the main challenges in designing routing protocols for WSNs is energy efficiency. The ultimate goal of the routing protocol is to keep the sensors running for as long as possible, extending the network's lifespan. Data transmission and reception account for the majority of the sensors' energy consumption. As a result, WSN routing protocols should be as energy efficient as possible in order to extend the lifetime of individual sensors, and thus the network's lifetime. We surveyed a sample of routing protocols in this paper, taking into account a variety of classification criteria such as location information, network layering and in-network processing, data centricity, path redundancy, network dynamics, QoS requirements, and network heterogeneity.

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A STUDY OF CRYPTOGRAPHY AND TECHNIQUES OF CRYPTOGRAPHY

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Abstract: — Security and privacy of information and communication have become very important aspects in today's era, which is experiencing a burst of technological innovation like never before. The benefits of cryptography and cryptanalysis can be found here. Cryptography ensures the integrity, availability, and identity of users, as well as the confidentiality, authentication, and protection and privacy of data that can be given to them. We described and analysed symmetric cryptographic algorithms such as DES, Triple DES, Blowfish, AES, and IDEA, as well as asymmetric key cryptographic algorithms such as RSA, in this paper. They were evaluated in terms of data security, key size, block size, and functionality. We've also dabbled in DNA cryptography, Elliptic Curves-based cryptography, and Quantum cryptography, all of which are newer trends in the field of cryptography but, in our opinion, have enormous potential.

Keywords: Cryptography, Encryption, DES, RC5, Triple DES, AES, RSA, Quantum Cryptography, DNA Cryptography

Article History

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I INTRODUCTION OF CRYPTOGRAPHY

Cryptography is the study of writing in secret code and is an ancient craft; the first documented use of cryptography in making dates back to about 1900 B.C., when an Egyptian recorder drew with non-standard pictographs. Cryptography came out of nowhere at some stage or another in the wake of making, with applications ranging from assuaging notes to war-time battle designs, according to many experts. It's not surprising that new types of cryptography appeared not long after the improvement in PC communications, regardless of how you look at it. Cryptography is fundamental in data and telecommunications when dealing with any untrusted medium,

which melds for all intents and purposes any structure, especially the Internet. There are some explicit security basics within the context of any application-to-application communication, including:Authentication: The path toward displaying one's character. (The fundamental sorts of host-to-have approval on the Internet today are name-based or address-based, the two of which are comprehensively slight.)

- Privacy/insurance: Ensuring that nobody can look at the message adjacent to the orchestrated gatherer.
- Integrity: Assuring the expert that the got message has not been changed at all from the first.
- Non-revocation: A section to demonstrate that the sender incredibly sent this message.

At that time, cryptography had been developed to protect data from theft or alteration, as well as to be used for customer verification. When in doubt, three types of cryptographic plans are consistently used to achieve these objectives: confuse key (or symmetric) cryptography, open key (or hilter kilter) cryptography, and hash works, all of which are depicted below. The simple decoded information is indicated as plaintext in all cases.

It is mixed into figure material, which will be decoded into accessible plaintext in this manner (for the most part). Two passing on gatherings would be proposed as Alice and Bob in a vital heap of the depictions beneath; this is the usual wording in the crypto sector and writing to make it less perplexing to see the passing on gatherings. They would be referred to as Carol and Dave if there is a third or fourth gathering to the correspondence. Eve is an eavesdropper, and Trent is a confided in outcast. Mallory is a pernicious get-together, Eve is an eavesdropper, and Trent is a confided in outcast.

II. STUDY OF CRYPTOGRAPHY

2.1 Types of Cryptography Algorithms

There are a few distinct procedures for dealing with cryptographic checks. For inspirations driving this paper, they will be coordinated reliant on the proportion of keys that are used for encryption and unscrambling, what's more portrayed by their application and use. The three sorts of estimations that will be analyzed are:

- Public Key Cryptography (PKC): Uses one key for encryption and another for unscrambling
- Secret Key Cryptography (SKC): Uses a solitary key for both encryption and unscrambling

- Hash Functions: Uses a numerical change to irreversibly "encode" data

2.2.1 Public Key Cryptography (PKC):

Public key cryptography has been same to be the foremost basic new overhaul in cryptography within the last 300-400 years. Gift day PKC was 1st sketched out freely by Stanford University teacher Martin Hellman and graduate understudy Whitfield Diffie in 1976. Their paper delineate a 2-enter crypto framework during which two get-togethers might worth a protected correspondence over a non-secure interchanges channel while not sharing an issue key.

- PKC depends upon the closeness of expected unidirectional works, or numerical limits that area unit verifiably not laborious to laptop whereas their opposite limit is often laborious to method. Empower Pine Tree State to allow each of you organize points of view:
- While the points of read higher than area unit insignificant, {they do|they area unit doing} address 2 of the practical sets that are used with PKC; to be express, the straightforwardness of duplication and operation versus the final weight of computation and enrolling logarithms, severally. the real "trap" in PKC is to seek out a gizmo passage in quite so much with the target that the contrary estimation lands up being basic given learning of one thing of knowledge. One key's accustomed inscribe the plaintext and also the different key's accustomed unravel the figure content. The essential purpose here is that it does not have any reasonably impact that key's connected 1st, at any rate that each keys area unit needed for the framework to figure. Since match of key's needed, this method is aside from referred to as uneven cryptography.

2.2.2 Secret Key Cryptography:

With Secret key cryptography, a singular key's used for each secret writing and unscrambling. As showed up in Figure 1A, the sender uses the key (or some course of action of checks) to inscribe the plaintext and sends the figure substance to the beneficiary. The recipient applies a comparable key (or run set) to disentangle the message and recover the plaintext. Since a selected key's used on the far side what several would take into account doable, mystery key cryptography is additionally referred to as even secret writing.

With this type of cryptography, clearly the key should be proverbial to each the sender and also the recipient; that, no 2 ways in which regarding it, is that the mystery. the most effective issue with this approach, obviously, is that the division of the key.

Secret key cryptography structures area unit usually requested as being either stream figures or sq. figures. Stream figures wear out one piece (byte or laptop word) like a shot and see a sort of investigation structure with the target that the key's faithfully demonstrating modification. A sq. figure is expressed in lightweight of the approach during which that the arrangement encodes one sq. of information at some irregular minute employing a comparable key on every sq.. With everything thought-about, the proportionate plaintext sq. can perpetually scramble to a comparative figure content whereas employing a shut key in a very sq. figure whereas the identical plaintext can inscribe to totally different figure message in a very stream figure.

Stream figures arrive in a very few flavors regardless 2 realism creating relevancy here. Self-synchronizing stream figures figure every bit within the key stream as a small amount of the past n bits within the key stream. it's named "self-synchronizing" in lightweight of the approach that the unscrambling procedure will keep synchronal with the secret writing framework primarily by knowing however so much into the n-bit key stream it's.

Electronic Codebook (ECB) mode is that the base difficult , most clear application: the mystery key's accustomed scramble the plaintext sq. to plot a figure content sq.. 2 not well characterised plaintext obstructs, by then, can perpetually create a for all intents and functions indistinguishable figure content sq..despite the approach during which this can be the foremost wide ascertained framework for sq. figures, it's helpless against a game-plan of brute power ambushes.

Cipher Block Chaining (CBC) mode adds AN investigation instrument to the secret writing plot. In CBC, the plaintext is simply O Red (X O Red) with the past figure content sq. before secret writing. during this mode, 2 dim squares of plaintext ne'er inscribe to a relative figure content.

Cipher Feedback (CFB) mode may be a sq. figure use as a self-synchronizing stream figure. CFB mode connects with information to be mixed in units a lot of minor than the unit of measurement, which could be prodigious in a very few uses, for example, secret writing savvy terminal information. If we have a tendency to were victimisation 1-byte CFB mode, as an example, every progressing toward character is about into a move choose

unclear size from the sq., encoded, and also the sq. transmitted. At the continued facet, the figure content is decoded and also the further bits within the sq. (i.e., everything right past the one byte) area unit discarded.

Output Feedback (OFB) mode may be a sq. figure use sanely sort of a synchronous stream figure. OFB keeps the relative plaintext keep from creating a comparable figure content sq. by victimisation AN inward examination half that's freed from each the plaintext and figure content piece streams.

Secret key cryptography figuring's that area unit being employed nowadays include:

Data Encryption commonplace (DES):

The most loosely ascertained SKC conspire used nowadays, DES was planned by IBM amid the Nineteen Seventies and understood by the National Bureau of Standards (NBS) [now the National Institute for Standards and Technology (NIST)] in 1977 for business and unclassified government applications. DES may be a sq. figure employing a 56-bit key that deals with 64-bit squares.

DES incorporates a gorgeous approach of models and changes that were pictured particularly to yield snappy equipment executions and moderate programming use, paying very little relevance however this last purpose is ending up less basic nowadays since the speed of laptop processors may be a few posing for of degree speedier nowadays than twenty years sooner.

IBM besides planned a 112-piece key for DES, that was rejected at the time by the affiliation; the utilization of 112-piece keys was thought-about amid the Nineteen Nineties, in any case, modification was ne'er really thought-about.

Hash Functions:

A hash function is any limit that may be used to stipulate of zealous size to data of a settled size. The attributes came back by a hash work area unit known as hash respects, hash codes, digests, or simply hashes. Hash limits area unit in several cases used in an exceedingly combine with a hash table, a standard data structure used in laptop programming for good data request. Hash limits invigorate table or information question by perceiving

reproduced records in an exceedingly general report. One such application is finding equivalent stretches in deoxyribonucleic acid game-plans.

2.2.3 Symmetric Key Cryptography

Symmetric-key cryptography implies encoding methods within which each the sender and beneficiary provide a comparative key (or, less normally, within which their keys area unit exceptional, however connected in an exceedingly viably measurable way). This was the elemental quite encoding in public well-known till Gregorian calendar month 1976.

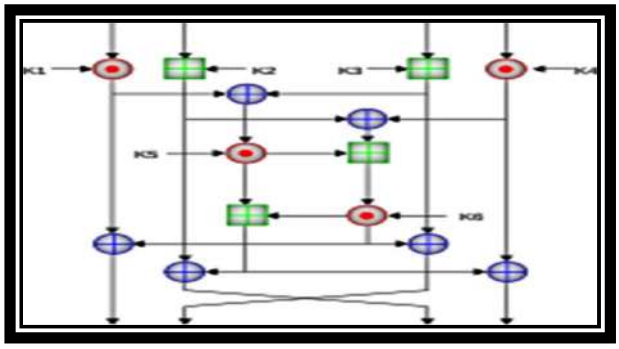

Fig 1.1Symmetric Key Cryptography

Symmetric-key cryptography construes encoding systems within which each the sender and master provide a comparable key (or, less for the foremost half, within which their keys area unit uncommon, at any rate-related in an exceedingly tastily quantitative manner). This was the focal quite encoding in public well-known till Gregorian calendar month 1976.

- One spherical (out of eight.5) of the secured plan cipher, used in an exceedingly few types of PGP for snappy encoding of, for instance, email.
- The contemporary examination of symmetric-key ciphers relates by and enormous to the examination of sq. ciphers and stream ciphers and to their applications. A sq. cipher is, therefore to talk, a up-to-date embodiment of Alberti's polyalphabetic cipher: sq. ciphers take as data a sq. of plaintext and a key and yield a sq. of cipher substance of an identical size. Since messages area unit systematically longer than a solitary sq., some framework for weaving along distinctive squares is needed. a handful has been created, some with favored

security in some purpose of read over others. they're the system for activities and have to be compelled to be purposefully determined as whereas utilizing a sq. cipher in an exceedingly cryptosystem.

- The encryption normal (DES) and also the Advanced encoding normal (AES) area unit sq. cipher plans that are parceled out cryptography norms by the United States government (in any case DES's assignment was at long last force back when the AES was gotten). Despite its swing down as a politician normal, DES (particularly its still-guaranteed associate degreed generously progressively secure triple-DES assortment) remains to a good degree observable; it's used over an expansive arrangement of employment, from ATM encoding to email protection and secures remote access. completely different alternative sq. ciphers are formed and discharged, with associate degree expansive sort of quality. several are utterly broken. See Category: Block Ciphers.
- Stream ciphers, rather than the 'square' kind, build a dynamically long stream of key material, or, toward the day's finish the plaintext a touch at some random minute or character-by-character, to some extent just like the one-time cushion. in an exceedingly stream cipher, the yield stream is formed smitten by an indoor state that changes because the cipher works. That physical change is controlled by the key, and, in some stream ciphers, by the plaintext stream moreover. RC4 could be a case of a noted and totally used stream cipher; see Category: Stream Ciphers.
- Cryptographic hash capacities (much of the time known as message method capacities) do not for the foremost half use keys, however area unit a connected and elementary category of science tallies. They take input data (reliably an entire message), and yield a brief, settled length hash, and do everything thought of as a unbroken limit. permanently ones, impacts (two plaintexts that die a close to hash) area unit to associate degree uncommon degree laborious to find.
- Message confirmation codes (MACs) area unit abundant kind of like science hash capacities, with the exception of that a secret secret is used to endorse the hash a assistance on receipt. These sq. a entice against plain hash capacities.

IV. CONCLUSION

The cryptographic world is evolving in ways it has never seen before. Newer and more modern approaches are becoming more popular. We have attempted to address Cryptography in all of its facets in this article. We've addressed elements of both traditional and modern cryptographic methods in this study of reverie. In this field,

the possibilities are limitless. In today's world, where information is force, security and privacy are not taken for granted. Cryptography and cryptanalysis are extremely useful tools that can make a big difference, but they should be used with extreme caution.

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Design And Development Of Microcontroller Base Pulse Oximeter

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Abstract:

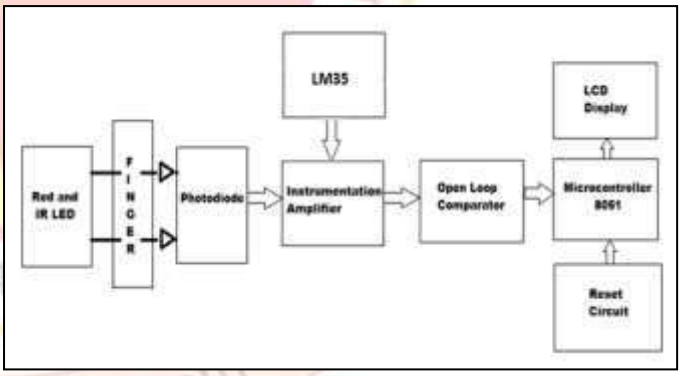
Percentage oxygen saturation in blood, Heart rate and the Body temperature are the prominent parameters to be known by the medical Technicians and Doctors for knowing the patient's health condition in general and in the situations like Covid-19 in particular, since the Doctor gets less than three minutes to survive the patient when the percentage oxygen level in blood starts going below the critical value of 89% followed by lowering of the heart rate. Here the designing of microcontroller based pulse oximeter is proposed in order to have direct [Non invasive] measurement of % oxygen saturation in the blood and the heart rate by even a non medical person. Microcontroller, a dedicated processor is universally employed in almost all the electronic gadgets, devices and machines which are popularly identified as embedded systems and have applicability in almost every field inclusive of biomedical electronics for the accurate, fast and even online readings. Also the designing of such pulse oximeter will be cost effective and hence can be used at small hospitals and even at small places

Index Terms - Percentage oxygen saturation in blood, Heart Rate, Covid-19, Non invasive, Dedicated Processor, Gadgets, Embedded Systems

1. Introduction

Entire circuit on a single chip is a concept of embedded system and it came into existence with the development of microcontrollers. Almost all the systems built around microcontrollers today follows the basic steps like sensing, processing and displaying or outputting the result as per the requirement. Since it's a dedicated system or a processor with limited amount of RAM, ROM, timer and counters; they are identified as a SYSTEM ON CHIP. The systems built around the microcontrollers are having an added advantage of portability. Here in this paper, the microcontroller is proposed to be used with the associated circuitry for the measurement of all the three prominent parameters namely Percentage oxygen saturation in blood, Heart rate and the Body temperature, which are considered as the most important parameters in a situation like COVID-19.Though the microcontroller 8051 is shown in the block diagram; since the parameters to be measured needs utmost accuracy being health related, hence one has to move to the higher versions of the microcontroller accordingly.[1]

2. Proposed Block Diagram



3. Various blocks in a Block Diagram

3.1 Red and IR LED & Photodiode:

Generally, two common methods are used in pulse oximetry namely; the ***Reflectance and the transmittance*** method. Of which the **transmittance method** is used here. Light from the Red LED (660 nm wavelength) and IR (Infrared) LED (940nm wavelength) is passed through the tissues of the finger and detected at the other end by the photo detector. Oxygenated hemoglobin absorbs more infrared light and allows more red light to pass through whereas Deoxygenated hemoglobin absorbs more red light and allows more infrared light to pass through. The change is detected by the photo

detector and the equivalent electrical signal (voltage) is obtain at its output. [2]

3.2 IC LM35:

Is a 3 terminal temperature sensor IC measuring the temperature in °C in the range of -55 °C to 150 °C with accuracy of ±0.5%. Universally the body temperature is measured in °C and hence the IC LM35 is chosen.

3.3 Instrumentation Amplifier:

Receives both the above measurand. Basically a Differential amplifier equipped with input buffer amplifiers (To eliminate the need for input impedance matching). Hence useful in measurement and test equipment from heavy duty industrial automation to precision medical devices.

When light from LEDs passes through tissues the interference of unwanted light signals (noise) takes place and the signal received by the photodiode may be with noise. The Instrumentation Amplifier has an advantage to measure small signal in noisy environment and hence are used for great accuracy and stability.

3.4 Open loop Comparator:

Compares, One Analogue signal with another or a reference voltage and outputs a binary signal based on the comparison. The comparator is basically an analogue-to-digital converter.

3.5 Microcontroller:

Needs to be programmed for the inputs received from the open loop comparator and sending the result i.e. Pulse Rate, Percentage Oxygen saturation in the blood and the body temperature in °F to LCD display. All computation part is done inside the controller.

3.6 LCD Display:

Is a 16x4 LCD Display used for displaying the actual Pulse rate, Percentage Oxygen saturation in the blood and the body temperature.

3.7 Reset Circuitry:

Resets the microcontroller, clearing the display so as to take the next measurement. [3]

4. Data processing:

Here the data for three major parameters namely percentage oxygen saturation in blood and heart rate from the photo detector's output and the body temperature from the IC LM35 will be received by the instrumentation amplifier at the first stage where the noiseless data will only be outputted by the instrumentation amplifier as it being the quality of an instrumentation amplifier and will be forwarded to the microcontroller through the open loop comparator (where these parameters will be compared with the standard or reference values for the further processing; for which the microcontroller needs to be programmed. On manipulating these parameters with the help of microcontroller the result will be displayed at LCD output. After taking the readings from the display to reset the system the reset circuitry is used, this will allow taking the readings for the next. [4]

5. Conclusion:

Ultimate intention behind the designing of pulse oximeter is to have quality and in time health assistance and is a great concern and the basic need in the medical field. Though, today's Multispecialty and Superspeciality hospitals are equipped with the high-tech facilities, they are complex and quite expensive. Under such circumstances the proposed design could have been proved to be much effective. The design as above using Red LED, IR LED, photo detector and IC LM35 for measuring the body temperature in degree Celsius. The components, design & technology used makes the system cost effective.

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Utilization of Green Electricity for Operation of Miniature Electronic Circuits

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ABSTRACT

On small scale basis, green electricity generation from trees or plants is possible. Almost all kind of the leaf contains trillions of plant cells. Throughout the process of photosynthesis, each cell of the leaf emits plenty of electrons. By the movement of these electrons, one can produce electricity called green electricity. In our day-to-day life, electric energy is playing a major and indispensable role for human being. Most all the fields are encompassed with electricity and related appliances. Also, there are number of ways by which electricity is being generated. To prevail the demand of electrical energy is ever growing problem and is creating several threats to the environment. To deal with the situation, various types of non-conventional and renewable energy sources are being invented and developed all over the world.

In this research paper, an influence is given to utilize the generated DC voltage from living plants like xerophytes and mesophytes. This kind of energy source is non-conventional as well as renewable energy source and is very useful. It is eco-friendly technique of low voltage generation and its utilization. The undertook research work describes the design aspect of low voltage energy source wherein various plants are used as natural electrolytes along with various electrodes and cells to operate miniature electronic circuits.

Keywords: Miniature circuit, Green electricity, eco-friendly, renewable source, electrodes and cells

I. INTRODUCTION

Now a day there are number of ways by which electricity is being generated. The conventional as well as non-conventional methods are being research and developed used by different agencies, boards and institutes. Everywhere scientific teams are contributing their shares in the field of electricity generation. The researcher is trying to introduce nonconventional method of generation of electricity by using living plants like xerophytes and mesophytes. After successful generation, it may be utilized as a new kind of power source for small electronic circuits, devices & gadgets. This may treat as one of the renewable emerging source of energy. Such type of low voltage can be generated without polluting any environmental parameters.

In the presented research work, a small amount of voltage was generated and utilized for actual working of few miniature electronic circuits and gadgets. By using the electrode pairs or cells in series combinations, the net output voltage was increased whereas by using parallel combinations, the net output current was increased. Thus, various miniature electronic circuits and gadgets can be operated by the virtue of this generated output

voltage. These circuits include Digital watch, LED circuit, 12 and ½ digit Calculator, Musical sound circuit, Quartz wall clock, Timer IC 555 circuit, Tiny DC motor, Small toy, Remotes of CD player, Tiny torch and Joule Thief circuit. Most of these miniature electronic circuits require 1.5 to 4.5V DC voltage with few milliamperes (mA) of current. Also, the simultaneous operation of few of above mentioned circuits were tested using such type of generated voltage from living plants. Few photographs and video clips of actual operation of the above miniature electronic circuits and gadgets are recorded locally and stored in the research laboratory as well as college center.

II. UTILIZATION OF GENERATED VOLTAGE FOR WORKING OF DIGITAL WATCH

Digital wrist watch (Model: Mint Silicone Strap -105 DDK) with liquid crystal display (LCD) requires the typical operating voltage of 1.5 volts and current of approximately 2.5 mA. Such the low values of the voltage and currents were produced by using series combination of the Ag-Zn or Cu-Zn or any suitable type of electrodes or cells. Following figure (1) shows the actual working of a digital wrist watch using such type of generated voltage from the living plants. The digital watch and other circuit components were assembled on a regular breadboard with the help of bus and terminal streams. The watch worked for next many days and months using such kind of generated voltage. Time setting, day-date settings and all other available functions worked in the proper manner.

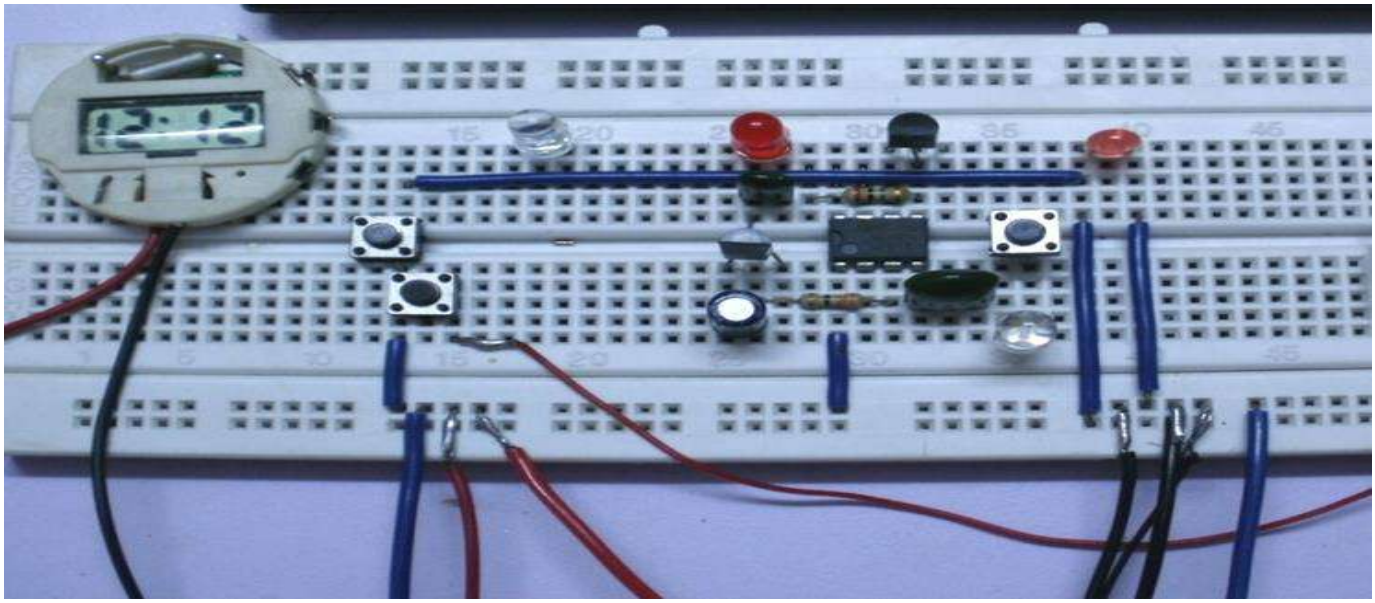

Figure (1) : Actual working of Digital Watch

III. UTILIZATION OF GENERATED VOLTAGE FOR WORKING OF LIGHT EMITTING DIODE

As per the requirement, various types of Light Emitting Diodes (LEDs) are available in the electronic market. The main types of LED are miniature, high power devices and custom designs such as alphanumeric or multi color device. A regular low current LED of 5mm size requires the typical operating voltage of 2 volts and current of 2.5 mA (approximately 5 mW consumption). Such values of the voltage and currents were produced by using series and parallel combination of the Ag-Zn or Cu-Zn or any suitable type of the electrodes or cells. Following figure (2) shows the actual working of such a regular low current Light Emitting Diode (LED) using

generated voltage from the living plants. In the given figure, LED circuit is arranged on a regular breadboard, along with few other components. In order to focus on the emitted light from the LED, the photograph was intentionally snapped in darkness.

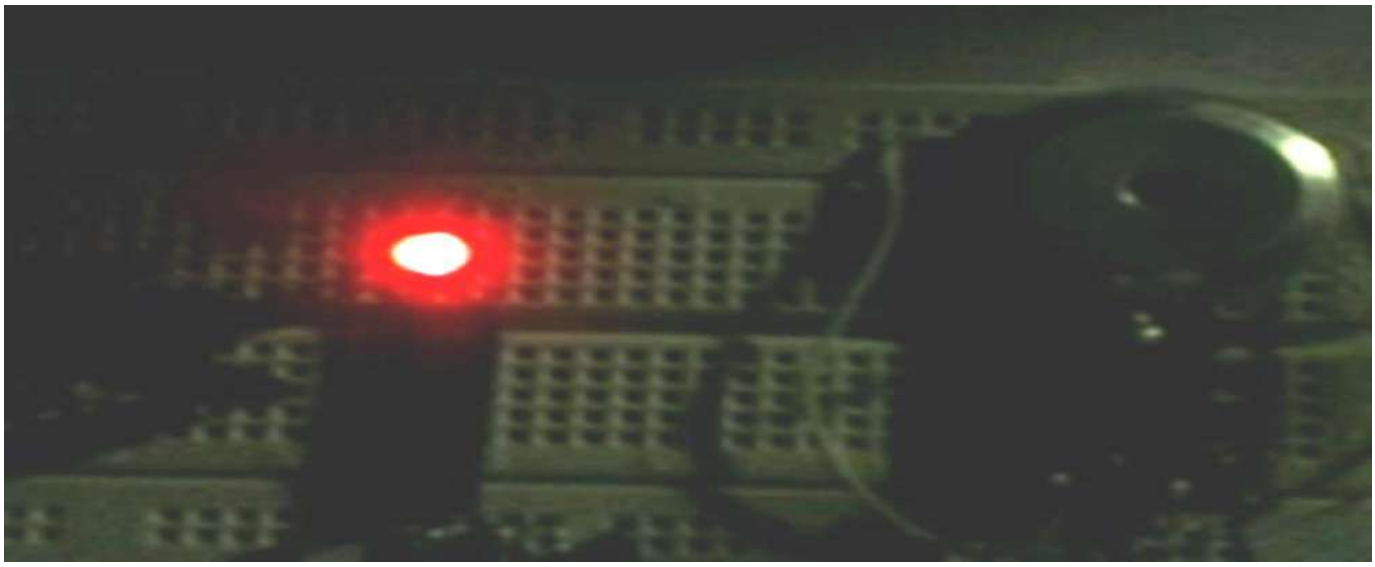

Figure (2) : Actual working of LED Circuit

IV. UTILIZATION OF GENERATED VOLTAGE FOR WORKING OF 12 AND ½ DIGIT CALCULATOR

A digital calculator with 12 and ½ digits (Model: CITIZEN – CT 512, Large Display) requires the typical operating voltage of 1.5 volts and current of 25 mA. By removing internal battery of the calculator, such values of the voltage and currents were produced by using series combination of the Ag-Zn, Au-Zn and Cu-Zn or any other suitable type of the electrodes and cells. Following figure (3) shows the actual working of such a calculator, using the generated voltage from living plants. All kind of available functions in the calculator like Auto checking, memory settings, auto power off and all other mathematical functions of the calculator worked in proper manner. A digital multimeter in the photograph of this figure shows the generated full load voltage of '2.10V', which is somewhat more than the actual voltage required for the working of calculator.

Figure (3): Actual working of 12 and ½ Digit Calculator

V. UTILIZATION OF GENERATED VOLTAGE FOR WORKING OF MUSICAL SOUND CIRCUIT

A miniature musical sound circuit or musical greeting card circuit with build in COB (Chip On Board) and buzzer as sound output was connected as the output load. Such a circuit works on 1.5V voltage and 25mA current ratings (approximately 50 mW power consumption). The required values of voltage and currents were generated by using series and parallel combinations of the Ag-Zn, Au-Zn and Cu-Zn or any other suitable type of the electrode pairs and cells. The musical sound circuit worked properly with suitable sound output. Following figure (4) shows the actual working of such a circuit with the help of voltage generated from living plants.

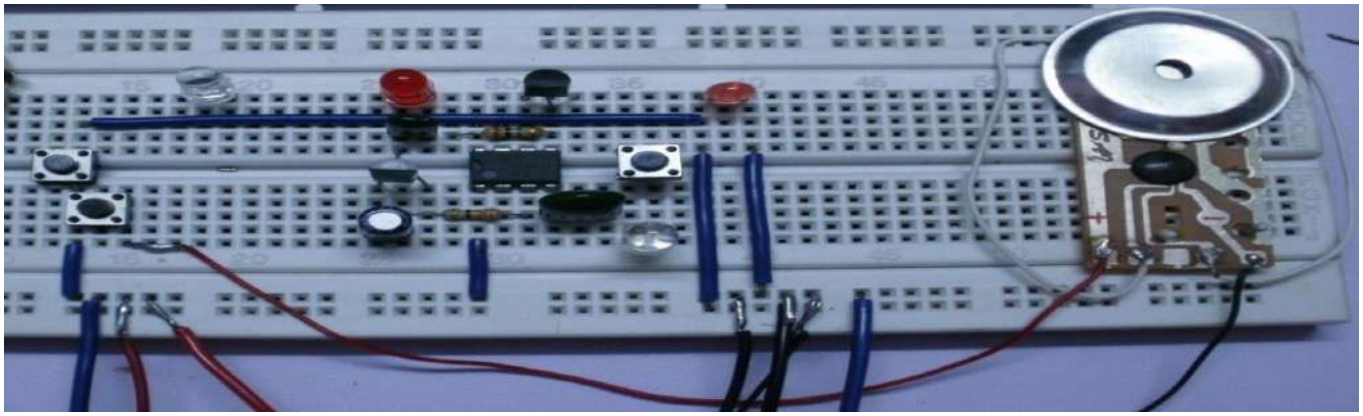

Figure (4) : Actual working of Musical sound circuit with buzzer as output load

VI. UTILIZATION OF GENERATED VOLTAGE FOR SIMULTANEOUS WORKING OF DIGITAL WATCH, LED CIRCUIT, CALCULATOR AND MUSICAL SOUND CIRCUIT

A digital watch, a LED circuit, a digital calculator and a miniature musical sound circuit were simultaneously connected as a parallel load at the output. The simultaneous working of all these four circuits were observed and studied carefully. All the circuits worked properly as long as they were connected to the living plant setup using suitable number of electrodes and cells. Following figure (5) shows an actual photograph of simultaneous working of all these circuits, using the voltage generated from living plants. LCD display of digital watch and calculator are showing particular values of time and calculations of that instant. The voltage requirement for such a simultaneous working was up to 4.5 volts, which was developed properly.

Figure (5): Simultaneous working of Digital watch, LED circuit, Musical circuit & Calculator

VII. CONCLUSION

It was observed that such kind of source is non-conventional, renewable and eco-friendly technique of low voltage generation and its small scale utilization. The undertook research work describes the design aspect of low voltage energy source wherein various plants are used as natural electrolytes along with various electrodes and cells to operate miniature electronic circuits which includes Digital watch, LED circuit, 12 and ½ digit Calculator, Musical sound circuit, Quartz wall clock, Timer IC 555 circuit, Tiny DC motor, Small toy, Remotes of CD and DVD players, Tiny torch and Joule Thief circuit. Such types of sources are of low cost, replenishable, sustainable, pollution free and an emerging low power source of electricity.

The presented research work is in early stages, but further research may open novel ways of using such type of green energy. Thus craving of human being on conventional resources may reduce on some extent. So let's expect that our imagination may cross boundaries and we might be plugging into the surrounding trees and plants to charge our mobile phones and other gadgets using such type of green electricity.

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Remote Sensing and GIS Based Extensive Morphotectonic Analysis of Tapti River Basin, Peninsular India

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Abstract: **The present study on Morphotectonics of the Tapti basin using remote sensing (RS) data and Geographic Information System (GIS) technique is an important input in deciphering the association between drainage morphometry and tectonics of the area. The basic structural elements like the established faults and other linear features of the study area were identified on the digitally processed remote sensing data and drainage pattern/morphometry was derived from the available Shuttle Radar Topography Mission, Digital Elevation Model (SRTM DEM) (90m) data. The various morphometric characters of the Tapti river basin were studied in detail. The drainage model of this area is a coarse sub-dendritic, trellis, and rectangular. The results of the preliminary morphometric analysis have been correlated with tectonic and seismotectonic characters exhibited by the study area. Overall, the morphometric and morphotectonic analysis revealed the area has periodically experienced tectonic and low order seismic instances.**

***Index Terms*: DEM, Drainage Morphometry, India, Morphotectonics, Remote Sensing and GIS, Tapti River Basin.**

I. INTRODUCTION

The study of short and long-term external evidence of tectonic activities is considered as Morphotectonics (Singh and Singh, 2011; Nongkynrih and Husain, 2011; Magesh et al. 2011; Nagare, 2014). The morphotectonic analysis of a river basin explains the geomorphological and hydrological processes working on the basin scale. Climate, topography, and geology are the major controlling parameters of drainage patterns (Thomas et al. 2012). The surface features of the tectonic activities are represented by relative movement such as uplifting, subsidence, and translation of the crust (Strahler, 1957; 1964). The drainage basin and its relationship with the structures are the most susceptible parameter which controls the river courses (Miller, 1953; Altaf et al. 2013). The formations of landforms are the manifestation of the controls of tectonics which are lead by the processes of weathering and erosion (Singh and Singh, 2011; Thomas et al. 2012).

Remote Sensing technology is an important input in deciphering the relationship between drainage morphometry and tectonics of the area (Altaf et al. 2013). GIS techniques provide an analytical tool for quantitative analysis in such studies (Cholke, 2018; Barman et al. 2020). The study of SRTM DEM of the area demonstrates the presence of a large number of lineaments (some are established faults) and fractures across which distinct elevation changes are seen. The Morphotectonics features are observed and mapped using advanced remote sensing and digital image processing techniques (Nongkynrih, and Husain, 2011). Basin elongation ratio (Re) and Asymmetric factor (AF) are important parameters for morphotectonical investigation (Miller, 1953; Schumm, 1956; Rawat et al. 2011; Waikar, and Nilawar, 2014; Cholke, 2018; Barman et al. 2020). River Profile sections are used to identify the evidence of active structures in the area (Copley et al, 2014). In areas, where the rate of tectonics is low, indication comes from the morphotectonic investigation, whereas in the present, the rate of tectonics is substantial resulting in field indications being directly observed.

The present work is done on the Tapti River (also known as Tapi River) which is one of the major rivers of peninsular India originating from Multai in the Betul district of Madhya Pradesh

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with a length of around 764.569 kilometers (Jain et al. 2007; Copley et al. 2014).

II. STUDY AREA

In the northern part of the Deccan plateau, over an area of 63725.02 sq. Km. Tapti river basin is extended (Raja et al. 2010; Giri et al. 2020). The Tapti river basin (Fig.1) lies between longitudes of 72º 38' to 78º 17' and latitudes of 20º 5' to 22º 3' (Jain et al. 2007; Copley et al. 2014; Sharma et al. 2019). It is enclosed by the hill ranges from three sides. Satpura range, in the north, Mahadeo hills, in the east, the Ajanta range and the Satmala hills, the on the south and the west by the Arabian Sea. Around 25% of the area of the Tapti river basin is covered by forest (Jain et al. 2007; Raja et al. 2010; Copley et al. 2014; Giri et al. 2020). The Tapti river basin typically is a basaltic landscape (Jain et al. 2007; Copley et al. 2014)

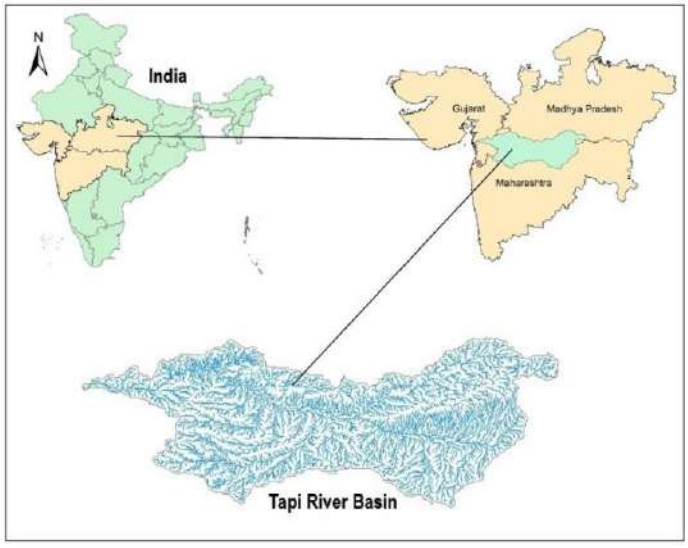

Fig.1: Location map of the study area showing the Tapti/Tapi river basin.

III. METHODOLOGY

This study is based on the quantitative investigation of geomorphic indices using SRTM DEM (90M Resolution). The periphery of the Tapti river Basin was delineated over the topographical maps and mosaic were created of satellite images and ArcGIS and Earth Resource Development Assessment System (ERDAS) Imagine software was used for georeferencing (Yadav et al. 2014). The rectification and resampling to a Universal Transverse Mercator (UTM) projection having World Geodetic System (WGS) 1984, Zone 43 North, as the datum was also completed. Some pre-processing function techniques to normalize the data were used to correct data error and noise. The sinks were removed by filling SRTM DEM data from the dataset (Giri et al. 2020).

Digital elevation model with 90m resolution was used for making Hill shed map overlay by contour lines with 100m intervals, slope map, aspect map. The morphometric parameter is used for landscape shape which accessing the tectonics of the area. Morphotectonic parameters such as basin elongation ratio (Re), Asymmetric factor, and study of longitudinal river profile section are useful for characterization of the topography and landforms features (Nongkynrih, and Husain, 2011; Thomas et al. 2012). The results obtained could be verified with the actual fieldwork carried out in the area.

IV. RESULT AND DISCUSSION

A. Hill Shed Map Overlay by Contour Lines

Hill shed map overlay by contour gives better comprehension of the topography. It can greatly enhance the visualization of the surface for analysis or geographical display, especially when using layer transparency (Schumm and Hadley, 1961; Waikar, and Nilawar, 2014). Most of the area exhibits elevation ranging from 100 to 300 m (Fig. 2). The NNW fringe of the area and the eastern and the northeastern part of the area exhibit comparatively higher elevation ranging from 500 to 1000 m (Giri et al. 2020).

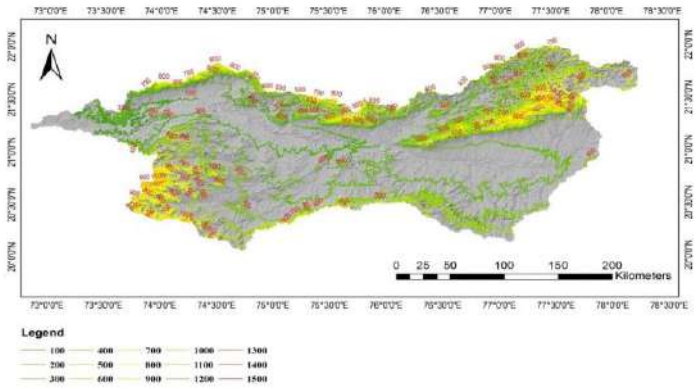

Fig. 2: Hill shed map overlay by contour lines of the Tapti river basin.

B. Slope Map

A slope map is a helpful tool for the identification of structural disturbances (Schumm and Hadley, 1961; Thomas et al. 2012; Waikar, and Nilawar, 2014). A slope map is constructed with the help of a surface tool utilizing a spatial analyst tool, highlighting the presence of fault scarps, tilting of strata, etc (Schumm and Hadley, 1961; Singh et al. 2021).

According to this slope map, regionally area has a gentle slope varying from 0^0 to 3^0 (Fig. 3). The north-northwestern fringe of the study area and the eastern–northeastern part of the area reflects 17^0-25^0 to 25^0-59.80^0 variations which have probably experienced tectonic disturbances. The scarp face of the Gavilgarh fault zone and Tapi north fault zone is characterised by a 3^0-5^0 slope (Giri et al. 2020).

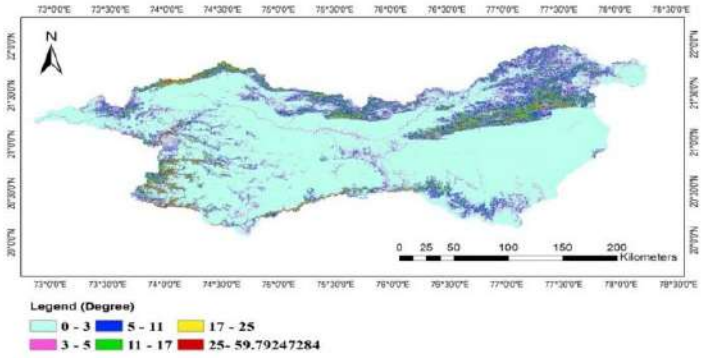

Fig. 3: Slope map of Tapti river basin.

C. Aspect Map

Aspect is used for recognition of the steepest downslope direction of each cell to its adjacent cell (Schumm and Hadley, 1961; Waikar, and Nilawar, 2014). The SRTM DEM has been used for the generation of the "Aspect map" of the area (Fig. 4) (Thomas et al. 2012; Giri et al. 2020).

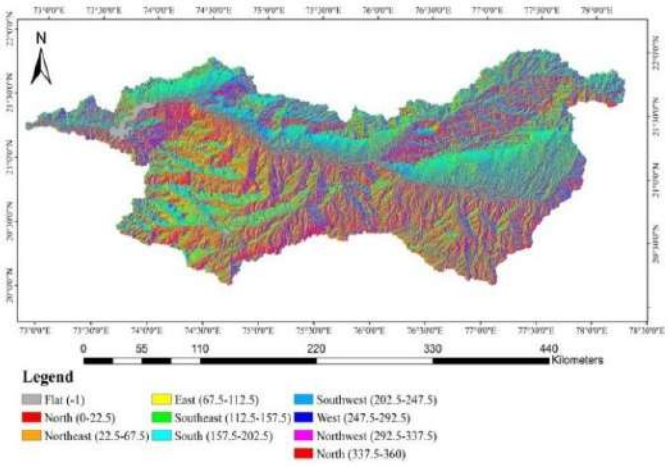

Fig. 4: Aspect map of Tapti river basin.

D. Geomorphological Map

Geomorphology is the systematic study of landforms concerning the climatology, geological and structural aspect (Schumm and Hadley, 1961). Landforms and drainage are the prime parameters in deciphering the geomorphology of an area. The geomorphological record best describes the landforms, plains, and plateau (Schumm and Hadley, 1961; Thomas et al. 2012).

Broadly areas can be classified in a variety of plateaus and plains (Fig. 5). Dissected, denudational plateaus and flood plains are dominant in this area. Denudational plateaus are the exposure of deeper rock structures by the erosion of the land surface, while dissected plateaus are characterised by the cutting of ravines, gullies, or valleys, especially by the stream (Schumm and Hadley, 1961; Thomas et al. 2012; Giri et al. 2020).

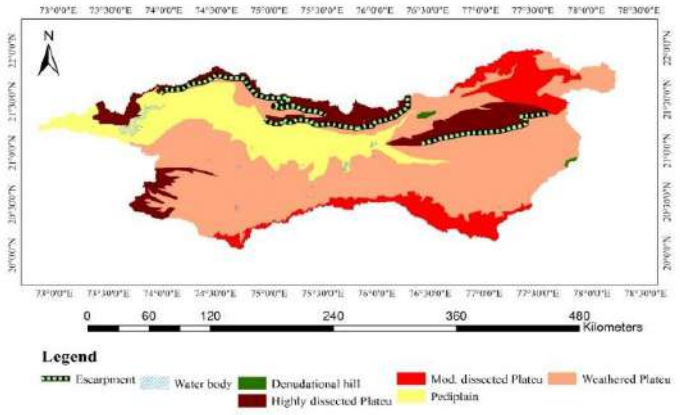

Fig.5: Geomorphology map of Tapti river basin.

E. Lineament map

Lineament is a linear feature that is thought to reflect the crustal structure, viz, Fault line, and straight stream courses. Lineament Mapping is the prime step that directly provides information on the tectonics of the area (Schumm and Hadley, 1961; Thomas et al. 2012; Singh et al. 2021). A structural plot of the area reveals the story of the tectonics of the area. There are several lineaments with some major & minor faults. Lineaments are haphazardly spread all over the Tapti river basin but when observed carefully they represent a crisscross pattern. Mostly a horizontal, vertical, NE-SW, and NW-SE were observed, often cross-cutting each other. There are four major faults, the NE-SW trending Tapti river fault, NE-SW trending Tapi north fault, E-W Gavilgarh fault, and SE-NW trending Purna fault (Fig. 6). Some minor faults were also observed having NE-SW and NW-SE trends (Nongkynrih, and Husain, 2011; Giri et al. 2020).

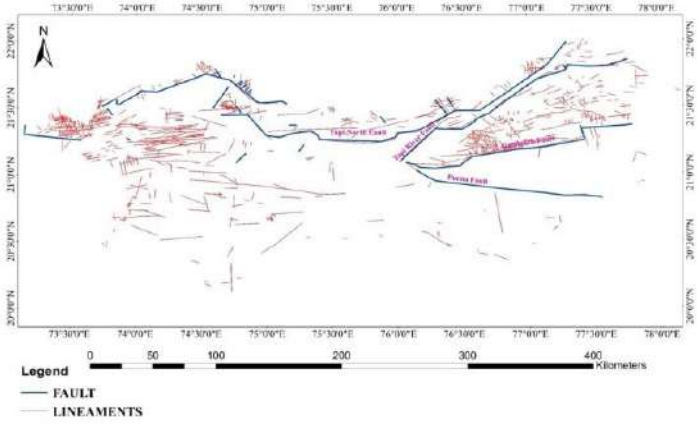

Fig.6: Structural map of Tapti river basin.

V. MORPHOMETRIC ANALYSIS OF BASIN

A. Relief Aspects

1) Relief Ratio (Rh)

The Rh value of the Tapti river basin is 0.002944, indicative of moderate relief and moderate slope (Waikar, and Nilawar, 2014; Giri et al. 2020).

2) Basin Relief

The term Basin relief (R) was given by Melton, 1957 (Fig. 7). Relief (R) (Table I) is 1558 m, indicative of moderate to a steep slope with high run-off (Schumm, 1956; Schumm and Hadley, 1961; Waikar, and Nilawar, 2014; Giri et al. 2020).

Basin Relief (R) is expressed as: R= Hh, Where H = maximum elevation (m), h = minimum elevation (m) (Giri et al, 2020)

Table I: Basin Relief (R)

Object Id	Shape	Major Stream Length in Km	Basin Area in Km²	Maximum Elevation	Minimum Elevation	Basin Relief (Bh)
13982	Polygon	761.775	63725.0264	1559	1	1558

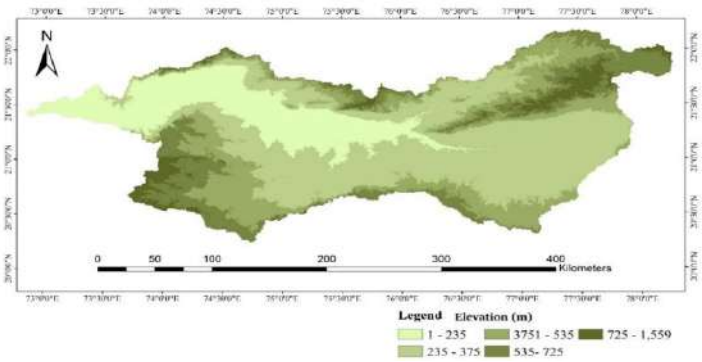

Fig.7: Digital Elevation Map (DEM) of the Tapti river basin.

B. Aerial Aspects

1) Drainage density (Dd)

Horton in 1945 introduced the term drainage density (Dd). The Dd (Table II) of the area is 0.439 km/km2 indicative of Low drainage density, signifying high porous soil and moderate vegetative cover (Giri et al. 2020).

Table II: Drainage density of all streams.

Full basin	Object ID	Basin area (Km²)	The total length of all stream order(Km)	Avg. drainage density
Polygon	13982	63725.0264	27967.844887667	0.439

2) Stream Frequency (Fs)

The Fs for the basin (Table. III) is 0.0883 km2 (Schumm and Hadley, 1961; Altaf et al. 2013; Waikar, and Nilawar, 2014; Giri et al. 2020).

Table III: Stream frequency of the study area.

Object Id	Shape	Shape Area in km2	No. of stream	Stream Frequency/km2
13982	Polygon	63725.0264	5630	0.0883

3) Texture Ratio (T)

The Drainage texture ratio (T) of the area is 0.452 (Giri et al. 2020).

4) Form Factor (Rf)

The (Rf) of the area is 0.1098, indicative of an extended basin with lower peak flows (Schumm and Hadley, 1961; Altaf et al. 2013; Waikar, and Nilawar, 2014; Giri et al. 2020).

5) Circulatory Ratio (Rc)

The Rc value of the area is 0.1862, indicative of moderate to low relief (Waikar, and Nilawar, 2014; Giri et al. 2020). The high value of the circularity ratio signifies The late maturity stage of topography.

6) Elongation Ratio (Re)

The elongation ratio (Re) in the area (Table IV) is 0.3740 indicative of moderate to a slightly steep ground slope, signifying an elongated shape (Altaf et al. 2013; Giri et al. 2020).

Table IV: Form factor, circulatory ratio, elongation ratio of the basin area.

Major Stream	Object ID	Stream Length(Km)	Form Factor	Circulatory Ratio	Elongation Ratio
Polyline	238	761.775	0.1098	0.1862	0.3740

C. Drainage Asymmetry Factor (Af)

The drainage asymmetry factor (AF) is used to estimate the extent of tectonic tilting at the scale of the drainage basin or relatively large area (Schumm and Hadley, 1961; Alaei et al. 2017; Giri et al. 2020).

Drainage asymmetry is defined by Hare and Gardner, 1985;

AF = Ar /At*100

Where Ar = Area of the basin to the right side of the stream

At = Area of the drainage basin

The area of the left part of the basin is greater than that of the right part, showing the effect of active tectonic or differential erosion or tilt (Fig. 8). If the AF of both parts of the basin is equal, then it indicates the presence of no or little tilting. An asymmetry factor

(Table V) of 22.66 indicates that the river basin is undergoing a probable active tilt in the northerly direction (Giri et al. 2020).

Table V: Drainage Asymmetry Factor of the Tapti River Basin.

Object Id	Shape	Grid code	Major Stream Length in Km	Basin Area in Km^2	Area of the Right Side Basin in Km^2	Drainage Asymmetry Factor
13982	Polygon	6	761.775	63725.0264	14441.9983558	22.66

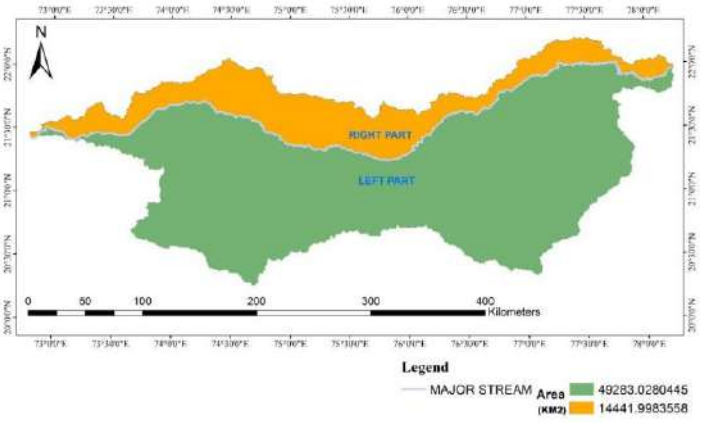

Fig.8: Drainage asymmetric map of Tapti river basin

VI. STUDY OF PROFILE SECTION

In morphotectonic studies, the digital elevation model can provide longitudinal as well as the cross profile of mountain ranges and active faults (Fig. 9). The longitudinal profile may display the youthfulness of the landform, highlighted by the presence of v-shaped valleys (Schumm and Hadley, 1961; Giri et al. 2020).

Also, such profile can be used to recognize structural features like major & minor faults, lineaments, V-shaped valley, dissected plateau, change in elevation along stream channel, evidence of differential block movement, etc. (Fig. 10)

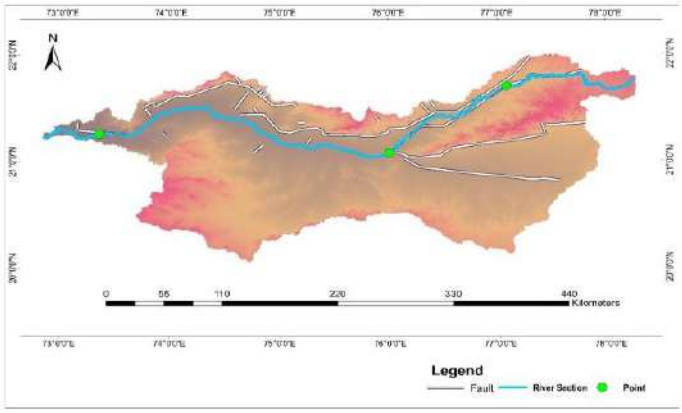

Fig.9: Map showing river section along which digital profiling has been done in the Tapti river basin.

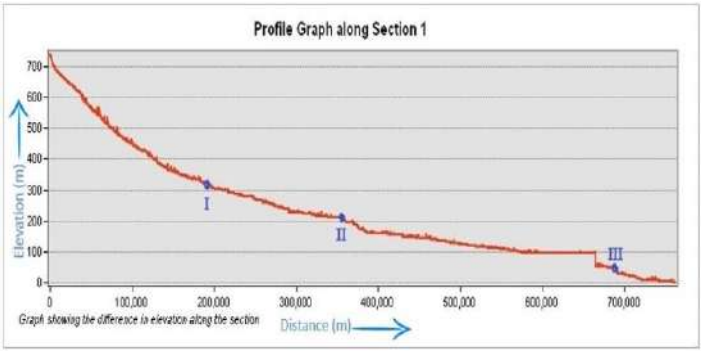

Fig. 10: Profile Graph of Tapti River section

Point I: Point I shows a sudden drop in elevation which co-relates with straight stream course. This convergence of evidence tallies with the previously established Tapti river fault.

Point II: In the central part of the Tapti drainage basin there is a sudden change in the route of the river which is also related to the drop in the elevation of about 20m. This location probably marks the intersection of the well-established NE-SW trending Tapi river fault & the nearly E to W Gavilgarh fault causing sudden flexure in the overall drainage characteristics of the area.

This is further substantiated by the fact that from this location toward the upstream side there is a drainage divide which has bifurcated the basin into two distinct parts in the north-eastern and eastern part of the basin. The originating eastern part of the main river course is depicting a clear NE-SW trend, which nearly follows the NE-SW trending of the Tapi river fault (Giri et al. 2020).

Point III: In the downstream side of the basin, the stream orientation is often controlled by a minor structural feature that has been locally established as a fault. This is to further state that the orientation of the major stream of the Tapi river basin is almost parallel to the Tapi north fault, which might be indicative of the presence of structural features in the southern part of the area sympathetic to the Tapi north fault (Giri et al. 2020).

VII. SEISMOTECTONICS

Seismotectonics is defined as the study of the correlation of individual fault of the area and the active tectonics present in the area. It involves extensive analysis of regional tectonics, recently recorded events using the latest instrumentation techniques, geomorphological evidence, and history of earthquakes in the area.

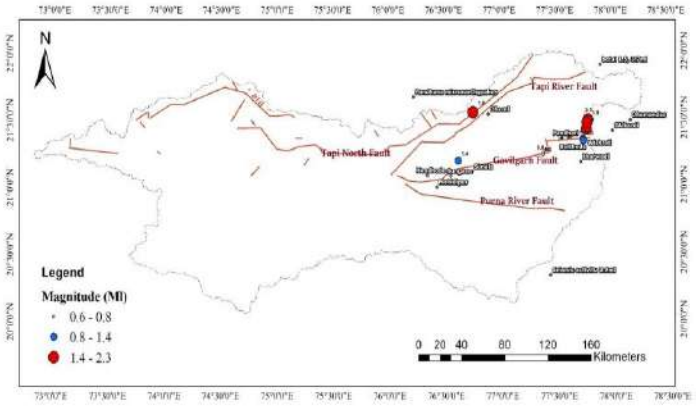

Fig. 11: Seismotectonic map of Tapti River Basin

Seismic events of 3.9ml magnitude on 10 march 2003 with epicenter south of Purna fault were recorded by GSI observatory (Fig. 11). One more event of magnitude 2.9ml at shallow depth was recorded with the epicenter near Dharni in Amravati district of Maharashtra on 1st April 2005 which falls south of the Tapti River fault. A seismic event with an epicenter north of Kharwadi has been recorded which is in close vicinity to the Gavilgarh fault. Few microearthquakes have also been recorded in the Pandhana area in the MP, north of Gavilgarh and Tapti north fault during 1998-1999 (Ghatak et al. 2009). Three distinct events of magnitude 2.3ml, 2ml, and 1.8ml have been recorded north of Belkund Dhana in a linear fashion which may be indicative of the existence of N-S structural entity in the eastern part of the basin cross-cutting the Gavilgarh fault. Two events of magnitude 3.7ml and 1.5ml have been notable near Betul which falls outside the basin in the northeastern part of the area. Few low order seismic events have been recorded near Daryapur, Wishroli, and Jambhal talav area (Ghatak et al. 2007; 2009; Copley et al. 2014;).

After examining the relationship between lineaments and seismic characteristics it can be interpreted, the area has experienced tectonic activities in its recent geological past (Sajadi et al. 2020). Careful observation shows that area is still experiencing tectonic activities as the morphology of the lineaments is changing and the area is continuing to experience low-level seismic instances (Jain et al. 2007; Copley et al. 2014; Giri et al. 2020). However, a thorough and detailed study on this aspect is quite essential to ascertain the prevailing seismic activity of the area and its relation to tectonics.

VIII. CONCLUSION

The Morphotectonic study of the Tapti basin with the help of RS and GIS technology established to be an important input in deciphering the relationship between drainage morphometry and tectonics of the area (Jain, 2007; Magesh et al. 2011; Altaf et al, 2013; Copley et al, 2014; Waikar, and Nilawar, 2014). The basic structural elements like the established faults and other linear feature of the study area were identified on the digitally processed remote sensing data and drainage pattern/morphometry as derived from the available DEM data (Nongkynrih, and Husain, 2011; Altaf et al. 2013; Waikar, and Nilawar, 2014). Since the present study pertains to use the freely available digital data using laboratory techniques, the results obtained need to be verified with the actual fieldwork carried out in the area (Giri et al. 2020).

The various morphometric characters of the Tapti, basin were studied in detail which suggested, that these basins, in general, are asymmetric and exhibit a northerly tilt. Gavilgarh fault zone and Tapti north fault zone are characterized by distinct scarp faces. The greater dissection of geomorphic landforms probably indicates the periodic structural disturbance the area has undergone. In general, the area is characterized by two dominant sets of lineaments viz. NW-SE and NE-SW. Also, a few NS and some EW lineaments have been found to cross-cut the regional trends. Based on the study of stream networks in the area, various morphometric characters were derived for the study area (Jain et al. 2007; Copley et al. 2014). The Relief ratio of the Tapti river basin is 0.002944, indicating moderate relief and moderate slope. The Basin relief is 1558 m which also indicates a moderate to steep slope. The low drainage density indicates the basin has highly permeable subsoil and moderate vegetative cover. The form factor for the Tapti river area is 0.1098, indicating the basin is elongated with lower peak flows of longer duration than the average. The high value of the circularity ratio shows the late maturity stage of topography. The elongation ratio of the study area is 0.3740, which indicates moderate to the slightly steep ground slope (Miller, 1953; Strahler, 1957; 1964; Schumm and Hadley, 1961; Altaf et al. 2013; Waikar, and Nilawar, 2014; Giri et al. 2020).

The Tapti basin exhibit high order of an asymmetric factor of the order 34% indicating the distinct effect of tectonic activity (Nongkynrih, and Husain, 2011; Giri et al. 2020). Study of various profile section indicated the effect of tectonic forces over the present-day geomorphic landforms in the form of a sudden drop in elevation (rapids) along with the river profile, offset of stream courses, sudden change in stream course orientation, change from depositional to the erosional regime, etc. (Schumm and Hadley, 1961; Waikar, and Nilawar, 2014). The low-level tectonic activity experienced by the area can be deciphered from the seismotectonic signatures noted in the area (Magesh et al. 2011). The area in general is characterized by few low-order seismic events. The relationship between seismicity and structural linears suggests that the area has experienced distinct tectonic activity in the geological past and continues to experience the same as indicated by the changes in the morphology of the lineaments in the study area (Raja et al. 2010). However, a thorough and detailed study is quite essential in the future to ascertain the prevalent seismic activity of the area and its relation to regional

tectonics (Strahler, 1957; 1964; Schumm and Hadley, 1961; Giri et al. 2020).

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ORIGINAL PAPER

Lithological controls on the groundwater fluoride enrichment in central India

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Abstract
Petrographic and mineralogical observations are corroborated with the hydrochemistry data to identify the exact lithological source of fluoride contamination in the central part of India. Groundwater samples ($n=57$) representing both shallow and deep aquifers and lithological formations ranging from Archean to Late Cretaceous from central part of India were studied, where fluoride contamination in drinking water is causing a serious environmental health hazard. About 90% samples show high fluoride content than the maximum permissible limit of 1.5 mg/L. Fluoride concentrations in different rock formations such as granite gneisses, limestones, sandstones, and basalts were studied which shows maximum fluoride values of up to 4.9 mg/L. Several parameters (including Saturation Index and Gibbs's plots) were evaluated to understand the factors which controlled the groundwater quality in the area. All signifies water–rock interaction as a major factor influencing composition of groundwater in both the seasons as well as support geogenic enrichment of fluoride. Low-temperature hydrothermal mineralization of fluorite in the limestone aquifers is responsible for the dissolution of fluorine in groundwaters with highest concentration. Moderate concentrations of fluoride up to 2.7 mg/L are observed in the basement granite gneisses. Our mineralogical studies recognized abundant fluor-apatite in granite gneiss aquifers, with high F^- content ranging from 2.5 to 4.2 wt%, as a major contributor of fluoride in groundwaters. Rock-water interactions amplified in alkaline environments played an important role in the dissolution of fluorine in both the aquifers. Identification of main geogenic source of fluoride will be helpful for proper management of drinking water sources in the highly affected areas.

Keywords Groundwater fluoride contamination · Fluoride mineralogy · Central India · Fluor-apatite · Rock-water interaction

Introduction

Groundwater is a major source for drinking water for more than 50% population on global scale (Amiri et al. 2021a). Groundwater chemistry and quality can be modified by the natural sources as well as anthropogenic activities (e.g., Gaikwad et al. 2020; Sohrabi et al. 2021). Various aspects like topography, rainfall, climatic conditions, aquifer properties, and rock-water interactions are the natural factors while large-scale extraction of groundwater for increasing demands of population, industrialization, and urbanization exerts pressure on groundwater resources. In addition, solid waste dumping, use of agrochemicals, sewage, and industrial effluents are also deteriorating the groundwater quality globally (Karunanidhi et al. 2019). All major element constituents of the groundwater are important for the human health if they are in desirable limit; however, their concentrations in more than permissible limits can cause serious health problems.

Groundwater contaminations occurring due to fluoride (F), arsenic (As), and iron (Fe) concentrations are reported from various parts of the world. The sources of fluoride concentrations particularly in the groundwater aquifers are reported to be of natural as well as anthropogenic in origin (Ali et al. 2016; Sharma et al. 2016; Poonia et al. 2021). Fluoride is a natural constituent of the Earth's crust and

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mostly hydrothermal in origin. Fluorine ions are unstable in chemical nature and can be easily replaced by other ions at any temperatures (e.g., Wenzel and Blum 1992). Primary and common contributing minerals are fluorite (CaF_2), apatite, topaz, and ferromagnesium silicate minerals (such as amphiboles and biotites) where hydroxyl ions being replaced by the F^- ions during alteration (e.g., Ramesham and Rajagopalan 1985; Totsche et al. 2000; Msonda et al. 2007; Jadhav et al. 2015; Keesari et al. 2021). Weathering and low-temperature alteration of host rocks and their constituent minerals plays an important role in chemical dissolution of fluoride from F^- bearing minerals and subsequent enrichment in the groundwaters (Singh et al. 2011).

Fluoride is an essential element in the formation of bones and teeth enamels (Dissanayake 1991). Adequate and/or desirable amount of fluoride in drinking water is beneficial for the overall dental and bone health (e.g., Kadam et al. 2020; Amiri and Berndtsson 2020). Lower intake of F^- (i.e., < 0.6 mg/L) will cause dental carries, while long-term intake of high F^- (> 1.5 mg/L) contaminated groundwater results in dental and skeletal fluorosis (Li et al. 2010; Wu et al. 2015; WHO 2017; Aqeel et al. 2017; Keesari et al. 2021). Fluoride contamination in groundwater is a significant environmental issue in India, and it is estimated that nearly 62 million peoples are suffering from different kinds of fluorosis (Pouwels and Ahmed 2007; Ali et al. 2016). Several studies reported the incidence of groundwater fluoride from many parts of India; however, an attempt to identify its exact lithological sources appears to be very limited (e.g., Jacks et al. 2005; Naaz and Anshumali 2015; Adimalla and Venkatayogi 2017).

Recent work by Xiao et al. (2021) have investigated sources of fluoride in groundwater in the present alluvial fan plain aquifers in China and found them to be geogenic. Cation exchange is identified to be a main process affecting the fluoride concentration of groundwater in China (Liu et al. 2021; Su et al. 2021). Zango et al. (2021) reported the source of fluoride in groundwater within the Vea catchment, north-eastern Ghana, using hydro-geochemical and isotopic studies and concluded that F^- enrichment in groundwater is due to silicate weathering and ion exchange reactions. High risk of diseases associated with excessive fluoride intake is also observed in the Iran (Toolabi et al. 2021; Ghanbarian et al. 2021). Recent studies from India reports highly vulnerable parts of fluoride contamination in SW of Rajasthan State (Keesari et al. 2021) and south India (Sajilkumar, 2021). Sajilkumar (2021) performed a systematic human health risk assessment from south India and observed that groundwater is undersaturated with fluoride, and in Hazard Quotient (HQ) studies, the groundwater is posing noncarcinogenic threats to 62% of children and 34% of female population.

Warora area of central India is endowed with varied lithologies like granites, basalts, limestones, shales, sandstones, and cherts. There are previous reports of high fluoride concentrations in the groundwater from this area but the lithological based investigations to identify the contamination sources are inadequate. So, in the present work, we are contributing a mineralogical and lithological based study corroborated with the detail groundwater chemistry to know natural or anthropogenic cause of fluoride contamination, and to detect the sources (mineral/rock) responsible for fluoride enrichment in the groundwater aquifers of central India. The outcomes of this study will further help to manage the drinking water sources in the affected areas.

Materials and methods

Total fifty-seven (57) groundwater samples were collected during pre-monsoon (month: May, after summer) and post-monsoon (month: December, after rains) seasons, 28 samples from deeper aquifers (bore wells), and 32 samples from shallower aquifers (dug wells). Groundwater samples were collected from both bore wells (tapping deeper aquifers, > 60-m depth) and dug wells (tapping shallow aquifers, < 15-m depth). Both the wells are being extensively used for drinking and domestic purposes. One litre (01 L) sample was collected in polyethylene bottles after filtering through 0.45-μm Millipore filter paper. The sampling bottles were soaked in 1:1 diluted HCl solution for 24 h., washed with distilled water, again cleaned prior to each sampling with the filtrates of the sample. Bore well water samples were collected after pumping the water for 10 min. Water samples were collected 30 cm below the water level from open wells. The standard procedures recommended by the American Public Health Association (APHA, 1995) were followed during the groundwater sampling and analyses.

The electrical conductivity (EC) and pH of the water samples were measured in the field using EC meter (Hanna Instruments Model number-CD-98303) and portable eco Tester pH1 respectively. Sodium (Na^+) and potassium (K^+) were measured by flame photometer. The magnesium (Mg^{2+}), calcium (Ca^{2+}), carbonate (CO_3^{2-}), bicarbonate (HCO_3^-), chloride (Cl^-), TDS (total dissolved solids), and TH (total hardness) were analysed by volumetric titration. The sulphate (SO_4^{2-}), nitrate (NO_3^-), and phosphorus (PO_4^-) were analysed by spectrophotometric technique using standard procedures. Fluoride (F^-) content in groundwater was estimated by SPADNS method (Dean 1990). The

quantitative mineral chemical analyses were conducted on a Cameca SX 100 electron probe micro-analyser (EPMA). An acceleration voltage of 20 kV, a beam current of 20 nA, and a beam diameter of 1 μm were used. Counting times varied from 12 to 40 s on the peaks, depending on the element. The EPMA was calibrated using natural minerals and synthetic pure oxides. Back scattered electron images were also obtained. The analytical results are given in Tables 1, 2, and 3.

Geology of the area

Study area of Warora town and its adjoining parts (72 km × 50 km) are situated on the western margin of the Bastar craton of central India (Fig. 1) and expose rocks covering Archean to Late Cretaceous successions. The study area is characterized by the dendritic drainage pattern (Fig. 2). The Archean basement rocks comprise granite gneisses, fractured at places, and composed mainly of quartz, amphiboles, and alkali feldspars (Fig. 3A). These basement rocks are overlain by the Precambrian metasediments (i.e., Vindhyan equivalents). The Vindhyan Supergroup rocks are represented mostly by the limestones, shales, and cherts in the study area. Fluorite mineralization (CaF_2 fluorspar or fluorite) in the form of cavity filling and disseminated veins occurs within limestone and brecciated chert (Fig. 3B) at Dongargaon area. Fluorite mineralization is formed from hydrothermal solutions trapped by carbonate rocks (Randive et al. 2020).The basement rocks are unconformably overlain by the sediments belonging to the Gondwana Supergroup comprising mostly sandstones and shales (Fig. 3C). The northern part of the study area is covered by the Late Cretaceous Deccan Trap basaltic lava flows (Fig. 3D). All the lava flows are simple in nature and forms the basal flows of less than 10-m thickness overlying mostly Precambrian limestone and shale. Groundwater in the Archaean granitic gneisses and Vindhyan metasediments occurs under the water table semi confined hydrogeological conditions in the weathered and fractured zones.

Results and discussion

Petrography and mineralogy

Deccan Trap basalts show fine-grained texture and dominantly composed of clinopyroxenes and plagioclase feldspars along with minor iron–titanium oxides (Fig. 4A). All minerals are fresh and show no traces of alteration to secondary minerals such as amphiboles. All pyroxenes are compositionally augites, and alkali pyroxenes are not present. Limestones and brecciated cherts are highly enriched with fluorite mineralization that occur in the form of cavity filling and disseminated veins (Fig. 4B). Fluorite shows violet, purple color, and massive, botryoidal form (Fig. 4B).

Granite gneisses have well-exposed outcrops in the study area and show distinct gneissose structure at places. They are composed dominantly of quartz, alkali feldspar, amphiboles, and apatites. Among these minerals, amphiboles and apatites may contain fluorine and therefore studied in detail for their major element compositions. Amphiboles are abundant in the rock and show distinct pleochroism (Fig. 4C). Its mineral composition (determined using EPMA) show negligible amounts of F^- (Table 3). Apatites are F^--enriched fluor-apatite (Fig. 4D), occurring as abundant, small accessory crystals in the groundmass. F^- content in fluor-apatite ranges from 2.5 to 4.2 wt% (Table 3).

Spatio-temporal variation of ions in groundwater

Average cation concentrations in groundwater tailed a declining order of $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ in pre-monsoon, while in post-monsoon, it is $Na^+ > Mg^{2+} > Ca^{2+} > K^+$. The dominant pattern for anionic hydrochemistry was in the order $HCO_3^- > Cl^- > SO_4^{2-} > NO_3^- > F^- > PO_4^{-3}$ for both the season. In general, concentrations of cations and anions in groundwater are controlled by lithological weathering, dissolution of minerals, and base-exchange processes (e.g., Nakhaei et al. 2016; Sohrabi et al. 2017; Amiri et al. 2021b).

Total 57 groundwater samples represent varied lithologies such as limestones (15), granite gneisses (06), sandstones (07), and basalts (29). The pH of groundwater in post-monsoon is alkaline and ranges from 7.35 to 8.61, while it is acidic to alkaline (ranges from 6.7 to 8.25) during the pre-monsoon. The average electrical conductivity (EC) is 774.03 during the pre-monsoon season as compared to 582 during post-monsoon season. Sodium (Na) is dominant among cations and its ranges from 28 to 180 mg/L (Fig. 5). Highest Na is reported in BW-23 located in basalt during post-monsoon. In pre-monsoon season, highest value is 145 mg/L reported in DW-53 located in granite gneiss aquifer. The dominance of Na in groundwater is due to the rock weathering (Stumm and Morgan 1996; Rao 2017). Average concentration of potassium (K) in groundwater is 2.81 mg/L, and 3.93 mg/L is studied during post- and pre-monsoon season respectively. The main source of K^+ in groundwater is dissolution of

Table 1 Chemical composition of groundwater from study area during pre-monsoon season

Sample no	Rock type	Type of well	pH	EC (μS cm^{-1})	TDS (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Mg^{2+} (mg/L)	Ca^{2+} (mg/L)	TH (mg/L)	HCO_3^- (mg/L)	SO_4^{2-} mg/L)	Cl^- (mg/L)	F^- (mg/L)	NO_3^- (mg/L)	$PO4^-$ (mg/L)
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
1	Lime-stone	BW	7.45	780	499.2	122	3	39.99	33.13	246.6	341	117	279	0.92	19	0.4
2	Lime-stone	DW	8.11	520	332.8	128	2	36.85	50.45	277.01	466	46	102	0.42	6	0.44
3	Lime-stone	BW	7.65	920	588.8	178	2	33.68	40.18	238.38	416	334	421	1.13	30	0.29
4	Lime-stone	DW	8.12	870	556.8	155	1	95.51	96.38	631.14	316	186	336	0.84	19	0.25
5	Lime-stone	BW	7.45	1210	774.4	152	4	66.13	51.73	400.18	179	409	663	1.11	36	0.46
6	Lime-stone	DW	7.87	1150	736	129	2	57.79	44.03	346.81	166	213	621	1.2	39	0.52
7	Lime-stone	DW	8.18	900	576	121	2	29.17	31.84	199.07	366	311	428	0.82	30	0.27
8	Lime-stone	BW	7.89	420	268.8	110	4	11.17	26.07	110.86	241	77	201	1.32	68	0.32
9	Lime-stone	DW	7.82	470	300.8	119	1	103.06	106.26	687.73	191	84	265	3.45	9	0.34
10	Lime-stone	BW	7.94	510	326.4	109	3	20.98	37.62	179.93	291	102	208	1.28	69	0.36
11	Lime-stone	DW	7.36	480	307.2	134	1	81.81	83.81	544.56	266	140	211	1.59	31	0.26
12	Lime-stone	DW	7.47	390	249.6	67	1	28.03	36.34	205.6	166	104	161	1.26	30	0.19
13	Lime-stone	BW	7.46	380	243.2	64	5	25.47	19.66	153.48	191	66	183	1.47	42	0.21
14	Basalt	DW	7.42	1010	646.4	98	3	105.05	119.09	727.93	216	260	414	1.38	50	0.18
15	Basalt	BW	7.68	410	262.4	115	3	52.03	55.58	352.01	116	124	232	0.73	33	0.07
16	Basalt	DW	8.01	200	128	59	8	16.98	22.86	126.68	216	39	113	0.69	10	0.62
17	Basalt	BW	7.58	460	294.4	162	12	15.4	19.66	112.18	166	113	275	2.8	8	0.5
18	Basalt	DW	8.12	320	204.8	49	4	23.14	13.88	129.48	175	66	144	2.1	20	0.29
19	Basalt	BW	8.05	500	320	140	1	23.56	38.9	193.68	171	102	258	1.8	25	0.34
20	Basalt	DW	7.84	210	134.4	37	1	25.91	42.11	211.34	191	61	95	2.86	8	0.36
21	Basalt	BW	8.61	310	198.4	120	1	87.65	87.02	576.5	266	104	180	1.8	20	0.38
22	Basalt	DW	7.45	200	128	42	2	51.09	61.35	362.58	216	60	95	1.84	37	5.6
23	Basalt	BW	8.41	610	390.4	180	1	19.31	19.66	128.22	166	232	400	1.18	5	0.69
24	Basalt	BW	7.75	210	134.4	46	3	18.08	26.71	140.79	191	33	130	2.7	8	0.55
25	Basalt	DW	7.45	290	185.6	79	2	26.59	44.03	218.93	216	26	80	4.13	14	0.35

Table 1 (continued)

Sample no	Rock type	Type of well	pH	EC (μS cm^{-1})	TDS (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Mg^{2+} (mg/L)	Ca^{2+} (mg/L)	TH (mg/L)	HCO_3^- (mg/L)	SO_4^{2-} mg/L)	Cl^- (mg/L)	F^- (mg/L)	NO_3^- (mg/L)	$PO4^-$ (mg/L)
26	Basalt	BW	7.91	250	160	52	5	26.49	43.39	216.91	291	44	76	0.82	38	0.22
27	Basalt	DW	8.31	500	320	28	2	33.25	45.31	249.4	391	47	87	1.1	31	0.26
28	Basalt	DW	8.05	340	217.6	70	3	25.05	28.63	174.16	291	64	116	0.83	30	0.326
29	Basalt	BW	7.85	690	441.6	64	1	40.5	12.6	197.46	216	210	237	0.23	9	0.24
30	Basalt	DW	7.74	840	537.6	98	2	22.93	15.81	133.46	266	233	350	1.47	24	0.46
31	Basalt	BW	8.41	950	608	132	2	54.49	42.11	328.46	82	212	357	0.8	19	0.34
32	Basalt	BW	8.13	620	396.8	179	2	18.42	16.34	113.37	556	98	123	1.64	28	0.24
33	Basalt	DW	8.13	520	332.8	164	2	16.06	15.16	103.69	316	47	66	1.2	39	0.143
34	Basalt	BW	7.94	570	364.8	65	1	31.59	14.78	167.32	391	89	166	1.05	19	0.116
35	Basalt	DW	8.18	990	633.6	98	2	58.3	20.94	291.22	341	300	464	0.96	22	0.53
36	Basalt	DW	7.91	870	556.8	120	2	43.34	26.07	242.72	266	146	379	1.06	33	0.26
37	Basalt	BW	7.99	300	192	103	2	27.82	42.11	219.16	341	61	73	0.73	43	0.35
38	Basalt	BW	7.94	560	358.4	87	2	35.73	36.34	237.18	291	53	123	0.93	18	0.52
39	Basalt	BW	7.35	340	217.6	86	1	62.93	72.9	439.93	491	525	1053	0.71	25	0.62
40	Basalt	DW	7.85	590	377.6	93	3	63.4	80.6	461.09	391	100	158	1.37	44	0.11
41	Basalt	DW	8.12	370	236.8	108	1	128.27	119.09	823.09	316	82	137	0.75	34	0.25
42	Basalt	BW	7.92	360	230.4	113	3	18.13	18.37	120.18	266	66	116	0.62	41	0.28
43	Sandstone	DW	7.85	1090	697.6	146	2	80.44	94.71	566.18	491	411	570	1.8	45	0.22
44	Sandstone	DW	8.11	1160	742.4	134	2	35.92	26.71	213.92	266	305	407	1.9	22	0.69
45	Sandstone	BW	7.5	100	64	64	2	36.24	51.73	277.68	566	62	45	1.7	34	0.55
46	Sandstone	DW	8.16	500	320	152	1	23.61	24.79	158.66	341	44	95	0.9	20	0.35
47	Sandstone	BW	8.24	260	166.4	95	4	24.77	38.9	198.67	266	52	38	0.74	28	0.22
48	Lime-stone	BW	8.09	490	313.6	99	3	55.7	70.98	405.5	616	95	130	1.37	29	0.26
49	Lime-stone	DW	8.16	780	499.2	125	3	37.79	51.73	284.03	566	144	244	1.39	72	0.326
50	Sandstone	BW	8.04	810	518.4	135	1	39.11	35.69	249.42	366	86	265	0.63	9	0.31
51	Sandstone	DW	8.24	1110	710.4	159	4	41.79	39.54	270.01	532	210	364	1.46	14	0.24
52	Granite Gneiss	BW	8.45	500	320	142	3	30.02	36.98	215.36	541	44	66	1.06	49	0.46
53	Granite Gneiss	DW	8.44	690	441.6	174	2	27.48	19.66	161.7	516	120	160	1.51	45	0.52
54	Granite Gneiss	BW	7.72	370	236.8	107	8	21.81	30.56	165.7	216	109	130	1.19	9	0.62
55	Granite Gneiss	DW	7.84	620	396.8	103	4	41.29	21.58	223.1	291	84	208	1.32	19	0.11

Table 1 (continued)

Sample no	Rock type	Type of well	pH	EC (µS cm^{-1})	TDS (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Mg^{2+} (mg/L)	Ca^{2+} (mg/L)	TH (mg/L)	HCO_3^- (mg/L)	SO_4^{2-} mg/L)	Cl^- (mg/L)	F^- (mg/L)	NO_3^- (mg/L)	$PO4^-$ (mg/L)
56	Granite Gneiss	BW	8.21	560	358.4	116	4	40.8	58.15	312.41	245	75	151	0.79	39	0.25
57	Granite Gneiss	DW	8.31	620	396.8	89	2	28.18	16.12	174.24	316	155	251	1.35	43	0.28
Minimum			*7.35*	*100.00*	*64.00*	*28.00*	*1.00*	*11.17*	*12.60*	*103.69*	*82.00*	*26.00*	*37.70*	*0.23*	*5.00*	*0.07*
Maximum			*8.61*	*1210.00*	*774.40*	*180.00*	*12.00*	*128.27*	*119.09*	*823.09*	*616.00*	*525.00*	*1053.00*	*4.13*	*72.00*	*5.60*
Average			*7.94*	*582.37*	*372.72*	*108.86*	*2.81*	*42.47*	*44.21*	*285.15*	*309.12*	*141.24*	*250.62*	*1.37*	*29.10*	*0.52*

potash feldspar (Keesari et al. 2021). The magnesium (Mg) in groundwater varies from 11.17 to 128.27 mg/L in post-monsoon samples, while it ranges from 26.32 to 140.4 mg/L during pre-monsoon season. Natural factors such as carbonate dissolution and silicate weathering usually control Mg concentration in groundwaters (Sajil Kumar and James, 2016; Sajilkumar 2021). Calcium (Ca) is second dominant cation with average values of 44.21 and 55.67 mg/L during post-monsoon and pre-monsoon season respectively. The Ca in groundwater is a function of the solubility of $CaCO_3$ along with silicates in rocks (Kadam et al. 2021). The bicarbonate (HCO_3) is a major among the anions. It ranges from 82 to 616 mg/L in post-monsoon samples. In pre-monsoon samples, the range of HCO_3 is from 193 to 939 mg/L. The high HCO_3 in groundwater generally occurs due to agricultural runoff as well as sourced from basaltic host rocks (Locsey and Cox 2003). High concentration of chloride in groundwater (Cl) in both the seasons (i.e., 1053 mg/L and 1164 mg/L) that is reported from the BW-39 (in basalt) may be due to the hydrochemical evolution along with high-residence time of groundwater (Jing et al. 2016; Amiri et al. 2021b). High concentration of sulphate (SO_4) (i.e., 525 mg/L and 647 mg/L) in post-monsoon and pre-monsoon seasons respectively may indicate domestic sewage drainage to the bore well (Raja and Neelakantan 2021). The NO_3 in groundwater is high during pre-monsoon (average 41.85 mg/L) than post-monsoon (average 29.10 mg/L). Probable sources are decomposing organic matter and fertilizers used in agriculture. The NO_3 concentration more than 10 mg/L signifies an anthropogenic pollution (Rao 2017). The average concentration of phosphate (PO_4) is 0.52 mg/L and 1.10 mg/L. High PO_4 in groundwater is mainly due to agricultural return flow from the irrigated fields (Vetrimurugan et al. 2013).

Geochemical behaviour of fluoride

Higher values of fluoride above the maximum permissible limit (i.e., > 1.5 mg/L; WHO 1984) are observed during post-monsoon season in about 90% samples from the study area (Fig. 6). Fluoride content in post-monsoon season is enriched and ranges from 1.2 to 4.9 mg/L as compared to the pre-monsoon season (i.e., 0.2–4.1 mg/L). Shallow aquifers appear to have relatively higher concentrations of F^- as compared to deeper aquifers from the same location (Fig. 6A, B). Groundwater samples with higher pH (~7.5 and more) show enriched contents of fluoride which is due to the leaching of F^- in more alkaline environments (e.g., Saxena and Ahmed 2003; Raja and Neelakantan 2021).

In both the seasons, groundwater samples show positive correlation of Ca^{2+} with F^- (Fig. 5). Higher concentrations

Table 2 Chemical composition of groundwater from study area during post-monsoon season

Sample no	Rock type	Type of well	pH	EC (μS cm^{-1})	TDS (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Mg^{2+} (mg/L)	Ca^{2+} (mg/L)	TH (mg/L)	HCO_3^- (mg/L)	SO_4^{2-} mg/L)	Cl^- (mg/L)	F − (mg/L)	NO_3^- (mg/L)	$PO4^-$ (mg/L)
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
1	Lime-stone	BW	7.12	980	637	79	2	66.66	46.67	389.73	540	261	394	1.31	42	0.90
2	Lime-stone	DW	7.38	1040	676	99	4	65.98	56.94	412.56	746	231	221	1.39	30	0.91
3	Lime-stone	BW	7.49	1250	813	131	3	57.31	52.61	366.24	630	460	546	1.78	38	0.86
4	Lime-stone	DW	7.6	923	600	133	2	101.63	105.05	678.84	589	361	446	1.89	20	0.61
5	Lime-stone	BW	6.7	1458	948	106	5	103.26	65.43	586.6	470	574	788	1.79	54	1.20
6	Lime-stone	DW	7.58	1269	825	99	4	92.72	57.1	522.55	458	348	723	1.58	48	1.31
7	Lime-stone	DW	7.5	1110	722	95	4	62	43.46	362.63	560	487	510	1.64	32	0.76
8	Lime-stone	BW	7.64	596	387	68	5	51.98	41.54	316.77	450	209	321	2.24	76	0.88
9	Lime-stone	PIT	7.42	786	511	70	4	124.22	113.39	792.25	462	220	340	4.1	15	0.69
10	Lime-stone	BW	7.64	646	420	82	4	52.07	44.1	323.52	573	210	319	2.34	67	0.92
11	Lime-stone	DW	7.18	793	515	89	2	101.38	100.08	665.4	494	288	345	2.14	41	0.74
12	Lime-stone	DW	7.31	578	376	48	2	61.1	44.1	360.54	458	235	284	2.12	30	0.79
13	Lime-stone	BW	7.15	458	298	36	3	55.07	34.32	311.4	320	246	260	2.36	48	0.84
14	Basalt	DW	7.14	1260	819	70	2	119.3	120.93	790.9	497	378	538	1.94	55	0.79
15	Basalt	BW	6.98	613	398	93	4	95.06	82.76	596.25	342	240	349	1.87	53	0.42
16	Basalt	DW	7.69	423	275	46	14	43.21	31.91	256.77	487	194	218	1.2	22	1.20
17	Basalt	BW	7.45	669	435	107	13	26.32	27.26	175.93	312	245	345	3.18	24	1.09
18	Basalt	DW	7.64	390	254	32	5	52.6	25.82	280.06	432	239	278	3.6	41	0.87
19	Basalt	BW	7.67	603	392	83	2	58.3	51.48	367.48	451	268	367	2.14	39	0.94
20	Basalt	DW	7.35	336	218	26	1	53.28	55.81	357.75	461	223	287	3.89	24	0.75
21	Basalt	BW	8.1	437	284	92	2	111.47	93.18	689.54	540	234	278	2.45	28	0.87
22	Basalt	DW	7.34	310	202	23	1	77.62	75.7	507.16	360	241	209	2.64	62	5.61
23	Basalt	BW	7.81	740	481	139	2	27.64	32.4	194.18	437	340	524	2.49	18	1.34
24	Basalt	BW	7.32	359	233	34	4	46.71	39.13	289.17	465	149	240	4.11	29	1.21
25	Basalt	DW	7.38	334	217	48	4	61.05	54.05	385.18	487	201	197	4.9	27	0.92

Table 2 (continued)

Sample no	Rock type	Type of well	pH	EC (μS cm^{-1})	TDS (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Mg^{2+} (mg/L)	Ca^{2+} (mg/L)	TH (mg/L)	HCO_3^- (mg/L)	SO_4^{2-} mg/L)	Cl^- (mg/L)	F − (mg/L)	NO_3^- (mg/L)	$PO4^-$ (mg/L)
26	Basalt	BW	7.58	409	266	30	6	62.54	56.14	396.5	574	231	188	1.74	47	0.97
27	Basalt	DW	7.41	632	411	24	3	68.51	57.9	425.36	560	214	201	2.13	37	0.85
28	Basalt	DW	7.68	546	355	44	5	56.49	38.33	327.24	560	167	234	1.75	36	0.88
29	Basalt	BW	7.57	879	571	48	2	61.14	25.02	313.06	503	381	345	1.27	18	1.23
30	Basalt	DW	7.36	922	599	75	4	51.33	27.59	279.23	434	364	471	1.79	31	0.97
31	Basalt	BW	7.67	1062	690	93	4	85.28	54.69	486.08	193	347	479	1.73	32	1.09
32	Basalt	BW	7.55	784	510	115	3	43.93	28.39	250.92	689	291	238	1.32	49	0.83
33	Basalt	DW	7.95	665	432	111	2	40.75	27.26	235.07	571	198	197	2.34	52	0.42
34	Basalt	BW	7.35	753	489	47	1	55.95	24.7	290.98	564	231	287	1.62	29	0.64
35	Basalt	DW	7.67	1258	818	75	3	86.14	33.04	435.52	469	486	598	1.76	31	1.10
36	Basalt	DW	7.58	1030	670	99	3	67.99	38.81	375.56	460	332	498	2.02	47	0.64
37	Basalt	BW	7.64	456	296	66	3	55.99	57.58	373.25	631	188	197	1.67	51	0.79
38	Basalt	BW	7.43	730	475	63	3	61.36	49.24	374.44	563	231	214	1.82	34	1.31
39	Basalt	BW	7.67	455	296	53	2	75.91	85.16	523.77	688	647	1164	1.73	44	1.10
40	Basalt	DW	7.41	789	513	67	4	94.04	87.89	604.86	506	274	275	2.37	67	0.67
41	Basalt	DW	7.47	510	332	68	2	140.4	126.86	892.2	530	243	264	1.76	56	0.85
42	Basalt	BW	7.52	513	333	69	4	39.09	29.51	233.9	422	210	261	1.69	61	0.76
43	Sand-stone	DW	7.54	1342	872	117	5	114.71	103.13	727.63	732	585	615	2.64	56	0.88
44	Sand-stone	DW	7.61	1238	805	87	4	67.24	38.33	371.29	510	491	498	2.71	34	1.61
45	Sand-stone	BW	7.5	332	216	38	3	58.26	58.54	384.95	872	115	120	2.45	57	1.32
46	Sand-stone	DW	7.62	745	484	113	3	42.33	37.21	266.38	498	143	204	1.89	40	0.94
47	Sand-stone	BW	8.06	495	322	56	5	49.49	51.48	331.38	514	160	157	1.74	39	0.87
48	Lime-stone	BW	7.68	795	517	69	5	92.49	84.52	590.12	850	216	213	1.87	43	0.92
49	Lime-stone	DW	7.58	991	644	84	4	72.13	65.76	459.83	846	264	357	1.89	76	1.10
50	Sand-stone	BW	7.7	1123	730	83	2	73.93	48.27	423.53	474	279	375	1.67	20	1.02
51	Sand-stone	DW	7.6	1348	876	116	6	77.75	52.77	450.41	939	323	494	1.68	21	0.81
52	Granite Gneiss	BW	8.21	749	487	123	2	62.42	50.04	380.76	846	240	151	2.17	61	0.68

Table 2 (continued)

Sample no	Rock type	Type of well	pH	EC (µS cm^{-1})	TDS (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Mg^{2+} (mg/L)	Ca^{2+} (mg/L)	TH (mg/L)	HCO_3^- (mg/L)	SO_4^{2-} mg/L)	Cl^- (mg/L)	F − (mg/L)	NO_3^- (mg/L)	$PO4^-$ (mg/L)
53	Granite Gneiss	DW	8.25	869	565	145	3	54.26	27.91	292.06	741	283	245	2.11	66	1.25
54	Granite Gneiss	BW	7.45	625	406	68	9	53.76	48.27	340.88	398	264	210	2.41	20	1.38
55	Granite Gneiss	DW	7.48	789	513	63	6	69.25	36.41	374.71	485	276	342	2.75	41	0.69
56	Granite Gneiss	BW	7.65	843	548	74	5	46.94	71.21	370.17	450	198	241	1.54	61	2.06
57	Granite Gneiss	DW	7.74	862	560	57	3	57.85	20.21	287.57	546	301	364	1.61	58	0.67
Minimum			*6.7*	*310*	*201.5*	*23*	*1*	*26.32*	*20.21*	*175.93*	*193*	*115*	*120*	*1.2*	*15*	*0.42*
Maximum			*8.25*	*1458*	*947.7*	*145*	*14*	*140.4*	*126.86*	*892.2*	*939*	*647*	*1164*	*4.9*	*76*	*5.61*
Average			*7.54*	*774.03*	*503.12*	*76.88*	*3.93*	*69.06*	*55.67*	*422.32*	*538.49*	*288.42*	*361.15*	*2.18*	*41.85*	*1.10*

of F^- in limestones and in basalts (overlying limestones) are observed and correlated positively with Ca due to leaching of more calcium from carbonates (Rao 2009). The Ca^{2+} shows higher contents in limestones and basalts (pre-monsoon: 119 mg/L, post-monsoon: 126 mg/L) as compared to sandstones and granite gneisses. Higher values of Ca^{2+} accompanied by elevated F^- contents have also been observed previously in the groundwater from limestone aquifers from NE parts of India (e.g., Chakraborti, 2000). The Na^+ and HCO_3 correlate negatively with F^- in both pre and post-monsoon seasons which reflects less contribution from the host rocks (Fig. 5). However, higher concentrations of HCO_3^- independent of F^- are indicative of carbonate weathering (e.g., Avtar et al. 2013). K^+ commonly shows no correlation with increased F^- contents (Gaikwad et al. 2019).

Mechanisms controlling groundwater chemistry

In the Na vs. Cl cross plot (Fig. 7A), most of the samples are fallowing the 1:1 line indicating Na may be released from silicate weathering reactions (Meybeck 1987; Al-Dabbas et al. 2018; Thapa et al. 2018). On the other hand, high Na/Cl ratio may reveal the anthropogenic contamination, such as fertilizers and agricultural runoff (Jones et al. 1999; Amiri and Berndtsson 2020; Gaikwad et al. 2020). In these high- F^- samples, the average (Ca + Mg) vs. ($HCO_3 + SO_4$) ratio is > 1.0 suggesting that these ions are associated with carbonate weathering rather than silicate minerals (Fig. 7B) (Hounslow 1995; Thapa et al. 2018; Amiri and Berndtsson 2020). Fluoride-enriched groundwater samples located in the carbonate weathering zone are dominant water type (i.e., carbonate Ca-Mg-HCO_3) in the study area. The scatter plot [(Na + K)-Cl] vs. [(Ca + Mg)–($HCO_3 + SO_4$)] indicates a role of dominant processes like ion exchange, reverse ion exchange, and silicate weathering for the modification of the groundwater chemistry (Datta and Tyagi 1996; Fisher and Mulican 1997; Pant et al. 2020) (Fig. 7C). In F vs. F/Cl plot samples follow trend of geogenic enrichment of fluoride. However, samples also show low F/Cl ratio which indicates role of other factors like evaporation also played an important role in the high F^- concentration of groundwater (Dehbandi et al. 2018; Amiri and Berndtsson 2020) (Fig. 7D).

The intensity of soluble minerals is expressed as Saturation Index (SI). Thus, it is used to evaluate the degree of equilibrium between water and respective mineral (Li et al. 2010; Rao 2017), which is calculated as

$$SI = K_{IAP}/K_{SP}$$

where IAP is the ion activity product and SP is the solubility product.

Table 3 Representative chemical compositions of constituent fluorine bearing minerals from basalt and granite gneiss determined using electron probe micro analyser (EPMA) in wt%

	1	2	3	4	1	2	3
Rock	Basalt				Granite Gneiss		
Mineral	Clinopyroxene				Amphibole		
SiO_2	50.45	50.01	50.66	49.15	44.93	46.16	45.02
TiO_2	1.18	0.84	0.75	0.60	1.15	0.77	1.14
Al_2O_3	1.75	1.18	0.92	0.60	8.43	7.34	8.25
FeO	15.66	19.64	20.73	28.08	17.17	18.43	17.27
MnO	0.34	0.49	0.48	0.65	n.a	n.a	n.a
MgO	13.71	12.89	12.95	10.07	11.38	10.28	11.36
CaO	16.33	13.75	13.27	9.90	11.17	11.53	11.18
K_2O	n.a	n.a	n.a	n.a	0.96	0.86	0.87
Na_2O	0.28	0.20	0.19	0.15	1.27	0.98	1.29
F	0.00	0.00	0.00	0.00	0.04	0.08	0.12
Cl	0.01	0.01	0.01	0.02	0.19	0.21	0.19
Total	99.71	99.01	99.96	99.22	96.69	96.64	96.69
	1	2	3	4	5	6	7
Rock	Granite Gneiss						
Mineral	Fluor-apatite						
SiO_2	0.07	0.05	0.05	0.09	0.06	0.08	0.02
TiO_2	–	0.01	0.02	–	–	0.01	0.01
Al_2O_3	–	–	–	0.01	–	–	–
FeO	0.02		0.07	0.12	0.08	0.04	0.06
CaO	53.63	53.79	53.30	53.47	53.60	53.02	53.31
K_2O	0.02	–	0.03	–	–	0.01	0.02
Na_2O	0.02	–	0.02	0.02	0.02	0.01	0.01
P_2O_5	40.54	40.82	40.48	39.72	40.05	39.36	39.02
F	4.27	4.00	4.27	3.55	3.75	2.67	2.54
Cl	0.40	0.29	0.38	0.52	0.47	0.41	0.38
Total	98.97	98.96	98.62	97.50	98.03	95.61	95.37

n.a. not analysed

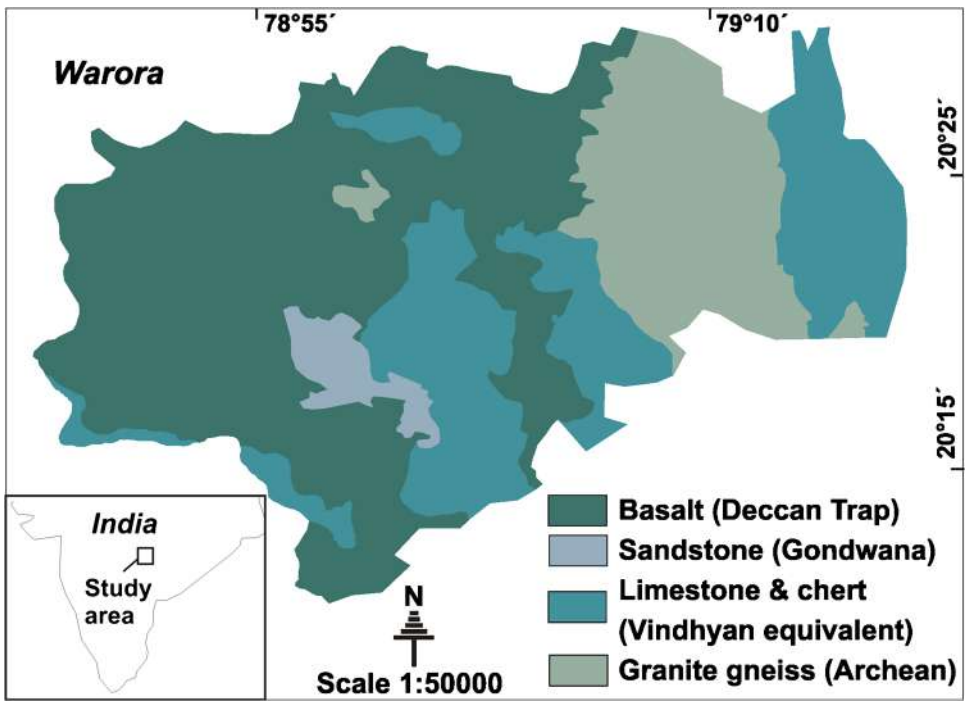

Fig. 1 Geological map of the study area of Warora in central India

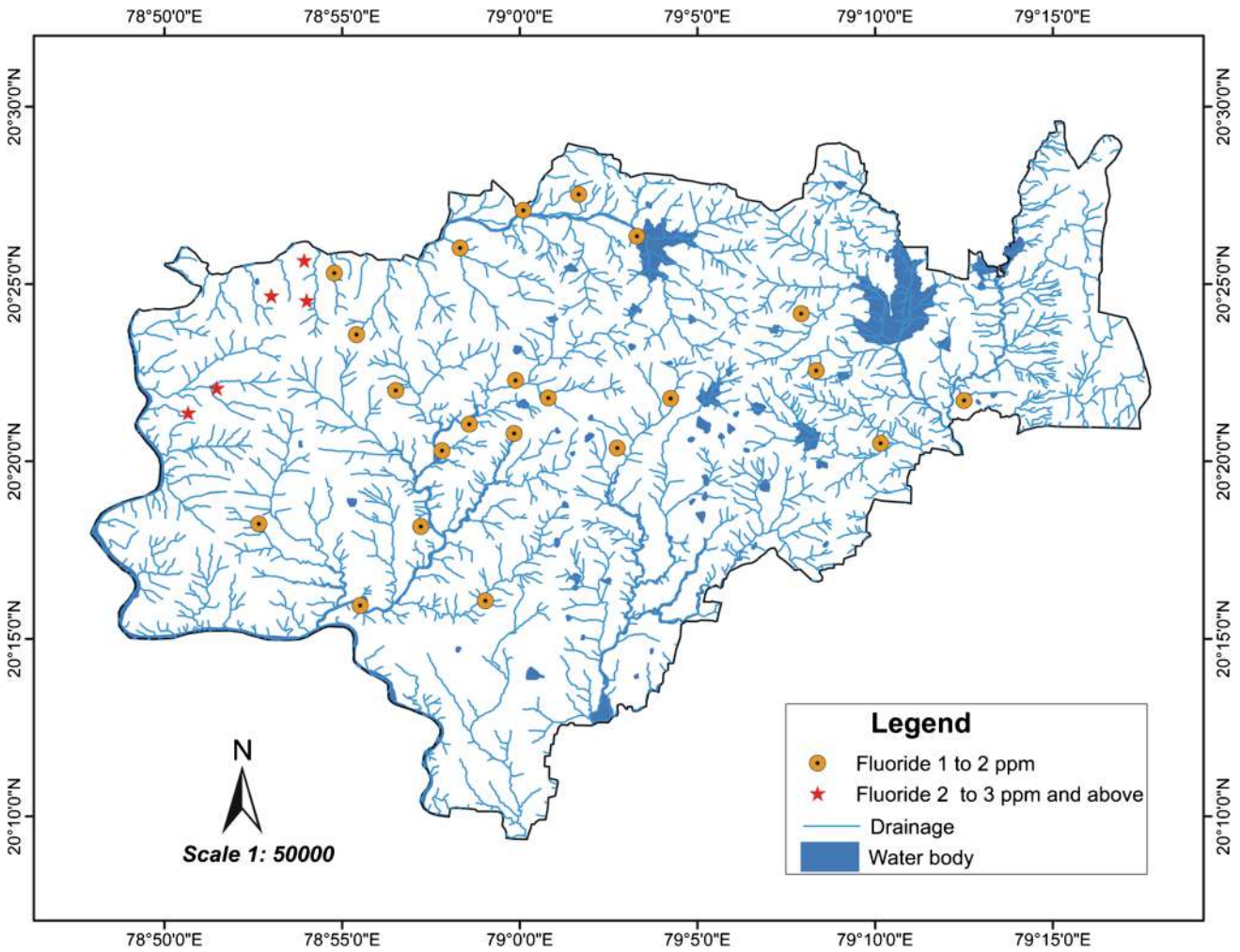

Fig. 2 Map showing drainage pattern in the Warora area along with sample location and distribution of fluoride

SI values were determined through the PHREEQC interactive 2.15, for determining the status of mineral equilibrium and feasibly controlling dissolved elements in the groundwater (Parkhurst and Appelo 1999). The details of SI are shown in Fig. 8. If SI is zero, it indicates saturated state (equilibrium) with respect to the particular mineral. If SI is less than zero, it shows under-saturated state (dissolution) with respect to the concerned mineral. If SI is more than zero, it suggests oversaturated state (precipitation) with respect to that particular mineral (Li et al. 2010; Rao, 2017). Computed saturation indices implied that all the samples are saturated in terms of both CaF_2 with $CaCO_3$ and CaF_2 with dolomite.

Gibbs's ratio is employed in this study to understand and differentiate the influences of rock-water interaction, evaporation, and precipitation on water chemistry (Gibbs 1970). Rock-water interaction shows dominance over evaporation and precipitation and therefore responsible for the release of fluorine in groundwater in both the seasons, as well as primarily controlling the major ion chemistry of groundwater of the study area. Samples plotted on modified Gibbs graph (Fig. 9) are influenced by water–rock reactions.

All above studied parameters indicate that groundwater chemistry and quality of the Warora area that are influenced mainly by the rock-water interaction and lithology played an important role in modifying its chemical composition including enrichment of fluoride.

Lithological controls in groundwater fluoride enrichment

Lithological variation in the study area appears to primarily control the variation of fluoride in different aquifers. Because of influence of rock-water interaction, post-monsoon samples show more enrichment of fluoride in groundwater (Brindha et al. 2011). Fluoride shows following range in post-monsoon samples in different rock formations/lithologies (in mg/L): granite gneiss, 1.5 to 2.4; limestone, 1.3 to 4.1; Gondwana (sedimentary), 1.6 to 2.7; and basalts, 1.2

Fig. 3 Field photographs showing **A** outcrops of granite gneiss, **B** silicified chert outcrops in the Dongargaon fluorite mine, **C** scattered outcrops of sandstones belonging to Gondwana Supergroup, and **D** outcrops of Deccan basalts

to 4.9. Very high values of fluoride are observed in basaltic rocks followed by the groundwater samples from limestone, whereas Archean granite gneisses and Gondwana sediments show comparatively lower values (Fig. 6).

Higher concentration of fluoride in limestones and cherts is expected due to the occurrence of rich fluorite deposits within these Precambrian rocks. However, groundwater samples from wells in basalts also show similar range of fluoride enrichment values. Secondary amphiboles and altered pyroxenes in basalts have been known to contribute fluorine in groundwaters aquifers (e.g., Madhurne et al. 2007). Our detail petrographic and mineralogical observations do not show any fluorine containing mineral in basalts (e.g., secondary veins/ minerals). Deuteric alteration products of pyroxenes (amphiboles and chlorite) may contain F^- due to the replacement of OH^-. However, pyroxenes from basalts in the area are fresh and contain CaO and MgO ranging from 9.9 to 16 wt% and 10 to 13.7 wt% respectively. These compositions are similar to the clinopyroxenes from Deccan basalts (e.g., Dongre et al., 2018) with undetectable fluorine (Table 3); therefore, the observed enrichment in basalts is intriguing. As mentioned above, study area is situated on the eastern fringe of the Deccan Trap province and occupied by the basal/ lower basaltic lava flows of simple type. Basaltic flows in the study area show thickness of < 10 m and overlain directly the Precambrian metasedimentary rocks (limestone and chert). Therefore, the contribution of high fluoride in basalt aquifers is inferred to be sourced from underlying limestones and cherts having hydrothermal mineralization of fluorite. Fluorite (CaF_2) occurs as late-crystallizing and low-temperature, hydrothermal mineral. Dissolution of fluorine from such hydrothermal sources in the study area is, therefore, responsible for very high concentrations of fluoride in meta-sedimentary aquifers. High fluoride values of up to 22 mg/L are also reported from the aquifers of north-eastern Tunisia due to leaching of F^- from the adjacent fluorite deposits (Ameur et al. 2019).

Other lithologies like granite gneisses and overlying sedimentary successions also show higher and similar values of fluoride concentrations. Granitic rocks are well

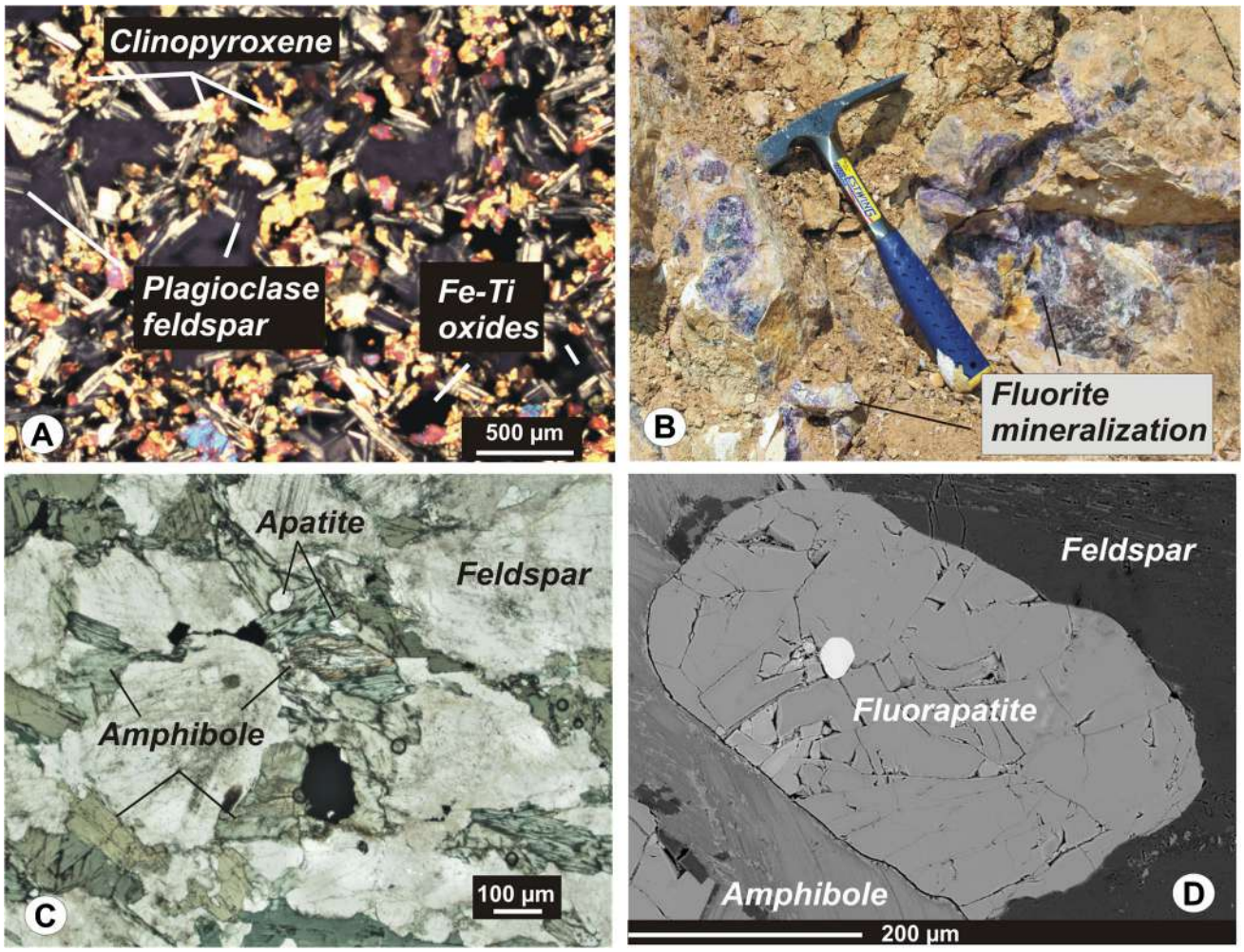

Fig. 4 **A** Photomicrograph of basalt showing fine-grained texture and presence of clinopyroxenes, plagioclase feldspars, and Fe-Ti oxides, in cross nicols; **B** field photograph showing occurrence of hydrothermal fluorite in Dongargaon fluorite mine; **C** photomicrograph of granite gneiss showing coarse-grained texture and presence of feldspar and abundant amphiboles; apatite crystal are also seen; **D** back scattered electron image (BSE) showing anhedral grain of fluor-apatite significantly rich in fluorine content

known for the fluoride contributing minerals in groundwaters (e.g., Ramamohana Rao et al. 1993; Apambire et al. 1997; Edmunds and Smedley 2005) such as amphiboles and apatites. Dissolution of silicate minerals particularly apatite, biotite, muscovite, and hornblende liberate fluoride ions from the aquifer matrix (rocks) into groundwater (Karunanidhi et al 2019; Vithanage and Bhattacharya 2015). Our mineralogical studies identified abundant fluor-apatite grains in the groundmass with F^- content ranging from 2.5 to 4.2 wt%, whereas amphiboles show very negligible F^- content (< 0.12 wt%). Member of apatite group [$(Ca_5(PO_4)_3(OH,F,Cl)$] are common primary accessory minerals in granites, and among them, fluor-apatite is the most common. Fluorine, chlorine, and the hydroxyl ions in the apatites mutually replace each other to form pure end-members. Alkaline environment favoured the dissolution of these volatile elements (dominantly F^-) from fluor-apatites causing important environmental health hazard in the study area. It is found that weathering and alteration of apatites and its batch dissolution can release > 4 mg/L fluoride concentrations in the waters (Chae et al. 2006). It is mentioned in several studies that occurrence of minerals like fluorite, apatite, topaz, villiamite, and ferromagnesium silicates in weathered and fractured granitic rocks is responsible for the enhancement of the concentration of fluoride in groundwater of southern India (e.g., Ramesham and Rajagopalan 1985). However, based on our detail mineralogical studies, the abundance of fluor-apatites in granitic aquifers of the central and southern India appears to be a primary and significant cause for fluoride enrichment.

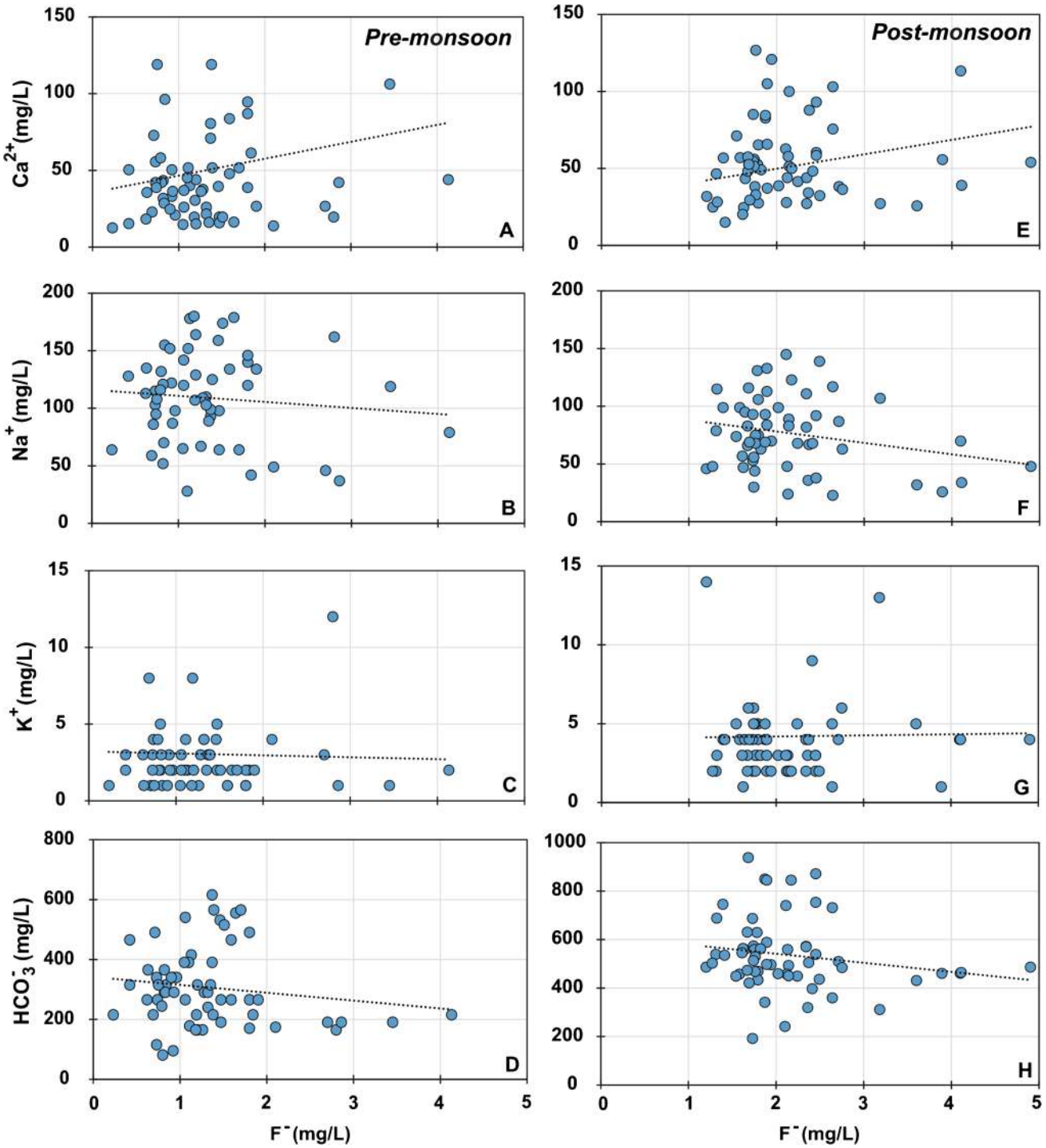

Fig. 5 Bivariate plots of F^- versus Ca^{2+} (**A**), Na^+ (**B**), K^+ (**C**), and HCO_3^- (**D**) (in mg/L) in pre and post-monsoon seasons

Conclusions

Average cation concentrations in groundwater from Warora area of central India tailed a declining order of $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ in pre-monsoon, while in post-monsoon, it is $Na^+ > Mg^{2+} > Ca^{2+} > K^+$. The dominant pattern for anionic hydrochemistry was in the order of $HCO_3^- > Cl^- > SO_4^{2-} > NO_3^- > F^- > PO_4^{-3}$ for both the season. Groundwater shows high concentrations of fluoride

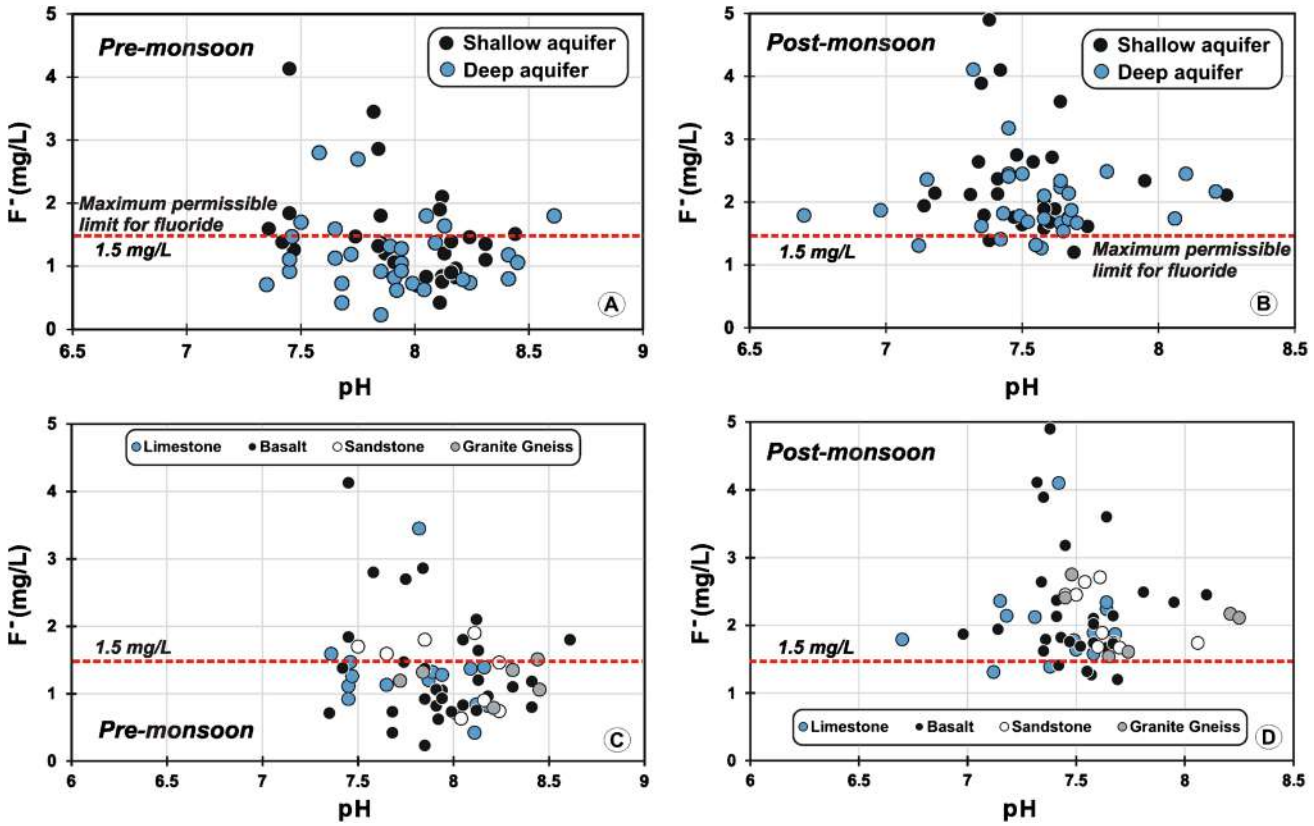

Fig. 6 Bivariate plots of pH versus F^- concentration during pre and post-monsoon seasons in the studied groundwater samples, showing variation of shallow and deep aquifers (**A** and **B**), and variation in different rock types (**C** and **D**)

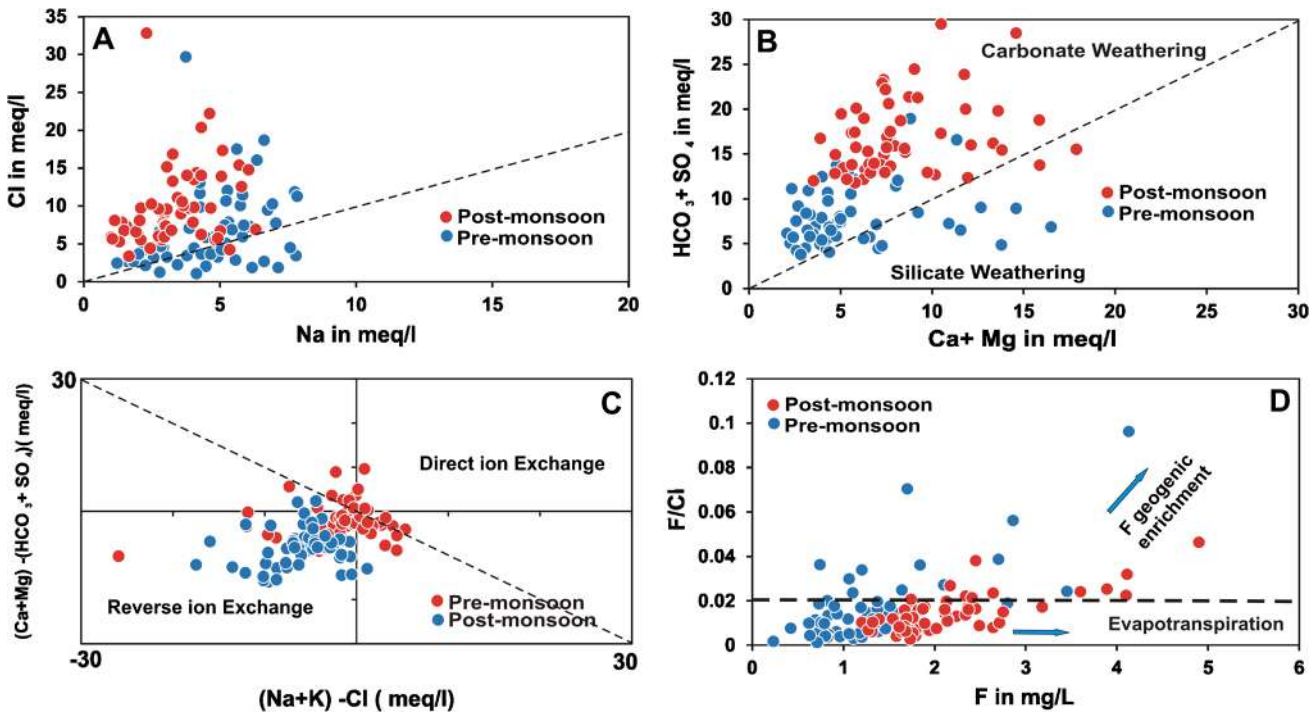

Fig. 7 Scatter plots of **A** Na vs. Cl, **B** Ca + Mg vs. $HCO_3 + SO_4$, **C** (Na + K)-Cl vs. (Ca + Mg)-($HCO_3 + SO_4$), and **D** F vs. F/Cl

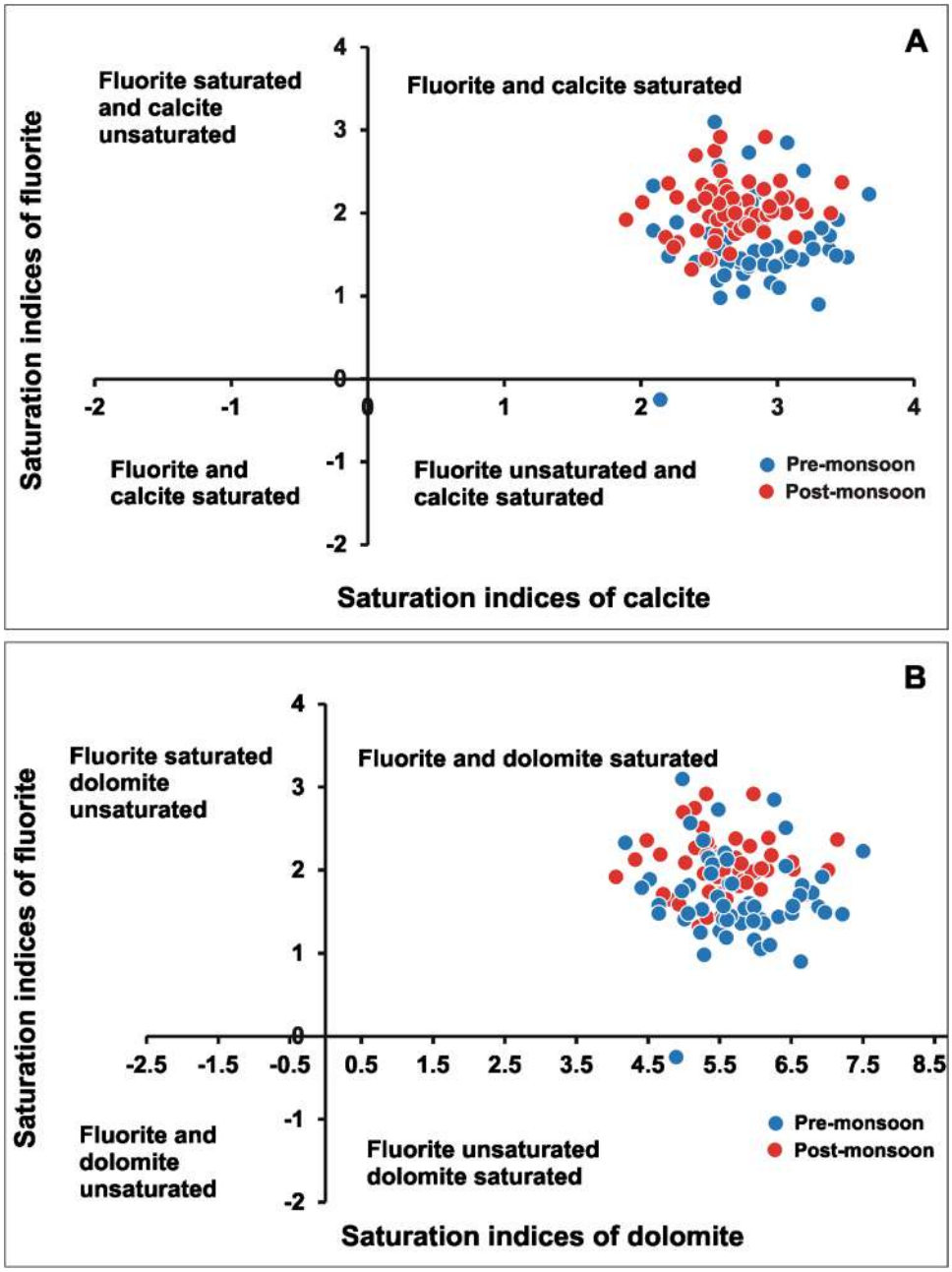

Fig. 8 Saturation Index (SI) data of water samples with respect to **A** fluorite and calcite and **B** fluorite and dolomite

up to 4.9 wt% in post-monsoon seasons. Around 90% of groundwater samples collected during this study contain fluoride concentrations above the maximum permissible limit of 1.5 mg/L. Groundwater samples are dominantly alkaline in nature and rock-water interaction in an alkaline environment appears to have favoured the dissolution of F^- in groundwaters. Several parameters (including Saturation Index and Gibbs's plots) evaluated to understand the influencing factors of groundwater composition. All suggest dominance of rock-water interaction and geogenic enrichment of fluoride.

Hydrothermal fluorite mineralization in Proterozoic metasedimentary successions is a main source of fluoride contamination in limestones and overlying basalts. Our detail mineralogical studies and reported absence of fluoride enrichment in basaltic aquifers of Deccan volcanic province indicate insignificant contribution of basalts and their constituent minerals in groundwater fluoride contamination. Fluor-apatite with F^- content ranging from 2.5 to 4.2 wt% is a primary source of fluoride in the groundwaters from granite gneiss aquifers. Fluor-apatite is also suggested as chief contributor of fluoride in granitic aquifers of central and southern India where groundwater fluoride contamination is

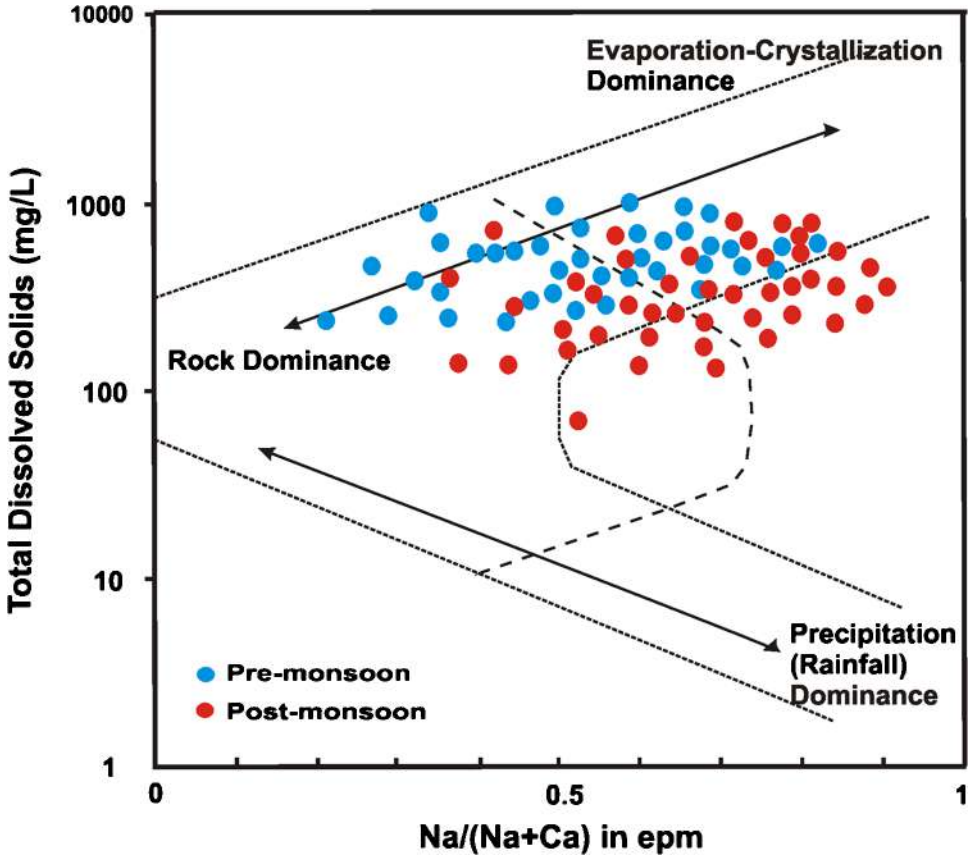

Fig. 9 Mechanisms controlling groundwater chemistry on Gibb's plot

more pronounced. An identification of the lithological influence on fluoride enrichment will help for the management of drinking water sources in high fluoride areas.

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Declarations

Conflict of interest The authors declare that they have no competing interests.

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Effect of Synthesis Techniques on VUV Properties of Eu^{3+} Doped YVO_4 Phosphors: A Comparative Study

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ABSTRACT

The europium doped yttrium vanadate (YVO4:Eu3+) doped phosphor have been synthesized by two different techniques viz., solution combustion (CM) and solid-state diffusion (SSD) techniques. X-ray diffraction patterns confirm the formation of a pure phase in the samples synthesized by both the methods; however, the luminescence intensities of the samples are different under vacuum ultraviolet (VUV) excitation i.e., 147 and 172nm. The effect of synthetic technique is also seen on morphology of materials studied with the help of scanning electron microscopy, which shows an agglomeration and increase in particle size with increasing calcination temperature in case of SSD. The luminescent properties of the synthesized material have been studied by using synchrotron radiation. The photoluminescence (PL) results clearly show the strongest red emission peak at the wavelength around 618 nm. The highest luminescent intensity is obtained for the sample prepared by the CM method compared to SSD method. It is also noted that wavelength of 172 nm is more efficient than the 147 nm for excitation of YVO4:Eu3+.

Keywords: Yttrium Vanadate, Combustion Synthesis, Solid State Diffusion, VUV Luminescence

I. INTRODUCTION

A plasma display panel (PDP) has been regarded as a promising candidate for a display with a large area mainly because its emissive features include a wide viewing angle and high brightness. PDP phosphors are expected to meet the critical requirements to yield a high luminous efficiency on excitation with vacuum ultraviolet (VUV) radiation of wavelengths 147 and 172 nm generated from a plasma of a mixture of He and Xe noble gases[1]. Oxide phosphors with aluminate, silicate, vanadate, phosphate, and borate groups generally exhibit strong absorption in the VUV spectral region[2-3].

The main weakness of red-emitting PDP phosphors currently used are the lack of colour purity, long decay lifetime and colour degradation due to material instability. For these reasons, the optical and luminescence properties such as luminous efficiency, purity of chromaticity and saturation, and decay lifetime of PDP phosphors have been widely investigated[5-7]. A search for red-emitting PDP phosphors with improved efficiency, brightness, and colour saturation has become an important task for which research is being actively pursued. Several synthesis routes have been described for the preparation of Eu^{3+}-doped YVO_4 such as co-precipitation, hydrothermal, solid-state reaction, combustion method[8-12]. However, there is no report on the comparison of structural and VUV properties of Eu^{3+}-doped YVO_4 sample synthesized via combustion and solid-state reaction routes. To develop satisfactory red-emitting PDP phosphor, we have thoroughly investigated the effect of preparation method on photoluminescence (PL) properties $YVO_4:Eu^{3+}$ phosphor under VUV excitation. Here, we report the synthesis and VUV PL spectral investigations of red-emitting $Y_{1-x}VO_4$: Eu_x phosphors in several series and also the dependence of luminescence performance on method of synthesis. The $YVO_4:Eu^{3+}$ phosphor has been prepared by low temperature, low cost and less time-consuming solution combustion method and high temperature conventional solid-state diffusion method. We have also studied the optimized composition of the dopant to obtain red-emitting phosphor with great potential for PDP application.

Pure and Eu^{3+}-doped YVO_4 phosphors were prepared following two techniques, namely the solution combustion synthesis and high-temperature solid-state diffusion method. Analytical graded yttrium oxide (Y_2O_3), europium oxide (Eu_2O_3), ammonium meta-vanadate (NH_4VO_3) and urea [$CO(NH_2)_2$] were taken as starting materials.

II. METHODS AND MATERIAL

2.1. Solution Combustion Method:

In the first step for solution combustion synthesis method, 0.5 mol of Y_2O_3 and xEu_2O_3 (x = 0.02, 0.04, 0.06, 0.08, 0.10) were dissolved in the concentrated HNO_3 (nitric acid) to form respective nitrates. Stoichiometric amount of NH_4VO_3 was dissolved in doubled distilled water and slowly added to the previously formed nitrates, which resulted in a dark brown solution. In this solution, appropriate amount of urea was added as a fuel and ammonium nitrate as a oxidizer was added. The required amount of fuel (urea) and oxidizer (ammonium nitrate) was calculated by the ratio of oxidizing and reducing valencies[11]. Then, the mixture was stirred until the clear solution is formed. The as-prepared solution of reaction mixture was placed in pre-heated muffle furnace at 550 ^{0}C temperature for 5 min and such process resulted in a black powder. Finally, the black powder was annealed at 800 C for 3 h resulting in the final product.

2.2. Solid State Diffusion Method:

$Y_{1-x}Eu_xVO_4$ (x = 0.02, 0.04, 0.06, 0.08, 0.10) phosphors were also prepared by conventional high-temperature solid-state reaction method. All the reagents (Y_2O_3, NH_4VO_3 and Eu_2O_3) were taken in stoichiometric ratio and mixed together in mortar–pestle for half an hour and heated at 700 ^{0}C for 6h. The last product was again ground properly and maintained in a muffle furnace at 1200 ^{0}C for 3h. Finally, the sample was removed out from the furnace and after normal cooling ground appropriately. The X-ray diffraction (XRD) pattern of the sample was recorded on Rigaku miniflex X-ray diffractometer with a scan speed 2.000 deg/min and with Cu Ka radiation. The morphology of the phosphor particles was studied by using Hitachi model S-4800 type-2 field-emission scanning electron microscope (SEM) and elemental analysis by Bruker EDS. The VUV spectra were

recorded at Department of Physics, S.G.B., Amravati University, Amravati, by using remote access mode of Beamline 4B8 in Beijing synchrotron radiation facilities (BSRF)[13] under dedicated synchrotron mode (2.5 GeV, 150 – 60 mA). The vacuum in the sample chamber was about 1×10^{-5} mbar. The effects of the experimental setup response on the relative VUV excitation intensities of the samples were corrected by dividing the measured excitation intensities of the samples with the excitation intensities of sodium salicylate measured simultaneously in the same excitation conditions. The region of excitation spectra was from 100 to 300 nm and the emission spectra recorded at 147 and 172 nm excitation.

III. RESULT AND DISCUSSION

3.1 X-ray Diffraction

The crystallinity and surface morphology have a great impact on optical behaviour such as photoluminescence of the material[14]. Fig.1 illustrate the XRD patterns of Eu^{3+}-doped YVO_4 prepared by combustion and solid-state reaction route, respectively. The formation of the crystalline phase of as-prepared products of SSD and CM method was confirmed by X-ray diffraction patterns of YVO_4 (as shown in Figure 1) to verify the phase purity and crystal structure. The X-ray pattern of both method samples indicated a pure phase of the standard YVO_4 and all the peaks are in good agreement with the (ICDD, 01-082-1968). There were no additional peaks found as the concentration of Eu ion was increased to 10%. Thus, it seen that pure phase of YVO_4 could be achieved using CM method at low temperature compared to solid state diffusion (SSD) synthesis, which require higher temperature and time for synthesizing YVO_4. This agreement indicates that the phosphor has been successfully prepared by using the CM and SSD method. It is also noticed that the crystal diffraction intensity of YVO_4 obtained by SSD is lower than that obtained from the CM method.

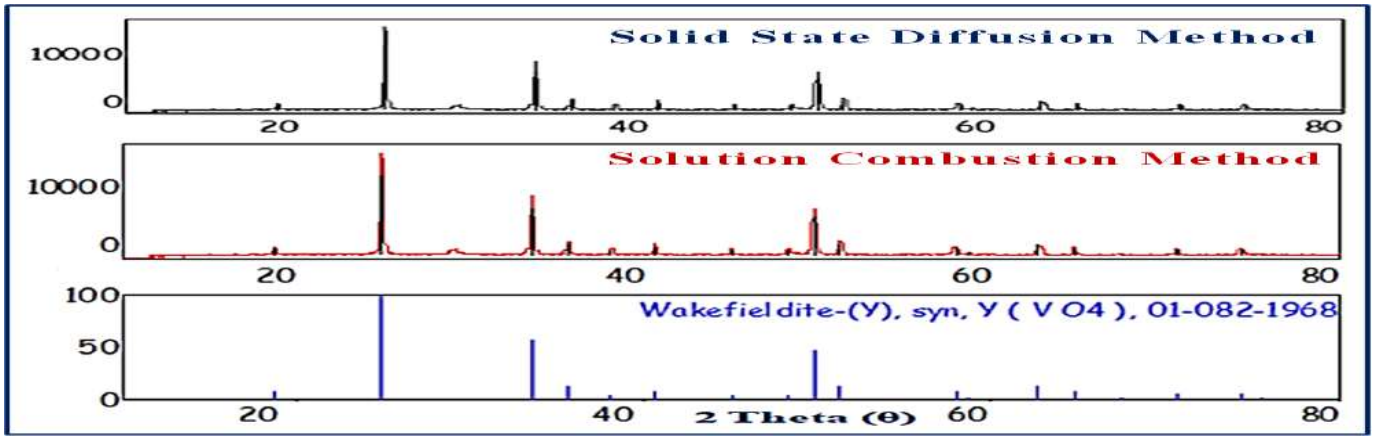

Figure 1: XRD patterns for undoped and Eu^{3+}-doped YVO_4 phosphors prepared by combustion method. Standard JCPDS pattern is also given for reference.

3.2 Scanning Electron Microscopy

The morphologies of YVO_4:Eu^{3+} prepared by conventional CM technique and SSD route are shown in Fig. 2(a) and (b), respectively. The YVO_4:Eu^{3+} particles prepared by conventional solid-state route have an irregular shape, coarse surface, wide size distribution, and are highly aggregated, whereas the YVO_4:Eu^{3+} particles prepared by CM technique have rod shape, smooth surface, narrow size distribution in 1um range, and are lowly aggregated. The morphology difference above mentioned should have originated from different preparation conditions and post-treatment techniques. In conventional solid-state reaction route, a high-

temperature calcination is required for obtaining the phosphor materials with high crystallinity, however, high-temperature calcinations make the phosphor particles large and easily agglomerated, thus, milling and grinding appear necessary to obtain suitable particle size for application, but these post-treatment techniques significantly damage the surface quality of phosphor particles[15], as shown in Fig. 2(a). Compared with solid-state reaction route, the CM route needs a lower calcination temperature for the host crystallization and no milling and grinding processes. It is known that the morphology of phosphor particles plays an important role in improving the performance of flat panel displays. The phosphor particles with smooth surfaces are able to increase the screen brightness and improve the resolution[16] because of lower scattering of evolved light and higher packing densities than irregularly shaped particles obtained by conventional solid-state route.

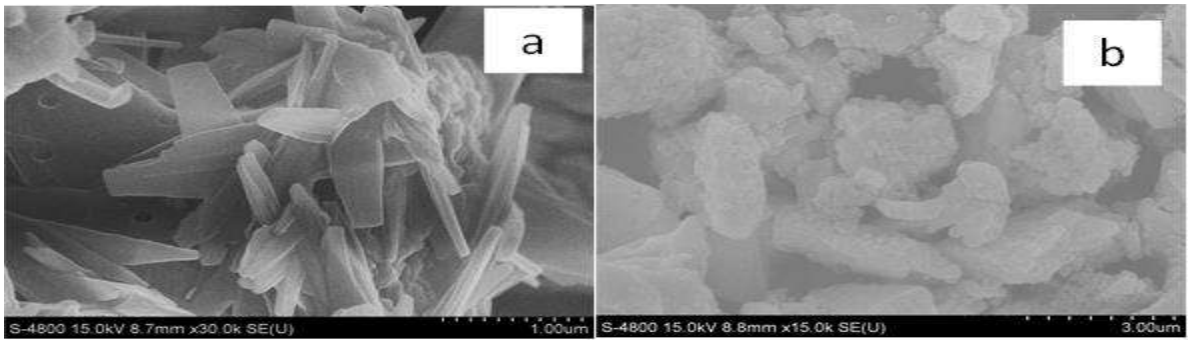

Figure 2: SEM images of 0.8 % Eu^{3+} doped YVO_4 prepared by: (a) CM and (b) SSD Method

Furthermore, recent studies revealed that the VUV energy is absorbed in a very thin layer at the surface of the phosphor particles[17,18], so the surface quality of phosphor particles seems to be very important for the luminescent efficiency. Milling and grinding processes are introduced in the phosphor prepared by conventional solid-state route, thus, the surface quality of phosphor is degraded, which is expected to influence the absorption of VUV energy significantly.

3.3 VUV Luminescence Studies

Emission spectra for samples prepared by CM and SSD methods of Eu^{3+}-doped YVO_4 phosphor shown in Fig. 3 along with insets, reveal the characteristic Eu^{3+} emission lines[19-21]. All the samples have been excited by VUV light of wavelength 147 and 172 nm, leading to an efficient energy transfer from the YVO_4 matrix to Eu^{3+} ions with subsequent f–f radiative relaxation ($^5D_0 \rightarrow ^7F_J$) transitions. All the emission spectra consist of the characteristic lines from $^5D_0 \rightarrow ^7F_J$ (J = 1, 2, 3 and 4) transitions of $Eu3^+$ ion at 596, 620, 653 and 702 nm, respectively, as shown in Fig. 3 along with insets, respectively. In all emission results, red emission line at 619 nm, attributed to the electric dipole transition $^5D_0 \rightarrow ^7F_2$ of Eu^{3+} ions, is found to be intense. The excitation spectra of 0.8 % Eu^{3+}-doped YVO_4 sample, prepared by two different methods, recorded at the emission wavelength of 619 nm are shown in the insets of Fig.4. Fig.5 illustrates the plot of Eu^{3+} concentration versus the emission intensity of the red line (at 619 nm) in the $Y_{1-x}Eu_xVO_4$ phosphors synthesized by two different methods. The optimum Eu^{3+} concentration of the samples, synthesized by SSD and CM technique, is observed to be 8 %. As a case, the luminescent efficiency of the Eu^{3+} under the excitation at wavelength 147 and 172 nm depends strongly on the absorption efficiency of the host. As mentioned above, the phosphor powders obtained from CM route have higher luminance than those obtained from SSD route, since they have higher absorption efficiency of energy due to their excellent morphology. The emission spectrum of Eu^{3+}-doped YVO_4 prepared by low temperature method CM method shows very similar characteristics with that from high temperature SSD with difference in emission intensity.

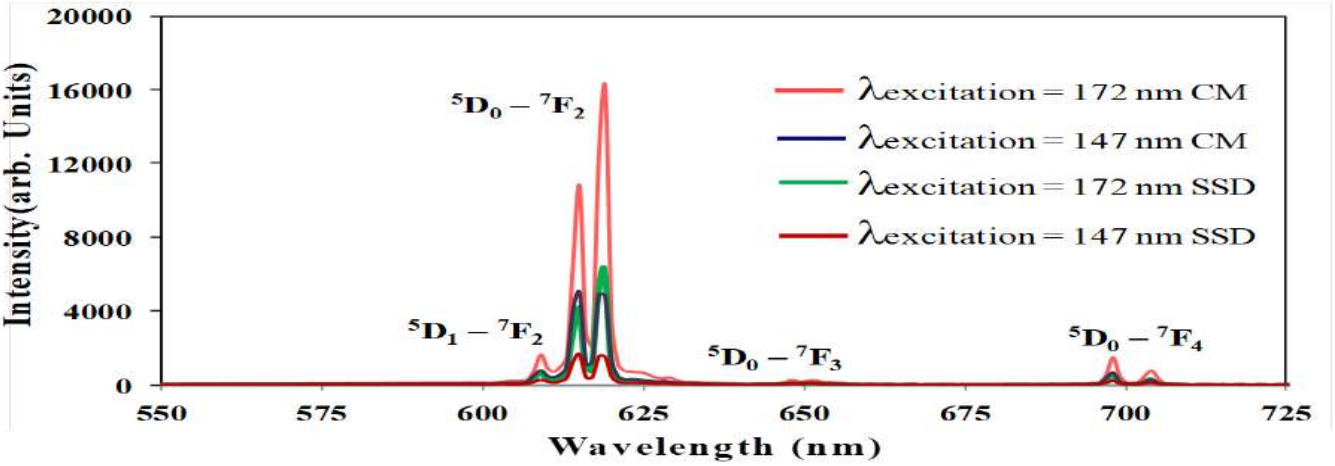

Figure 3: Photoluminescence emission spectra of $YVO_4:xEu^{3+}$ prepared by: (a) CM and SSD method (λex = 147 and 172 nm).

The intensity ratio of $^5D_0 \rightarrow {}^7F_1$ to $^5D_0 \rightarrow {}^7F_2$ bands varies with the changing of the preparation method at different excitation. It is interesting to note that the emission intensity of Eu^{3+}-doped YVO_4 crystals prepared by the CM method is about 2 times as much as that by the SSD method. The difference in the emission intensity of Eu^{3+}- doped YVO_4 crystals prepared by different methods can be explained if we consider the morphology of crystals and the phase formation during the processes.

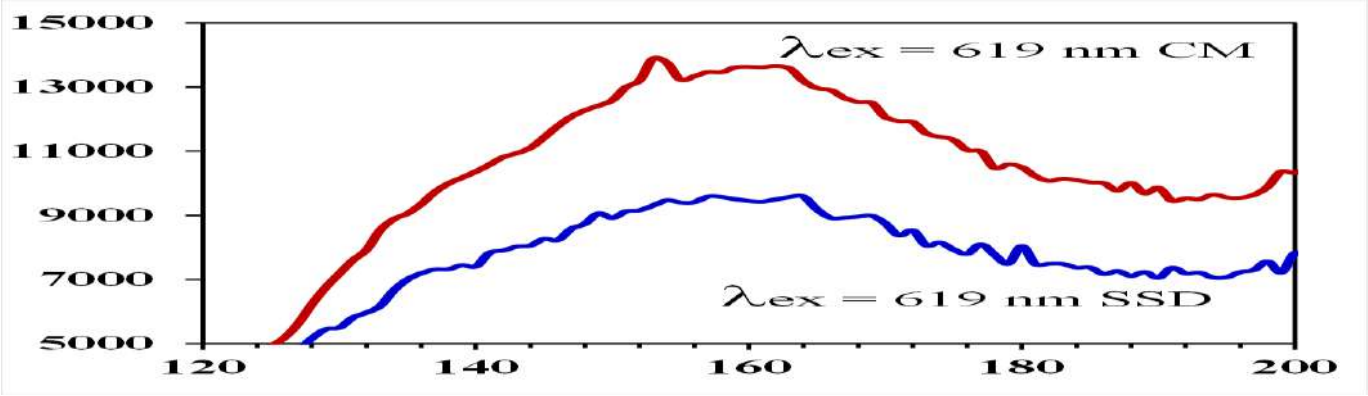

Figure 4: PL excitation spectra of the optimum Eu^{3+}-doped YVO_4 samples prepared by CM and SSD route (λemi = 619 nm)

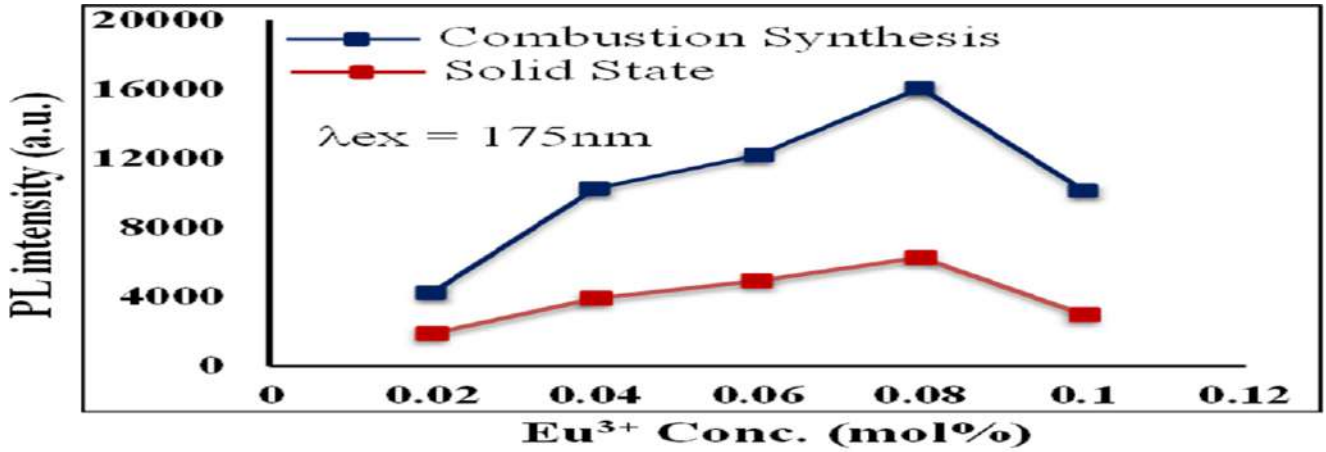

Figure 4: Plot of PL emission intensity as a function of Eu^{3+} concentrations of Eu^{3+}-doped YVO_4 prepared by combustion route and solid-state route (λex = 172 nm)

The particles of the YVO_4 prepared via the high temperature method were agglomerated (Fig.2b) and the extent of crystallization of YVO_4 prepared from the high temperature process is lower than that obtained from the low temperature CM method (Fig.2a). As mentioned earlier in the process of photoluminescence of Eu^{3+}-doped YVO_4 crystals, the energy is absorbed by the host lattice YVO_4 first and then it is transferred to the activator Eu^{3+} ions then lead to the luminescence. The absorbed energy by the host lattice in the agglomerated Eu^{3+}-doped YVO_4 particles would be lower than that in the YVO_4 crystals with uniform shape. Furthermore, there would be more defects in the crystals with lower crystallization obtained from the high temperature system.

IV. CONCLUSION

Solid-state and solution combustion methods were used to synthesize the red-emitting phosphor for PDP applications. By comparison, advantages of low temperature solution combustion method are summarized as follows: lower calcinations temperature, excellent particle morphology, and higher compositional homogeneity. YVO_4:Eu^{3+} phosphors have strong excitation bands in VUV range, indicating high VUV energy absorption. The phosphors prepared by low temperature solution combustion method have superior luminescence, since they have excellent particle morphology and high compositional homogeneity, compared with those prepared by solid-state reaction route.

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Novel Molten Salts Synthesis and Photoluminescence Properties of Eu (III) Doped Y_2O_3 Phosphor

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ABSTRACT

A novel molten salt method used for the synthesis of Eu^{3+} doped yttriumbased phosphor. It is well known that $Y_2O_3:Eu^{3+}$ is highly efficient red phosphors used for Lamp phosphor. The $Y_2O_3:Eu^{3+}$ phosphor was synthesized by reactions in molten salts method.The red emitting phosphor characterized through powder X-ray diffraction (XRD), and PL spectra. A novel molten salt is one step methodand decrease calcining temperature.

Keywords : $Y_2O_3:Eu^{3+}$,Molten salts method, PL spectra.

I. INTRODUCTION

The production of reliable and reproducible ceramic materials for high technology applications require strict control over their powder characteristics, which includes chemical homogeneity, low impurity levels, small particle size, narrow size distribution and freedom from agglomeration. A variety of methods e.g. sol-gel, chemical precipitation of precursors in aqueous or organic solutions, thermal decomposition of solutions by spraying technique, high alkaline and hydrothermal precipitation have been proposed for obtaining small, uniform un-agglomerated powders. These methods so-called wet chemical method, have been found to be successful for number of systems. Also self-sustaining combustion synthesis is a simple, inexpensive and quick way of synthesizing various oxide materials in comparison to the wet chemical techniques [1].

Compounds containing rare earths have long been used as phosphors and laser materials because of their sharp, intensely luminescent f-f electronic transitions.In particular, Eu^{3+} has five narrow emission bands corresponding to the $^5D_0 \rightarrow {}^7F_j$ transitions where, j = 0,1,2,3,4. The strongest transition, $^5D_0 \rightarrow {}^7F_2$ occurs at 613 nm, which is a characteristic of red fluorescence of Eu^{3+}. This transition has also been shown to exhibit laser emission under appropriate conditions in Eu^{3+} doped crystals [2, 3]. It is well known that the $Y_2O_3:Eu^{3+}$ is highly efficient red phosphor and has its own importance in scintillation, lamp and color TV picture tubes [4].

The preparation of these red emitting phosphors is critical and requires special methods such as wet chemical methods. Recently preparation of Eu^{3+} doped yttria was carried out by the alkoxide route and combustion process [5, 6]. Though these processes are efficient, requires expensive chemicals and special

equipment. Here we report the preparation of Y_2O_3: Eu^{3+} by the novel method of reactions in molten salts.

The term molten salt refersto the liquid state of compound, which melts to give liquids displaying a degree of ionic properties [7, 8]. Alkali metal nitrates have relatively low melting points (Table:1) whereas even lower melting points are obtained in their eutectic mixtures. A molten salt can behave as a solvent or as a reactant. Thus in a nitrate melt acid-base reactions can occur according to the Lux -flood formalism, whereby an acid is an oxide ion acceptor and a base is an oxide ion donor; nitrate ions are bases in this formalism [9]. Nitrite melts are more basic than nitrate melts whereas addition of Lux-flood bases such as Na_2O_2, Na_2O and NaOH to a nitrate melt, which its basicity.

The precursors are the inorganic compounds, in particular sulphates and chlorides that are blended with the alkali metal nitrates or nitrites as a powder mixture before heating to the reaction temperature. Table:1 shows the various eutectic mixtures and corresponding melting points.

Table-1 Melting points for alkali metal nitrates and eutectic mixtures.

Metal Nitrate	Melting point (^{0}C)
$NaNO_3$	307
KNO_3	334
50 mol% $NaNO_3$-50 mol% KNO_3	220
43 mol% $LiNO_3$- 57 mol% KNO_3	132

II. METHODS AND MATERIAL

2.1 Synthesis of $Y_2O_3:Eu^{3+}$

The precursors used were Y_2O_3 (AR) and Eu_2O_3 (AR). Both were mixed together in a china basin. A small quantity of double distilled (DD) water was added and paste was formed. Then HCl was added drop by drop and mixture was heated slowly under observation at 50^{0}C till the paste dissolved completely. The solution was further heated till the excess of acid was boiled off. Little quantity of double distilled (DD)water was again added and slowly evaporated to dryness. The resulting powder was YCl_3: Eu. The chemical reaction is $0.97\ Y_2O_3 + 0.03\ Eu_2O_3 + HCl \rightarrow 2\ Y_{0.97}Cl_3 : Eu_{0.03} + 3H_2O$ ---------- (1)

The eutectic mixture of nitrates $LiNO_3.3H_2O$ (43 mole %) and KNO_3 (57 mole %) were taken in a china basin and mixture was dried at 50^{0}C.The dry chloride YCl_3:Eu was added to this mixture of dried nitrates and thoroughly ground in a china basin. This mixture was then heated in a resistive furnace first at 100^{0}C for 1h and then with the gradual rise of temperature it was further heated at 425^{0}C for12 hours. The chemical reaction is $2Y_{0.97}Cl_3 :Eu_{0.03} + 0.43\ LiNO_3.3H_2O + 0.57\ KNO_3 \rightarrow Y_{1.94}O_3 : Eu_{0.06}$ --------- (2)

The mixture was then cooled slowly. A semi convex white solid was formed. With the help of sufficient lukewarm DD water, the solid was transferred to a glass beaker. Keeping the beaker in an oven at 60^{0}C for 10 minutes, the white solid was partly dissolved in water and the fine particles of Y_2O_3:Eu started settling down at the bottom. The precipitate was washed repeatedly by DD water and then dried. The dried precipitate was then calcinated at 800°C for 2h and quenched suddenly at room temperature.The calcinated and quenched powder was $Y_2O_3:Eu^{3+}$ phosphor.

2.2 Material characterization

The phase purities of $Y_2O_3:Eu^{3+}$ phosphor was studied using Rigaku miniflex II X-ray Diffractometer with scan speed of 2.000°/min and Cu Kα (λ = 1.5406 Å) radiation in the range 10° to 90°. PL and PL excitation (PLE) spectra were measured on (Hitachi F-7000) fluorescence spectrophotometer at room temperature. The parameters such as spectral resolution, width of the monochromatic slits (1.0 nm), photomultiplier

tube (PMT) detector voltage and scan speed were kept constant throughout the analysis of samples

III. RESULTS AND DISCUSSION

3.1 Powder XRD pattern of $Y_2O_3:Eu^{3+}$

The formation of the phase purity and crystal structure of Y_2O_3 synthesized by using molten salts at 800°C was confirmed by XRD pattern as shown in Figure. 1. All the peaks in XRD pattern very well agree with the standard data from ICDD file no. 01-071-0049. Also the XRD shows that the formed material was completely crystalline and was in single phase with cubic structure where a=b=c=10.5957 Å. The space group for Y_2O_3 is Ia-3 (206).The average crystallite size of $Y_2O_3:Eu^{3+}$determined from XRD pattern using Scherrer formula and it was found to be 965.52 nm [10]

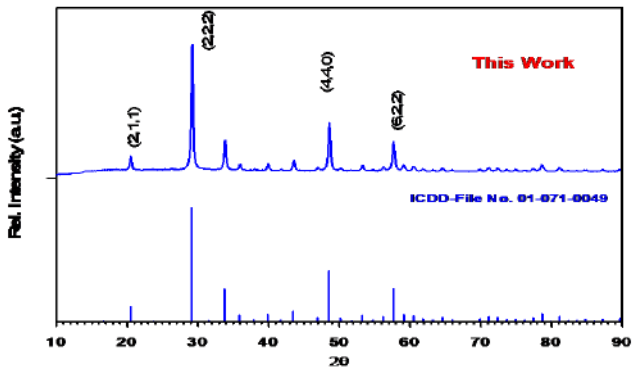

Figure:2 XRD pattern of $Y_2O_3:Eu^{3+}$.

Figure 2 shows PL spectra of $Y_2O_3:Eu^{3+}$ phosphor. It consists of a broadband excitation spectrum peaking at 246 nm, monitored at emission wavelength 613 nm. The emission spectrum is sharp peaking at 613 nm at excitation wavelength 254 nm, corresponding to the transition $^5D_0 \rightarrow {}^7F_2$ of Eu^{3+}. The intensity of emission is found to be comparable and excitation, emission wavelengths matches well with those of reported in literature.

The rare earth compounds such as $Y_2O_3:Eu^{3+}$ mainly belong to luminescent materials with individual luminescent center. Luminescence of these materials is due to the transition between 4f energy levels. Because of spin-orbit interaction, the degenerate 4f configuration is split into several energy levels such as ^5Dj and ^7Fj. The crystal field of host lattice affects the electronic transitions in Eu^{3+} [11]. For $^5D_0$ term, j = 0, so it cannot split (only one energy level). For the term $^7F_2$, j = 2 and $2_{j+1}=5$, so it can split into five energy levels (Γ_1, Γ_2,Γ_3, Γ_4, Γ_5). The strongest peak at 613 nm in $Y_2O_3:Eu^{3+}$ phosphor corresponds to the transition $^5D_0 \rightarrow {}^7F_2$ of Eu^{3+}. This method of reactions in molten salts is a low temperature and single step synthesis. This method is easy to synthesis and precursors used are readily available. The sample synthesized is a snow-white powder and particle size varies from sub-micron to nano. Frequent washing and calcinations enhances the PL intensity.

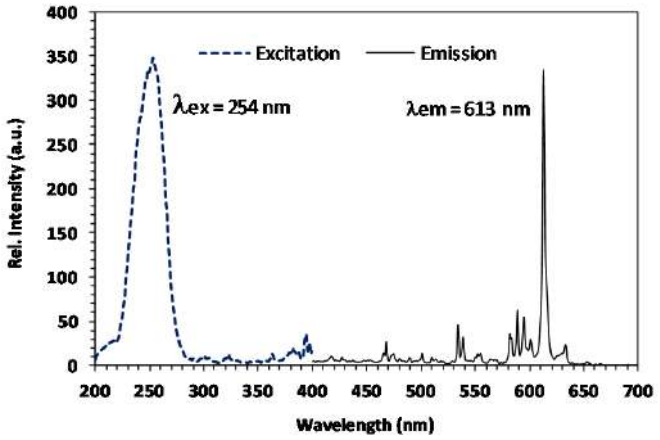

Figure:1 Photoluminescence emission and excitation Spectrum of $Y_2O_3:Eu^{3+}$

This method of reactions in molten salts is a low temperature and single step synthesis. This method is easy to synthesis and precursors used are readily available. The sample synthesized is a snow-white powder and particle size varies from sub-micron to nano. Frequent washing and calcinations enhances the PL intensity.

IV. CONCLUSION

The excitation and emission wavelengths in PL spectra of $Y_2O_3:Eu^{3+}$ synthesized by molten salts method confirms the formation of desired phase and crystal structure in the compounds. As phosphors

with particles of required size and colour are needed for their use in the display devices and other applications. This method has new horizons in the lighting industries.

V. ACKNOWLEDGEMENT

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Aldo-Keto Gel Synthesis and Photoluminescence Properties of $YVO_4 : Eu^{3+}$ Microsphere

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ABSTRACT

The Eu^{3+} doped YVO_4 phosphor synthesized via simple aldo-keto gel method by using Benzaldehyde and Acetone which then compared with conventional solid state diffusion. Powder X-ray diffraction (XRD) and field emission scanning electron microscopy (FE-SEM) studies indicate that the prepared samples were well crystalline and free from organic impurities. However, the nature of as-prepared phosphor by using aldo-keto gel method does not having any agglomeration. Further photoluminescence (PL), photoluminescence excitation (PLE) spectra and decay curves were superior as compared to solid state diffusion method.

Keywords: Aldo-keto gel method; aldehydes and ketones; spherical particle, PL properties; CIE diagram.

I. INTRODUCTION

Yttrium based materials doped with europium (III) have attracted more attentions among the many researcher group because these are important excellent commercial red-emitting phosphors used in various applications such as color television, the cathode ray tube and plasma display panel [1-3] due to its high quantum efficiency, dip red color purity, and high thermal stability [4]. Among all these yttrium based phosphors, the Eu^{3+} doped YVO_4 is still more demanding in the field of luminescence for the upcoming research because, its wide band gap. Also, absorption spectrum of YVO_4 shows strong and broad bands in the ultraviolet (UV) region [5].

The effect of synthesis method is important in the rare earth doped host lattice because luminescence efficiency is depending on nature of particles (agglomerated or un-agglomerated) [6]. A lot of efforts have been focused on the enhancement in luminescent properties of $YVO_4:Eu^{3+}$ phosphor with non agglomerated and narrow particle size. For the synthesis of phosphors, a variety of conventional and non conventional techniques have been adopted. The conventional method such as solid-state reaction is required lot of time with high temperature for preparation of phosphor [7]. Therefore, there is need to synthesis of such a phosphors at low temperature. The particle size of material prepared by solid state method is in the range of few micrometers and non homogeneous nature of as-prepared phosphor particle size.

All conventional and non conventional synthesis approach is sophisticated synthesis techniques for preparation of $YVO_4:Eu^{3+}$, but suffers with drawback. Because precursor require for synthesis is very costly and other additive chemical required for these methods are very expensive which leads to increase cost of application devices. Therefore in progressive

research we developed a novel synthesis technique for preparation of phosphors.

Inspiring from the above discussions, the present work planned to study the luminescent properties of $YVO_4:Eu^{3+}$ phosphor synthesized by using aldo-keto gel method and compared with very famous method is known as solid state diffusion.

II. METHODS AND MATERIAL

2.1 Solid state diffusion

The phosphor YVO_4: Eu^{3+} was synthesized by solid state methods with Eu concentration 0.01 mole. The precursor Y_2O_3 (99.99%, AR), NH_4VO_3 (AR) and Eu_2O_3 (99.90%, AR) were mixed thoroughly in a mortar with small amount of acetone. The resultant mixture was transferred to an alumina crucible and oven dried at 50°C. The mixture was heated in a resistive furnace at 1100ºC for 10h with intermittent grindings. The white powder of $YVO_4:Eu^{3+}$ so obtained was used for characterization.

2.2 Aldo-keto gel method

Aldo-keto gel method is uses to synthesis of $YVO_4:Eu^{3+}$ phosphor as per the previous work [8]. The precursors used $Y(NO_3)_3$ (99.99%, AR) and $Eu(NO_3)_3$ (99.99%, AR) were mixed together in a china clay basin. In basin $VOSO_4$ (AR) were mixed with some amount of water. On slowly heating to dryness, precipitated changed its color to reddish black. The acidic traces were removed by adding small quantity of deionized water to precipitated and drying 2-3 times; it finally changes to red color.

The red dried compound was finally milled. The benzaldehyde (1M) and acetone (1M) were added to this compound after that NaOH added drop by drop with increasing temperature.

On further slow heating, pyrolysis of foam was started at 450°C and shining black foam was formed at 500°C, which started burning from 700°C. After that one time washing and drying is required for better luminescence properties.

2.3 Material characterization

The phase purities of $YVO_4:Eu^{3+}$ samples were studied using Rigaku miniflex II X-ray diffractometer with scan speed of 2.000°/min and CuK_α (λ = 1.5406 Å) radiation in the range 10° to 90°. The PL and PLE spectra were measured on (Hitachi F-7000) fluorescence spectrophotometer at room temperature. The parameters such as spectral resolution, width of the monochromatic slits (1.0 nm), photomultiplier tube (PMT) detector voltage and scan speed were kept constant throughout the analysis of samples.

III. RESULTS AND DISCUSSION

3.1 XRD analysis

The formation of the crystalline phase of as-prepared products of solid state diffusion and aldo-keto gel method was confirmed by X-ray diffraction patterns as shown in Fig.1, to verify the phase purity and crystal structure. The X-ray pattern of both method samples indicated a pure phase of the standard YVO_4 and all the peaks are in good agreement with the (ICDD, 01-082-1968). Also the XRD shows that the formed material is completely crystalline and is in single phase, where a = b = 7.11 and c = 6.28 Å. The space group for YVO_4 is a I41/amd(141).

3.2 Morphology of $YVO_4:Eu^{3+}$ phosphors

FE-SEM analysis was done and resulting image displayed in Fig. 2 (A and D). The representative micrograph (A) for solid state diffusion and (D) for aldo-keto gel method shows that synthesized sample comprises regular shape with agglomerated and non agglomeration particles. The $YVO_4:Eu^{3+}$ phosphor prepared by aldo-keto gel method gives the non agglomerated and fine spherical particles. Also the grain boundaries of as-prepared materials were fine and well separated with no organic additives. On the other hand, sample prepared by solid state diffusion method reflects the agglomerated irregular nature of particles.

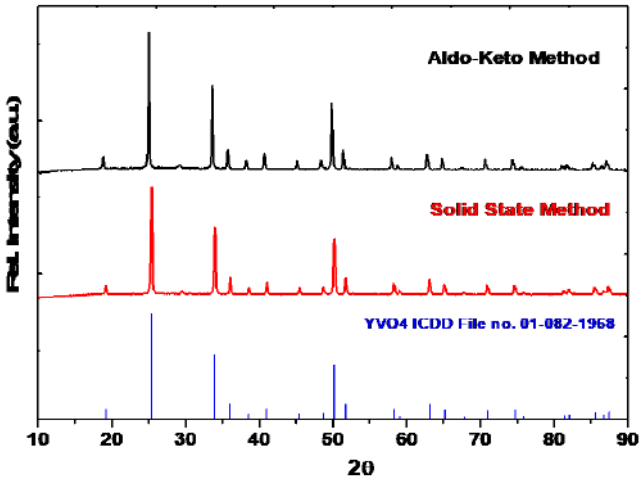

Fig. 1 XRD patterns of the $YVO_4:Eu^{3+}$ nanophosphor synthesized through solid state diffusion and aldo-keto gel method.

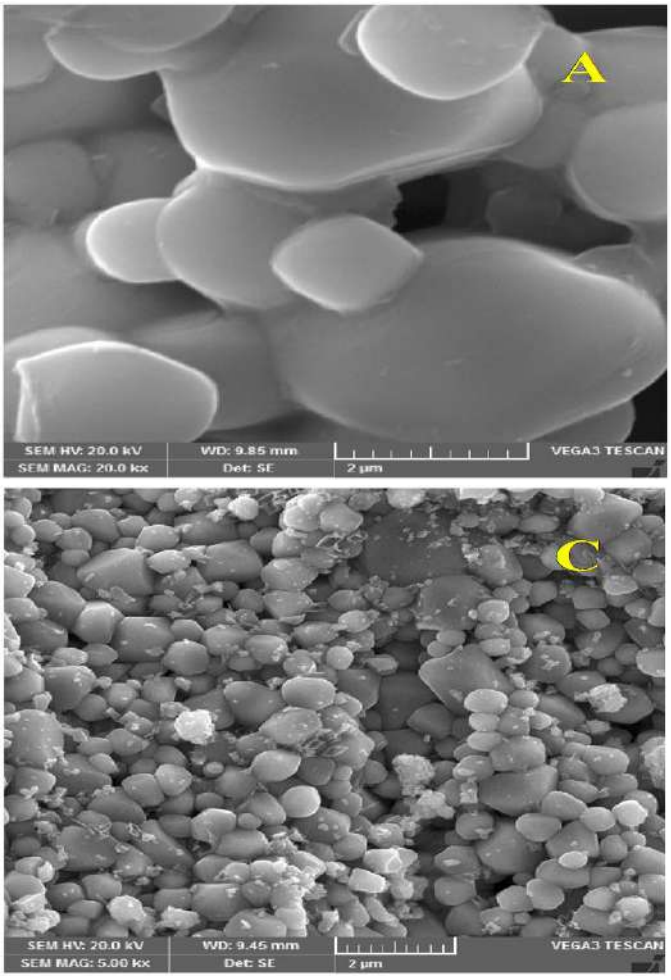

Fig. 2 FE-SEM images of the $YVO_{4:0.01}Eu^{3+}$ phosphor synthesized through solid state diffusion (A) and aldo-keto gel method D).

3.3 Photoluminescence properties

Fig. 3 demonstrates excitation and emission spectra of $YVO_4:Eu^{3+}$ phosphor synthesized by using solid state method and aldo-keto method with same concentration of Eu^{3+} ions (0.01 mole). The excitation and emission spectrum reflects that the phosphor prepared by aldo-keto gel method gives highest PL emission intensity as compared to solid state diffusion. The excitation attributed at 615 nm and emission monitored at 621 nm wavelength. The excitation spectrum shows similar nature except for a difference in intensity. It consists of a broad band with high intensity from 200 to 350 nm centered at 315 nm due to a charge-transfer transition from the oxygen ligands to the central vanadium atom inside the VO^{3-}_4 ion. Also, several narrow bands with low intensity in the range of 350–500 nm are due to the f–f transitions within Eu^{3+} 4f6 electron configuration [9].

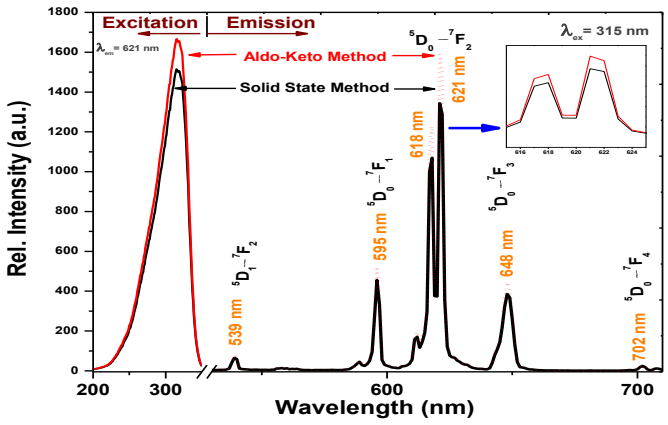

Fig. 3 PL excitation and emission spectra of $YVO_{4:0.01}Eu^{3+}$ phosphor synthesized via solid state diffusion (Black lines) and aldo-keto gel method (Red lines) (Inset of emission at 618 nm and 621 nm.

The emission spectra of $YVO_4:Eu^{3+}$ is as shown in Fig. 3. It consist of number of emission peaks in the ranging 550 to 710 nm corresponding to of $^5D_0 \rightarrow {}^7F_J$ (J = 1, 2, 3, 4) transitions of Eu^{3+} ions. The peak at 595 nm is corresponding to $^5D_0 \rightarrow {}^7F_1$ transition in the orange region due to magnetic dipole interaction and peaks at 618 and 621 nm are corresponding to $^5D_0 \rightarrow {}^7F_2$ transition in the red region due to electric dipole transition. The electric dipole transition is sensitive to

chemical bonds in the vicinity of the Eu^{3+} ion. On the other hand, the magnetic dipole transition is changes with the crystal field strength around the Eu^{3+} ion. Therefore, the PL intensity ratio of $^5D_0 \rightarrow {}^7F_2$ (Red) to $^5D_0 \rightarrow {}^7F_1$ (Orange) transitions is depend on the Eu^{3+} ions local surrounding environment. Generally, Eu^{3+} ions occupies an inversion symmetry site in the host matrix, then the orange emission ($^5D_0 \rightarrow {}^7F_1$) could be a dominant emission. Moreover, The peaks at 648 and 702 are corresponding to $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$ transition respectively. In $YVO_4:Eu^{3+}$ phosphor the electric dipole transition ($^5D_0 \rightarrow {}^7F_1$) shows superior PL intensity than magnetic dipole transition ($^5D_0 \rightarrow {}^7F_2$). The small peak at 539 nm is attributed to $^5D_1 \rightarrow {}^7F_2$ transition. [10].

IV. CONCLUSION

The inorganic intense red emitting $YVO_4:Eu^{3+}$ phosphor was first time successfully prepared by aldo-keto gel method and compared with solid state diffusion method. The experimental results indicate that aldo-keto gel method requires low temperature than that of solid state reaction and also reaction complete in less time.

The aldo-keto gel method does not need expensive equipment and result in good PL intensity. The aldo-keto gel method is based on molecular synthesis of particles so that agglomeration of phosphor particle can be avoided.

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Study of Haemoglobin Level in The Group Of 18-24 Year in Boys and Girls

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ABSTRACT: *In the survey we determined the quantity of Hb (8/dl). We divided the the subjects into different groups, based on age and sex. We make a comparison about percentage of haemoglobin between the College Students and between Boy's and Girl's. We divide the subjects into the age groups i.e. 20-24 (15 Subjects) in Girls and 18-24 (15 Subjects) in Boy's. In girls between 18 and 24 years of age the haemoglobin values decreased slightly, reaching about 11.36 gm/100 ml. In boys of corresponding ages there was an increase to about 16.10 gm. The quantity of the haemoglobin is very important in the diagnosis of the anaemia. Anaemia is a normal quantity of Haemoglobin present in the blood. To compare the percentage of Hb, we take the mean Hb (gm/dl) of male and females as well as of the four age groups. The mean Hb of the male was 12.83 gm/dl and for the female it is 11.83 gm/dl and for the female it is 11.93 g/dl male subjects have more amount of HB (12.83gm/dl) that the female subsets (11.93 gm/dl). By this we said that bared on the sex percentage of Hb varies, the male subjects having more amount of Hb than the female subjects.*

1. INTRODUCTION:

Haemoglobin is the most familiar, most efficient respiratory pigment. It is a crystallized, Conjugated protein consisting of an iron – containing pigment and a simple protein, globin. It occurs in majority of vertebrate and invertebrates. In invertebrates is found dissolved in plasma, whereas in vertebrate it is contained in the special cell called red blood corpuscles. Each Haemoglobin molecule is made up of four heme groups. Surrounding a globin groups forming tetrahedral structure.

Haemoglobin is involved in the transport of other gases it carries some of the body's respiratory carbon dioxide about 10 % of the total as carbanion haemoglobin in Which O2 is bound to the globin protein. The molecule also carrier the important regulatory molecule nitric oxide bound to a globin protein thiol group releasing it at the same time as oxygen. Haemoglobin is also found outside red blood cells and their progenitor lines. Other cells that contain haemoglobin include the A9 dopaminergic neurons in the substantiate nigra, macrophage and meningeal cells in the kidney in these tissues haemoglobin has a non – oxygen Carrying function as an antioxidant and regulator of iron metabolism.

2. MATERIALS AND METHODS:

Material Used in Estimation of haemoglobin percentage with the help of haemometer are as follows

Haemometer (Sahli's Haemometer)

Decinormal (N/10) HCl (1.2 CC Of Conc. HCl Dissolved in 100 cc of distilled water), Distilled water, own blood Sample, Pricking needle, spirit lamp, Cotton and beaker.

Fig. No.1:- Haemometer

Apparatus: The Haemometer consists of two sealed lateral comparison tube containing a suspension of acid haematin. This are held in a black frame against a white back round glasses Besides, a graduated test tube of the same diameter is also provided which can fit in the haemometer in between the two side tubes for comparison. A micropipette of 20 cm is also provided thither things provided are a small glass rod, a small bottle to contain the decinormal acid solution.

Fig. No. 2 Apparatus

3. METHOD:

- The Graduated tube is first Clean with distilled water and then with methylated spirit or 90% alcohol.
- It is thoroughly dried up before being used.
- Now with the help of dropper. Then 10N HCl Solution is filled is graduated tube up to 2gms mark.
- Micropipette is now filled up by sucking fresh blood of the vertebrate under experimentation up to the mark of 20 cm.
- The small amount of blood adhering to outside of micropipette should be aspired off by sterilized cotton.
- The blood of micropipette is now added to n/10 HCl solution in the graduated tube.
- The Pipette should be introduced carefully into tube and its lower mouth should. Pass right up to the bottom into HCl solution.
- When blood has been expelled pipette is rinse by distilled water,
- Every time the content of micropipette should be expelled into graduated tube.
- The acid haematin solution is now thoroughly, Stir with the help of glass rod and then allow to stand at least for 10 min.
- Afterwards the acid haematin solution is gradually diluted by adding distilled water in a drop wise manner with addition of each drop of distilled water the solution should be stirred and it's colour match with that standard sealed tube.
- This should continue till the colour of acid haematin solution just feds away as compared to that of standard comparison tube.
- The reading before the colour just fed's taken as correct and final reading.

4. OBSERVATIONS AND RESULTS:

In the survey we determined the quantity of Hb (8/dl). We divided the subjects into different groups, based on age and sex. We make a comparison about percentage of haemoglobin between the College Students and between Boy's and Girl's. We divide the subjects into the age groups i.e. 20-24 (15 Subjects) in Girls and 18-24 (15 Subjects) in Boy's.

Table No. 1 :- Mean Hb (g/dl) based on the age and sex.

Age groups (years)	Sex	Mean HB (g/dl)
18 – 20	Boy	15.50
	Girl	10.21
21 -22	Boy	14.50
	Girl	8.15
23 -24	Boy	16.10
	Girl	11.36

Normal Haemoglobin levels according to the world health Organization (WHO) is a healthy haemoglobin level depends on maintaining good nutrition and regular physical exercise. Haemoglobin helps you stay active by transporting oxygen through your blood stream around your body and by removing poisonous carbon dioxide. But in our survey of the college students shows the boy's Hb percentage. It is because of the reason of good nutrition, habits and regular diet. Normal Hb levels depends on your sex, age and health status.

Table No. 2 :- Normal HB (g/dl) level given by WHO

Groups (years)/Gender.	Normal HB level (g/dl)
0.6-4	11 g/dl
5-12	11.s g/dl
12-15	Equal or above 12 g/dl
Adult male	13.8 -17.2 g/dl
Adult Female	12.1 1s.1 g/dl
Pregnant women	Equal or above 11 g/dl

5. DISCUSSION:

The quantity of the haemoglobin is very important in the diagnosis of the anaemia. Anaemia is a normal quantity of Haemoglobin present in the blood. To compare the percentage of Hb, we take the mean Hb (g/dl) of male and females as well as of the four age groups. The mean Hb of the male was 12.83 g/dl and for the female it is 11.83 g/dl and for the female it is 11.93 g/dl. Male subjects have more amount of HB (12.83g/dl) That the female subsets (11.93 g/dl). By this we said that bared on the sex percentage of Hb varies, the male subjects having more amount of Hb than the female subjects.

The main reason for having less amount of Hb due to by taking important diet and some habits, like smoking. Because iron is an important component of Haemoglobin, consuming iron-rich component foods, like fortified foods, (these products include breakfast cereals, Pasta, bread, malted drinks and grits . The food and nutrition board recommends 18 mg of iron for women and 8mg for men), animal sources (seafood, Poultry, eggs and beef), plant sources (Red Kidney beans , lentils, Soybeans, black, beans, white beans and Cowpeas).

6. SUMMARY AND CONCLUSION:

HB is a very important metal -protein in the blood. By find out amount of hb present in the blood, we diagnosis that whether the patient is suffering with anaemia or not by our survey we conclude that the maximum peoples are having healthy amount of Hb (g/dl) the limits which is given by the who. Some of the people are having very less amount of Hb they consider as a anaemia patients, there is a significant difference between the amount of Hb present in the male and female subjects and the difference is age groups by this we said that the amount of Hb on the blood varies depends on age and the sex.

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IMPACT OF SYNTHETIC PYRETHROID ON DNA, RNA,AND DNA/RNA RATIO ON FRESHWATER FISH *CHANNA PUNCTATUS*

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ABSTRACT:

In the present investigation an attempt was made to evaluate the impact of sub lethal concentration of pyrethroid exposed to freshwater fish. The DNA, RNA and RNA/DNA ratio were estimated in kidney and brain of freshwater fish *Channa punctatus*. The sub lethal concentration of pyrethroid (0.00078 µl/lit) for 24, 48, 72 and 96 hours of different time intervals. The concentration of pyrethroid showed reduced level of DNA content 0.22, 0.27, 0.23, 0.25 in control whereas 0.25, 0.23, 0.22, 0.28 was observed in experimental. RNA content 0.001, 0.001, 0001, 0.002 in control and 0.0018, 0.0017, 0.0015, 0.0012 in experimental. While the DNA / RNA ratio significantly changed 0.0071, 0.0070, 0.0074, 0.0041 respectively at the different periods as compared with control of the experimental in *Channa punctatus*.

KEY WORDS: *Channa punctatus*, Pyrethroid, DNA, Kidney, RNA

INTRODUCTION:

Environmental problem in the developing world is clearly linked to imbalanced ecosystem. Environmental contamination by pesticides has been documented in both biotic and abiotic components. Pollution is impairment of quality of some part of environment by addition of the harmful impurities. There are many reasons for environmental pollution. The industrial waste materials discharged in river water contains waste material, due to which water gets highly polluted or contaminated. In industrial waste many harmful subjects are preset, which cannot destroy, means some subjects are non-degredable and some reacts with water and forms poisonous substances which results in pollution of water. The increased use of the insecticides in agriculture has contributed to the improvement of agriculture production. However, many adverse effects have been recognized. The mode of action of these compounds has been subjected to intensive study The pollution of environment due to use of

pesticides have become an increasing problem over the last century with the development of industry agriculture and increase in population. The random use of different pesticides often causes lot of damage on non- target organism.

Modern agricultural pesticides undoubtedly contributed to increase crop yield but also produce widespread pollution of the natural environment with damage to inland fisheries (Johnson 1968). Environmental problem in the developing world is clearly linked to unbalanced ecosystem. The random use of the different pesticides often caused lot of the damage on non-target organism. Organophosphate pesticide constitutes a large proportion of total synthetic chemical employed for the control of pests in the field of the agriculture, veterinary pesticides, and public health.

Pyrethroid insecticides shows their toxic effect by inhibiting impulse transmission Caside et al; (1983) most studies carried out with pyrethroid deals with its acute toxicity rather than biochemical effect (Reddy and Yellema 1991). In invertbrates and vertebrates, pyrethroid acts mainly on the nervous system pyrethroid affected to both a stomach poison and contact insecticide (Jin 1998).

The action is especially critical to fishes and aquatic insects where ATP are enzymes provides the energy necessary to active transport and are very important at site of oxygen exchange. Synthetic pyrethroids are extremely effective against insects but are relatively safe to mammals and birds. One potential problem of pyrethroid is the extrem toxicity to aquatic organisms which will produce toxic effects. Sieghfried also suggested that aquatic insects show higher susceptibility to the pyrethroid than terrestrial insects because of lower level of expore to lipophilic compounds in the aquatic environment which leads to lower potential to detoxify lipohilic xenobioties such as insecticides.

The synthetic pyrethorid a new class of agricultural insecticides has emerged as a complement to organophasphate and other type of pesticides.

Therefore it was considered to analyse the effect of pyrethroid on DNA, RNA, RNA/ DNA Ratio in muscles of a freshwater fish *Channa punctatus.*

Materials and Methods:

The experimental fish *Channa punctatus* were collected from Sonala Dam around Sonala village and local market. The fishes were measuring 12-13 cm in length and about 13-25 gm in weight. The fish were brought to the laboratory in polythene bags containing aerated water and acclimatizing in glass aquaria in the laboratory conditions for about a week. During this period fish were fed on commercially available food for experimental purpose the pesticide mixture was prepared by dissolving enough pesticide in 100ml of water. A calculated quantity of stalk solution was added to fresh water in the industrial aquarium.

Fishes were divided into two groups control and experimental. The fish were acclimatizing for a week according to APHA (AWWA/WPCA, 1998) standard method. The tap water was used as experimental medium for holding different test. The test fish was fed on food available in the market

excess food and fecal matter were removed from the glass, aquaria ones in a day or thrice at least in week the test fish was handled carefully so that the stress was minimum.

For toxicity evaluation synthetic pyrethroid was selected. These synthetic pyrethroid was cypermethrin. The cypermethrin is alternative for oganophosphate and organachlorine. The insecticide diluted in laboratory tap water.The LC_{50} of cypermethrin is 0.0007 ul/ltr for 96 hours was determined to decide its sub lethal concentration for experimentation. Control and experimental groups of fishes were scarified after 24 hr. of 96 hrs. The pesticides used in present works.Brain and kidney were removes and washed in saline and deep frozen.A 10% homogenate was prepared in buffered saline (0.15 mol/l Nacl and 0.15 mol/l sodium citrate, pH (7.0). Homogenate was centrifuged at 8,000 rpm for 15 minute and resulting supernatant was taken for estimation of macromolecular constituents. DNA and RNA were estimated by diphenylamine and orcinol method respectively (Schneider, 1957). Absorbance was recorded at 595, 665 and 660 nm for DNA, RNA respectively.

RESULT AND DISCUSSION:

In the present study observed that when the freshwater fish *Channa punctatus* exposed to sub lethal concentration of cypermethrin showed a significant observation, of biochemical such as DNA, RNA and RNA/DNA ratio.

Pyrethroid a, cypermethrin was treated with freshwater fish *Channa punctuates* for toxicity evaluation the freshwater fish *Channa punctatus* exposed to sublethal concentration of cypermethrin showed histological alternation in the DNA and RNA ratio.

Pyretheroids are not well known for their toxic action in animals therefore repeated administrations of subtethal and lethal doses of cypermethrin were found to be induced behavior tolerance in the aquatic animals.

Sublethal concentration of the cypermethrin increased the mucus secretion, fast movement and it is believed that the behavioural changes are the most sensitive measure of the neurotoxicity.

The fish *Channa punctatus* exposed to the cypermethrin showed irregular and erratic swimming, and slow movement of fishes. It is also losing their swimming balance and showed irregular movements. The body colour of fishes gets whitish due to sublethal concentration of the cypermethrin.

DNA :

In the present investigation the freshwater fish *Channa punctatus* exposed to sub lethal concentration of cypermethrin observed in muscle that, the DNA content were (0.22, 0.27, 0.23, 0.25) in control whereas (0.25, 0.23, 0.22, 0.28) which are decreasing in order observed in

experimental (Table -1). The result showed that all the values of DNA contain showed decreasing tread.

RNA :

In the present investigation the fresh water fish *Channa punctatus* exposed to the sub lethal concentration of cypermethrin and observed in muscle of fish 0.001, 0.001, 0001, 0.002 in control and 0.0018, 0.0017,0.0015, 0.0012 RNA contains of experimental values of the fish *Channa punctatus* showed decreasing trend.

DNA / RNA Ratio :

While the DNA / RNA ratio significantly changed (0.0071, 0.0070, 0.0074, 0.0041) respectively at the different periods as compared with control of the experimental in *Channa punctatus*.

In this study it is observed that when freshwater fish *Channa punctatus* is exposed to sub lethal concentration of the pyretheroids showed a significant decreased in level of DNA, RNA, while DNA/RNA ratio significantly changed From the above result it is noticed the that effect of sub lethal concentration affected the DNA, RNA and RNA/DNA ratio.

Hrs.	Control (DNA)	DNA (Expt)	Control (RNA)	RNA (Expt.)	RNA/DNA Contra	RNA/DNA (Expt.)
24	0.2278 ± 0.0181	0.2517 ± 0.0065	0.0012 ± 0.0027	0.0018 ± 0.0308	0.0052 ± 0.0013	0.0071 ± 0.0014
48	0.2755 ± 0.022	0.2398 ± 0.0053	0.0018 ± 0.003	0.0017 ± 0.044	0.0065 ± 0.0015	0.0070 ± 0.0012
72	0.2517 ± 0.025	0.2878 ± 0.0297	0.0020 ± 0.004	0.0012 ± 0.0019	0.0079 ± 0.0012	0.0041 ± 0.0018
96	0.2398 ± 0.020	0.2278 ± 0.0321	0.0019 ± 0.003	0.0015 ± 0.0046	0.0079 ± 0.0012	0.0065 ± 0.0016

CONCLUSION:

The purpose of present study was to investigation on different aspect of fish Channa punctatus. The LC50 values of cypermethrin 0.0007 □/ at 24, 48, 72, hrs. were determined. The DNA, RNA and DNA/RNA ratio from muscle of fish *Channa punctatus* was determined. The results showed that effect of sublethal concentration affected the DNA, RNA and RNA/DNA ratio, so very lower concentration may affect fishes. Therefore, prevention must be taken to save the aquatic environment and health of fish from pesticides in toxification.

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WEB ECOLOGY OF COMMON ARANEIDS OF SATPUDA LANDSCAPE, INDIA

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Abstract
In India, Spiders from only 11 families are known till date and they are **Araneidae** Clerck, 1757; **Deinopidae** C. L. Koch, 1850; **Linyphiidae** Blackwall, 1859; **Mimetidae** Simon, 1881; **Mysmenidae** Petrunkevitch, 1928; **Nephilidae** Simon, 1894; **Pimoidae** Wunderlich, 1986; **Tetragnathidae** Menge, 1866; **Theridiidae** Sundevall, 1833; **Theridiosomatidae** Simon, 1881 and **Uloboridae** Thorell, 1869. 7 Orb-web Builder families namely Araneidae, Deinopidae, Linyphiidae, Nephilidae, Tetragnathidae, Theridiidae and Uloboridae out of the 11 orb-web builder during 2013-2015 from Satpuda Landscape were collected. Webs can be an identifying character of a particular family and even the genera of a particular family can be identified by the web. Here, a brief Web comparison of the collected genera from the Araneidae is done to have an idea about the web including parameters like **Web Orientation & Measurement/ Web Description/ Related Activities**.

Keywords: Satpuda, Araneidae, Orb-Weavers, Ecology, Web.

Introduction

'Orb-web' is a peculiar web usually fulfilling almost all the requirements for which a web is being built i.e. prey capturing and retaining it, quite strong with significant elasticity, resistant to moderate climatic tampering and so on. Family Araneidae is one of the orb-web builder family currently having 177 genera and 3059 species (WSC, V-22.0). It was described by Clerck in 1757.Web pattern of different genera which were collected during the field work were studied in details aspect for documentation purpose.

Materials and Methods

Spiders from the 7 families were observed day and night for their web pattern. Web images were taken by Sony Cyber- shot DSCH-50. Web images with and without specimen wherever possible were taken and measurement of web segments were done with the help of scale and vernier caliper.

Observations and Results

Satpuda Landscape was surveyed day and night for studying the web patterns of different genera from Family Araneidae Clerck, 1757. Here, a tabulated documentation of 7 genera with their respective webs is done.

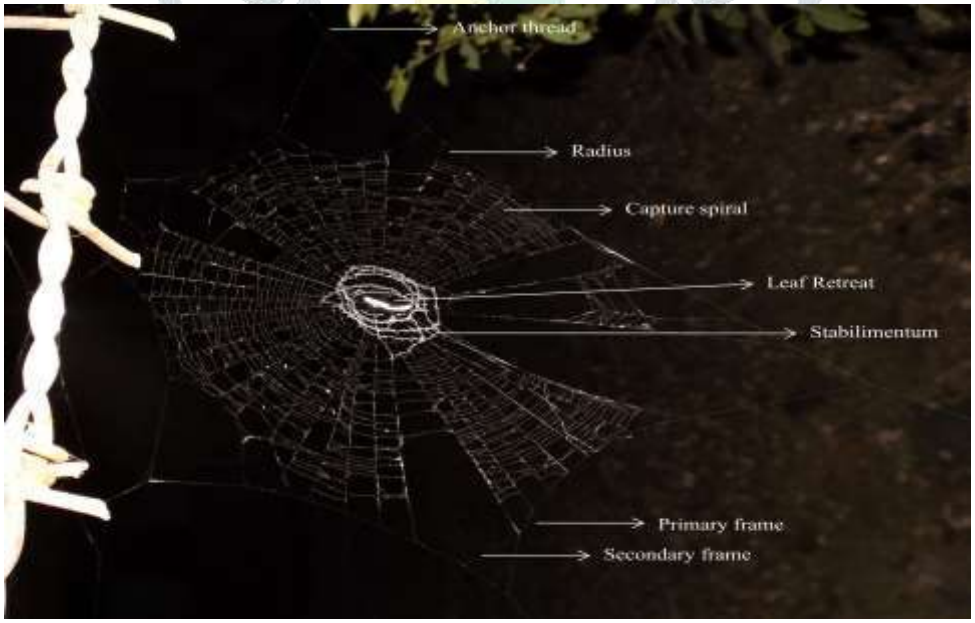

Fig. 1: General parts of a web (Web of *Cyclosa* sp.)

ARANEIDAE Clerck, 1757			
Genera	**Web Orientation & Measurement**	**Web Description**	**Related Activities**
Araneus	**Vertical:** Measurements of three webs of *Araneus* were taken for comparision: web 1, 2 & 3 respectively Total area of web (16cm/ 22 cm/24cm); Height from ground (2 feet/ 1.5 feet/ 2feet); Dist. (above) From the hub (9cm/13cm/9.5cm); Dist. (below) From the hub (9cm/11cm/9cm); No. of radials (27/28/28); Dist. b/w adjacent radials near centre (2mm/3mm/3mm); Dist. b/w adjacent radials near pheriphery (1.4cm/1.8cm/2cm); No. of spirals (24/31/30); Dist. b/w adjacent spirals (5mm/6mm/6mm); No. of attachment threads (8/7); Dist. of retreat from web (13cm/21cm/22cm)	Web of *Araneus* sp., less pronounced at the upper half. The upper half of the web is comparatively broader while lower half is more in area and a bit narrowed as compared to the upper half region of the web. Spider sitting at hub of the web, which is at a distance from the spirals and also the spirals of the web are spaced. Some of the spirals are discontinued and a small missing block is formed in the web, instead of the usual complete spiral pattern of the orb-web.	
Argiope	**Vertical:** Measurements of two webs of *Argiope* were taken for comparision: web 1 & 2 respectively Total area of web (18cm/ 24 cm); Height from ground (2 feet/ 1.5 feet); Dist. (above) From the hub (9cm/13cm); Dist. (below) From the hub (9cm/11cm); No. of radials (27/28); Dist. b/w adjacent radials near centre (2mm/3mm); Dist. b/w adjacent radials near pheriphery (1.4cm/1.8cm); No. of spirals (24/31); Dist. b/w adjacent spirals (5mm/6mm); No. of attachment threads (8/7); Area of stabilimentum (1.5cm/2.5cm); Dist. Of retreat from web (13cm/21cm)	Popularly known as "signature spider". This spider shows unique decoration of stabilimentum, which are called as signature. *Argiope* changes its stabilimentum shape from zig-zag to round shape. The species which was collected changes its stabilimentum design after 2-3 days. The height of the web from the ground is not much i.e. it usually built its web near to the ground, ranging app. from 1 foot to 3.5 feet in height.	

Cyclosa	**Vertical**: 3 webs of *Cyclosa* were measured; web1, 2 & 3 respectively: Total area of web (12cm/ 17cm/14cm); Height from ground (5feet/ 3.5 feet/1.8feet); Dist. (above) From the hub (6cm/9.5cm/7cm); Dist. (below) From the hub (6cm/8.5cm/7cm); No. of radials (34/46/43); Dist. b/w adjacent radials near centre (1mm/1.5mm/1.5mm); Dist. b/w adjacent radials near pheriphery (6mm/7mm/7mm); No. of spirals (32/41/32); Dist. b/w adjacent spirals (1.5mm/1.8mm/1.5mm); No. of attachment threads (5/6/5); Area of stabilimentum (2.2cm/11.5cm/6cm).	This spider builds a web which allows it to a remarkable degree of camouflage since its web is occupied by the leftovers of the prey and other debris. The stabilimentum is often occupied by these materials only and the female deposits its egg sacs, which passes vertically from the hub. The spider usually sits in the midst of these structures, fooling their predators. *Cyclosa* can be noticed sitting in its web during the whole day, but the web usually found vacant in night. *Cyclosa insulana* builds both linear and circular stabilimenta. The shape, size and design of stabilimenta varied depending upon the website location and environmental conditions. For example, in exposed or quite windy sites, *Cyclosa* builds smaller webs with greater number of circular stabilimenta while in normal conditions, it builds linear stabilimenta and also the web is large. I have noticed 4 webs of *Cyclosa insulana* which are present in forests of Melghat region at a bit of exposed site, which shows the presence of circular stabilimenta with size variations in the web.	**Egg Sacs:** **Shape:** round to oval **Size:** 4-5mm **Count:** 1 **Silk colour:** golden yellow **No. of eggs (total):** app. 60 **Site of egg sac laying:** laid within the web along with debris hanging with stabilimenta and also on under and upperside of leaf. **Parental Care:** Egg sac is guarded by the female till hatching. 
Cyrtophora	**Horizontal**: Web of *Cyrtophora* quite complex and therefore, the detailed measurements were not able to be taken , only the distinctly available measurements were taken of the 2 webs of *Cyrtophora:* web 1 & 2 respectively Total area of web (32cm/24cm); Height from the ground (3.6feet/1.8feet);	Commonly called as Tent-web spiders. *Cyrtophora* shows a degree of high technical aspect while building a web, which is quite complex and is rather not a complete orb web instead it is a horizontal web forming a cone in the middle, with many support lines holding it. The web is not sticky in nature, spirals and radials are constructed from the same silk. Unless in orb webs, all cells in the web are rectangular. Web height 2 to 5 feet.	**Egg Sacs:** Shape: oval to elliptical Size: 4-5mm Count: 2-7 **Silk colour:** off white with greenish tinch. **No. of eggs (total):** app. 150 **Site of egg sac laying:** laid at the center of the web, hangs with silk. **Parental Care:** Egg sac is guarded by the female till hatching and also accessory tents are built within the existing web, for accommodation of the hatchlings.

			
Neoscona	**Vertical**: Total area of web (2.6feet/ 1.8feet/1.4feet); Height from ground (2feet/ 3feet/2.8feet); Dist. (above) From the hub (28cm/24cm/17cm); Dist. (below) From the hub (38cm/28cm/25cm); No. of radials (27/25/22); Dist. b/w adjacent radials near centre (7mm/6mm/6mm); Dist. b/w adjacent radials near pheriphery (5cm/3cm/3.5cm); No. of spirals (32/34/28); Dist. b/w adjacent spirals (1.1cm/0.8cm/1cm); No. of attachment threads (7/4/6); Area of stabilimentum (1feet /3feet).	*Neoscona*, which are commonly cited in the webs, on shrubs, fences, poles, fields etc. builds a nearly vertical web ranging from 20- 70 cm in diameter. Hub of *Neoscona* sp. is not that prominent, showing few cross threads. The spider usually remains in retreat, within a curled leaf or beneath tree trunks, during the daytime. The height of the web from the ground is variable ranging from 2 feet to 7 feet.	**Egg Sacs:** **Shape:** round **Size**: 5-6mm **Count:** 1 **Silk colour:** yellowish white **No. of eggs (total):** - **Site of egg sac laying: -** **Parental Care:** Egg sac guarded by the female. 
Poltys	**Vertical**: Total area of web (20cm/2feet/1.2feet); Height from ground (2.2feet/ 3.6 feet/2.8feet); Dist. (above) From the hub (10cm/30cm/18cm); Dist. (below) From the hub (10cm/30cm/18cm); No. of radials (22/34/44); Dist. b/w adjacent radials near	These spiders are nocturnally active, building finely meshed orb webs at night and reingesting them around dawn. *Poltys* builds a very fine web, equally spaced spirals and neatly radiating radial threads. Usually the centre of the web i.e. the hub shows spaced cubical blocks of thread; while these blocks are absent in the webs of *P. columnaris* species.	**Egg Sacs:** **Shape:** oval to elliptical **Size:** 4.4-6mm **Silk colour:** yellowish with some brown threads **No. of eggs (total):** app.40 **Site of egg sac laying:** laid adhered to any surface, especially twigs with the help of silk. **Parental Care:** *Poltys* spider appears to show least parental care, as it is not seen guarding its egg sac.

	centre (3mm/5mm/3mm); Dist. b/w adjacent radials near pheriphery (1.5cm/2.6cm/1.6cm); No. of spirals (60/190/140); Dist. b/w adjacent spirals (1mm/1mm/1mm); No. of attachment threads (8/6/10); Area of stabilimentum (1.2feet/3.6feet).		
Zygiella	**Vertical**: 2 webs were compared, web 1 & 2 respectively; Total area of web (1.2feet/1.4feet); Height from ground (1.5feet/ 5 feet); Dist. (above) From the hub (17cm/20cm); Dist. (below) From the hub (19cm/22cm); No. of radials (18/22); Dist. b/w adjacent radials near centre (5mm/6mm); Dist. b/w adjacent radials near pheriphery (3cm/3.4cm); No. of spirals (12/16); Dist. b/w adjacent spirals (5mm/6mm); No. of attachment threads (5/9); Area of stabilimentum (2feet/1.5feet).	*Zygiella*, nocturnal in habit, hunts in the night and its web has a unique characteristic of having a missing sector in the upperhalf of the web. The missing sector usually shows a signal thread which connects the hub to the retreat through this missing sector. The spider rests in its retreat during the daylight hours and is informed for the presence of any prey through that signal thread, which is connected to the hub.	

CONCLUSION

The orb-weavers include more or less 12,000 species and make up about 26% of spider diversity. Web constitute an essential part in understanding the ecological as well as behavioural aspect of the spiders and by studying the detailed web characters; structures and related activities, one can easily understand and can identify and characterise the spider by seeing the web.

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Species Richness and Distribution of Ostracoda of Sonala Dam, Sonala, Dist. Washim (M.S.) India

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Abstract: *The paper deals with Species Richness and Distribution of Ostracoda of Sonala Dam, Sonala, Distt. Washim (M.S.) India. Sonala dam is an earthen dam, constructed by irrigation department of Maharashtra Govt. The dam is presently used for irrigation and drinking for regional rural areas. Ostracods are bivalved micro crustaceans found almost in all types of water bodies and are one of the most diverse groups of living crustaceans. The population density of ostracod of Sonala Dam, Sonala was monitored for one year. Samples were collected using plankton net of bolting silk cloth No.25 (56 mesh size and analysed with standard keys. Quantitative estimation was done by drop count method of Lackey. A total of 4 species from the dam water were identified. Results indicate that the population of Ostracoda was maximum during the summer season and minimum during the winter season. Distribution of Ostracoda was influenced by environmental factors like temperature, DO, salinity and sediment decomposition. Conservation of this water body is essential, as this habitat may reveal interesting ostracod fauna present there. There is no report of study on the species richness and distribution of ostracods in this reservoir and that is the reason the present study was planned.*

Key Words: *Sonala dam, Diversity, Ostracods, Zooplanktons*

1. INTRODUCTION:

Dams are the most important water resources. Unfortunately, large quantities of pollutants are accumulated in the reservoir due to indiscriminate disposal of sewage and wastes from anthropogenic activities (Shinde et al., 2011). Studies on freshwater bodies, natural or manmade have recently gained much importance, mainly because of their multiple uses. Aquatic ecosystems are known to support work to range of organism. Ostracods are one of the most diverse groups of living crustaceans. They are bivalved micro crustaceans found almost in all types of water bodies. Although ostracods are abundant and widely distributed but they have received much less attention than Cladocera and Copepoda (Pennak, 1978). They are a vital component of an ecosystem and form an essential link in the food chain and energy transfer at secondary level in aquatic food web between autotrophs and heterotrophs (Dievanni et. al, 2004). Ostracods are extremely sensitive to environmental variations. Their abundance and species diversity can provide important indication of environmental changes. The result will contribute to the understanding of the present status of the ostracods fauna in Indian freshwater lakes. There is no report of study on the species richness and distribution of ostracods in this reservoir and that is the reason the present study was planned.

2. MATERIALS AND METHODS:

2.1 STUDY AREA:

Sonala dam is an earthen dam constructed on River Adan, a tributary of River Godavari. It lays between 77^0, 12', 30" E Longitude and Latitude of 20^0, 19', 00" N in Sonala village of Washim district in Maharashtra (India). Maximum height is 19.20 meter and 446.90 hectares of submergence with 132.50 square kilometre of catchment area. The reservoir is mainly used for drinking water supply to nearby villages and for irrigation. The selection of six sampling station was made based on human and other domestic activities.

2.2 COLLECTION OF SAMPLES:

The acquisition of meaningful data demands correct sampling and preservation procedures. Water samples were collected from six sampling stations every month in the forenoon (between 7:00 am to 9:00 am.) for one year. 50 litres of water sample were filtered through standard plankton net of bolting silk cloth No.25 (56 mesh size). The sample was

taken in 125 ml plastic bottle and labelled mentioning the time, date and place of sampling. The samples were preserved by adding 2ml of 4% formalin. Quantitative analysis was done by Drop Count Method. Detailed taxonomic identification was carried out with Pennak (1989), Koradkar (1992) and Dhanpati (2000).

3. OBSERVATION AND RESULTS:

In the present study, Ostracoda represented by 4 species in dam water namely *Centro cypris, Cypris species, Hetero cypris, Stenocypris malcomsonii.* Seasonally, Ostracoda showed dominance in summer season, showed maximum 190 ± 3.08 ind/l in summer season and minimum 45 ± 4.5 ind/l in winter season. The yearly mean average of Ostracoda during the study was 77.5 ± 2.9 ind/l. In summer growth of algal blooms and macrophytes is high due to anthropogenic activities and contamination of brick factories. Hence, the abundance of ostracods, especially those of cosmopolitans, could be the indicator of pollution (Padmnabha, 2008; Sontakke et al, 2010). During the study period ***Cypris species 33.5±2.0*** ind/l showed dominance at all stations followed by ***Centro cypris* 28.2±1.2 *ind*/l**. Less appearance was shown by ***Hetero cypris* 17.8±1.5** ind/l and ***Stenocypris malcomsonii* 17.9±1.8.** Stationwise abundance of Ostracoda was in the order.

Station S_3 > Station S_1 > Station S_6 > Station S_5 > Station S_2 > Station S

TABLE NO. 1. Station wise Average values of Ostracoda

Sr. No.	Ostracoda	S1	S2	S3	S4	S5	S6	Average
1	*Centro cypris*	43.3±2.9	19.2±1.6	45.0±2.1	15.8±1.9	20.8±1.6	25.0±1.3	28.2±1.2
2	*Cypris species*	51.7±3.4	22.5±1.0	55.0±3.3	16.7±1.3	27.5±1.7	27.5±1.0	33.5±2.0
3	*Hetero cypris*	26.7±1.1	11.7±1.0	29.2±1.5	13.3±1.3	10.8±1.7	15.0±1.3	17.8±1.5
4	*Stenocypris malcomsonii*	31.7±2.9	10.0±6.6	31.7±2.3	13.3±1.1	9.2±5.5	11.7±1.2	17.9±1.8

4. DISCUSSION:

Data harvested during the study period, the population of Ostracoda was maximum during the summer season and minimum the winter. Distribution of Ostracoda was influenced by environmental factors like temperature, DO, salinity and sediment decomposition. There abundance is also dependent upon the availability of food as opined by Swain (1995) and Clark (1977). Four different species of Ostracoda were identified from this group. The population abundance of Ostracoda was observed at all the sampling stations but found in lesser number at station S_4. The Ostracoda population was abundant and dominated at stations S_1, S_3, S_6. It forms a good food chain and hence more fish catches have been recorded at station S_3. Seasonal variations in abundance of Ostracoda fauna was in order summer>winter>Monsoon. During the monsoon, Ostracoda population was found meagre at almost all stations except stations S_1 and S_2 which indicated productive nature of water.

5. CONCLUSION:

Sonala dam is nutrient rich and contain diversified Ostracoda fauna. They are bivalved micro crustaceans found almost in all types of water bodies, which have often been used to indicate the tropic status of a water body. They are a vital component of an ecosystem and form an essential link in the food chain and energy transfer at secondary level in aquatic food web between autotrophs and heterotrophs. They were most abundant during summer season and showed least abundance during winter season. They utilize the nutrients as well as phytoplankton more rapidly to build up their population and due to their enormous reproductive potential; they play a significant role in aquatic ecosystem to maintain the ecological balance.

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Molecular identification of a forensically relevant blowfly species (Diptera: Calliphoridae) from the Nagpur region of Maharashtra, India

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RESEARCH PAPER

Molecular identification of a forensically relevant blowfly species (Diptera: Calliphoridae) from the Nagpur region of Maharashtra, India

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Abstract

Blowflies (Diptera: Calliphoridae) are widely distributed in many parts of the world. These flies have forensic importance, as they infest carrion soon after death; this helps not only to estimate the post-mortem interval, but also other forensic interpretations. However, the forensic value of most entomofauna found at crime scenes is dependent on accurate species identification. Traditional identification of blowflies is based on morphology, but this has limitations when it comes to identifying degraded or damaged samples, or immature stages of the flies. To increase the accuracy of species identification, DNA-based technologies have been applied. Molecular identification, using the mitochondrial cytochrome C oxidase I gene coupled with its phylogenetic analysis, has demonstrated the potential for rapid and accurate identification of Calliphoridae species. The present study used this process of molecular identification to identify blowflies collected from the Nagpur region (Maharashtra, India). Five flies belonging to two species (*Chrysoma megacephala* and *Chrysomya rufifacies*) have been identified by mitochondrial cytochrome C oxidase I gene sequences, and have been added to GenBank [Accession nos: - (MT502110, MT502109 *Chrysomya megacephala*) (MT502108, MT502111 – *Chrysomya rufifacies*) to aid researchers in the correct identification of blowfly species for future research or forensic applications.

Key words: Calliphoridae, *Chrysomya megacephala*, *Chrysomya rufifacies*, Cytochrome Oxidase gene, Molecular identification

Introduction

Within entomofauna, necrophagous insects such as blowflies (Diptera: Calliphoridae) are attracted by decaying corpses, and colonize a body immediately after death (Reed 1958). Therefore, analyzing the infestation pattern of insects on a corpse can facilitate criminal investigations related to crimes such as homicide (Harvey *et al.* 2003), suicide (Vasconcelos *et al.* 2017), sexual molestation, wildlife crimes (Anderson 1999; Simon 2019), and others. They also provide clues as to the time of death, child neglect and abuse, chemical intoxication (Byrd & Castner 2001), disfigurement of corpses, the path followed by a culprit, and the location of death (Anderson 2004; Byrd & Castner 2001; Catts & Goff 1992; Singh *et al.* 1999). As, generally, forensic flies found at the crime scenes have a similar appearance, the accurate identification of fly species is crucial and should be more precise. If a species determination is incorrect, the estimated

post-mortem interval and other interpretations may be invalid and inaccurate (Byrd & Castner 2001).

Traditional morphological study is the most common method to identify adult insects, which includes various species characteristics (identification marks) used for the identification of Calliphoridae species. Unfortunately, in many cases, the traditional morphological identification is very difficult or impossible to perform (Prins 1982; Wallman & Donnellan 2001) due to lack of expertise in entomological studies, or to the high degree of morphological similarity between species of the same genus, or even by loss of morphological characteristics during collection, preservation, and packaging of the entomological samples (Wallman & Donnellan 2001). For this reason, the mt-DNA-based analysis using the mitochondrial cytochrome oxidase I (COI) gene is a powerful tool that can be used to resolve these issues, even when no appropriate specimen for morphological identification is obtained (Harvey *et al*. 2003; Sperling *et al*. 1994; Wallman & Donnellan 2001).

Since different succession patterns, geographic distributions, elevations, environmental temperature, and humidity (Siddiki & Zambare 2017) can affect the composition, development, and life cycle of insect fauna, the knowledge of local entomofauna of necrophagous insects is very important in order to introduce evidence into a forensic investigation. Many studies of forensic entomology have reported the entomofauna of India (Abd-Algalil & Zambare 2017; Bharamal 2016; Bharti & Sing 2017; Jadav & Sathe 2014; Sathe *et al*. 2013), but there is a paucity of data on the entomofauna of central India (Nagpur). As the temperature in Nagpur ranges from 48.6°C to 3.9°C, and has an average rainfall of 1064.1 mm throughout the year (online report, Government of India 2020), a survey of the entomofauna of the Nagpur region has become a necessary step for forensic entomological investigation in nearby regions.

The objective of this study was to identify blowfly species (Diptera: Calliphoridae) from the Nagpur region of Maharashtra, India. The COI gene of the mt-DNA sequence was used as a based approach coupled with phylogenetic analysis for the identification of two common blowfly species, *Chrysomya megacephala* and *Chrysomya rufifacies* (Diptera: Calliphoridae).

Material and Methods

Specimen collection

Adult flies were collected from various locations (Table 1) of Nagpur city using the decayed meat of sheep for attecting the flies as a trap. The adult flies were collected with the help of insect collecting nets, and were preserved in collecting vials containing 70% ethanol. Prior to the addition of 70% ethanol (Kanan & Tulung 2018), one to two legs of each fly were removed and stored in separate vessels for the extraction of DNA (**Fig.** 1).

DNA extraction

The mt-DNA from each fly was extracted by using the Wizard® Genomic DNA Purification Kit (Promega, Madison, WI, USA) following the manufacturer's protocol. The fly sample was ground into powder form and mixed with 700 μL of lysis buffer and 4 μL of RNAse in a 2-mL microcentrifuge tube. After DNA extraction, DNA concentration was measured using a Nanodrop ND 1000.

Polymerase chain reaction amplification and purification

The sequence of COI gene was amplified via polymerase chain reaction (PCR) using two universal primers (Abd-Algalil & Zambare 2017) (Table 2). PCR reactions were performed using a Kapa biosystems kit in 96-well plates. The reaction master mix was prepared by adding 9.6 μL of 10% trehalose, 7.0 μL H_2O, 2.5 μL of 10 × PCR buffer "B," 0.8 μL $MgCl_2$, 2.0 μL of 2.5 mM dNTP, 1.0 μL of 10 mM forward and reverse primers each, and 0.1 μL of Taq polymerase (5 units/μL) per reaction; 24 μL of the master mix was then distributed into each PCR tube, to which 1 μL of the DNA template (30–100 ng/μL) was added.

Polymerase Chain Reaction 35 cycles were performed with an initial denaturation temperature of 95°C, to break DNA down for single strands. Repeated amplification cycles performed at 94°C for 30 s, 52°C for 40 s, and 72°C for 60 s, with a final extension at 72°C for 10 min. Following this process, the amplified DNA fragments were harvested. The

Table 1 Species, collection data, and Genbank Accession numbers of blowfly specimens used in this study

Sr. no.	Species	Label	Collection locality	Genbank Accession no.
1	*Chrysomya megacephala*	NO2	Omkar Nagar, Nagpur	MT502109
2	*Chrysomya megacephala*	GO2	Godhani, Nagpur	MT502110
3	*Chrysomya rufifacies*	GO3	Godhani, Nagpur	MT502108
4	*Chrysomya rufifacies*	DP5	Dharampeth, Nagpur	MT502111

Chrysomya megacephala

Chrysomya rufifacies

Figure 1 The adult insect to *Chrysomya megacephala* and *Chrysomya rufifacies*.

Table 2 Primer sequences used to amplify the COI gene

Primer Name	Target Marker	Sequence Details
HCO2198_t1	COI-5P	CAGGAAACAGCTATGACTAAACTTCAGGGTGACCAAAAAATCA
LCO1490_t1	COI-5P	TGTAAAACGACGGCCAGTGGTCAACAAATCATAAAGATATTGG

unincorporated PCR primers and dNTPs were removed from the PCR products using the Exo-SAP enzyme.

DNA sequencing

PCR amplicons were purified from the unincorporated primers using the Exo-SAP enzyme. The samples were resuspended in distilled water, subjected to electrophoresis, and then cycle sequencing reactions of purified DNA were carried out using the BigDye® Terminator v.3.1 Cycle Sequencing Kit (Applied Biosystems, Foster City, CA, USA) with the LCO1490/HCO2198 primers. The PCR amplification cycle sequencing conditions were as follows: an initial step of 2 min at 96°C, then 35 cycles of 30 s at 96°C, 15 s at 55°C, and 4 min at 60°C. The cycle sequencing was followed by ethanol precipitation, then the template was dissolved in Hi-Di formamide. These samples were bidirectionally sequenced using an ABI 3730 Genetic analyzer.

DNA sequence alignment and phylogenetic analysis

A BLAST search was performed using the NCBI blast similarity search tool from the web (http://blast.ncbi.nlm.nih.gov/) on sequences of blowflies. The multiple alignments of sequences were carried out using the program MUSCLE 3.8.31. The resulting alignment curation was carried out using the program Gblocks to eliminate divergent regions and poorly aligned positions. Finally, the construction of a phylogenetic tree was carried out using PhyML. The program TreeDyn was used for tree rendering (Fig. 2). All of the above operations were carried out using https://www.phylogeny.fr/. The verified sequences were submitted to NCBI, and GenBank accession numbers of the samples are reported (Table 1).

Results

The aligned sequences of the COI gene of five Calliphoridae specimens showed no insertions or deletions. Nucleotide

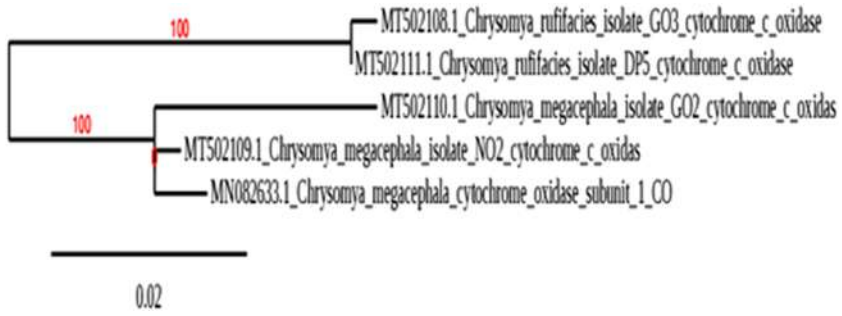

Figure 2 Phylogenetic tree showing phylogenetic relationships of all specimens with supporting bootstrap values.

composition frequency distribution within isolated specimens was 30.6% adenine (A), 38.6% thymine (T), 15.3% cytosine (C), and 15.5% guanine (Gdata not shown).

A phylogenetic tree constructed by multiple sequence alignment shows the classification of the five collected Calliphoridae specimens into two major clades. The separated clades indicate the two congeneric species, i.e., *Chrysomya megacephala* and *Chrysomya rufifacies* (Fig. 2). The phylogenetic tree forms a single cluster with minor nucleotide variations for all specimens belonging to the same species. The strong bootstrap value indicates the importance of the COI gene in providing a distinction between species.

The study compared the sequence of each of the collected specimens to each other to calculate the genetic variations interspecifically and intraspecifically. The pairwise divergence between each isolated specimen was calculated and are indicated as percentages in Table 3. The interspecies diversion between *Chrysomya megacephala* and *Chrysomya rufifacies* was found to be approximately 6.75% (minimum 6.54%, maximum 7.01%), while the intraspecific diversion between the sequences of the same species was found to be approximately 2.21% (minimum 1.39%, maximum 2.77%) for *Chrysomya megacephala* (DP4, GO2, and NO2) and 0.15% for *Chrysomya rufifacies* (GO3 and DP5).

Sequence comparisons of specimens belonging to the same species showed the percentage of sequence similarity was 98% and 99.5% for *Chrysomya megacephala* and *Chrysomya rufifacies*, respectively. The results indicate that there is a high degree of similarity in partial COI gene sequences within the same species isolated from different regions of Nagpur. On the other hand, sequence comparisons among different blowfly species showed that the percentage of sequence similarity between *Chrysomya megacephala* and *Chrysomya rufifacies* ranged from 93.7% to 94.6% (mean 94.26%). The interspecies sequence comparison indicated that the partial COI gene sequence was productive for differentiation between these two blowfly species in Nagpur. The similarity matrix in Table 4 showed the percentage of similarity in the COI gene sequences among specimens.

Discussion

The used of mt-DNA- COI gene as a based analysis is a powerful tool whereby specimens can be identified by comparing the similarities between sequences of other specimens (Abd-Algalil & Zambare 2017; Shinde *et al*. 2019). The chosen COI sequence was specific enough to differentiate between the collected blowfly specimens, despite its short length (Harvey *et al*. 2003). This method can only be used, however, if a reference sample of the same species is known (Wells & Sperling 2001). If an accurate reference sample is missing from the data set, a strong relationship may be found with the most closely related species; therefore, there is a need

Table 3 Pairwise divergence matrix showing the percentage of sequence variation between each specimen

SR. NO.	SPECIES	MT502110.1 *Chrysomya megacephala* (GO2)	MT502109.1 *Chrysomya megacephala* (NO2)	MT502108.1 *Chrysomya rufifacies* (GO3)
1	**MT502110.1 *Chrysomya megacephala* (GO2)**	-	-	-
2	**MT502109.1 *Chrysomya megacephala* (NO2)**	**2.47**	-	-
3	**MT502108.1 *Chrysomya rufifacies* (GO3)**	**7.01**	**6.76**	-
4	**MT502111.1 *Chrysomya rufifacies* (DP5)**	**6.70**	**6.54**	**0.15**

Table 4 Identity matrix showing the percentage sequence similarity between each specimen

SR. NO.	SPECIES	MT502110.1 *Chrysomya megacephala* (GO2)	MT502109.1 *Chrysomya megacephala* (NO2)	MT502108.1 *Chrysomya rufifacies* (GO3)
1	**MT502110.1 *Chrysomya megacephala* (GO2)**	-	-	-
2	**MT502109.1 *Chrysomya megacephala* (NO2)**	**97.6**	-	-
3	**MT502108.1 *Chrysomya rufifacies* (GO3)**	**93.7**	**94.5**	-
4	**MT502111.1 *Chrysomya rufifacies* (DP5)**	**93.9**	**94.6**	**99.5**

for a database of all known species likely to belong to local entomofauna for use in forensic investigations.

In India, *Chrysomya megacephala* and *Chrysomya rufifacies* are common blowfly species associated with human corpses (Abd-Algalil & Zambare 2017; Singh & Bharti 2000). Therefore, species identification of these two blowflies can be performed using partial COI gene sequencing. After sequencing of the COI gene, the nucleotide composition frequency distribution within *Chrysomya* species isolates can be compared to previous studies. Abd-Algalil and Zambare (2017) reported that the mean values of nucleotide composition frequency were 30.6% A, 15.5% C, 38.3% T, and 15.5% G, while Harvey *et al*. (2003) reported 40% A, 15% C, 30% T, and 15% G. The high frequencies of adenine and thymine observed in the isolated sequences are often characteristic of insect mt-DNA (Bernasconi *et al*. 2000; Harvey *et al*. 2003).

The phylogenetic analyses in this study produced similar results to previous studies (Harvey *et al*. 2003; Kavitha *et al*. 2013; Tan *et al*. 2009; Wells & Sperling 2001), supporting the single clustering of conspecific individuals and separation between individuals of congeneric species. The strong bootstrap value indicates the importance of the COI gene region in providing a distinction between species.

This study showed interspecific sequence divergence of 6.75% between *Chrysomya megacephala* and *Chrysomya rufifacies*, similar to previous studies that also found greater than 3% divergence among Chrysomyinae flies (Abd-Algalil & Zambare 2017; Harvey *et al*. 2003; Singh & Bharti 2000; Wells & Sperling 2001). The intraspecific genetic distances between the *Chrysomya rufifacies* specimens were found to be 0.15%, which also supports the results of many studies on Calliphoridae. The high degree of intraspecific variation observed in *Chrysomya megacephala* specimens (2.21%) was not expected, as previous studies have shown that intraspecific divergence rarely exceeds 1% (Harvey *et al*. 2003, Preativatanyou *et al*. 2010) or ranges from 0.14% to 1.59% (Otranto *et al*. 2003). Thus, there is a need to study new regions of DNA, like the cytochrome oxidase subunit II (COII) gene and tRNA-encoding genes (Sperling *et al*. 1994), to map intraspecific variation.

In conclusion, the present study represents the first attempt to report forensically relevant species in the Nagpur region, and reveals that the mt-DNA-based analysis using partial COI gene sequencing provides a strong foundation to identify species irrespective of nature, sex, and number of collected flies, which can be difficult to distinguish by traditional morphological methods. This study may serve as the basis of a database of sequences and methodologies that are useful to forensic entomology as an investigative tool in Nagpur (Maharashtra, India). Future studies will also need be needed to consider other forensically important species in the Nagpur region and bridge the gap of morphological- and mt-DNA-based taxonomy to obtain phylogenetic data.

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First Record of the Genus *Angaeus* (Arachnida, Araneae, Thomisidae) from Gujarat – India

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Abstract

While undertaking the study on diversity of spiders in different parts of Navsari District (Gujarat), a very rare species of Thomisidae family and genus Angaeus (Thorell, 1881) commonly known as Diamond- bellied Crab spider female specimen was collected from the surface of the under lying low shrubs Discorea bulbifera (Yam family Discoreaceae) in one of the Sapota (Chiku plant) agro-systems in early morning during monsoon season of the year 2016. Male spider was not found. Moreover, the researchers have not come across any past records or evidences of finding this extremely rare spider in the state of Gujarat (India) till date. Only one species of Angaeus pentagonaalis was so far reported by Pocock, 1901 in India (Sebastian and Peter, 2012; Keswaniat. al. 2012).

Key words: *Crab spider, agricultural ecosystem, diversity, sapota, taxonomy.*

Introduction

Arachnids inhabit the whole world and are believed to be the first land animals from the fossils discovered so far. Small and insignificant looking carnivorous spiders, members of Araneae order, class Arachnida, are very important predators and prey to multitude of other animals. Thomisidae, the sixth largest family, includes 7 subfamilies, 170 genera and 2154 species, of which 40 genera and 176 species were recorded from India (WSC, MNBE, 2020 Ver. 21; ISC, 2012). The crab spider genus *Angaeus* presently includes 10 species; *A. canalis,* Tang and Li, 2010; *A. christa* Banjamin, 2013; *A. comotulu* Simon, 1909; *A. lelniculosus* Simon, 1903; *A. Liangweii* Tang and Li, 2010; *A. pentagonalis* Pocock, 1901; *A. pudicus* Thoell, 188; *A. rhombifer* Thorell, 1890; *A. rhombus* Tang and Li, 2009; and *A. zhengi* Tang and Li, 2009 (WSC, NMBE, 2020 Version 21). This type of species *A. puducus* is known from male; *A. comolutus* from juvenile; the three species *A. canalis, A.lelniculosus* and *A. pentagonalis* from female and the five remaining species are from both males and females. All species are restricted to tropical Asia, majority are from China. Only one species *A. pentagonalis*is reported from India, Andaman Islands and Karnataka. Other than these, *A. zhengi* is reported for first time as new species *Paraborboropactus canalis* in Xishuangbanna, Yunnan, China, by Tang and Li, 2009. Benjamin S.P., 2013; Tang and Li, 2009, 2010 described morphological description, illustrations and photographs of the Angaeus species. It is important to mention that this species is reported for the first time in India which is illustrated in this paper. The spiders work as guards and check the population of number of insects in various food chains and food webs of different ecosystems. With this view, the present study was undertaken to understand the diversity and role spiders play, in an agricultural ecosystem.

Materials and Methods

A female specimen were collected by hand picking from the surface of the under lying low shrubs *Discorea bulbifera* (Yam family Discoreaceae) in *Sappota* (Chiku plant) agro ecosystem in rainy season at early morning during 20th August, 2016 from District Navsari, (Gujarat- India). The male spider was not found. The photographs of live specimen were taken with 16 megapixel Gionee S-plus mobile camera. The material was preserved in 70% alcohol with all legs spread properly. The detail examination were carried out by an Olympus SZ 4E Binocular Stereomicroscope, attached with Cat Cam I-30 camera bearing measurement scale (to the nearest 0.01 mm). All measurements are in millimeter scale. The taxonomic studies and identification of the specimen were done by using the methods as suggested by different scientists like B. Tikader,1980; Joseph K.H. Koh and Leong Tzi Ming, 2014; Suresh P. Benjamin, 2013; Tang and Li, 2009, 2010. Under this taxonomical study the salient features of the spiders along with ecological habitat and different morphological characters were recorded.

Abbreviations used: AER = anterior eye row; PER = posterior eye row; AME = anterior median eyes; ALE = anterior lateral eyes; PME = posterior median eyes; PLE = posterior lateral eyes; MOA = median ocular area; AS = anterior spinnerets; PS = posterior spinnerets; MS = median spinnerets

Taxonomy

Family *Thomisidae*, Sundevall, 1833

Genus *Angaeus* Thorell, 1881

Angaeus Thorell, 1881: 346
Paraborboropactus Tang and Li, 2009 713, = *Angaeus* Thorell, 1881: 346 (Benjamin, 2013:720)
2010a: 49, 2010b: 44

Entomology: The generic name is a compound word with the prefix *para* and the generic name of *Borboropactus*, referring to its similarity to the genus *Borboropactus* Simon, 1884.

Identifiacation:

Morphologically the genus *Angaeus* Thorell, 1881 related to the senior synonym of the *Paraborboropactus*, and can be separated from other thomisids, except for *Borboropoactus* Simon, 1884 by the presence of epigynal teeth in females (Benjamin 2013: figs 2D, 5C). Separated from *Borboropoactus* by the absence of a sensory patch on tarsi (Benjamin 2011: figs 24C-E), and by the presence of an anterior epigynal cavity or hood (Benjamin 2013: figs 1C, 3D, 4B, 5C). *Angaeus and Borboropoactus* possess chelicerae with teeth, femur swollen in the median and bear spurs, palp with a soft tegular apophysis, epigynum with epigynal teeth, median epigynal septum and terminal epigynal fold (Benjamin 2011, Tang and Li, 2009).

Description:

***Angaeus zhengi* Tang and Li, 2009 (Plates 1: a-d)**

Paraborboropactus zhengi trasfered to *Angaeus zhengi* by Benjamin, 2013.

Type material: Isotype / Syntype of female *Angaeus zhengi*

Morphology:

Natural habitat: Body of spider appears rough and warty, blackish brown with whitish cream colored pinchs under microscope. The body is actually covered with a densely packed setae or hairs of different shapes (**Plate -1a**). In resting condition, legs I and II are always drawn toward cephalic region. When disturbed, it moves like Crab, at that time first two legs lies nearer to each other in forward direction. When collected it mimics the fruits of *Discorea bulbifera* (Yam family Discoreaceae) plant (**Plate -1b**).

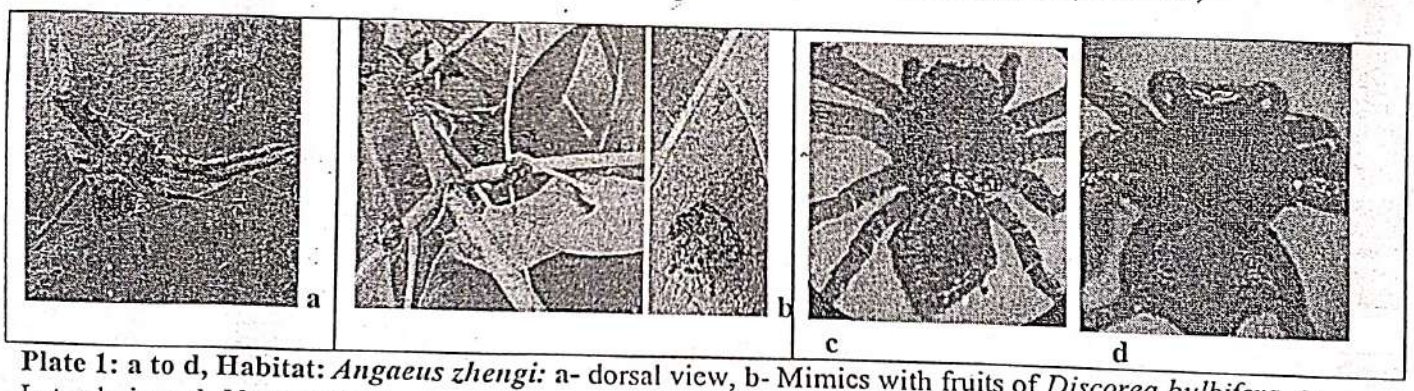

Plate 1: a to d, Habitat: ***Angaeus zhengi:*** **a-** dorsal view, b- Mimics with fruits of *Discorea bulbifera*, c- Lateral view, d- Ventral view

Female: Total Body length: 6.57 mm; Prosoma flat, clung with dense short and clustered hairs, radish brown in colour, slightly longer than wide (3.36 L/ 3.19 W), narrowing anteriorly, cephalic region elevated, thoracic fovea distinct, thorax with dark chevron or stripe (**Plate - 2a**). Eyes area elevated, AER slightly recurved, PER recurved, tubercle of ALE with clustered hairs. Eye measurements; AME 0.10; ALE 0.22; PME 0.18; PLE 0.23; AME-AME 0.33; AME-ALE 0.34; PME-PME 0.59; PME-PLE 0.55; AME-PME 0.42; AME-ALE 076; ALE-ALE 1.15; ALE-PLE 0.57; AME-PLE 0.39; PLE-PLE 1.49; PLE-ALE 0.57. MOA length 0.42mm with front width 0.33mm and back width 0.59mm (**Plate - 2a**). Sternum blackish brown, heart shaped, distinctly bordered, wider than long (1.48L/1.51W); Labium blackish brown, wider than long (0.55L/0.63), distally with bifurcate clustered hairs, triangular in outline (**Plate - 2b**); Maxillae longer than wide (0.85/0.61), blackish brown with three promarginal and three retromarginal teeth, the basal of the 2 large retromarginal teeth combined (**Plate - 2c**). Legs long, robust, dark brown with white patches or spots, covered with hairs and clusters of hairs (nodes) with spines; Femora of all legs ventrally creams white while III and IV only dorsally creams white, whereas femora I slightly swollen and bears 8 thick spines with clusters of hairs, tibia and metatarsi of I and II with 4, 3 pairs of ventral spines respectively (**Plate - 2d & e**). Formula of Leg is II, I, IV, III (**Table -1**).

Table - 1 Measurement of leg segments (in mm)

Leg	Coxa	Trochanter	Femur	Patella	Tibia	Metatarsus	Tarsus	Total
I	1.14	0.39	3.62	1.35	3.24	1.31	0.79	11.84
II	1.17	0.31	3.78	1.24	3.27	1.37	1.00	12.14
III	1.10	0.36	2.10	0.82	1.30	0.71	1.02	07.41
IV	0.84	0.34	2.39	0.93	1.58	0.68	0.79	07.55

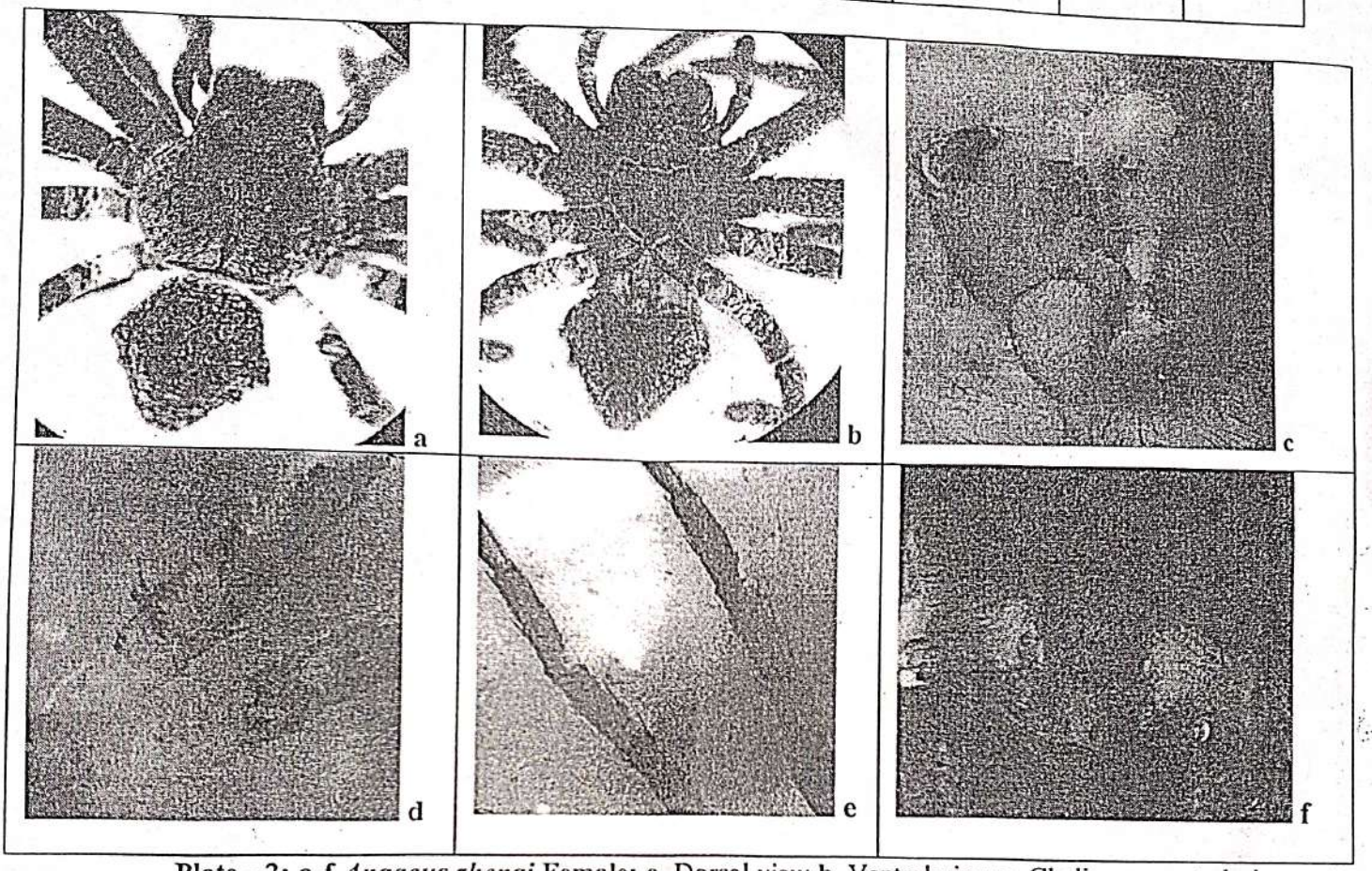

Plate - 2: a-f *Angaeus zhengi* **Female: a.** Dorsal view **b.** Ventral view **c.** Chelicerae ventral view **d.** Dorsal part of femur I & II **e.** Ventral part of Tibia and Metatarsus of I & II **f.** Epigynal ventral view

Opisthosoma longer than wide (3.36 L/3.19 W), blackish brown, and diamond shaped or nearly pentagonal with blunt posterior end; dorsally with 2 pairs of sagilla and a pair of longitudinal break lines antero-dorsally and toward posterior side bearing 2 pairs of rows of clustered hairs, dorsolaterally (**Plate 2a**). The Ventrum dark brown, with two pairs of yellowish white rows with spotted lines. Spinnerets surrounded with yellowish border (**Plate - 2b**). Epigynum with an anterior cavity or hood and a pair of epigynal teeth medially and pointed backwardly, copulatory duct invisible, Spermatheca convoluted, with longitudinal epigynal ridge slender anteriorly and wide posteriorly (**Plate - 2f**).

Distribution: Yunnan (China) and now in Dist. Navsari (Gujarat, India).

Remarks: So far crab spider ***Angaeus zhengi*** was not recorded anywhere in the world except China. Now it was found in Navsari (Gujarat state –India) for the first time. So after confirming with the experts, it was found that in India this spider ***Angaeus zhengi*** is a new record. But presently it's difficult to state anything about the history of crab spider ***Angaeus zhengi*** distribution in India. And it's a matter of further research about the biodiversity of this spider in India. Moreover, no details are available regarding the orchards or plants of China (Yunnan) where this spider normally mimics. Still we found only female specimen in Navsari. So if male specimen of crab spider is found than it can unfold much important information.

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Benjamin, Institute of Fundamental Studies (Kandy - Sri Lanka) for helping me in identification of this spider species.

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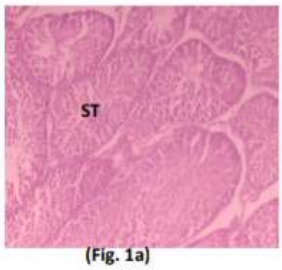
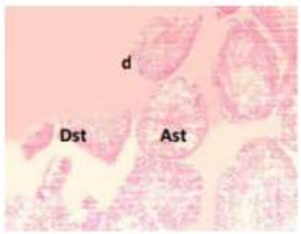
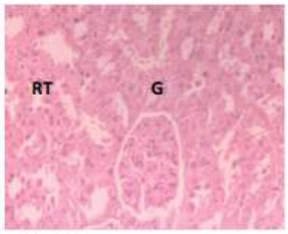


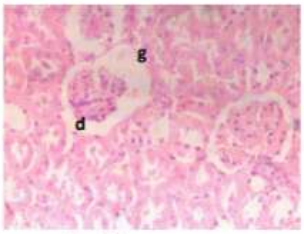
(Fig. 1a)



(Fig. 1b)



(Fig. 2a)



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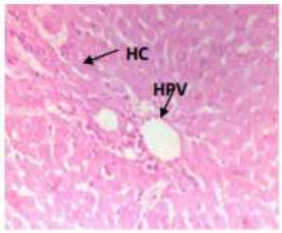
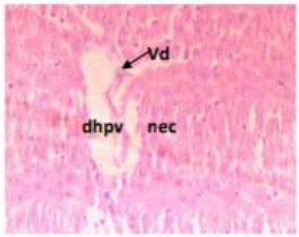


(Fig. 3a)



(Fig. 3b)

(Fig 1a): T.S. Testis of control albino male wistar rat, Hematoxylin- eosin X 400, ST- Seminiferous tubule, **(Fig. 1b):** T.S. Testis of experimental rat showing , (HE) X 100 dilation of seminiferous tubule **(Dst),** atrophy of testis **(At)** various degenerative changes **(d)**

(Fig. 2a): T.S. Kidney of control albino rat (male), (HE) X 400. **G-** Glomerulus, **RT-** Renal tubule. **(Fig. 2b):** T.S Kidney of experimental rat (male), (HE) X 400, atrophy of a glomerulus**(g)** and degenerated renal tubules**(d)** **(Fig. 3a)** : T.S. Liver of control Wistar albino rat (male) shows regular hepatic cords, Hematoxylin-eosin (HE) X 400, **HPV**- Hepatic portal vein, **HC**- Hepatic cord. **(Fig. 3b):** T.S. Liver of experimental rat (male) showing vacuolar degeneration of hepatocytes **(Vd)**, diffuse necrosis **(nec)**, degeneration of hepatic portal vein **(dhpv).**

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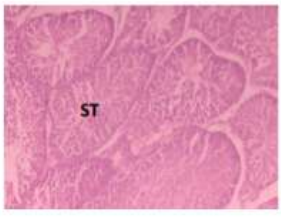

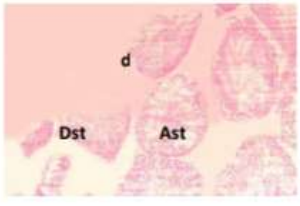

level has been observed. However slight decrease in SGOT and SGPT level has been observed in experimental rats. Elevated level of urea, creatinine and uric acid along with decrease in potassium level may be as a result of destruction of kidney cells. Similar results were observed by Bakke *et al*., (1972) Atrazine exposure result in a significant increase in serum creatinine in male rats compared with control groups. Nephrotoxicity of Atrazine is a consequence of its elimination through the kidneys which leads to a decrease in creatinine clearance and proteinuria.

The testis of Atrazine treated rats exhibited dilation of seminiferous tubules and atrophy of testis and various degenerative changes. (Fig.1b). However, normal cellular architecture is seen showing normal germinal epithelial cells primary and secondary spermocytes in control rats .(Fig.1a) According to Kniewald (2000) Atrazine causes changes in sperm morphology and a reduction in sperm motility.

T.S. of kidney of control rats revealed normal renal tubule and glomerulus (Fig. 2a). Atrazine treated rats show atrophy of a glomerulus and degenerated renal tubules (Fig. 2b). Toxicological Profile for Atrazine (2003) were observed sub-acute glomerulitis and degeneration and desquamation of the proximal tubules in female pigs receiving 2 mg/kg/day atrazine in the diet for 19 days.

Hepatocytes of control rats were polygonal in shape, mononucleate or binucleate.(Fig. 3a) Atrazine herbicide treated rats, shows vacuolar degeneration of hepatocytes, diffuse necrosis and degeneration of hepatic portal vein. (Fig.3b) Toxicological Profile for Atrazine (2003) reported Intermediate-duration exposure of pigs to 2 mg/kg/day resulted in a 35% increase in serum γ-glutamyltransferase activity and mild histopathological changes, including chronic interstitial inflammation, lymphocyte and eosinophill infiltration, and narrowing and irregular forms of bile canaliculi in liver.

Conclusion:

The result obtained in the present investigation reveal that the sub chronic dose of Atrazine herbicide i.e., 25% of LD50 induced considerable alteration in biochemical parameters and architecture of the liver, kidney & testis of rats. Therefore widespread use of this herbicide in public place and agriculture field is to be prohibited or restricted.

Discussion:

Male Wister rats were exposed to Atrazine by giving a dose 25% (124 mg/ kg/bw/day) of LD50 (3090 mg/kg/bw) for 120 days and then animals were sacrificed for tissues and blood.

During the period of exposure of Atrazine rats were observed for their behavioral changes. No Change in food intake and no significant change in weight were observed. According to Cantemir (1997) many rat studies involving acute, intermediate or chronic exposure to Atrazine in the diet or by gavage showed mild to severe weight loss. No mortality was observed during exposure period. After giving the oral dose, rats showed symptoms of lethargy, red nasal and ocular discharge, dehydration and pasty diarrhea. Hyperactivity was seen just after the administration of dose for 5-10 minutes and rats became more aggressive. After long term exposure (nearly after 90 days of exposure) hair fall has been observed. Williams (1997) observed that Atrazine is a skin sensitizer and cyanazine which is toxic by the oral route. Overexposure to triazine herbicides (atrazine, simazine, propazine) may induce fatigue, dizziness, nausea, irritation of the skin, eyes and respiratory tract, allergic eczema or asthma. Schlicher (1972) revealed that 40-year-old white male farmer developed blisters on his hands and forearms one afternoon after having applied Atrazine to crops in the morning using a spray ring and cleaning the plugged nozzles several times with his hands.

In case of Atrazine treated rats it has been also observed that excreta were semisolid with pungent smell. Bakke (1972) investigated specific data on elimination and excretion of Atrazine by any route was limited. However, the primary route of excretion appears to be in urine, as indicated by the detection of urinary Atrazine and its metabolites in a number of species exposed via oral and dermal routes. When rats were dissected it has been observed that the testis were shrinked, (comparative reduction in weight), development of edema on kidney and liver, stomach filled with fluid having pungent smell was observed in all most all experimental rats. Wilhelms *et al*. (2005) findings indicate that the absorption of Atrazine in humans following oral exposure was indicated in a single case report of a 38-year-old man who died of progressive organ failure and shock 3 days after ingesting 500 mL of a weed killer that contained 100 g Atrazine, 25 g of aminotriazole, 25 g of ethylene glycol, and 0.15 g of formaldehyde.

Biochemical analysis of control as well as Atrazine exposed rats was done to compare the sub-chronic effects of Atrazine, Table I. Significant increase in urea, creatinine and uric acid

Table 1. Significant increase in urea, creatinine and uric acid level has been observed. However slight decrease in SGOT and SGPT level has been observed in experimental rats.

Table- 1: Biochemical analysis results of control and Atrazine treated rat.

Parameters	Control rats	Atrazine treated rats
Urea	16.16±2.6394	**44.5**±9.7039**
Creatinine	0.45±0.1870	**0.92**±0.1649**
SGOT	139.33±94.9245	67.5±13.126
SGPT	54.5±16.8967	48.83±8.8863
Uric acid	1.5±0.5477	**9.05**±2.1431**

Values are given as mean of six separate animals ± standards deviations. *p<0.05; **p<0.01 (Student's t-t).

Histological changes

Alteration in Testis architecture

T.S. of testis shows normal cellular architecture, with normal seminiferous tubules, germinal epithelial cells, primary and secondary spermatocytes in control rats (Fig. 1a). T.S. of testis of Atrazine treated rats exhibited atrophy of testis, dilation of seminiferous tubules and various degenerative changes (Fig. 1b).

Alteration in kidney architecture:

Transverse section of kidney of control rats revealed normal renal tubule and glomerulus (Fig. 2a). In Atrazine treated rats kidney shows atrophy of a glomerulus and degenerated renal tubules. (Fig. 2b)

Alteration in Liver architecture:

Hepatocytes of liver in control rats were polygonal in shape, mononucleate or binucleate (Fig.3a). In Atrazine herbicide treated rats liver shows vacuolar degeneration of hepatocytes, diffuse necrosis and degeneration of hepatic portal vein. (Fig.3b).

Material and Methods:

Healthy Wister rats (male) were acclimatized to laboratory condition. During acclimatization rats were provided with food and water *adlibitum*. The animals were kept in clean polypropylene cages (measuring 12"x10"x8") with chrome plates grills. The rats were grouped in to two groups, six rats in each group; one group was kept as control whiles other as experimental. Experimental rats were given the 25% (124 mg/kg/body weight) of LD50 (3090 mg/kg/bw) dose of the Atrazine (dissolved in tap water) for 120 days. The control rats were sacrificed on 120th day. Whereas experimental rats were sacrificed on 121st day after giving 120 days oral dose (according to rules of ethical committee registration no. is 1060/ac/07/CPCSEA). The tissues like liver, testis & kidney of male rats were removed, fixed in Bouin's fixative for at least 24 hrs, processed by paraffin wax impregnation method, cut using a rotary microtome at 5 µm thickness and stained with Hematoxylin and Eosin (H X E) for light microscopic examination.

Statistical analysis:

In each assay, the experimental data represent the mean of six independent assay ± standards deviation. Mean were compared using the student t-test. Differences were considered significant at the level $p < 0.05$ and very significant at the level $p < 0.01$.

Results:

Male Wister rats were exposed to Atrazine by giving a dose 25% (124 mg/ kg/bw/day) of LD50 (3090 mg/kg/bw), for 120 days and then animals were sacrificed for tissue and blood. When rats were dissected it has been observed that the testis were shrinked, (comparative reduction in weight), development of edema on kidney and liver, stomach filled with fluid having pungent smell was observed in all most all experimental rats. Biochemical analysis of control as well as Atrazine exposed rats was done to compare the sub-chronic effects of Atrazine,

et. al. 2003). This herbicide was first introduced in 1958. Its commercial name is 'Atrax' and in Iran is marketed under the name of 'Gesaprim'. This compound is a white crystalline solid with the solubility of 33 ppm in water at 27°C. Its molecular weight is 215.68 gr/M; Atrazine does not degrade significantly in ground water and in surface water. It has a half life of more than 200 days to 2 years (ATSDR 2003).

Atrazine is absorbed through roots and transmitted via apoplast; it is also absorbed through leaves. This herbicide inhibits plant growth through interference with photosynthesis and leaf death. Other effects on the leaves include membrane and chloroplast destruction. It is known that all the plant organs are inhibited by Atrazine herbicides; in addition, it interferes with the metabolism of phytohormons, prevents stomata opening in light and causes their closure in normal temperature. The translocation of Atrazine from soil and water to plants and aquatic animals, results in its entry into food chain and bioaccumulation. Chronic exposure of this herbicide leads to non-Hodgkin type lymphoma, multiple myeloma and sarcoma in agricultural workers (Chiu *et. al.,* 2004). Since Atrazine is now most commonly used in the world to control weeds therefore the relative risk and benefits of this herbicide must be compared to the existing herbicides. Studies show that Atrazine causes adverse effects on the liver, kidney and cardiovascular system in animals exposed to it (Chan *et al.* 2006). However, the patterns of accumulation of xenobiotics varies depending on the organism, characteristics of the chemical compound, quantity of this substance present in the environment, and the balance between assimilation and metabolic rates (Nwani *et al.*, 2011).

The demand of herbicide is increasing day by day in India. Anything that is in excess is always harmful, so with the herbicides tremendous and repeated use of herbicides now adding one more head to environmental pollution. Accumulation / bioaccumulation of herbicides may have toxic effects on animals, plants or human beings, those who directly or indirectly get exposed to it. So considering the effect of herbicide, work was carried out to study the effect of sub-chronic exposure of Atrazine on albino male Wistar rats with reference to variation in histophysiology of liver, kidney and testis.

HISTOPHYSIOLOGICAL ALTERATIONS CAUSED DUE TO INTOXICATION OF ATRAZINE HERBICIDE IN WISTAR ALBINO RATS (MALE)

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ABSTRACT:

Atrazine is one of the most commonly used herbicides in the US and the world. More than 76 million pounds are used on US fields every year, particularly in the Central Plains. Because of its selective nature in India the use of Atrazine is tremendously increased, but unawareness and accidents may results into toxic effects. Therefore an attempt was made to study the sub chronic effect on histophysiology of some organs in male Wistar Albino rats exposed to Atrazine. Experimental rats were given oral dose of 25% (124 mg/kg/body weight) of LD50 (3090 mg/kg/body weight) of the Atrazine dissolved in water for 120 days. The histological study shows alterations in liver, kidney and testis of rats. Hepatic cells of liver show vacuolar degeneration of hepatocytes diffuse necrosis and degeneration of hepatic portal vein. Examination of kidney sections showed atrophy of a glomerulus and degenerated renal tubules. The testis exhibited dilation of seminiferous tubules and atrophy of testis and various degenerative changes.

Keywords: Herbicides, Atrazine, Histology, liver, kidney, Testis.

Introduction:

Atrazine is an organophosphate herbicide which is extensively used against long and broad leaf herbaceous plants in corn fields and gardens. This herbicide is most efficient against weeds when applied prior to growth. In some areas, Atrazine is used for the selective control of weeds in re-establishment of pine forest, cultivation of Christmas trees, long leaf seed fields. In addition, it is used in dry areas as a nonselective herbicide. Atrazine is a common name for 2-chloro-4-(ethylamino)-4-(isopropylamino)-s-triazine. Its chemical formula is C8H14ClN5 (Cai

ECO-PRINTING: NEW DIMENSIONS IN TEXTILE PRINTING

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Abstract

Globalization has totally changed the design business and its methodology toward supportability. Quick changing patterns are significantly centered on engineered colors and textures. Also, these items have bombed fabricating the extension among maintainability and climate well disposed plans. Hence there is a need to focus on the methodology toward plan advancement and improvement of maintainable eco-accommodating methodology for ecoprinting by utilizing colors from nature on textures like silk and cotton. The section depends on feasible plan approach which gives a lot of arrangement for utilizing common colors for regular change in style. The part additionally centers on shading speed properties of the pre-owned colors. These outcomes were assessed via doing shading quickness tests for light, wash and scouring. Plan strategy utilized in the investigation likewise has the potential for ability improvement programs for business visionaries and furthermore adds to country advancement programs by making maintainable development.

Key words: ecoprinting, colors, textures,

Introduction

Material imprinting in India has been polished over hundreds of years.

Long periods of human obliviousness has reduced our characteristic assets and matured our planet. Presently, individuals are putting forth an attempt to change the manner in which they are treating the planet. Being all the more earth cognizant about the effect materials utilized for style have on our planet is single direction creators can lessen waste and help

empower a superior world. By going eco-accommodating can be less unsafe to our common assets. Not all style is following this eco-accommodating pattern, yet more planners are accepting the pattern toward eco-design than any time in recent memory. In the event that the whole style industry became eco-accommodating, it would have a colossal effect for people in the future on the grounds that the design business utilizes over a billion groups all around the world. Eco-accommodating preparing is likewise called as eco-handling. Eco-handling is an appropriate material preparing strategy that conveys eco-accommodating completed items as well as doesn't hamper the encompassing climate and climate via contaminating the air and water individually, because of emanation and profluent releases from dirtying enterprises like material industry. Material enterprises utilize various synthetics in various cycles like coloring, completing the process of scouring, fading, relaxing, washing and so forth. The material synthetics and coloring Industry burn-through enormous amounts of water and produce huge volumes of wastewater in various interactions. Wastewater from material preparing and coloring containing buildups requires proper treatment prior to being delivered into the climate.

M. M. Islam, K. Mahmud, O. Faruk, and M. S. Billah -(2011),in their paper- Textile Dyeing Industries in Bangladesh for Sustainable Development, state that the textile dyeing and washing industry plays an important role in the economical growth as well as the environmental sectors of Bangladesh. The textile dyeing industries has been condemned as being one of the world's most offenders in terms of pollution. This study was aimed at the dyeing industries to assess the present situation of environmental impacts arising from the activities of dyeing industries in Bangladesh.

GeetaMahale, in her paper 'Ecoprinting of Cotton with Reactive Dyes ', opines- there have been a number of options developed to overcome the polluted effluentproblem of dyeing cotton fabric with reactive dyes. This paper reviews the options to improve
sustainability of the dyeing process through development of reactive dyes, modification of dyeingmachinery and processes, chemical modification of cotton brief prior to dyeing, use of
biodegradable organic compounds in dye bath formulation.

Most cotton fabrics are dyed with reactive dyes because they produce a full range of bright fashion colours with a high degree of wash fastness. Application of these dyes, however, causes high and undesirable levels of dissolved solids and oxygen demand in the effluent. This is due to the use of considerable quantities of inorganic salt and alkali to ensure efficient utilization and fixation of the reactive dyes. Dye that is unfixed on cotton also contributes to effluent pollution. There are two approaches to deal with the effluent problem:

Alternative dyeing techniques and technology;

Effluent treatment after dyeing. The effluent treatment requires additional capital investment and high treatment and maintenance costs.

This paper reviews the options to improve sustainability of the dyeing process through development of reactive dyes, modification of dyeing machinery and processes, chemical modification of cotton brief prior to dyeing, use of biodegradable organic compounds in dye bath formulation.

House of Commons Environmental Audit Committee Fixing Fashion: Clothing Consumption and Sustainability, Sixteenth Report of Session 2017–19 Report, together with formal minutes relating to the report-
The fashion designer Phoebe English says that 'fast fashion' has made the sector a 'monstrous disposable industry': The overproduction of 'fast' fashion which will never be purchased or used and the insane speed which the sector churns out new designs almost every week means that the never-ending production of cheap fashion which is poorly made and will last only a few weeks and then be thrown away, has made our sector a monstrous disposable industry. The entire way the sector is structured so that the prospective sales orders are put into production rather than only making the production which has been actually ordered means that countless levels of wasted garments are produced.19

Enrico Fatarella, Daniele Spinelli, Rebecca Pogni, Riccardo , 'Environmental impact assessment of an eco-efficient production for coloured textiles'-The textile and clothing industry is one of the world most global industries and constitutes an important source of income and employment for several EU countries. The textile manufacturing process is characterized by high consumption of resources such as water, fuel and a variety of chemicals in a long process sequence generating a significant load on the environment. Therefore, in order to meet the consumer's demand of eco-friendly products, more sustainable production processes are under investigation in order to reduce the environmental burdens. The feasibility of these alternative solutions has been demonstrated during the EU BISCOL project proposing a new dyeing process as a global alternative for the conversion of raw materials into competitive eco-viable final products. This has been achieved through the integration of enzymatic synthesis of dyes at semi-industrial scale, textile pre-treatment based on plasma technology and synthesis of new auxiliaries at lower environmental impact. A life cycle assessment has been performed to evaluate the environmental impact associated with the development of new strategies for textile industry in comparison to classical dyeing processes. Results based on primary data from the consortium partners involved in the project show that relevant benefits are achievable with an innovative protocol in terms of reducing energy, water and raw materials consumption.

Practical handling of materials:

There is need for eco-accommodating wet handling that is maintainable and useful techniques. Number of feasible practices has been carried out by different material preparing ventures, for example, Eco-accommodating blanching; Peroxide fading; Eco-accommodating coloring and Printing; Low effect colors; Natural colors; Azo Free colors; Phthalates Free Printing. There is an assortment of materials considered "harmless to the ecosystem" for an assortment of reasons. Above all else, the inexhaustibility of the item. Inexhaustible assets are things that can be recharged in a generally short measure of time. The subsequent factor is the environmental impression of the asset - how much land (typically estimated in sections of land) it takes to bring one of the people (plants or creatures) to full development and backing it. The third interesting point in deciding the eco-neighborliness of a specific item is the number of synthetic compounds it needs to develop/measure it to prepare it for market.

What is Eco printing?

Eco-printing is a technique for packaging leaves and different plants in texture, and steaming the bundle(s) to print their common shades onto the texture. The tools and equipments needed are-

fabric for imprinting on (cotton fabric)

freshly gathered plants ,flowers

vinegar

old nails, or other corroded salvaged material

dowel bars, or straight-dish sticks, somewhat more limited than the measurement of the pot you intend to steam them in

String and scissors

A container

A huge pot, and extra pots/basins

Plastic wrap (discretionary)

The common procedure of eco printing is-

Stage 1: Making a vinegar solution

The cotton texture must be dealt with so it takes up the regular color. It will require about seven days for the hand crafted form to sit and arrive at power, so the initial step has to be done long time before any one wraps up of the real eco printing.

A small bunch of the nails is put into the container, filled with a proportion of 2 sections water to 1 section vinegar. The container is sealed, and let to set for possibly more than seven days. That is it for this progression.

In the event one the nails can be strained out of the subsequent alcohol so the fluid is simpler to work with.

Stage 2: Gathering and Pre-dousing all materials

About a day prior to do the printing, the plants and flowers to print with are gathered. It's an exceptionally trial cycle, and results will differ a ton. Whenever one has the texture and collection of plants and flowers, everything is pre-drenched short-term (independently) to prepare it for printing:

The plants are put in a tub of 2 sections water to 1 section vinegar, and let douse.

The cotton texture is put in a different pot (this can be a similar pot intended to use for the steaming advance), and is covered with 2 sections water to 1 section iron acetic acid derivation arrangement. This is carriedto stew for a thirty minutes, and eliminated from heat. It is allowed to cool in the pot for the time being.

Stage 3: Assemblingthe Plants, flowers and Fabric for Printing

The cotton texture is spotted on a level surface, and some additional iron arrangement isput in an extra container. The leaves are taken from the tub where they've been drenching, dunked into the iron arrangement, and are organized on the texture anyway one likes.

On the off chance that one puts some face up and others face down, they may give various outcomes. One can likewise have a go at skirting the iron plunge; iron influences the shade of common colors, making them 'more troubled' (that is, inclining toward greens and dim purples instead of tones on the hotter finish of the range). So undipped leaves may give various outcomes, however since the whole texture is treated with iron, an over the top distinction will not be seen. This is a lot of an experimentation interaction.

Stage 4: Rolling and Bindingthe Prints

The following stage is to prepare the print for steaming. A dowel bar (or a straight stick, which works comparably well) is taken and is spotted aside of the texture. The texture edge is accumulated with the dowel pole, and moved up as firmly as possible. The leaves are needed to be pressed against the texture, so the texture can take up however much of their color as could reasonably be expected. For a tight move, a piece of string is attached to one end, and the string is wound firmly around the pack, through and through. It is tied off. The preparation of steaming is done.

Stage 5: Setting of Prints with Steam

The bundles are taken bundle(s) and organized in a pot to be steamed. An additional dowel bar can be utilized to lift the texture packages out of the water. In the first place, the additional dowel bar is propped askew against the side of the pot. At that point, it is crossed down low in the pot like a 't.' Then, in the event if there are additional packs to steam, they are propped in a triangle arrangement on top.

After the texture packs are organized in the pot, some water is poured in the lower part of the pot and heated to the point of boiling. A top on top is spotted to keep in the steam, and

kept for bubbling for an hour or two. Intermittent checking is done to ensure the water doesn't bubble off totally; more water is added depending on the situation.

Stage 6: Revealing the Results and Finish

Following an hour or two, after allowing it to cool for a piece, the top is eliminated from the steam pot. When everything is adequately cool to deal with, a texture pack is taken out and the string is cut. The print is carried out on a perfect surface, the color materials are eliminated and the completed print is uncovered.

A common eco-print is derived.

The printed texture is washed tenderly and draped to dry. The regular colors in general blur moderately rapidly.The texture is kept out of direct daylight.

Conclusion

Eco-printing is a procedure where plants, leaves and blossoms leave their shapes, shading, and stamps on texture. Plant material packaged within fabric is steamed or bubbled to deliver the color discovered normally inside the plant, making a contact print looking like the leaf or blossom utilized. These contact prints are alluded to as "eco-prints."

In the current universe of quick design, there is an expanded concern all around the world toward the utilization of dangerous and cancer-causing manufactured colors like azo and benzidine; these colors affect nature and humanity. The developing mindfulness about supportability and climate well disposed colors has made a fundamental stage for youthful scientists to restore and try different things with customary methodology of material coloring and printing. Notwithstanding, the material colored from common colors needs esteem expansion to arrive at the ideal market acknowledgment; printing various themes utilizing normal colors can help beat the necessities of significant worth expansion for materials.

In eco printing, dyeing and printing is done by using natural pigments present in flora. These pigments appear in different colours depending on the season and time of the year.

This process helps the natural pigments to leave incredible details of form and colours on fabrics.

Ecoprinting, or botanical contact printing, is a contemporary adaptation of the ancient art of dyeing cloth with plant based pigments. The naturally produced colours are soft and harmonious, and the process is non polluting and respectful of the environment. The smallest change in plant species, climatic conditions or water source can produce marked variations in the prints, meaning every piece of cloth is unique.

An eco print can never be repeated, because every leaf on this planet is different, even the two sides of that leaf are different.

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Department of Economics

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A) Research Papers publication:

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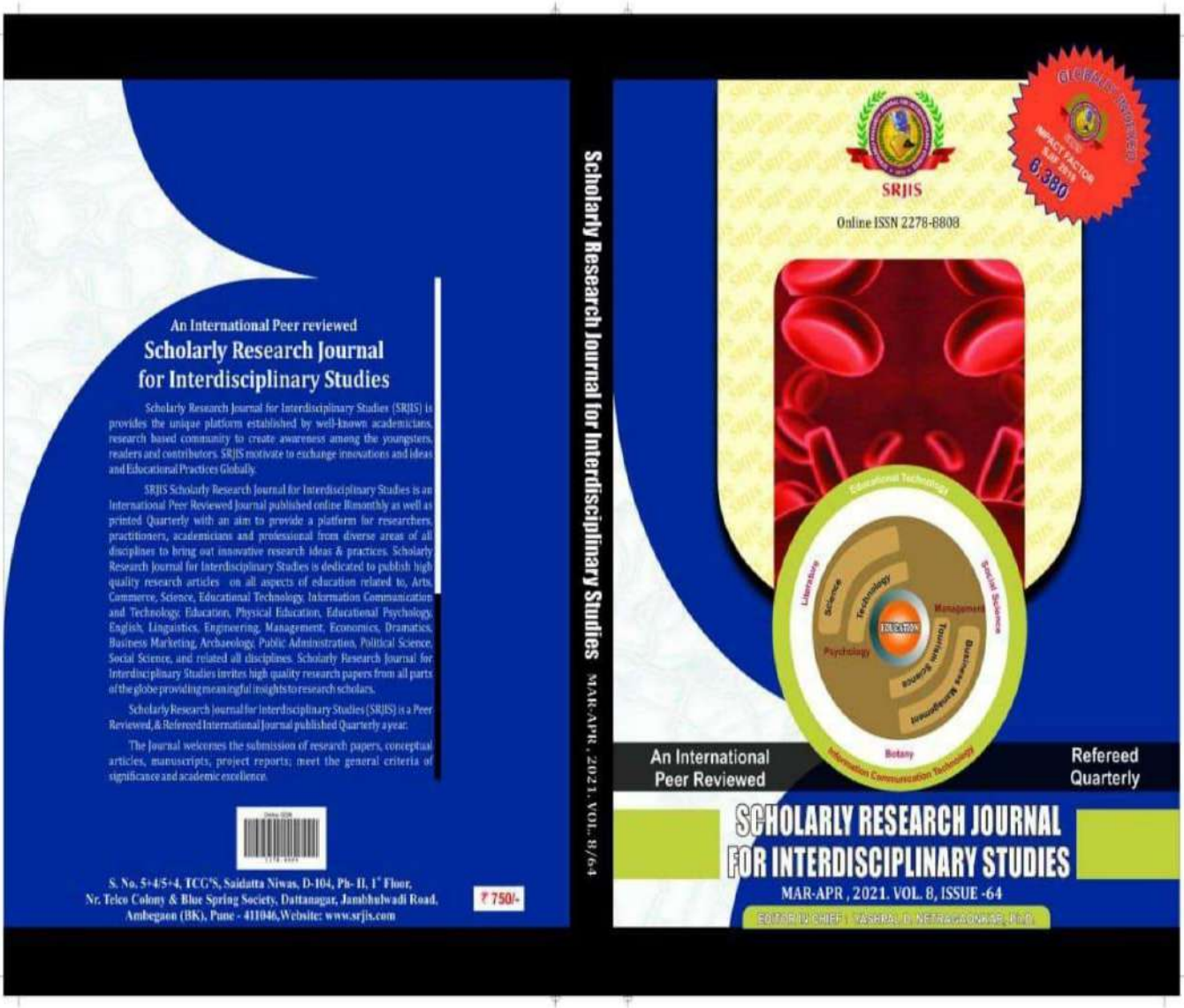
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कोव्हीड –19 चा भारतीय अर्थव्यवस्थेवरील परीणाम

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अर्थशास्त्र विभाग, श्री शिवाजी महाविद्यालय अकोला
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प्रस्तावना –

कोरोनाव्हायरस साथीचा भारतावर होणारा परिणाम आर्थिक हालचालींच्या दृष्टीने तसेच मानवी जीवितहानीच्या दृष्टीने मोठ्या प्रमाणात व्यत्यय आणत आहे. देशांतर्गत मागणी आणि निर्यात काही उल्लेखनीय अपवाद वगळता झपाट्याने घट झाल्याने जवळजवळ सर्वच क्षेत्रांवर विपरीत परिणाम झाला आहे. काही महत्त्वाच्या क्षेत्रांचा प्रभाव आणि संभाव्य उपाय यांचे विश्लेषण करण्याचा प्रयत्न केला जातो. साथीच्या रोगामुळे होणारा व्यत्यय लक्षात घेता, रूग्णांची मंदी भूतकाळ मंदीपेक्षा वेगळी असल्याचे स्पष्ट झाले आहे. अचानक झालेली मागणी आणि वाढती बेरोजगारी यामुळे व्यावसायिक दृष्टिकोन बदलणार आहे. 'स्थानिकीकरण, रोख संवर्धन, पुरवठा साखळी लवचिकता आणि नवनिर्मिती' यासारख्या नव्या तत्त्वांचा अवलंब केल्यास या अनिश्चित वातावरणात व्यवसायांना नव्या मार्गावर चालण्यास मदत होईल.

आकडेवारीनुसार भारताचा चालू जीडीपी तोटा अंदाजे 5 ते 10 अब्ज डॉलर (0.15 – 0.35 टक्के) असण्याची शक्यता आहे. बेंचमार्क निर्देशांकात 20 टक्के पेक्षा जास्त कपात भारतीय शेअर बाजाराने अस्थल बाजारक्षेत्रात प्रवेश केला. जागतिक आरोग्य संघटनेने (डब्ल्यूएचओ) 12 मार्च रोजी कोरोनाव्हायरस रोगाचा (ब्रेक्ट–19) मुकताच उद्रेक झाल्याचे जाहीर केले आणि 11.4 ट्रिलियन भागधारकांची संपत्ती उद्ध्वस्त केली. अलीकडच्या काळात भारताची अर्थव्यवस्था मंदावली आहे. गेल्या 11 वर्षांतील सर्वात मंद असलेल्या कोविड–19 च्या अडोगतीच्या धोक्यांमुळे मूडीजने २०२० मध्ये भारताचा विकास दर 5.3 टक्क्यांवर आणला आहे. एका अर्थतज्ज्ञाच्या मते, 'सप्लाय साईड कौन्टमइफेक्ट' उत्पादन, कृषी आणि औषध उद्योगावर परिणाम करेल. कोरोनाव्हायरसने विविध विभाग स्थिर राहण्यासाठी आगले आहेत.

संशोधनाची उद्दीष्टये – कोव्हीड – 19 चा भारतीय अर्थव्यवस्थेवरील परीणामांचे अध्ययन करणे.
संशोधनाची गृहीते – कोव्हीड – 19 चा भारतीय अर्थव्यवस्थेवर विपरीत परीणाम झाला.

अन्न आणि शेती

शेती हा देशाचा कणा आहे आणि सरकारने अत्यावश्यक सेवी जाहीर केल्यामुळे प्राथमिक कृषी उत्पादन आणि कृषी माहितीचा वापर या दोन्हीवर कमी परिणाम होण्याची शक्यता आहे. अनेक राज्य सरकारांनी फळे, भाजीपाला, दूध इत्यादींची मोकत हालचाल करण्याची परवानगी दिली आहे. ऑनलाइन खाद्यपदार्थांच्या किराणा प्लॅटफॉर्मवर हालचाली आणि लॉजिस्टिक वाहने बंद करण्यावर अस्पष्ट निर्बंध असल्यामुळे ऑनलाइन खाद्यपदार्थांच्या किराणा प्लॅटफॉर्मवर मोठा परिणाम होतो. आरबीआय आणि अर्थमंत्र्यांनी अल्पावधीत उद्योग आणि कर्मचाऱ्यांना मदत करणार असल्याचे जाहीर केले. गेल्या काही आठवड्यात ग्रामीण अन्न उत्पादन क्षेत्राला इन्सुलेट केल्यास कोव्हीड – 19 चा भारतीय अन्न क्षेत्रावर तसेच मोठ्या अर्थव्यवस्थेवर होणाऱ्या व्यापक परिणामाचे उत्तम उत्तर मिळेल.

एव्हिएशन अँड टुरिझम

आपल्या जीडीपीमध्ये एव्हिएशन सेक्टर आणि टुरिझमचे योगदान अनुक्रमे 2.4 टक्के आणि 9.2 टक्के आहे. पर्यटन क्षेत्राने आर्थिक वर्ष 18–19 मध्ये सुमारे 4.3 कोटी लोकांना सेवा दिली. एव्हिएशन अँड टुरिझम या पहिल्या उद्योगाना साथीचा मोठा फटका बसला. सर्वसामान्य एकमत असे आहे की कोव्हीड –19 पेक्षा या उद्योगांना आणि २००8 च्या आर्थिक संकटाला अधिक फटका देईल. हे दोन्ही उद्योग साथीच्या रोगाच्या सुरुवातीपासून चलनप्रवाहाच्या गंभीर समस्याहाताळत आहेत आणि एकूण मनुष्यबळाच्या 70 टक्के मनुष्यबळ असलेल्या संभाव्य 3.8 कोटी ले–ऑफकडे पाहत आहेत. व्हाईट आणि ब्लू कॉलर या दोन्ही नोक–यांवर याचा परिणाम होणार आहे. आयएटीएच्या अंदाजानुसार, प्रवास निर्बंधामुळे या उद्योगांना सुमारे 85 अब्ज रुपयांचा तोटा सहन करावा लागू शकतो. साथीच्या रोगामुळे कॉन्टैक्टलेस बोर्डिंग आणि ट्रैव्हल टेक्नोलॉजी या क्षेत्रातही नावीन्याची लाट आली आहे.

दूरसंचार

सेवा पुरवठादारांमधील संक्षिप्त किंमत युद्धामुळे सीओव्हीआयडी –19 च्या आधीही भारतातील दूरसंचार क्षेत्रात लक्षणीय बदल झाले आहेत. निर्बंधामुळे 'घरकाम' लागू झाल्यामुळे बहुतेक अत्यावश्यक सेवा आणि क्षेत्रे साथीच्या रोगाच्या काळात चालू राहिली आहेत. 2019 पर्यंत 1 अब्जाहून अधिक कनेक्शन असलेले दूरसंचार क्षेत्र जीडीपीच्या सुमारे 6.5 टक्के योगदान देते आणि सुमारे 40 लाख लोकांना रोजगार देते. ब्रॉडबँडच्या वाढत्या वापराचा थेट परिणाम झाला आणि नेटवर्कवर दबाव आला. मागणी तपासून सुमारे 10 टक्क्यांनी वाढली आहे. तथापि, टेल्कोमध्ये नवीन ग्राहक जोडण्यात घसरलीची घट होण्याची शक्यता आहे. धोरणात्मक शिफारशीनुसार, सरकार नियामक अनुपालन शिथिल करून या क्षेत्राला मदत करू शकते आणि स्पेक्ट्रम देय साठी स्थगिती प्रदान करू शकते, जे कंपन्यांकडून नेटवर्क विस्तारासाठी वापरले जाऊ शकते.

औषधे

जागतिक पातळीवर जेनेरिक औषधांचे सर्वात मोठे उत्पादक असलेल्या कोविड– 19 साथीच्या रोगाच्या प्रारंभापासून औषध उद्योग वाढत आहे. २०२० च्या सुरुवातीला बाजारपेठेचा आकार 55 अब्ज डॉलर असून, भारतात हायड्रॉक्सिक्लोरोक्विनची निर्यात अमेरिका, यूके, कॅनडा आणि मध्यपूर्वेत होत आहे.

साथीच्या रोगामुळे चीनमधून आयात केलेल्या कच्च्या मालाच्या किंमतीत नुकतीच वाढ झाली आहे. आयातीवर मोठ्या प्रमाणावर अवलंबून राहणे, पुरवठा साखळी विस्कळीत होणे आणि सामाजिक दुराव्यामुळे उद्योगात श्रमाची अनुपलब्धता यामुळे जेनेरिक औषधांचा सर्वाधिक परिणाम होतो. त्याचबरोबर देशासाठी परदेशी औषधे, उपकरणे आणि पीपीई किट्सच्या निर्यातीवर सरकारने घातलेल्या बंदीमुळे औषध उद्योग संघर्ष करत आहे. या औषधांच्या वाढत्या मागणीमुळे आणि प्रवेशात अडथळा आणण्याबरोबरच परिस्थिती कठीण होत चालली आहे. औषध कंपन्यांवरील आर्थिक ताण कमी करणे, कर–शिथिलता आणि श्रमशक्तीच्या कमतरतेवर मात करणे हे अशा निराशाजनक काळात करकाचे घटक असू शकतात.

तेल आणि वायू

जागतिक संदर्भात भारतीय तेल आणि वायू उद्योग अतिशय महत्त्वाचा आहे– हा अमेरिका आणि चीनच्या मागे तिसरा सर्वात मोठा ऊर्जा ग्राहक आहे आणि जागतिक तेलाच्या मागणीच्या 5.2 टक्के योगदान देतो. देशभरातील वाहतूक इंधनाची मागणी मंदावली (तेल आणि वायू क्षेत्रातील 2/3 वी मागणी) ऑटो अँड औद्योगिक उत्पादन घटले आणि वस्तू आणि प्रवासी चळवळ (दोन्ही बल्क आणि वैयक्तिक) कमी झाली. या काळात कच्च्या तेलाच्या किंमती कमी झाल्या असल्या तरी महसुलाचे नुकसान करण्यासाठी सरकारने उत्पादन शुल्क आणि विशेष उत्पादन शुल्कात वाढ केली आणि याशिवाय रस्ते उपकरही वाढवण्यात आला. धोरणात्मक शिफारशींनुसार, मागणीला चालना देण्यासाठी किरकोळ दुकानांमध्ये ग्राहकांना संपवण्यासाठी कच्च्या तेलाच्या कमी किंमतीचे फायदे देण्याचा सरकार विचार करू शकते.

पर्यटन

पर्यटन, विमानवाहतूक, आदरातिथ्य आणि व्यापार यासारख्या क्षेत्रांना पहिल्या आव्हानांना तोंड द्यावे लागेलच इतर क्षेत्रांनाही चक्रीय परिणामाला सामोरे जावे लागेल. अहवालानुसार, देशांतर्गत प्रवासात 20 टक्के कपात झाली आहे आणि आंतरराष्ट्रीय प्रवासबुकिंगमध्ये सुमारे 75 टक्के घट झाली आहे. हॉटेल बुकिंगचे प्रमाणही 70 टक्क्यांवरून 20 टक्क्यांपर्यंत घसरले आहे. रेस्टॉरंट व्यवसायात 30 ते 35 टक्क्यांनी घट झाली आहे. पोल्ट्री क्षेत्राच्या विक्रीतही दररोज सुमारे 1500 – 20 कोटी रुपयांच्या व्यवसायाचे 80 टक्क्यांनी नुकसान झाले आहे. व्हायरसचा प्रादुर्भाव हा जागतिक अर्थव्यवस्था आणि वित्तीय बाजारपेठांना सर्वात मोठा धोका बनला आहे. जागतिक ग्रामीण भारताचा भाग असणे हा या विषाणूपासून मुक्त नाही. भारत सरकार तसेच राज्य सरकार कोरोनाव्हायरस साथीच्या रोगावर नियंत्रण ठेवण्यासाठी परिस्थितीवर बारकाईने उपचार आणि देखरेख करत आहेत समस्येचे स्पष्ट चित्र मिळवण्यासाठी 1 – 2 महिने लागू शकतात. प्रत्येक भारतीयाने जागरूक आणि जागरूक राहणे अत्यंत महत्त्वाचे आहे.

जागतिक आरोग्य संघटनेने (डब्ल्यूएचओ) 12 मार्च रोजी कोरोनाव्हायरस रोगाचा (कोव्हीड–19) नुकताच साथीचा रोग सुरू करण्याची घोषणा केली आणि 11.4 ट्रिलियन भागधारकांची संपत्ती ढासळली. अलीकडच्या काळात भारताची अर्थव्यवस्था मंदावली आहे. गेल्या 11 वर्षांतील सर्वात मंद असलेल्या कोविड–19 च्या अधोगतीच्या धोक्यामुळे मूडीजने 2020 मध्ये भारताचा विकास दर 5.3 टक्क्यांवर आणला आहे. एका अर्थतज्ज्ञाच्या मते, 'सप्लाय साईड कॉन्टमइफेक्ट' उत्पादन, कृषी आणि औषध उद्योगावर परिणाम करेल. कोरोनाव्हायरसने विविध विभाग स्थिर राहण्यासाठी आणले आहेत.

आकडेवारीनुसार भारताचा चालू जीडीपी तोटा अंदाजे 5 ते 10 अब्ज डॉलर (0.15 – 0.35 टक्के) असण्याची शक्यता आहे. बेंचमार्क निर्देशांकात 20 पेक्षा जास्त कपातय भारतीय शेअर बाजाराने बाजारक्षेत्रात प्रवेश केला आहे. नव्या कोरोना व्हायरसमुळे गुंतवणूकदारांना बाँडच्या किंमती वर बोली लावली आहे आणि परिणामी प्रमुख अर्थव्यवस्थांमधील उत्पन्न इच कमी झाले आहे. सौदी अरेबिया आणि रशिया यांच्यातील कच्च्या तेलाच्या युद्धामुळे इतर मालमत्तेत अस्थिरता निर्माण झाली आहे. रंग, वैशिष्ट्यपूर्ण रसायने, हेअर ऑइल, सिमेंट, पीव्हीसी पाइप इत्यादी क्षेत्रांना कच्च्या तेलाच्या किंमती कमी झाल्यामुळे फायदा होणार आहे. मोठ्या वित्तीय संस्थाच्या अपयशामुळे देशांतर्गत उपभोग मंदावल्याने येस बँक संकटाच्या स्वरूपात आणखी एक परिस्थिती निर्माण झाली आहे. इतर वस्तू कमी झाल्या असल्या तरी अनिश्चिततेत सुरक्षित आश्रयाच्या मागणीमुळे सोने वाढले आहे.

देशातील संकटपरिस्थितीचा सामना करण्यासाठी आरबीआय आवश्यक पावले उचलत आहे. आरबीआयने उदयोन्मुख परिस्थितीत व्यवसाय सातत्य योजना आणली आणि कर्मचारी सदस्य आणि इतर ग्राहक यांच्यातील धोरणे आखून सूचना सानायिक करत आहे. आरबीआयने ओपन मार्केटही सुरू केले आहे. 20 मार्चपासून एकूण 10,000 कोटी रुपयांच्या सरकारी सिक्युरिटीज खरेदीच्या स्वरूपात काम केले जाते. सिक्युरिटीजची कोणतीही अधिसूचित रक्कम नमूद केलेली नाही, पण आरबीआयकडे 10,000 कोटी रुपयांची मर्यादा आहे ज्यामध्ये वैयक्तिक सिक्युरिटीज खरेदीचा निर्णय घेण्याचा. ऑफर स्वीकारण्याचा आणि ऑफर स्वीकारण्याचा किंवा नाकारण्याचा त्यांना एकमेव अधिकार आहे. म्हणतात त्याप्रमाणे प्रत्येक ढगाला चांदीची रेषा असते. पंतप्रधान मोदींनी आश्वासन दिले की, सरकार आमच्यासोबत आहे आणि सेल्फ क्वारंटाईन करून आपण स्वतःला मदत करण्याची गरज आहे. नागरिक या नात्याने आपण एकत्र येऊन जागतिक संकटाशी लढण्याची गरज आहे आणि भारत सरकारच्या निर्देशानुसार आरोग्य आणि स्वच्छतेच्या मूलभूत सूचनांचे पालन केले पाहिजे. आपल्याला आपल्या कृतीची काळजी घ्यावी लागेल आणि आपण एकत्र मिळून या विषाणूवर नक्कीच मात करू आणि या ग्रहाला राहण्यासाठी अधिक चांगले ठिकाण बनवू. आशा आहे की बाजारपेठेची चिंता लवकरच नाहीशी होईल आणि अर्थव्यवस्था उलटी होईल.

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NAAC 3.3.2

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प्रा. धनजय पी काळे
अर्थशास्त्र विभाग, श्री शिवाजी महाविद्यालय अकोला

प्रस्तावना – २०२० मधील कोरोना व्हायरस (कोव्हीड – 19 साथीच्या रोगाचा) साथीच्या रोगामुळे भारताची आर्थिक घडी मोठया प्रमाणात विस्कळीत झाला आहे. सांख्यिकी मंत्रालयाच्या म्हणण्यानुसार सन २०२० च्या आर्थिक वर्षातील चौथ्या तिमाहीत भारताची वाढ घसरून 1.1 टक्क्यांवर गेली आहे. भारत सरकारचे मुख्य आर्थिक सल्लागार म्हणाले की, ही घसरण प्रामुख्याने भारतीय अर्थव्यवस्थेवरील कोरोनाव्हायरस (साथीचा रोग) सर्व देशभर (किंवा (साथीचा रोग)) सर्वत्र पसरला आहे. विशेष म्हणजे, देशातील (साथीचा रोग) सर्व देशभर (साथीचा रोग)पसरलेला आहे. दीवसेन दीवस मंदीत वाढ होत आहे आणि जागतिक बँकेच्या म्हणन्यानुसार सध्याच्या साथीच्या रोगाने "भारताच्या आर्थिक दृष्टिकोनातून पूर्वीच्या अस्तित्वातील जोखीम" वाढविली आहेत.

1990 च्या दशकात भारताच्या आर्थिक उदारीकरणानंतरच्या तीन दशकात भारताने सर्वात कमी आकडेवारीसह जागतिक बँक आणि रेटिंग एजन्सीनी सुरुवातीच्या आर्थिक वर्ष २०२० च्या वाढीमध्ये सुधारणा केली होती. तथापि, मे च्या मध्यभागी आर्थिक पॅकेजची घोषणा झाल्यानंतर, भारताच्या जीडीपीच्या अंदाजानुसार नकारात्मक आकडेवारीत आणखी घसरण झाली आणि हे मंदीचे संकेत दर्शविते. (या कालावधीत 38 पेक्षा जास्त देशाच्या रेटिंगचे मूल्य कमी करण्यात आले आहे.) 26 मे रोजी क्रिसिलने जाहीर केले की ही कदाचित स्वातंत्र्यानंतरची सर्वात वाईट मंदी असेल. स्टेट बँक ऑफ इंडियाच्या संशोधनानुसार, जीडीपीमध्ये 40 पेक्षा जास्त आकुंचन होण्याचा अंदाज आहे. आकुंचन एकसारखे होणार नाही. तर राज्य आणि क्षेत्रासारख्या विविध पॅरामीटर्सनुसार ते वेगळे असेल. 1 सप्टेंबर 2020 रोजी सांख्यिकी मंत्रालयाने वित्तीय वर्ष 21 (एप्रिल ते जून) च्या जीडीपी आकडेवारी जाहीर केली, ज्यात मागील वर्षाच्या याच कालावधीच्या तुलनेत 24 घट झाली.

संशोधनाची उद्दीष्टये – कोव्हीड – 19 चा भारतीय अर्थव्यवस्थेवरील परीणामांचे अध्ययन करणे.

संशोधनाची गृहीते – कोव्हीड – 19 चा भारतीय अर्थव्यवस्थेवर विपरीत परीणाम झाला.

रोजगारावरील परीणाम

नोमुरा इंडियाच्या मते इंडिया बिझिनेस सेंटिमेन्ट इंडेक्सची आर्थिक क्रिया 22 मार्च रोजी 82.9 वरून घसरून 26 एप्रिल रोजी 44.7 वर आली. 13 सप्टेंबर 2020 पर्यंत आर्थिक क्रियाकलाप पूर्व-लॉकडाउनकडे परत आला होता. 1 मार्च रोजी बेरोजगारी 7.7: वरून 1 एप्रिल रोजी २: पर्यंत वाढली आणि नंतर जूनच्या मध्यापर्यंत पूर्व-लॉकडाऊन पातळीवर खाली आली.

२) लॉकडाऊन दरम्यान, अंदाजे 1 कोटी (1 दशलक्ष) लोकांचा रोजगार गमावला तर बँयाच जणांच्या पगारावर कपात केली. २. मागील वर्षाच्या तुलनेत देशभरातील 45: पेक्षा जास्त कुटुंबांनी उत्पन्नामध्ये घट नोंदविली आहे. कोरोनाव्हायरसच्या उद्रेकानंतर जाहीर झालेल्या 21 दिवसांच्या संपूर्ण लॉकडाऊन दरम्यान भारतीय अर्थव्यवस्थेला दररोज 32,000 कोटी (यूएस + 4.5 अब्ज डॉलर्स) कमी होणे अपेक्षित होते. संपूर्ण लॉकडाऊन अंतर्गत, भारताच्या 2.8 ट्रिलियन डॉलर्सच्या आर्थिक चक्रापैकी एका चतुर्थांशपेक्षा कमी कामकाज होते. देशातील सुमारे 53: व्यवसायांवर लक्षणीय परिणाम होण्याचा अंदाज होता. लॉकडाउन निर्बंधाच्या ठिकाणी पुरवठा साखळ्यांना तणावात आणले गेले आहे. प्रारंभी, "अत्यावश्यक" म्हणजे काय आणि काय नाही हे सुलझ करण्यात स्पष्टतेचा अभाव होता. अनौपचारिक क्षेत्रातील आणि दैनंदिन वेतन मजुरीतील लोकांना सर्वाधिक धोका आहे. , नाशवंत पीक पेर्णाया देशभरातील मोठया संख्येने शेतकऱ्यानाही अनिश्चिततेचा सामना करावा लागला.

सीमेंट उद्योग व शेअर बाजारावरील परीणाम

लार्सन अँड टुब्रो, भारत फोर्ज, अल्ट्राटेक सिमेंट, ग्रासिम इंडस्ट्रीज, आदित्य बिर्ला ग्रुप, बीएचईएल आणि टाटा मोटर्स यासारख्या मोठया कंपन्यांनी ऑपरेशन तात्पुरते स्थगित केले किंवा कमी केले. निधी कमी झाल्यामुळे यंग स्टार्टअपवर परिणाम झाला. देशातील देशाने चालवलेल्या ग्राहक वस्तू कंपन्यांनी ऑपरेशन्समध्ये लक्षणीय घट केली आहे आणि आवश्यक वस्तूंवर लक्ष केंद्रित केले आहे. 23 मार्च 2020 रोजी भारतातील शेअर बाजार इतिहासातील सर्वात वाईट घसरला तथापि, 25 मार्च रोजी पंतप्रधानांनी 21 दिवसांच्या संपूर्ण लॉकडाउनच्या घोषणेनंतर एका दिवसानंतर सेन्सेक्स आणि निफ्टीने 11 वर्षात सर्वात मोठा नफा मिळविला.

अन्न सुरक्षा आणि आरोग्य

निर्देशांक % S&P BSE 500 (जानेवारी 2015 ते नोव्हेंबर 2020) ब्लू डायलाइट कोविड –१ कालावधी प्रतिबिंबित करते अन्न सुरक्षा आणि आरोग्यासाठी आणि राज्यांसाठी अतिरिक्त निधी, सेक्टरशी संबंधित प्रोत्साहन व कर मुदत वाढ यासाठी विविध उपाययोजनांची घोषणा भारत सरकारने केली. २ मार्च रोजी गरिबांसाठी अनेक आर्थिक मदत उपायांची घोषणा केली गेली की एकूण 1,000 कोटी (यूएस + २अब्ज) आहे. दुर्दैवाच दिवशी रिझर्व्ह बँकेनेही अनेक उपाययोजना जाहीर केल्या ज्यामुळे देशाच्या वित्तीय यंत्रणेला 44,००० कोटी (यूएस +२ अब्ज डॉलर्स) उपलब्ध होतील. १ कोरोनव्हायरस (साथीचा रोग) सर्व देशभर (किंवा खंडभर) पसरलेला रोग सोडविण्यासाठी जागतिक बँक आणि आशियाई विकास बँकेने भारताला पाठिंबा मंजूर केला.

१ जून रोजी "फर्स्ट अनलॉक" पर्यंतच्या भारताच्या लॉकडाऊनच्या वेगवेगळ्या टप्प्यांमध्ये अर्थव्यवस्थेच्या उद्घाटनाचे वेगवेगळे अश होते. १ एप्रिल रोजी रिझर्व्ह बँकेच्या गाहर्नरने नाबार्ड, सिडबी आणि एनएचबीला 50,००० कोटी (यूएस 17 अब्ज डॉलर्स) चे विशेष तिलपुरवठा साथीच्या रोगाकरीत आर्थिक परिणामाचा प्रतिकार करण्यासाठी अधिक उपायांची घोषणा केली. 18 एप्रिल रोजी, साथीच्या आजाराच्या वेळी भारतीय कंपन्यांच्या संरक्षणासाठी सरकारने भारताचे थेट परकीय गुंतवणूक धोरण बदलले. सैनिकी व्यवहार विभागाने

आर्थिक वर्षाच्या सुरुवातीस सर्व मांडवल अधिग्रहण रोखले आहे. संस्थेने दलाचे प्रमुख यांनी जाहीर केले आहे की भारताने कमी खर्चात संसाधन आयात करावे आणि देशांतर्गत उत्पादनाला संधी द्यावी.

पंतप्रधान पॅकेज

१२ मे रोजी पंतप्रधानांनी २० लाख कोटी डॉलर्स (२ अब्ज अमेरिकन डॉलर्स) किमतीची एकूण आर्थिक उत्तेजन पॅकेज जाहीर केली, जी भारताच्या जीडीपीच्या १०. आहे, ज्याने भारतावर स्वावलंबी राष्ट्र म्हणून भर दिला. डिसेंबर २०२० मध्ये, माहितीच्या अधिकाराच्या अर्जाने असे निष्कर्ष काढले की या उत्तेजनापैकी १०. पेक्षा कमी प्रत्यक्षात वितरित केले गेले होते. २०, पुढील पाच दिवसांत अर्थमंत्र्यांनी आर्थिक पॅकेजचे तपशील जाहीर केला. दोन दिवसांनंतर मंत्रिमंडळाने आर्थिक पॅकेजमधील अनेक प्रस्तावांना मौकत अन्नधान्याच्या पॅकेजेससह मान्यता दिली. 2 जुलै 2020 पर्यंत अनेक आर्थिक निर्देशकांनी घरताव व पुनर्प्राप्तीची चिन्हे दर्शविली. २ जुलै रोजी भारताचे वित्त सचिव म्हणाले की, अर्थव्यवस्था अपेक्षेपेक्षा वेगवान दराने पुनर्प्राप्तीची चिन्हे दर्शवित आहे, तर आर्थिक व्यवहार सचिव म्हणाले की, त्यांना भारताच्या वसुलीच्या पुनर्प्राप्तीची अपेक्षा आहे. जुलैमध्ये केंद्रीय मंत्रिमंडळाने अर्थव्यवस्था मजबूत करण्याच्या उद्देशाने राष्ट्रीय शैक्षणिक धोरण 2020 पास केले. १२ ऑक्टोबर आणि १२ नोव्हेंबर रोजी सरकारने आणखी दोन आर्थिक प्रोत्साहन पॅकेजेसची घोषणा केली आणि एकूण आर्थिक उत्तेजन २ (7 लाख कोटी (यूएस + 420 अब्ज डॉलर्स) – राष्ट्रीय जीडीपीच्या 15% – 31 ऑक्टोबर 2020 पर्यंत तेव्हले.

भारतात आजीविका विरुद्ध उदरनिर्वाहाची चर्चादेखील सुरू झाली. सरकारने प्रथम जाहीर केले की जीवनापेक्षा जीवनाला प्राधान्य दिले जाईल, जे नंतर जीवन आणि रोजीरोटीला दिले जाणारे समान महत्त्व बदलले. २ मेच्या मध्यापर्यंत केंद्र आर्थिक क्रियाकलाप पुन्हा सुरू करण्यास उत्सुक होता, तर मुख्यमंत्र्यांची संमिश्र प्रतिक्रिया होती.

पंतप्रधान मोदींनी 24 मार्च रोजी भारताच्या पहिल्या 21 दिवसांच्या लॉकडाऊनची घोषणा केली. देशाला या संबोधनादरम्यान ते म्हणाले, "जान है तो जहां है है" (जर जीवन असेल तरच रोजीरोटी होईल). ११ एप्रिल रोजी भारताच्या मुख्यमंत्र्यांसमवेत झालेल्या बैठकीत पंतप्रधान म्हणाले, "आपका मंत्र आधी जान है तो होता है, परंतु आता तो जान भी जान भी (दोन्ही, जीवन आणि जीवनमान समान आहे)." १ एप्रिल रोजी, मोदींनी देशाला आणखी एक संबोधित केले, ज्यात त्यांनी लॉकडाउन,, मे पर्यंत वाढविला 11 मे रोजी मुख्यमंत्र्यांसमवेत पंतप्रधानाच्या पाचव्या बैठकीत पंतप्रधान म्हणाले की, जागतिक युद्धानंतर जसा जग बदलला तसाच भारतीयांनी कोरोनाव्हायरस (साथीचा रोग) सर्व देशभर (किंवा खंडभर) असलेला जगासाठी तयारी करायलाच हवी. बैठकीत मोदी म्हणाले, "जन से लेकर जग तक" (एक व्यक्तीपासून संपूर्ण मानुसकीपर्यंतचे भाषांतर) हे नवीन तत्व आणि जीवनशैली असेल. 12 मे रोजी पंतप्रधानांनी देशाला उद्देशून असे संबोधित केले कोरोनव्हायरस (साथीचा रोग) सर्व देशभर (किंवा खंडभर) असलेला देशभर स्वावलंबन वाढविण्याची संधी होती. त्यांनी आत्मनिर्भर भारत अभियान (स्वावलंबी भारत मिशन) आर्थिक पॅकेज प्रस्तावित केले.

१ मार्च रोजी कोविड – १ आर्थिक प्रतिसाद टास्क फोर्सच्या स्थापनेची घोषणा पंतप्रधान नरेंद्र मोदी यांनी देशाला थेट भाषण करताना केली. टास्क फोर्सचे नेतृत्व अर्थमंत्री निर्मला सीतारमण करीत होते. औपचारिकरित्या गठित केलेली नसल्यास किंवा मदत पॅकेजेसची अधिकृत तारीख नसली तरी संबंधित पक्षांशी सल्लामसलत त्वरित सुरू झाली होती. विमान मंत्रालय, आतिथ्य आणि एमएसएमई सारख्या सर्वाधिक बाधित क्षेत्रांचा साठा घेण्यासाठी वित्त मंत्रालयाने तातडीने आरबीआय आणि मंत्रालयांशी सल्लामसलत सुरू केली. २१ मार्च २०२० रोजी केंद्रीय मंत्रिमंडळाने इलेक्ट्रॉनिक उत्पादनाच्या ०,३३३५ कोटी (+.7 अब्ज डॉलर्स) च्या प्रोत्साहनांना मान्यता दिली.

विविध राज्य सरकारांनी असंघटित क्षेत्रातील गरिबांना आर्थिक मदतीची घोषणा केली. २१ मार्च रोजी उत्तर प्रदेश सरकारने राज्यातील सर्व दैनंदिन मजुरीसाठी १,००० डॉलर्स (यूएस + १) चे थेट पैसे हस्तांतरित करण्याचे ठरविले आणि दुर्संया दिवशी पंजाबने सर्व नोंदणीकृत बांधकाम कामगारांना प्रत्येकी 1,000, (यूएस +२) जाहीर केले. राज्यात, २ मार्च रोजी हरियाणा मजूर, पथ विक्रेते आणि रिक्षा चालकांना त्यांच्या बँक खात्यात थेट दर आठवड्याला १,००० डॉलर्सची मदत दिली जाईल. अशी घोषणा करण्यात आली. दारिद्र्यरेषेखालील कुटुंबांना एप्रिल महिन्यात मोफत राशन (तांदूळ, गहू, मोहरी तेल, साखर) दिले जाईल.

२ मार्च रोजी देशाला संबोधित करताना पंतप्रधानांनी आरोग्य सेवा क्षेत्रासाठी 1,000, कोटी (यूएस + २.१ अब्ज डॉलर्स) निधीची घोषणा केली.

२ मार्च रोजी अर्थमंत्र्यांनी अर्थसंकल्पसादर्भात अनेक घोषणा केल्या जसे की जीएसटी रिटर्न भरण्यासाठी शेवटची तारीख वाढविणे आणि आयकर विवरणपत्र भरणे. सबका विश्वास (लेगसी डिस्प्युट रेझोल्यूशन) स्कीम २०१ वित्त, कस्टम्स विलजरन्स आणि कस्टम ॲक्ट अंतर्गत संबंधित बाबींच्या अनुषंगाने आणि संबंधित कार्यवाहीसाठी जून २०२० पर्यंत मुदत देण्यात आली.

25 मार्च रोजी मोदी सरकारने देशातील 800 दशलक्ष लोकांसाठी जगातील सर्वात मोठी अन्न सुरक्षा योजना जाहीर केली. कॅबिनेट मंत्री प्रकाश जावडेकर यांनी पत्रकार परिषदेत जाहीर केले की दरमहा रेशन ७ किलो असेल (ज्यामध्ये प्रति किलो ₹ २ (२.8 अमेरिकन डॉलर्स) गहू आणि तांदूळ ₹ (२ अमेरिकन डॉलर) असेल.

२ मार्च रोजी उत्तर प्रदेश सरकारने पॅन मसाल्याच्या निर्मितीवर आणि विक्रीवर बंदी घातली. "रिपटिंग पैन मसाला कोविड –१ चतनकपदष्ट प्रसार करण्यास मदत करू शकतो" या आदेशात नमूद केले. यानंतर आंध्र प्रदेश, राजस्थान आणि गुजरातसारख्या इतर राज्यांनीही सार्वजनिक ठिकाणी थुंकण्यावर बंदी घातली.

२ मार्च रोजी अर्थमंत्र्यांनी गरिबांसाठी अनेक आर्थिक मदत उपायांची घोषणा केली. लॉकडाऊन दरम्यान भुकेलेला. प्रधानमंत्री उज्ज्वला योजना लाभार्थ्यांना तीन महिने मोफत सिलिंडर मिळतील. दारिद्र्यरेषेखालील 80 दशलक्षाहून अधिक लोकांना याचा फायदा होईल.. एप्रिलमध्येच २०२०–२१ मध्ये पहिल्या हप्त्याचे (₹ ००० डॉलर्स) भरणे सरकार वेगवान करेल.

प्रधानमंत्री किसान सम्मान निधी (पीएम–किसन) अंतर्गत संघटित क्षेत्रातील कामगारांसाठी, महिन्यात १,००० डॉलर्स पर्यंत कमाई करणाऱ्या छोट्या कंपन्यांच्या उपस्संपदद दशलक्ष कर्मचाऱ्यांना सरकार दोन्ही बाजूंचे कर्मचारी भविष्य निर्वाह निधी (ईपीएफ) चे योगदान देईल. दिवाळखोरी व दिवाळखोरी संहिता (आयबीसी) अंतर्गत दिवाळखोरीची कार्यवाही करण्यासाठी १००,००० डॉलर्स वरून १० दशलक्षापर्यंतची उंची एमएसएमईला मदत करण्यासाठी करण्यात आली. साथीच्या रोगाशी संबंधित आरोग्यविषयक गरजांसाठी जिल्हा खनिज निधी वळविणे यासारख्या राज्य सरकारांना विविध सूचना व मार्गदर्शक सूचना देण्यात आल्या.

२ मार्च रोजी भारताने आभासी 'एक्स्ट्राऑर्डिनरी जी –20 लीडर' समिटमध्ये भाग घेतला. जी –20 देशांनी (साथीचा रोग) सर्व देशभर (किंवा खंडभर) असलेला होणारा परिणाम टाळण्यासाठी जागतिक अर्थव्यवस्थेत 5 ट्रिलियन डॉलर्सपेक्षा जास्त इंजेक्ट करण्याचा निर्णय घेतला. त्यांनी एकत्र काम करण्यास, जागतिक आरोग्य संघटनेला बळकटी देण्यासाठी, एक लस विकसित करून ती उपलब्ध करुन देण्याचे मान्य केले. त्यांनी वेक्टर आणि पारदर्शक माहिती, संशोधन आणि विकासासाठी साहित्य आणि डेटा सामायिक करण्याचे ठरविले. वैद्यकीय पुरवठ्यासाठी उत्पादन क्षमता वाढविण्याव्यतिरिक्त, गंभीर पुरवठा सुरळीत होण्याची खात्री करण्यास त्यांनी सहमती दर्शविली. २ मार्च रोजी रिझर्व्ह बँक ऑफ इंडियाचे (आरबीआय) गव्हर्नर शक्तिकांत दास यांनी तीन महिन्यासाठी ईएमआय स्थगित ठेवून रेपो दर कमी करण्यासह अनेक घोषणा केल्या. सुरू केलेल्या इतर उपाययोजनामुळे देशाच्या वित्तीय व्यवस्थेला एकूण 4,000 कोटी (यूएस +२ अब्ज डॉलर्स) उपलब्ध होतील. दिल्ली सरकारने जाहीर केले की २ तारखेपासून ते दररोज 10,000 लोकांना मोफत भोजन पुरवतील. दिल्ली सरकारने 500 हून अधिक उपासमार केंद्रे स्थापन केली आहेत. 2 मार्च रोजी राजस्थान सरकारने आपल्या सर्व अधिकारी व कर्मचाऱ्यांचे पगार एक ते पाच दिवसांच्या कालावधीत कपात करण्याचा निर्णय घेतला, ज्यातून मुख्यमंत्री फंडात पैसे जमा झाले.

28 मार्च रोजी पंतप्रधानांनी कोरोनाव्हायरससारख्या परिस्थितीचा सामना करण्यासाठी पंतप्रधान केअरेस फंड नावाचा एक नवीन फंड सुरू केला. मार्च रोजी उत्तर प्रदेश सरकार मनरेगा योजनेतर्गत २,151,000,000 कामगारांना 1111 कोटी (यूएस + 88 दशलक्ष) हस्तांतरित करेल अशी घोषणा केली गेली.

1 एप्रिल रोजी आरबीआयने कोविड –१ च्या आर्थिक घसरण सामोरे जाण्यासाठी अलगची उपाययोजनांची घोषणा केली. राज्य सरकारांना दिलासा देण्यासाठी डब्ल्यूएमए आणि अल्प मुदतीची तरलता वाढविली गेलीय निर्यातदारांनाही लवलवीच्या स्वदेशी मर्यादेच्या स्वरूपात थोडा दिलासा मिळाला आहे.

एप्रिल रोजी जागतिक बँकेने 'इंडिया कोविड –१ इमर्जेन्सी रिस्पॉन्स अँड हेल्थ सिस्टम्स सज्जता प्रकल्प' अशी लेबल असलेली कोरोनाव्हायरससी सामना करण्यासाठी अमेरिकेला १ अब्ज डॉलर्सच्या आपत्कालीन वित्तपुरवठा मंजूर केला.

एप्रिल रोजी कोरोनाव्हायरससी लढा देण्यासाठी केंद्र सरकारने विविध राज्यांना ₹ 1,२ 7 कोटी (यूएस + २.4 अब्ज डॉलर्स) जाहीर केले. राज्य आपत्ती जोखीम व्यवस्थापन निधी अंतर्गत राज्यांना गृह मंत्रालयाने ११,० २ कोटी (यूएस 2 1.8 अब्ज) मंजूर केले.

6 एप्रिल रोजी राष्ट्रपती, उपराष्ट्रपती, पंतप्रधान, राज्यपाल, संसद सदस्य आणि मंत्री यांच्यासाठी एका वर्षासाठी 30 पगारातील घोषणा केली गेली. एमपीएलएडीएसला दोन वर्षांसाठी निलंबित करण्याचा आणि सुमारे ₹ ., ४तयतम०० कोटी (यूएस + 1.1 अब्ज डॉलर्स) पैसा भारतीय एकत्रित निधीमध्ये हस्तांतरित करण्याचा निर्णय घेण्यात आला.

8 एप्रिल रोजी वित्त मंत्रालयाच्या खर्चाच्या विभागाने एप्रिल ते डिसेंबर दरम्यान राज्यांना 320,451 कोटी (यूएस + 45 अब्ज डॉलर्स) निव्वळ बाजारातील कर्ज घेण्यास परवानगी दिली. पंतप्रधान गरीब कल्याण योजनेतर्गत (यूएस + निदर्क २० दशलक्ष) निधी बांधकामात गुंतलेल्या २० दशलक्ष कामगारांना देण्यात आला.

शांघाई कोऑपरेशन ऑर्गनायझेशन (एससीओ) च्या 23–24 एप्रिल रोजी बैठकीनी "आर्थिक पुनर्प्राप्तीसाठी संयुक्त रोडमैप" वर सहमती दर्शविली.

२ एप्रिल रोजी गृह मंत्रालयाने काही निर्बंधानुसार काही दुकाने पुन्हा उघडण्यास परवानगी दिली. "कोविड –१ उदहमउनदज व्यवस्थापनासाठी राष्ट्रीय निर्देशानुसार" दारू आणि इतर दुकाने बंद राहतील. या विश्रांती हॉटस्पॉटवर लागू होत नाहीत. २ एप्रिल रोजी एडीबीने साथीच्या रोगाचा सामना करण्यासाठी 10,500 कॉटी डॉलर (यूएस + 1.5 अब्ज डॉलर्स) चे कर्ज मंजूर केले. 92. मॉन्टेकसिंग अहलुवालिया यांच्या नेतृत्वात आणि माजी पंतप्रधान डॉ. मनमोहन सिंग यांच्या मार्गदर्शनासाठी, साथीचे साथीचे पतन करीत पंजाब सरकारने अर्थव्यवस्थेला चालना देण्यासाठी तज्ज्ञांचा एक गट तयार केला. मे रोजी भारत लॉकडाऊनच्या तिस जीयतक्या टप्प्यात गेला. देशाला वेगवेगळ्या झोनमध्ये विभागले गेले (डिरवे, केशरी, लाल, कंटेट) आणि झोननुसार अर्थव्यवस्था उघडली गेली.

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RESEARCH PAPER

GENDER STUDY IN LITERATURE

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ABSTRACT

Literature is the reflection of life .It depicts ,the panoramic view of the society. ,Moreover literature is the mirror through which we can understand the values of life. So far as human being is concerned relationships develops, where Gender differenciates man and woman. Therefore in literature and social life Gender study is consider to study from literary aspects.Mostly Gender study is being done from literary devices like novels and dramas. When we think about Modern Litrature,. Fiction is the tool through which we can study Gender related issues and in what sense it differentiates from man and woman.

A "gender-equal society" is a "society in which both men and women, as equal members, have the opportunity to participate in all kinds of social activities at will, equally enjoy political, economical and cultural benefits, and share responsibilities." In such a society, the human rights of men and women are equally respected. Women who desire an active role in society may participate in activities of their own choosing, while men could enjoy a fulfilling home and community life. A gender-equal society is a society built by men and women as equal partners.

No doubt ,Gender roles play an important role in society whether it is for good or for bad. These roles have been placed in society since the beginning of time. The term gender is socially created and it therefore The term gender can be defined as the characteristics by which people determine if their classification is to be male or female. Gender role expectations are things that a society deems normal and acceptable behavior, attitudes, and desires for a person. The question as to weather or not society influences the gender of a person or if it is an innate .

In Modern Literature ,Gender is a commonly discussed subject in society. Gender role simply defined is a person's inner sense of how a male or female should feel and behave. Society and culture are also very important in relation to this subject. This means different societies and cultures may produce children and later, grown men and women, who have quite different views of a man or a woman's place in the world around them, often determined by their culture's gender stereotypes.

But Traditionally, Society has stamped an image into the minds of people of how the role of each gender should be played out. There are two recognized types of gender, a man and a woman, however there are many types of gender roles a man or a woman may assume or be placed into by society. The ideas of how one should act and behave are often times ascribed by their gender by society, but these ascribed statuses and roles are sometimes un-welcomed, and people will assume who they want to be as individuals by going against the stereotypes set forth by society..

Gender, like all social identities, is social construction of male-female sexual differences in society. Social constructionism is one of the key theories sociologists use to put gender into historical and cultural focus. Social constructionism is a social theory about how meaning is created through social interaction – through the things we do and say with other people. This theory shows that gender it is not a fixed or innate fact, but instead it varies across time and place.

In the twenty-first century the results of this process are easily seen. As gender roles as a whole are becoming more flexible, gender roles in literature are also slowly coming out of the box. This, however, does not mean that

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gender stereotypes are gone. They still exist in literature, in movies and in the media.

Many feminists argue that early upbringing can play a crucial role in imposing assigned gender roles to both boys and girls. From birth children are attacked by gender rules and regulations. Literature, for one, creates the image of the girl as a woman and of the boy as a man, with different roles. The way in which gender is portrayed in children's books shapes the images that a child develops about his or her own role in society. The presence of gender bias in the content and language of a huge number of children's books has been proven more than once.

The way in which gender is represented in children's books and in literature as a whole is so important because most readers tend to identify themselves with the characters in books of their own sex. Literature's influence is especially strong with children. They often use the gender scripts and ideologies in children's books when role playing and thus gradually they form an impression of femaleness and maleness.

As a result, gender stereotypes in literature deprive boys and girls of the freedom the express themselves the way they are. They are forced to behave in the way the society considers appropriate. Gender stereotypes confine both sexes to traditional duties, ambitions and responsibilities. Women English Novelist including Kamals Das,Shashi deshpande,Manju Kapur,Anita Desai and more others bears testimony to the fact that a woman has been moving towards a definite feminist position, so that the Women's experiences do not merely provide data but are actually organized in such a way that they become an exercise in raising consciousness and critique of society with its unequal gender roles and the power distribution involved in them.

To start with, as Virginia Woolf was to write later, "a woman must have money and a room of her own if she is to write fiction". A comparison of the output of 18th and 19th century female novelists with those of their male contemporaries suggests that many women writers like Elizabeth Gaskell found it difficult to reconcile the demands of serious writing with their 'normal' household duties, to the detriment of the former.

Considering the manifold limitations that women writers and readers experienced, it is little surprise to find that related themes would have found their way into the writing of and about women. Restriction did, in fact, become one of the most enduring motifs of English fiction dealing with women's lives, manifesting itself in various disguises as the abduction and incarceration of women characters by male ones in carriages, castles, madhouses, brothels and seemingly comfortable homes.

From R. K. Narayan to till date, Indian English novelists have felt an upsurge of inner clash between consciousnesses of tradition with the modernity. Most of the female writers in India who have advocated feminism in their works, have physically presented the clash of tradition and modernity with the support of their characters. Under the aegis of feminism, gender studies looks for ways through which discrimination in the name of gender can be highlighted, brought to the forefront and thus exposed in the literary texts which however seem to propagate it through stories of glorifying masculinity against under-nourished femininity. In this context, the famous African proverb stands true that until the lion learns how to write, every story will glorify the hunter. Thus the first foundational achievement of feminism world over is women's participation in creative writings. It is from her pen that narrative about her are being expressed through ecriture feminine – a phrase coined by Helene Cixous. Following this call for exclusive feminine writing, women around the world reveal how they think about the nature of world, masculinity and their own selves. The echoes of this call do reach to women in India and result in a large corpus of writings defining existing life and ideas from their perspective.

What is remarkable about Indian women writing in English is that they have expressed themselves largely in poetry and fiction. Drama has been a less explored

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territory for them. It seems they are more comfortable in either meditating in poetry or creating large spaces for themselves in fiction. The fictional narratives based upon their personal experiences as 'female' form the very heart of Indian English women's fiction. The depth and element of truth they hold is a direct outcome of their personal struggle to accept themselves as creative writers. Many contemporary Hence Gender study in Modern literature has become important aspect in modern literature.

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Study of Implication of Tourism on Regional Development of Amravati District.

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Abstract :

Tourism is currently an important industry that is growing. Its activities have been expanded towards eco and rural tourism. This has created opportunities that make the novel demands from tourists coincide with rural communities' need for economic development. So this study aims to determine the effects to regional economic development of tourism sector and draw attention for raising awareness to tourism potential of Amravati District.

Keywords : tourism, sustainable development, regional development

Introduction :

Tourism is the temporary movement of people to the destinations externalto their normal places of work and residence, the activities undertaken during their stay in those destinations, and the facilities created to cater their needs. The study of tourism is the study of public away from their usual habitat, of the establishments, which responds to the necessities of travelers, and of the impact that they have on the economic, physical and social well-being of their hosts. It includes the motivations and experiences of the tourists, the expectation of and adjustments made by residents of reception areas, and the roles played by many agencies and institutions which intercede between them.

Tourism is a major economic activity, a form of expenditure which enables as well as absorbs on worldwide basis about 5% of the total consumer expenditure. In view of its significant in our National Economy, surprisingly little attention has been paid on its fundamental economic factors, which have controlled the past development of Tourism and which may be expected to shape its future development.

Travel for pleasure has frolicsome connotation which seems to have made it unattractive as a field for serious economic study. Another reason why moderately little attention has been paid to the economic significance of tourism is somewhat the amorphous nature of this trade. Fortunately this type of perception has changed in the past decade and tourism is definitely identified as an important factor in countries balance of payments and as means of developing regions or sites with little other economic potential. Apart from being huge revenue earner

tourism is particularly important to a vast and varied country like India as it promotes social and cultural ambience and plays a key role in socio-economic development.

Objectives :

1. To study the tourism potential in the Amravati District.
2. To access the impact of tourism on the regional development

Hypothesis :

Ho : There is no significance association between tourism development and regional development of Amravati District.

H_1 : There is a significance association between tourism development and regional development of Amravati District.

Tourism Development

The tourism as a contemporary activity has attracted the entire world. The development of communication and transportation has made different places practically accessible to wider segments of population around the world. It offers an opportunity to millions to enjoy the prospect from moving one country to another in a matter of hours. Tourism as a socio-economic phenomenon has become the world's major and fastest growing industry in terms of revenue and the number of people involved.

Generally people leave their homes to enjoy their holidays in distant places. People in the developed countries of the world, the annual holiday tour are an accepted way of life. 'Many countries reorganizing the economic benefits that will acquire from tourism, have as a result, established programmes promote international travel and have assisted in the better physical provision of facilities for the accommodation of tourists. In over many countries tourism has become one of the top export items in their national economy' (Maneet Kumar,1992). Tourism has become one of the fastest growing industry in the word. It has become the main sector of the economy while in others it serves to provide major sources of income for development purpose in some countries. In either case it is a major source of earning foreign exchange. Tourism is also being regarded as a source of employment. Besides, providing employment to a large number of people, tourism can be the instrument of a regional policy aimed at achieving an equitable balance between major industrial area and the rest of the country.

Almost every country in the world is now looking positively towards tourism (Maneet Kumar, 1992). Tourism also makes contribution to the improvement of social and political understanding. Travel between the countries fosters a better rapport between populations. Political ideologies and cultural misconceptions are minimized.

Communications are established in many instances to better political understanding. Tourism is thus an important means of promoting cultural exchanges international co-operations. So, it is very clear that tourism has its impact on national economy, social and cultural life and an international understanding. Tourism is today becoming increasingly crucial because of the growing size of the tourist market. Tourism today is the world's largest and fastest growing industry in terms of revenue and the number of people involved. many countries in the world live by tourism.

Amravati District

Amravati District is situated in the northern part of Maharashtra. The district is situated between 20°32' and 21°46' north latitudes and 76°37' and 78°27' east longitudes. The district occupies an area of 12,235 km². Melghat has potential for tourism. Melghat means 'meeting of the ghats' which is just what the area is, a large tract of unending hills and ravines scarred by jagged cliffs and steep climbs. At the northern extreme of the Amravati district of Maharashtra on the border of Madhya Pradesh, lies the Melghat in the South-western Satpura mountain ranges. Melghat area was declared a Tiger Reserve in 1974. Presently, the total area of the Reserve is around 1677 sq. km. There are no villages in the core area. There are 61 villages in the Reserve - 22 in the buffer zone and 39 in the Multiple Use Area. Human population in the buffer zone and MUA is 11024 and 15642 respectively, as per 1994 census. It forms the major part of Amaravati district of Maharashtra in India.

The region has three distinct seasons namely Monsoon, Rainy season and Winter season. The considerable altitudinal variations in Amravati gives rise to smart variations in rainfall which ranges from 1000 mm to 2050 mm. The rainfall is received in 50 to 60 rainy days during July to September. Winter is cooled and summer is extremely hot. Temperature varies from 6 degrees Celsius to 43.6 degrees Celsius

Amravati district has many tourist destinations including pilgrimage, wild life tourism, nature tourism, etc..

Role of Tourism in the Regional Development

Tourism is the emerging sector which has positive effects on regional development. It is amost important development tool that provides economic, social and political development in the region. Therefore, development in a region of tourism in rural or underdeveloped areas can help eliminate economic imbalances.

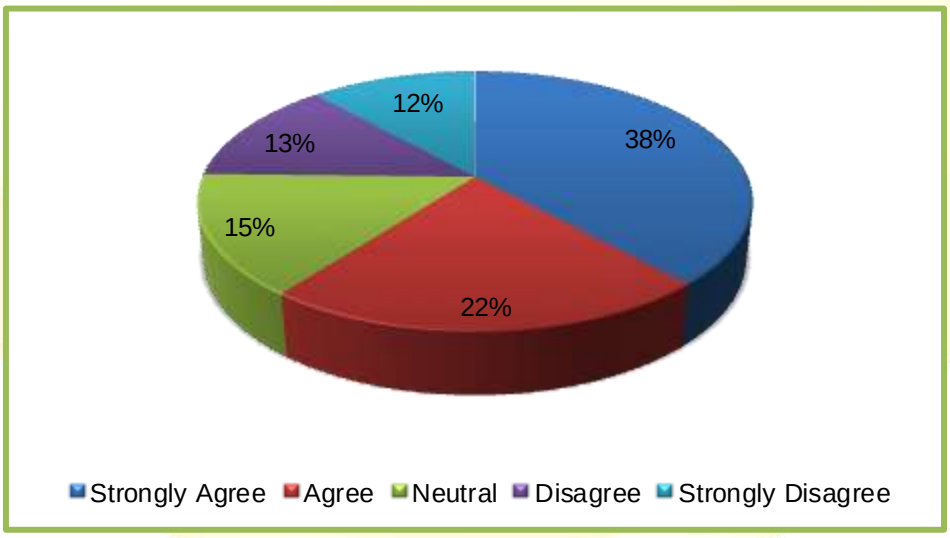
The region's tourism potential accelerates the development of the region's multi-faceted. With the tourism development of the tourism sector, are growing fast therefore, and the existing

tourism potential should be considered very well. Thus, development in a region of tourism in rural or underdeveloped areas can help eliminate economic imbalances. In this context, in order to upsurge the contribution of tourism to the local economy, the demand and the attractiveness for tourist attraction for the existing tourism values should be increased. If more tourists can be involved to the region by using all the opportunities; employment, income and value-added are increased and sustainable development can be performed. Tourism is considered by main economic, social and environmental indicators and its basic problems and impacts are strongminded by thinking of tourism as a crucial development tool in a region.

Table1 : Tourism development impacts on the regional development of Amravati District
Total numbers of respondents :560

Strongly Agree	Agree	Neutral	Disagree	Strongly Disagree
214	124	84	73	65

Graph 1 : Tourism development impacts on the regional development of Amravati District



The above graph shows the impact of tourism on the regional development.

As per the above graph, it is found that out of 560respondents; 38% people are strongly agree with the statement 'Tourism development impacts on the regional development of Amravati District', while 22% respondent are agree with the statement, 15% are neutral with the statement, 13% respondents are disagree with the statement and 12% respondents are strongly disagree with the statement.

That means majority of respondents feel that tourism development impacts on the regional development of Amravati District.

Hypothesis Testing

Ho : There is no significance association between tourism development and regional development of Amravati District.

H_1 : There is a significance association between tourism development and regional development of Amravati District.

This hypothesis regarding role of tourism development and regional development is tested through the One Sample t-test using statistical software SPSS.

One-Sample Statistics			
N	Mean	Std. Deviation	Std. Error Mean
560	2.3768	1.39991	.05916

One-Sample Test					
Test Value = 5					
t	df	Sig. (2-tailed)	Mean Difference	95% Confidence Interval of the Difference	
				Lower	Upper
40.178	559	.000	2.37679	2.26.6	2.4930

To test this hypothesis; a Likert scale is used. Response of 560 respondents are recorded and inputted in the SPSS software. The mean value generated is 2.3768 and Standard Deviation is 0.000. The test value is set as 5 as Likert scale is two level scale to record the responses. From the above One Sample t-test hypothesis is significant i.e. 0.000. So the NULL hypothesis is rejected and the alternate hypothesis 'There is a significance association between tourism development and regional development of Amravati District' is accepted.

Conclusion :

The tourism sector plays an important role on sustainable regional development. It rouses infrastructure investment and its benefits spill over to other activities. However, when implementing tourism projects, the full impact on such actions must be assessed in terms of natural resource degradation and unstable seasonal employment. The tourism has a potential to improve the sector and consequently to boost its sustainable development. Thus from the analysis of data it is found that There is a significance association between tourism development and regional development of Amravati District.

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Study of Role of Tourism in the Socio-Economic Growth and Employment Generation

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Abstract :

As tourism-related activities have grown and changed, many different definitions and ways of classifying the industry have emerged. Use of the term tourism has evolved as attempts have been made to place a title on a difficult-to-define group of naturally related service activities and participants.

Keywords : tourism, sustainable development, regional development

Introduction :

The tourism as a modern activity has attracted the entire world. The development of communication and transportation has made different places practically accessible to wider segments of population around the world. It provides an opportunity to millions to enjoy the prospect from moving one country to another in a matter of hours. Tourism as a socio-economic phenomenon has become the world's largest and fastest growing industry in terms of revenue and the number of people involved.

Generally people leave their homes to enjoy their vacations in distant places. People in the developed countries of the world, the annual holiday tour are an accepted way of life. 'Many countries reorganizing the economic benefits that will acquire from tourism, have as a result, established programmes promote international travel and have assisted in the better physical provision of facilities for the accommodation of tourists. In over many countries tourism has become one of the top export items in their national economy' (Maneet Kumar,1992)*. Tourism has become one of the fastest growing industry in the word. It has become the main sector of the economy while in others it serves to provide major sources of income for development purpose in some

* Kumar Manet, Tourism today, an Indian perspective, foreword by K.C. Malhotra, 1992

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countries. In either case it is a major source of earning foreign exchange. Tourism is also being regarded as a source of employment. Besides, providing employment to a large number of people, tourism can be the instrument of a regional policy aimed at achieving an equitable balance between major industrial area and the rest of the country.

Practically every country in the world is now looking positively towards tourism[†]. Tourism also makes contribution to the improvement of social and political understanding. Travel between the countries fosters a better rapport between populations. Political ideologies and cultural misconceptions are minimized. Communications are established in many instances to better political understanding. Tourism is thus an important means of promoting cultural exchanges international co-operations. So, it is very clear that tourism has its impact on national economy, social and cultural life and an international understanding. Tourism is today becoming increasingly crucial because of the growing size of the tourist market. As stated earlier tourism today is the world's largest and fastest growing industry in terms of revenue and the number of people involved. Many countries in the world live by tourism.

Tourism is an integral part of human life. It is a situation where person from one country, or region to other region and country for a short run period, is included in the concept of tourism. Now-a-days the tourism industry has a greater importance. India has a great heritage of historical place like the Taj Mahal, Various Forts, Natural sites etc. Since 2000 tourism industry has been giving number of benefits to India. The number of foreign tourist visited to India which has given foreign exchange earning to the Country. Here, we have focused the growth and performance of the Indian tourism industry. We have also analyzed the causal analysis of the Indian tourism industry for overall development of the Indian economy. National tourism policy 2002 and its implications are important in this context.

Objectives :

1. To study the tourism development in Amravati District.
2. To access the role of of tourism on socio-economic growth.

[†] Kumar Manet, Tourism today, an Indian perspective, foreword by K.C. Malhotra, 1992

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Hypothesis :

Ho : Tourism cannot be an engine of socio-economic growth in Amravati District and at the same time open avenues of employment.

H_1 : Tourism can be an engine of socio-economic growth in Amravati District and at the same time open avenues of employment.

Tourism Development

Tourism has developed into a truly worldwide activity that knows no political, ideological, geographic, or cultural boundaries. For a long time, tourism was disparate and fragmented, but as this industry has continued to grow and mature, a sense of professional identity has emerged. It has formed lobbying groups such as the World Travel and Tourism Council (WCTT), which includes executives of airlines, hotel chains, and travel agents among its members and concentrates on making the case for tourism's global importance and economic value. The future prospects for tourism are brighter than ever as people continue to travel for work or pleasure. "Given its historical performance as a luxury good during expansions and a necessity during recessions, travel and tourism's future economic prospects look quite bright".[‡] As we will see later, the growth and popularity of tourism activities have not been accidental. Growth projections indicate that tourism will support almost 350 million jobs worldwide by 2025. This will be an increase of over 70 million jobs when compared to 2015.[§]

Tourism in Maharashtra has much potential. Tourism can become a powerful growth engine for the Maharashtra economy only within efficient tourism infrastructure in place. Tourism & Tourism Infrastructure coverage is vast and growing. It encompasses both soft as well as physical infrastructure and contains a variety of facilities like medical & wellness tourism; adventure tourism; leisure &recreational tourism, beach tourism, Gandhian tourism, rural tourism, religious tourism, wine tourism and recently added mines tourism. All these require soft infrastructure which includes mainly governance aspects especially observance of just in time principle, least wastages, quality & suitable skills, best management norms and experience of a healthy swatch life.

[‡] Wilkerson, C. (2003). Travel and tourism: An overlooked industry in the U.S. and Tenth District. Economic Review, Third Quarter. Federal Reserve Bank of Kansas City. Available at: http://www.kc.frb.org
[§]Economic Impact of Tourism (2015). World Travel and Tourism Council, 1–2.

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Amravati District

Amravati District is situated in the northern part of Maharashtra. The district is situated between 20°32' and 21°46' north latitudes and 76°37' and 78°27' east longitudes. The district occupies an area of 12,235 km². Melghat has potential for tourism. Melghat means 'meeting of the ghats' which is just what the area is, a large tract of unending hills and ravines scarred by jagged cliffs and steep climbs. At the northern extreme of the Amravati district of Maharashtra on the border of Madhya Pradesh, lies the Melghat in the South-western Satpura mountain ranges. Melghat area was declared a Tiger Reserve in 1974. Presently, the total area of the Reserve is around 1677 sq. km. There are no villages in the core area. There are 61 villages in the Reserve - 22 in the buffer zone and 39 in the Multiple Use Area. Human population in the buffer zone and MUA is 11024 and 15642 respectively, as per 1994 census. It forms the major part of Amaravati district of Maharashtra in India.

The region has three distinct seasons namely Monsoon, Rainy season and Winter season. The considerable altitudinal variations in Amravati gives rise to smart variations in rainfall which ranges from 1000 mm to 2050 mm. The rainfall is received in 50 to 60 rainy days during July to September. Winter is cooled and summer is extremely hot. Temperature varies from 6 degrees Celsius to 43.6 degrees Celsius

Amravati district has many tourist destinations including pilgrimage, wild life tourism, nature tourism, etc..

Role of Tourism in Employment Generation& Socio-Economic Development of the region

Tourism plays a significant role in to the creation of the wide range of jobs and economic development. The substantial profit from this industry attracts to the investor and young generation to work in it. It is highly developed in all countries due to its economic benefits. The domestic market aspects play a noteworthy role in to the employment creation. Lot of peoples works with the tourist aspects and generates the income from it. It becomes a major source of income. Some countries and cities fully involved into the tourism and create lot of revenues. The tourism industry is one of the fastest growing

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industries in the world. In 2022 it may create 328 million jobs and supports approximate 10 percent work force in to the world. Important contributions to the country's economy are created by creating new jobs through this field. The direct jobs include the tour guide, tour planner, travel concealment, tour operators, hotels, resorts and restaurants.

The tourism and hospitality creates inter relevant jobs. The various other relevant industries like event management, airlines, amusement park, cruise industry etc also created lot of jobs. The agriculture, food production sector, retail industry etc also indirectly involved in to the tourism. The service sector is growing due to the tourism in various areas. The indirect sector also greatly contributed into the gross domestic product of the country. The tourism sectors included the individual; business and government also earn much. Besides this the income also generated through the use of services like hotels, restaurants and various tourist attractions.Otherwise the medicines, cloths, entertainment, food, transportations etc economic activities supports to the tourism. Thus the tourism creates significant contributions in the economics of the various countries in the world at various ways.

Tourism is now one of the world's largest industries and one of its fastest growing economic sectors. For many countries tourism is seen as a main instrument for regional development, as it stimulates new economic activities. Tourism may have a positive economic impact on the balance of payments, on employment, on gross income and production, but it may also have negative effects, particularly on the environment. Unplanned and uncontrolled tourism growth can result in such a deterioration of the environment that tourist growth can be compromised. The environment, being the major source of tourist product, should therefore be protected in order to have further growth of tourism and economic development in the future. This is especially true with regard to tourism based on the natural environment as well as on historical-cultural heritage. Sustainable tourism has three interconnected aspects: environmental, socio-cultural, and economic. Sustainability implies permanence, so sustainable tourism includes optimum use of resources, including biological diversity; minimization of ecological, cultural and social impacts; and maximization of benefits for conservation and local communities. It also refers to the management structures that are needed to achieve this. The paper provides a theoretical framework for sustainable tourism. It comprises two parts. The first part

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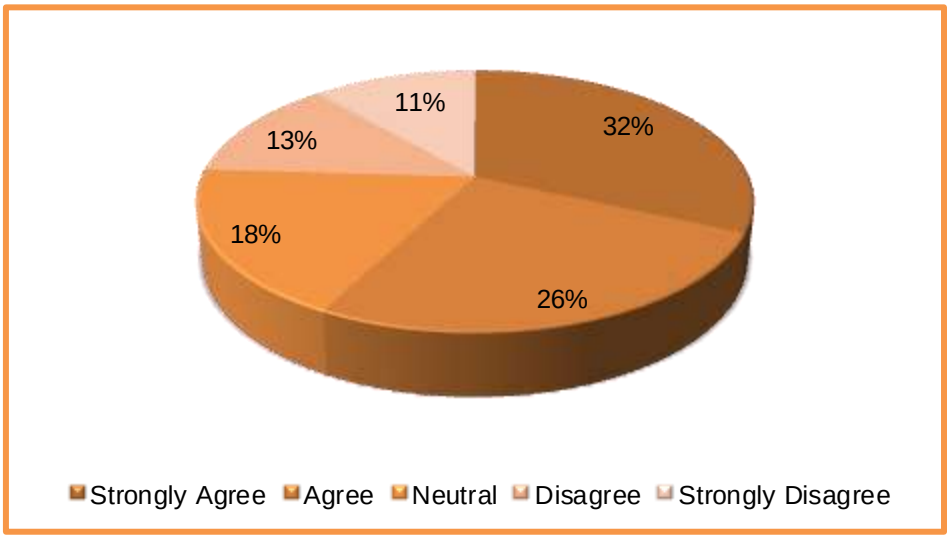
presents general views on tourism and sustainable economic development, and some opinions on the relationship between tourism and the environment.

Table 1 : Role of Tourism on the socio-economic growth in Amravati District and employmentgeneration.

Total numbers of respondents : 560

Strongly Agree	Agree	Neutral	Disagree	Strongly Disagree
178	145	102	71	64

Graph 1 : Role of Tourism on the socio-economic growth in Amravati District and employment generation.



The above graph shows the role of Tourism on the socio-economic growth in Amravati District and employment.

As per the above graph, it is found that out of 560 respondents; 32% people are strongly agree with the statement 'Tourism plays important role in the socio-economic growth in Amravati District and employment generation', while 26% respondent are agree with the statement, 18% are neutral with the statement, 13% respondents are disagree with the statement and 11% respondents are strongly disagree with the statement.

That means majority of respondents feel that Tourism plays important role in the socio-economic growth in Amravati District and employment generation.

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Hypothesis Testing

Ho : Tourism cannot be an engine of socio-economic growth in Amravati District and at the same time open avenues of employment.

H_1 : Tourism can be an engine of socio-economic growth in Amravati District and at the same time open avenues of employment.

This hypothesis regarding role of tourism development and regional development is tested through the One Sample t-test using statistical software SPSS.

One-Sample Statistics			
N	Mean	Std. Deviation	Std. Error Mean
560	2.4607	1.35156	.05711

One-Sample Test					
Test Value = 5					
t	df	Sig. (2-tailed)	Mean Difference	95% Confidence Interval of the Difference	
				Lower	Upper
-44.460	559	.000	-2.53929	-2.6515	-2.4271

To test this hypothesis; a Likert scale is used. Response of 560 respondents are recorded and inputted in the SPSS software. The mean value generated is 2.4607 and Standard Deviation is 0.000. The test value is set as 5 as Likert scale is two level scale to record the responses. From the above One Sample t-test hypothesis is significant i.e. 0.000. So the NULL hypothesis is rejected and the alternate hypothesis 'Tourism can be an engine of socio-economic growth in Amravati District and at the same time open avenues of employment' is accepted.

Conclusion :

The Amravati District offers variety of sightseeing desirability. The tourism becomes is an important sector for employment generation in region. The tourism sector plays an important role in the socio-economic growth of the region; as people of the region get

employment or they start their own startups. The tourism boost economy by increasing the spendings in the region which leads to the socio-economic development of the region as well as employment generation. The tourism has a potential to improve the sector and consequently to boost its sustainable development. Thus from the analysis of data it is found that Tourism can be an engine of socio-economic growth in Amravati District and at the same time open avenues of employment.

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विदर्भातील नव्वदोत्तर गझलेचे शिलेदार

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1990 नंतरच्या काळात माहिती तंत्रज्ञानात क्रांती घडली. संगणक, इंटरनेट, पोर्टल, ब्लॉग्ज, फेसबुक, यूटयूब, व्हॉट्सॲप, गझल गायनाच्या मैफली, गझल, मुशायरे अशी नवी माध्यमे मराठी गझलेला उपलब्ध झाली. नवीन पिढीने या आयुधांचा या तंत्रज्ञानाचा योग्य तो उपयोग केला आणि गेल्या 10 ते 5 वर्षात संख्येने फार मोठ्या प्रमाणात मराठीत गझल लिहिली गेली. अत्यंत माफक दरात मोबाइल डेटा उपलब्ध झाला, त्यामुळे 24 तास सहज हाताशी असलेले फेसबुक आणि व्हॉट्सॲप ही आजच्या मराठी गझलेची हक्काची माध्यमे झालीत. नव्या माध्यमांची नवलाई आणि अतिउत्साही तरूणाई असा दुथडी भरून मराठी गझलेचा प्रवाह सध्या वाहतो आहे. प्रत्येक कालखंडात चांगल्या कवितेचे, सुमार कवितेचे असणारे प्रमाण या डिजिटल माध्यमातून प्रसिध्द होत असलेल्या रचनांमध्येही आहे.

प्रवाहीपणा जीवंतपणाचे लक्षण असतं, त्याप्रमाणे गझलेच्या आकृतीबंधांची जाचक बंधने सहज–सोपे करण्याकडे या गझल प्रवाहाचा कल आहे. उदा. "आजची मराठी गझल केवळ अक्षरगुण वृत्तात लिहिली जात नाही. आशयाच्या सहज अभिव्यक्तिसाठी अक्षरगणवृत्तातला क्लिष्ट लगक्रम बाधा आणतो आणि काही अंशी कृत्रिमतेला वाव देतो, याची जाणीव झाल्याने आज फार मोठ्या प्रमाणात मराठी गझल मात्रावृत्तात लिहिली जाते."[1] ठराविक लगावलीचे बंधन नसल्याने मात्रावृत्तात गझल लिहिणे सोपे जाते. माधव जूलियन आणि सुरेश भट यांनी एखादं दुसऱ्या गझलेत, योजलेला स्वरकाफिया अलीकडच्या मराठी रचनेत फार मोठ्या प्रमाणात आढळतो. नव्वदोत्तर पिढीचे महत्त्वाचे वैशिष्ट्य आहे. नव्वदोत्तर गझलेविषयी प्रदीप निफाडकर म्हणतात, "भट यांच्या नंतर खूपच चांगली गझल आणि प्रयोगशील गझल लिहिली जाऊ लागली आहे. मात्र गझलकारांना एकत्र बांधण्याचा बहाणा करीत जे नतद्रष्ट स्वपोळीवर तूप ओतून घेऊ लागले आहेत, त्यांचा बंदोबस्त करण्यासाठीही गझलकारांनीच सज्ज झाले पाहिजे. आज मराठी कवितेला चांगले दिवस आले आहेत. गझलेला नाके मुरडणारे गझलेचा मुका घेऊ लागले आहेत. अशा वेळी सकस आणि दर्जेदार गझल लिहिण्यासाठी प्रयत्न झाले पाहिजेत. केवळ 'मी अमूक गझलेचा प्रकार प्रथम मराठीत आणला' याची फुशारकी मारण्यापेक्षा 'मी दर्जेदार गझल मराठीला दिली' याचा मराठी भाषा अभिमान बाळगेल, असे काही लिहिले पाहिजे."[2] नव्वदोत्तर गझल लिहिणाऱ्या पिढीकडून अपेक्षा वाढलेल्या आहेत. सुरेश भटानंतर गझल लिहिणाऱ्या पहिल्या पिढीने वयाची साठी ओलांडलेली आहे. अनुभवाची परिपक्वता आणि गझल आकृतीबंधात लोकप्रियतेचे असणारे योगदान पुढील पिढीपर्यंत पोहोचवण्याचे महत्त्वाचे काम त्यांनी केले आहे. नव्वदोत्तर गझल लिहिणाऱ्या पिढींकडून गझलरचनेचे वेगळेपण दिसून लागले आहेत.

नव्वदोत्तर पिढी 1990 ते 2020 पर्यंत गझल लिहिणारी सांगता येईल. मराठी गझलेचे काही ठळक टप्पे जसे – माधव जूलियन, मराठी संगीत नाटकातील गझल आणि सुरेश भट. यामध्ये माधव जूलियन आणि सुरेश भट या दोन गझलकारांवर मराठीमध्ये फार गझल समीक्षा झालेली आहे. बाकी सर्व त्यांच्या अनुषंगानेच झालेली दिसून येते. मराठी गझलेतील बरेच असे सुटलेले दुवे आहेत. त्यांना त्यांच्या कालखंडानुसार अभ्यासणे गरजेचे आहे. बदलत्या काळानुसार काही कालखंडाचा विचार केला आहे. जोपर्यंत गझलेच्या नवीन कालखंडावर अभ्यास होत नाही, तोपर्यंत प्रस्थापित गझलकारांवर समीक्षा होत राहते. कारण नवीन गझलकारांच्या अभ्यासांकडे प्रस्थापित समीक्षक डोळेझाक करीत असतात आणि पुनः पुन्हा आधीच्याच गझलकारांची समीक्षा करीत असतात. समीक्षकांच्या चर्चेतून नवीन गझलेवर लिहिले जात नाही, बोलले जात नाही म्हणूनही ते दुर्लक्षित राहण्याची शक्यता नाकारता येत नाही.

सुरेश भटांच्या गझल रचनेवर विपुल समीक्षा झाली, त्यामुळे भटांच्या विविध पैलूंचा अभ्यास आज उपलब्ध आहे. तसे नव्वदोत्तर गझलकाराच्या गझलेचा अभ्यासही होणे महत्त्वाचे आहे. "भटांचा प्रभाव म्हणजे रदीफ, काफिया, छंद आणि त्याची मोहक शब्दावली इतपतच होता. प्रत्येक

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गझलकाराच्या कल्पना, अभिव्यक्ति शैली मात्र त्याही वेळी विलग होतीच आणि त्यामुळे ते आजही आपले स्थान अढळपणे टिकवून आहेत."[3] भटोत्तर गझल किती पुढे गेली. तिने तिच्या कालखंडानुसार कोणत्या आणि कशा प्रतिमा, प्रतीके वापरले आहेत. त्या काळातील सामाजिक आणि राजकीय परिस्थितीचा धांडोळा घेणे महत्त्वाचे आहे. त्यामुळे नव्वदोत्तर काही निवडक गझलकारांच्या गझलेचा विश्लेषणात्मक अभ्यास करणे गरजेचे आहे.

नव्वदोत्तर गझल लिहिणारी पिढी (1990 – 2020) :–

नव्वदोत्तर पिढी अत्याधुनिक तंत्रज्ञानावर कुशलतेने स्वार होऊन मार्गक्रमण करणारी आहे. आधीच्या पिढीच्या वाचन–लेखनाच्या संकल्पना बदललेल्या आहेत. ग्रंथालयात बसून अभ्यास होतो, असे नाही, तर ग्रंथालये खिशात घालून आजचा गझलकार फिरतो आहे. आधीच्या कवींच्या जीभेवर सरस्वती नांदायची तर आताच्या पिढीच्या बोटांवर सरस्वती खेळत आहे. नव्वदोत्तर पिढीमध्ये गझलकार म्हणून काही गझलकारांचा उल्लेख जन्मतारखेनुसार केला आहे. त्यामध्ये विजयकुमार राऊत (1/5/71), प्रसेनजित गायकवाड (19/9/71). विद्यानंद हाडके (28/10/72), प्रा. गिरीश खारकर (7/2/73), गणेश भाकरे (1/7/73), प्रमोद चोबितकर (5/9/73), नितीन भट (15/11/73), लक्ष्मण जेवणे (19/8/73), प्रकाश बनसोड (6/6/74), प्रफुल्ल भुजाडे (10/8/74), ओमप्रकाश ढोरे (19/2/75), नितीन देशमुख (13/3/75), नामदेव राऊत (28/5/75), संदीप वाकोडे (1/6/76), डॉ. उज्वल बारंगे (30/3/76), आबेद शेख (9/8/78), मोहन महाजन (29/9/78), रूपेश देशमुख (18/12/78), सतीश दराडे (10/3/81), शेख गनी शेख मियॉ (9/7/81), किशोर बळी (30/7/81), गजानन रोडे (8/10/81), किरण मडावी (7/6/82), संदीप गवई (7/6/82), अभिषेक उदावंत (10/10/82), मंगेश गजभिये (16/10/82), मनोज सोनोने (8/3/82), मिलिंद हिवराळे (1/5/83), अमित वाघ (17/8/83), प्रविण हटकर (20/1/84), सिध्दार्थ धुळध्वज (25/1/84), अमोल शिरसाट (4/4/84), प्रशांत मडपूवार (6/2/85), शीलवंत सिरसाट (12/4/85), चंद्रशेखर तरारे (5/4/85), पवन नालट (4/2/89), वैभव देशमुख, सुधीर बल्लेवार, निर्मिती कोलते, एजाज शेख, रोशन गजभिये, गौतम राऊत, राहुल गडेकर, अझिझ खान पठाण, लतिफ शेख, आनंद रघुनाथ, अल्पना देशमुख, दिनेश मोडोकार, विशाल मोहिते, रमेश आराख, अभिजित नागले, शिवाजी खडे, प्रमोद राठोड, प्रमोद देशमुख, डॉ. अमिता गोसावी, सुरेश इंगळे, दिनेश गावंडे, डॉ. विजयालक्ष्मी वानखेडे, गजानन वाघमारे, गजानन दरोडे, जगन अवचार; मिलिंद इंगळे, नजीम खान, निर्मला सोनी, प्रशांत नामदार, रोशन पिलेवान, प्रीती जामगडे, राजेश देवलकर, राम रोगे, सुरेश शेंडे, राजु आठवले, विश्वजीत गुडघे, श्वेता पंडित, गणेश धामोडकर, पूजा फाटे, देवेंद्र गाडेकर, रवि चापके, अरविंद पोहरकर, तुळशीराम खराटे, नीलेश कवडे, संजय खांडेकर, देवानंद गवई, गोपाल मापारी, ईश्वर मते, अमोल गोंडचवर, अविनाश येलकर आदि गझलकारांचा उल्लेख करता येतो.

या पिढीच्या गझलकारांची गझल लेखनांची माध्यमे बदललेली आहेत. यातील बऱ्याच गझलकारांनी वेबपेज, ब्लॉग्जस्, फेसबुक, गझल मुशायरे, प्रातिनिधिक गझल संग्रह, दिवाळी अंक आदींच्या माध्यमातून स्वतःची एक वेगळी ओळख निर्माण केली आहे. गझलेसाठी आवड, अनुकरण, ध्यास आकृतीबंधाचे ज्ञान, अभ्यास, सातत्य आणि सराव अशा जिद्दीने समोर येणारी ही पिढी आहे या पिढीचे गझलसंग्रह जास्ते उपलब्ध नाहीत. कारण माहिती तंत्रज्ञानाच्या प्रचंड प्रभावामुळे जलद इंटरनेट आणि डिजीटल सुविधा आदि अत्याधुनिक सोईमुळे पूर्वीची पुस्तक प्रकाशनाच्या खर्च हाताची इच्छा, या माध्यमातूनच पूर्ण होत असल्यामुळे त्यावरच शुभेच्छा आणि प्रतिक्रिया मिळत असतात. त्यांची मानसिक आनंदाची भूक येथे अंशतः तरी पूर्ण होताना दिसते. त्यामुळे खरोखर गझलसंग्रहाकडे ही पिढी फारशी वळताना दिसत नाही. या पिढीच्या गझलांचा शोध घेण्यासाठी प्रातिनिधिक गझल संग्रहाबरोबर अंतर्जाल पाहणे क्रमप्राप्त आहे. समीक्षा करताना काही मार्गदर्शक तत्वे म्हणून ही सर्व माहिती महत्वाची. या पिढीचा समीक्षात्मक आढावा घेण्यासाठी सर्वप्रथम मिळू शकलेल्या या विकसित झालेल्या साधनांचा साठ वर्षांची मराठी गझल अद्याप त्या वयाला पोहचलेली नाही. सर्वांचे डोळ्यात हे आलेले माध्यमांहून अधिक गतीने जाईल पण मराठी वाङ्मयातील गझल विषय काही काही गझल मुशायरे कुठे दिशाभरस्थेकडे झुकली

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आहे. या काळात रसग्रहणात्मक प्रोत्साहन देणेच उचित ठरते."[4] मराठी कवितेच्या तुलनेत मराठी गझलेचा प्रवास हा फार नूतन आहे आणि त्यामध्येच सर्व गुणसंपन्न गझल बाहेर यावी, ही अपेक्षा न करता प्रोत्साहनपर समीक्षा करणे महत्वाचे आणि योग्य वाटते. त्यामुळे लिहिणाऱ्यांचा उत्साह द्विगुणीत होतो आणि पुढे आपल्या चुका लक्षात येवून तो तंत्रशुध्द गझलेच्या मार्गावर येईल, अशी आशा करता येवू शकते.

नव्वदोत्तर गझल लेखन करणाऱ्या पिढीचे स्फुलिंग चेतवण्यात सुरेश भटांचे योगदान मुख्यतत्त्वे मानावे लागते, अद्याप त्याची धग कायम आहे. गझलेला मराठी साहित्य विश्वात कायम दुय्यमत्व दिले गेले. त्यामुळे माधव जूलियनांना सुरेश भटांना त्या–त्या काळात संघर्ष करावा लागला. अनेक आक्षेपांना उत्तरे द्यावी लागलीत. याची जाणीव या पिढींच्या गझलकारांना असल्याचे जाणवते. अशाच निवडक नव्वदोत्तर गझलकारांचा थोडक्यात आढावा घेता येईल.

किशोर बळी :–

किशोर बळी हे अकोला जिल्हयातील असून ते बार्शीटाकळी तालुक्यातील टाकळी छबिले येथील शाळेत अध्यापनाचे कार्य करतात. त्यांचे 'पाकळया', 'पहाटेच्या प्रतीक्षेत', माझ्या बालमित्रानों', 'अक्षरांचे सूर' आणि 'धुम्मस' ही त्यांची पुस्तके प्रकाशित आहेत. 'झरी', 'शिरपा', 'संपर्क क्रांती', 'आसूड' या चित्रपटाचे त्यांनी गीतलेखन केले आहे. त्यांची गीते नामवंत गायकांनी गायलेली आहेत. त्यामध्ये भीमराव पांचाळे, वैशाली सामंत, आदर्श शिंदे, वैशाली माडे, आनंदी जोशी, अनिरूध्द जोशी, रोहित राऊत, प्रवीण कुंवर आदींचा समावेश आहे.

वऱ्हाडी बोलीतील स्तंभलेखक म्हणून ते विदर्भात वाचकप्रिय आहेत. गझल नवाज भीमराव पांचाळे यांच्या मैफलींचे 2009 पासून ते निवेदन करतात. झी मराठी चॅनलवरील 'हास्यसम्राट' या विनोदी कार्यक्रमात अंतिम फेरीपर्यंत ते सहभागी झालेले होते. 'हास्य बळी डॉट कॉम' या प्रबोधनात्मक विनोदी कार्यक्रमाचे त्यांनी 1998 पासून शेकडो प्रयोग केलेले आहेत. महाराष्ट्र राज्य पाठ्यपुस्तक निर्मिती मंडळाने इयत्ता आठवी सुलभ भारती या पुस्तकात त्यांच्या कवितेचा समावेश केला आहे. जानेवारी 2018 मध्ये दर्यापूर येथे झालेल्या युवा मराठी साहित्य संमेलनाचे त्यांनी अध्यक्षपद भूषवले आहे. ग्रामीण जीवनातील दुःख चितारताना शेतकऱ्यांना जगण्याचे बळ देण्याचा ते प्रयत्न करतात. त्याचप्रमाणे अनेक समाजाभिमुख विषयांसंदर्भात प्रबोधन करतानाच समतेचा विचार मांडत ते त्यातून देशप्रेमाचे स्फुल्लिंग चेतवतात.

लखलाभ तुम्हाला पाऊस सौख्याचा रिमझिमणारा
मज आता या दुनियेच्या अश्रूत न्हायचे आहे.[5]

वरवर विनोदी वाटणाऱ्या किशोर बळी यांचा पिंड मात्र सामाजिक जाणिवेचा आहे. रिमझिमणाऱ्या प्रेमाच्या पावसापेक्षा त्यांना दुःखीतांच्या दुःखात सहभागी होऊन त्यांना आनंद प्रदान करणारा आहे. समाजातील दुःख हे निसर्ग निर्मित नसून, ते मानव निर्मित आहे.– हया धरेचा धर्म सांगा कोणता ? त्या नभाची जात सांगा कोणती ?[6]

असा रोखठोक प्रश्न विचारून खोट्या प्रतिष्ठेत, कर्मकांडात राहणाऱ्यांचे बेगडी चेहरे उघडे करताना ते म्हणतात– ना सुखाचा घास तोंडी जीवनी आणि मेल्यावर किती हया पंगती ?[7]

रदीफ नसलेली ही गझल गैरमुरद्द गझल म्हणून ओळखली जाते. या गझलेतून किशोर बळी यांनी 'संगती', 'सोबती', 'पंगती', 'पावती', 'कोणती' अशा प्रकारचे कवाफी वापरलेले आहेत. साध्या–सोप्या रचना आणि आशयदृष्ट्या गझलेचे हे उदाहरण म्हणता येईल.

अमोल शिरसाट :–

अमोल बी. शिरसाट, अकोला हे नव्वदोत्तर पिढीतील एक आश्वासक गझलकार आहेत. मराठी गझल अभ्यासक आणि मराठी गझल चळवळीतील एक धडाडीचा कार्यकर्ता म्हणून आपले वेगळे स्थान निर्माण करीत आहेत. श्रीकृष्ण राऊत यांच्या मुख्य संपादनात 'गझलकार सीमोल्लंघन' हा ऑनलाईन विशेषांक दरवर्षी दसऱ्याला प्रकाशित होत असतो, यामध्ये सहसंपादक म्हणून अमोल शिरसाट यांची महत्त्वाची भूमिका आहे. मराठी गझलेच्या प्रचार प्रसारासाठी झटणारा गझल चळवळीतील एक धडाडीचा कार्यकर्ता म्हणूनही अमोल शिरसाट यांची कामगिरी महत्त्वाची आहे. युवा गझल अभ्यासक म्हणून त्यांचे पाक्षिक प्रबुध्द भारतामधील गझलविषयक लेख व दै. अजिंक्य भारत या वृत्तपत्रातील 'गझलयात्रा' या सदरातून ते गझल समीक्षण करीत असतात.

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अनेक गझलेमधून विविध विषयांबरोबर सामाजिक आशय प्रखरपणे मांडताना दिसतात. व्यवसायाने शिक्षक असलेले अमोल शिरसाट यांचे मानवी संबंधांबद्दलचे चिंतन त्यांच्या गझलेतून दिसून येते. – रानफुले शिकतात उन्हातच – कुठली शाळा ?कुठले दप्तर ?[8]

या शेराची मांडणी अभिव्यक्तिच्या अंगाने अत्यंत वेगळी आहे. उत्तम शेराच्या लक्षणामध्ये महत्त्वाची असते ती शब्दकळा. शेरमध्ये वापरले गेलेले शब्द हे वाचणाऱ्याच्या भाषेतील असणे आवश्यक असते. याबरोबरच शेरात कोणत्या प्रतिमा वापरल्या गेल्यात हे पाहणेही महत्वाचे असते. शब्दकळा आणि प्रतिमा या दोन्हींच्या कसोटीवर अमोल शिरसाट यांचा उपरोक्त शेर खरा उतरतो. शेरात वापरली गेलेली 'रानफुले' ही प्रतिमा मुख्य प्रवाहापासून वेगळे राहिलेल्या वंचित घटकांचे प्रतिनिधित्व करते आणि अशा वंचित घटकांचे अनुभवातून मिळालेले ज्ञान हे खऱ्या अर्थाने जीवनाचे ज्ञान असते. वंचितांची वेदना त्यांच्या पुढील शेरातून अधिक प्रखरपणे व्यक्त झाली आहे.

लेकरू आज गेले उपाशी पुन्हा
घुटमळे मायचा जीव शाळेपुढे. [9]

इंडियातल्या भारतातील लहानग्यांना आजही उपाशी पोटीच शाळेत जावे लागते. शाळेपुढून मोलमजुरीसाठी जाणाऱ्या कित्येक मातांचा पाय शाळेपुढे अडल्याशिवाय राहत नाही. याचे अचूक चित्रण अमोल शिरसाट यांच्या शेरातून आले आहे. रोजच्या वापरातील भाषा हे त्यांच्या लिखाणाचे वैशिष्ट्य सांगता येईल.

अमित वाघ :–

प्रेमाची गझल म्हटली तर काही मोजक्या गझलकारांमध्ये अमित वाघ यांचे नाव अग्रक्रमाने घ्यावे लागते. रोमॅंटिसिझमची भावना कवितेतून, कथा–कादंबऱ्यामधून आली, तरी आमचे ते प्रेम इतरांचे ते लफडे या युक्तिप्रमाणे समाज त्या प्रेमाच्या भावनेकडे पाहताना दिसते. प्रेमाच्या विविध छटा अमित वाघ यांच्या गझलेतून त्यामध्ये आलेल्या प्रतिमा–प्रतीकातून पाहायला मिळतात. प्रेमाच्या प्रतिमेतून धृतराष्ट्र, गांधारी, राधा, विठ्ठल अशा प्रतिमा येतात.

बघ... तिच्या प्रेमात झालो आंधळा मी
ती कधी होणार गांधारी विठोबा...[10]

प्रेमातून निर्माण झालेल्या पवित्र नात्याला समाजात फारसे महत्त्व दिले जात नाही. यामध्ये मुलींकडून बहुधा नकार देण्याची वेळ येते. तिच्या मनाची होणारी घालमेल गझलकार समजून घेण्याचा प्रयत्न येथे करताना दिसतात,–"संपले संबंध अपुले" सांगतांना / का तुझ्या ओठास मग थरकाप होता?[11] " काय कळे काय अवस्था मनाची / तिचा चेहरा होतसे पारदर्शी"

एखाद्या सिनेमातील नायकाप्रमाणे गझलेतून व्यक्त होणारा गझलकार आपल्या गझलेकडे लक्ष वेधून घेतो. हे करत असताना मात्र त्यांच्या काही गझला मुसलसल या स्वरूपाकडे झुकताना दिसतात.

संतोष गाजरेदे :–

[illegible]

प्रवीण हटकर :–

यांच्या गझलेचा केंद्रबिंदू माणूस हाच आहे. यांच्यासारखी विचार करणारी पिढी गझल लेखन करणारी असेल तर संत ज्ञानेश्वरांना अपेक्षित 'हे विश्वची माझे घर' ही धारणा दूर नाही. या अर्थाच्या एका शेरामध्ये ते म्हणतात –

गाव माझे, शहर माझे, विश्व माझे
पेरका मज ठरवणारा कोण आहे [12]

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संत ज्ञानेश्वरांना माऊली असेच म्हटले जाते. आईची ममता काय असते तर घरातला एक राबता, घराचे घरपण, जिव्हाळ्याचे मूर्तिमंत रूप, अशा शब्दात तिचे वर्णन करता येईल. आई माणसाच्या सर्व दुःखावरची ममतेची फुंकर, अशा नाना प्रतिमांनी मराठी कवितेमध्ये जिचे वर्णन केलेले आहे.

गोपाल मापारी :–

गोपाल तुळशीराम मापारी, बुलडाणा जिल्हयातील मोताळा तालुक्यातील चिंचपूर या छोट्याशा गावातील असून, सध्या अकोला येथे पाटबंधारे विभागात कार्यरत आहेत. मराठी–उर्दू गझलेची चांगली जाण आणि अभ्यास असल्यामुळे त्यांनी अनेक मुशायऱ्यांतून बहारदार निवेदनाने मैफली फुलवल्या आहेत. महाराष्ट्रातील विविध वर्तमानपत्रे, नियतकालिके आणि दिवाळी अंक यातून गोपाल मापारींच्या गझल विशेषत्त्वाने भेटतात. सुरेश भटांनंतर तिसऱ्या पिढीतील गझलकारांमध्ये त्यांच्या उल्लेख करावा लागेल. शेती–मातीच्या, ग्रामीण भाव–भावना आपल्या गझलेतून अभिव्यक्त करणारे सामान्य माणसाच्या जगण्याचे अस्सल संदर्भ त्यांच्या लिखाणात दिसून येतात.

"पोटात ठेवतो आम्ही, ज्या अंधाराला दिवसा
त्याचीच घरावर आमुच्या, रात्रीला असते पाळी"[13]

'अंधार' या प्रतिमेतून दिवस–रात्र दुःखासोबत सामना करणाऱ्या हातावर पोट असणाऱ्या खेड्यातील जीवनाचे चित्र यातून ते उभे करतात.

उगवलो मातीतुनी, मिळणारही मातीत मी,
मूठभर माती सदा अपुल्या मुळाशी ठेवतो. [14]

यशाच्या शिखरावर फुलत असताना मूळाशी असलेल्या मातीशी घट्ट नाते सांगणारा हा शेर आहे.

मनोज सोनोने :–

प्रत्येकच गोष्ट जीवनात माणसाच्या मनाप्रमाणे होत नाही. कुणाकडे आई आहे तर परिस्थिती नाही. त्यामुळे शिक्षण घेण्याची ईच्छा पूर्ण होत नाही असेच मुळावा, यवतमाळचे गझलकार शेख गनी शेख मियॉ म्हणतात. आईच्या विषयी व्यक्त करताना म्हणतात,

जाणीव फार होते घरट्यास माणसांच्या
सोडून जीव जातो जेव्हा धुरात आई [15]
फेकून पुस्तके मी कामास दूर गेलो
होत्या घरा बहिणी, आई बिमार होती [16]

कुणाची मग कितीही साधी अपेक्षा का असेना, अशीच साधी सुधी अपेक्षा गजानन दरोडे ठेवतात की, आपल्या घरी कोणी हक्काचे, मानसन्मानाने पाहूणे यावेत.

"कधीच अमुच्या मनासारखे घडले नाही
दारापुढे पाय कुणाचे पडले नाही" [17]

येथे दारापुढे कोणी आले नाही, अशी खंत आहे तर कोठे गर्दीही मतलबी लोकांची असते म्हणून साध्या–सुध्या माणसाचे कोठेही काही खरे नाही, अशीच जाणीव करून देणारा शेर मूर्तिजापूर येथील गझलकार संदीप वाकोडे म्हणतात,

"स्वार्थीच लोक होते गर्दीत भोवतीच्या
मझयाच मतलबाचे बघता मला न आले"[18]

आजुबाजूला स्वार्थीच लोकं असतील तर नितीन भट यांचा अनुभव सांगतो तो मोलाचा वाटतो. "सावलीवरही भरवसा येत नाही ठेवता/ अनुभवाने सांगतो हे एवढे ठासून मी"[19]

रमेश बुरबुरे :–

रमेश बुरबुरे हे नव्वदोत्तर आंबेडकरी गझलेतील प्रभावी आणि प्रखर वास्तवाचे भान असणारे गझलकार म्हणून त्यांचा उल्लेख करता येईल. त्यांच्या 'अस्वस्थ वर्तमानावे संदर्भ' हा 2019 मध्ये प्रकाशित झालेला पहिलाच गझलसंग्रह आहे. यावर भाष्य करताना विनोद बुरबुरे म्हणतात, "साहित्य हे जीवनाचे सर्वांगसुंदर अविष्करण असते. त्यातून मूलगामी विचारांचे सांस्कृतिक उत्सर्जन घडत असते, अशी धारणाच या धम्म प्रतिभेची असल्याने त्याच्या संबंध कवितेतून मानवीय दृष्टीची विशालता उजागर होते."[20]या भाष्यावरून रमेश बुरबुरे यांची

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लेखनविषयक जाणीव सजग आहे. ते गझलेला एक कलाकृती म्हणून पाहतात. सामाजिक जाणिवेतून गझल लिहितात.

समोगतात गझलकार स्वतःचा उल्लेख करताना जगाचा पोशिंदा असणाऱ्या शेतकऱ्यांचा पुत्र म्हणून घेतात. दुःख आणि दारिद्र्य जणू पाचविला पुजलेले असल्यागत शेतकऱ्यांची अवस्था त्यांना अस्वस्थ करते. शेतकरी कुटुंबाची धग त्यांनी स्वतः अनुभवलेली वाटते. गझलकाराची भूमिका स्पष्टवक्तेपणाची आहे. जे वास्तव अनुभवास येते. त्याला कसल्याही पुराव्याची गरज त्यांना भासत नाही. त्याविषयी व्यक्त होताना ते कोणाची भीड, मूर्वत ठेवताना दिसत नाहीत. संघर्षाच्या चळवळीचा बाणा त्यांनी आंबेडकरी विचारातून स्वीकारलेला आहे.

"त्यांना हवे तसे मग केलेत पंचनामे
शेतातल्या शवांचे आपापल्या मनाने" [21]

माणूस मेल्यावर त्याच्या मागे चांगले बोलण्याची पध्दत आहे, पण शेतकऱ्याच्या नशिबी तेही नाही. अतिव्यसनामुळे, कर्जबाजारीपणातून, अव्यवहारीपणा, अशिक्षितपणा आदि कारणांमुळे आत्महत्या केली, अशा शंका व्यक्त केल्या जातात. राजकारण, सामाजिकता, धार्मिकता, कृषिविषयक आदि विषयांचे आत्मचिंतन त्यांच्या गझलेतून घडते. त्यांच्या गझलेमध्ये येणाऱ्या प्रतिमा आणि प्रतीके ही 1990 नंतरच्या वास्तव जगण्यातील आहेत. बुध्द तत्वज्ञानातील विचार घेऊन आधुनिक माहिती तंत्रज्ञानाच्या प्रतिमा कवी उभ्या करतात. 'सद्धम्माचे सीम', 'सिस्टीम' अशा नवीन युगाच्या प्रतिमातून सूचकता अधोरेखित करतात.

"वाजून राहिली बघ विजयोत्सवात माझ्या
ती पानेही पिंपळाची सळसळ करून दोस्ता" [22]

पिंपळाच्या पानांचा सळसळात जणू त्यांच्या विजयाचे स्वागत करीत आहेत. आणि हा विजय निश्चितच मानव कल्याणाचा म्हणून आलेला आहे. या गझलकाराचा बौध्द तत्वज्ञानावर पूर्ण विश्वास आहे. डॉ. बाबासाहेब आंबेडकरांनी निर्माण केलेल्या भारतीय संविधानाच्या माध्यमातून कल्याणकारी समाजाची निर्मिती होईल, असे त्यांना वाटते.

राहूल गडेकर :–

आदिम काळापासून माणूस स्वतःच्या स्पर्धेसोबत इतरांशी स्पर्धा करीत आला आहे. आपल्या अपयशापेक्षा इतरांच्या यशाने दुःखी होणारा मानवी स्वभाव दिसून येतो. 'कुत्र्याला गती आणि माणसाला प्रगती सहन होत नाही.' अशी एक म्हण प्रचलित आहे. असा एक अर्थ या शेरमधून निघतो. त्याचप्रमाणे आपल्या जवळच्या मित्राची प्रगती पाहून त्या मार्गाकडे वळण्यासाठी प्रेरणा मिळते. त्यामुळे यशाकडे धावण्याचा वेग वाढतो. एका शेरमधून अनेकार्थता गझलकार देऊन जातो.

–"स्वतःची राहते स्पर्धा स्वतःशी... हे खरे तरीही / गती ही वाढते बघुनी जवळचा धावता कोणी" [23]

"शब्दाने शब्द वाढला हा फार गौण मुद्दा आहे, हो ! / मुद्दा आहे, समंजसांनी निष्कारण री ओढली कशी" [24]

कोणत्याही समाजाची धुरा त्या समाजातील बुध्दिवादी, समजंस माणसाच्या खांद्यावर उभी असते. असे म्हटल्यास अतिशयोक्ती होणार नाही. कारण अज्ञानी माणसाच्या जगण्याच्या कल्पना मर्यादित विचारावर आधारलेल्या असतात. दूरदृष्टीचा तेथे अभाव दिसून येतो. परंतु समजदार माणसांनी वेगवेगळ्या दृष्टीकोनातून न पटणाऱ्या बाबींचे समर्थन करणे हे गझलकाराला पटल्यासारखे वाटत नाही. यासाठी गझलकारांचा सत्याला धीटपणे समोर जाणे महत्त्वाचे आहे, असे म्हणता येतात.

नीलेश डहाके :–

नीलेश डहाके हे नवोदित पिढीचे प्रतिनिधीत्व करणारे तरुण उमदा गझलकार म्हणून नीलेश यांच्या गझलेकडे पाहता येतात. त्यांच्या गझलेला शोभेल अशीच त्यांची रोखठोक शैली आपल्या गझलेतून मांडण्याचे काम अवगत झाले आहे.

[illegible]

नीलेश यांच्या गझलेतून पिढीजात चालत आलेल्या परंपरेच्या खंडण्यावर उभ्या असलेल्या प्रतीके ढाल बदलत असतांना तसे काही नवे संकेत दिसतात. जर विश्वासातून नवसंज्ञा नव

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सुटत नसेल तर अशा पदव्यांचे करायचे काय ?असा आत्मपरिक्षण करायला लावणारा शेर नीलेश कवडे व्यक्त करून जातो. कालखंड बदलला पण प्रश्न अजून तोच आहे. याच आशयाच्या शेरमध्ये अरविंद पोहरकर म्हणतात– "उगा जातोय हात बाहेर मी धुवाया / उपाशी झोपतो जगाला नको कळाया"[26]

गरिबांमधील स्वाभीमानीवृत्तीचे प्रतीक म्हणजे हा शेर आहे. वेळ पडला तर तो उपाशी राहील पण कोणासमोर हात पसरणार नाही. हा मानी स्वभावविशेष यातून प्रकट होतो.

"वाढले प्रेमाविना त्यांचे कुपोषण
लेकरांना दे जरासा वेळ मित्रा"[27]

उपरोक्त शेरमधून अमोल शिरसाट परिवाराला इतर सर्व गरजांसोबत आपला वेळही अत्यंत महत्त्वाचा असल्याचे सांगतात. जागतिकीकरणाच्या परिणामातून माणसाच्या धावपळीत भरच पडलेली आहे. तो आपल्या कामाच्या व्यापातून पोटाची खळगी भरण्याच्या व्यवस्थेतून आपल्या मुला–बाळांनाही वेळ देऊ शकत नाही.

"आजन्म खेळलो मी मस्तीत विस्तवाशी
लाचार लाकडांना मज जाळता न आले" [28]

रवी चापके कमी वयात अधिक अनुभवाची शिदोरी असणारा गझलकार आहे. त्यामुळे स्वभावामध्ये कणखरपणा, आलेल्या कोणत्याही प्रसंगाला तोंड देण्याची ताकद अग्नीपूजक असणाऱ्या धगधगत्या विस्तवाला कोणी द्यावी. तो आलेला प्रसंगच लाचार तेथे वाटतो.

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सुटत नसेल तर अशा पदव्यांचे करायचे काय ?असा आत्मपरिक्षण करायला लावणारा शेर नीलेश कवडे व्यक्त करून जातो. कालखंड बदलला पण प्रश्न अजून तोच आहे. याच आशयाच्या शेरमध्ये अरविंद पोहरकर म्हणतात– "उगा जातोय हात बाहेर मी धुवाया / उपाशी झोपतो जगाला नको कळाया"[26]

गरिबांमधील स्वाभीमानीवृत्तीचे प्रतीक म्हणजे हा शेर आहे. वेळ पडला तर तो उपाशी राहील पण कोणासमोर हात पसरणार नाही. हा मानी स्वभावविशेष यातून प्रकट होतो.

"वाढले प्रेमाविना त्यांचे कुपोषण
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रवी चापके कमी वयात अधिक अनुभवाची शिदोरी असणारा गझलकार आहे. त्यामुळे स्वभावामध्ये कणखरपणा, आलेल्या कोणत्याही प्रसंगाला तोंड देण्याची ताकद अग्नीपूजक असणाऱ्या धगधगत्या विस्तवाला कोणी द्यावी. तो आलेला प्रसंगच लाचार तेथे वाटतो.

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बंदीशीतील भाषा काव्य संस्कृती यातील समन्वय

प्रा.डॉ. किशोर निळकंठराव देशमुख
संगीत विभाग प्रमुख,
श्री शिवाजी कला, वाणिज्य व विज्ञान
महाविद्यालय, अकोला

मनुष्य हा एक भावना प्रधान प्राणी आहे. त्याच्या हृदयात अनेक प्रकारच्या भावना असतात. त्या भावना प्रकट करण्याची त्याच्या मनात तिव्र ईच्छा असते कारण भावना या प्रत्येक व्यक्तीच्या जीवनातील आधाररूप असतात व त्या भावनांच्या आदान–प्रदानातून मनुष्य एक दुसऱ्या जवळ पोहचु शकतात आपल्या हृदयातील भावना वेगवेगळया प्रकारे व्यक्त करण्याचा तो सतत प्रयत्न करीत असतो. हीच त्याची अभिव्यक्ति. जेंव्हा संगीतातील स्वर तालास काव्यातील निर्माण केलेल्या बंदीशीला महत्व देवून जाते तेंव्हा मनुष्य आपल्या अंतरंगातील कल्पनांना साकार करू शकतो. संगीत शिक्षणाच्या ऐतीहासीक टप्प्यांना समजून घेण्यासाठी प्राचीन काळातील शिक्षण पध्दतीवर विचार करणे गरजेचे आहे.

संगीत कलेच्या सदंर्भात सद्यस्थितीत म्हणजे विदयालय, महाविदयालय व विदयापीठ या स्तरावर स्थान मिळवून अतिशय लोकप्रियतेच्या शिखरावर पोहचले आहे. कलावंतांच्या विचारात व दृष्टित पुर्वीपेक्षा आज अतिशय परिवर्तन झाले आहे. राग गायनामध्ये बंदीश व त्यातील सौंदर्य दाखवितांना काही महत्वाच्या बाबी पुढे येतात त्या म्हणजे बंदीश–भाषा–काव्य आणि संस्कृती यांचा परस्परांशी संबंध एकमेकांशी पुरक आहे.

बंदीश : हिंदुस्थानी संगीताच्या क्षेत्रात बंदिश या संकल्पनेला केंद्रवर्ती अतिमहत्वाचे स्थान आहे. हिंदुस्थानी संगीताच्या कोणताही अविष्कार, बंदिश वजा घटकाच्या आधाराशिवाय संभवने अशक्य आहे. कारण संगीत हा सौंदर्याविष्कार आहे आणि कोणतेही सौंदर्य विधान हे रूप, आकार किंवा घाट यांच्या उपस्थितीशिवाय संवेदनगम्य होऊ शकत नाही. म्हणूनच सौंदर्यशास्त्रा मध्ये कला उपस्थितीशिवाय व कलाकृतीचा घाट या संबंधीची चर्चा ही प्राथमिक अवस्थेपासून तर आजपर्यंत होत आलेली आहे. हिंदुस्थानी संगीताच्या क्षेत्रात बंदीश या शब्दाला अनेक अर्थ प्राप्त झाले आहे.

१. ख्याल गायनासाठी किंवा व्यापकदृष्टया रागदारी गायनासाठी योजीलेले कवन याकरिता मराठीत 'चीज' असा ही शब्दप्रयोग अधीक करून वापरल्या जातो हिंदी भाषेत सुध्दा हा शब्द ऐकायला मिळतो.

२. कोणत्याही संगीतविष्काराचे काहीसे लवचिक व बरेचसे ठराविक असे रूपतत्व कधी धृपद, ख्याल, ठुमरी, दादरा, गझल, भावगीत, भजन, नाटयगीत याचे म्हणून एक रूपतत्व आहे ते कलाव्यवहारातील सातत्य आणि वारंवारीता यामुळे ठरून गेले आहे. त्यात अकस्मात काही बदल केला तर ते रूपतत्व विस्कळीत होईल. पं. वि.रा. आठवले यांनी भक्तीसंगीत व शास्त्रीयसंगीत हया लेखामध्ये एक आठवण सांगीतली आहे. सं. क. विहार जुलै– १९८२ ''आकाशवाणीवरील त्यांच्या एका संगीत निर्मात्या मित्राने तुकारामबुवांच्या एका अभंगाला गझलच्या सुरावटीत निबध्द केले. हे संगीत कसे काय वाटेल''. हे त्याने दुसऱ्या एका बुजुर्ग दिग्दर्शकाला विचारले ते ''दिग्दर्शक म्हणाले तुमची ही चाल चांगली आहे पण तो अभंग ऐकताना असे वाटले, की तुकारामबुवांच्या मांडीवर बसुन बेगम अख्तर गात आहे''. अशाच प्रकारे एखादा पारंपारिक अभंग ख्यालाच्या शैलीने म्हटला तर मराठी आहे की हिंदी बोलीभाषेत आहे हे ओळखणे काही क्षण अवघड जाईल. सारांश हा की बंदिश याचा आनखी एक अर्थ व अमूर्त अशी काल्पनिक आधार चौकट असा आहे. दुसऱ्या शब्दात बंदीश म्हणजे चाल असा अर्थ येथे गश्हीत धरलेला नाही.

३. बंदिश म्हणजे चाल नव्हे अस म्हणण्याचं कारण हे की, भावगीत, गझल, भजन, नाटयगीत

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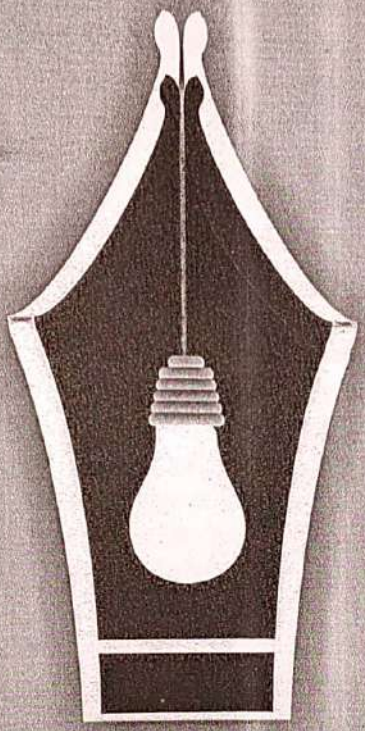

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"बंदीशीतील भाषा काव्य संस्कृती यातील समन्वय"

प्रा. डॉ. किशोर निळकंठराव देशमुख
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श्री शिवाजी कला, वाणिज्य व विज्ञान
महाविदद्यालय, अकोला

मनुष्य हा एक भावना प्रधान प्राणी आहे. त्याच्या हृदयात अनेक प्रकारच्या भावना असतात. त्या भावना प्रकट करण्याची त्याच्या मनात तिव्र ईच्छा असते कारण भावना या प्रत्येक व्यक्तीच्या जीवनातील आधाररूप असतात व त्या भावनांच्या आदान–प्रदानातून मनुष्य एक दुसऱ्या जवळ पोहचु शकतात आपल्या हृदयातील भावना वेगवेगळया प्रकारे व्यक्त करण्याचा तो सतत प्रयत्न करीत असतो. हीच त्याची अभिव्यक्ति. जेंव्हा संगीतातील स्वर तालास काव्यातील निर्माण केलेल्या बंदीशीला महत्व देवून जाते तेंव्हा मनुष्य आपल्या अंतरंगातील कल्पनांना साकार करू शकतो. संगीत शिक्षणाच्या ऐतीहासीक टप्यांना समजून घेण्यासाठी प्राचीन काळातील शिक्षण पध्दतीवर विचार करणे गरजेचे आहे.

संगीत कलेच्या सदंर्भात सद्यस्थितीत म्हणजे विदयालय, महाविदयालय व विदयापीठ या स्तरावर स्थान मिळवून अतिशय लोकप्रियतेच्या शिखरावर पोहचले आहे. कलावंतांच्या विचारात व दृष्टित पुर्वीपेक्षा आज अतिशय परिवर्तन झाले आहे. राग गायनामध्ये बंदीश व त्यातील सौंदर्य दाखवितांना काही महत्वाच्या बाबी पुढे येतात त्या म्हणजे बंदीश–भाषा–काव्य आणि संस्कश्ती यांचा परस्परांशी संबंध एकमेकांशी पुरक आहे.

बंदीश : हिंदुस्थानी संगीताच्या क्षेत्रात बंदिश या संकल्पनेला केंद्रवर्ती अतिमहत्वाचे स्थान आहे. हिंदुस्थानी संगीताच्या कोणताही अविष्कार, बंदिश वजा घटकाच्या आधाराशिवाय संभवने अशक्य आहे. कारण संगीत हा सौंदर्याविष्कार आहे आणि कोणतेही सौंदर्य विधान हे रूप, आकार किंवा घाट यांच्या उपस्थितीशिवाय संवेदनगम्य होउ शकत नाही. म्हणूनच सौंदर्यशास्त्रामध्ये कला उपस्थितीशिवाय व कलाकृतीचा घाट या संबंधीची चर्चा ही प्राथमिक अवस्थेपासून तर आजपर्यंत होत आलेली आहे. हिंदुस्थानी संगीताच्या क्षेत्रात बंदीश या शब्दाला अनेक अर्थ प्राप्त झाले आहे.

१. ख्याल गायनासाठी किंवा व्यापकदृष्टया रागदारी गायनासाठी योजीलेले कवन याकरिता मराठीत 'चीज' असा ही शब्दप्रयोग अधीक करून वापरल्या जातो हिंदी भाषेत सुध्दा हा शब्द ऐकायला मिळतो.

२. कोणत्याही संगीतविष्काराचे काहीसे लवचिक व बरेचसे ठराविक असे रूपतत्व कधी धृपद, ख्याल, ठुमरी, दादरा, गझल, भावगीत, भजन, नाटयगीत याचे म्हणून एक रूपतत्व आहे ते कलाव्यवहारातील सातत्य आणि वारंवारीता यामुळे ठरून गेले आहे. त्यात अकस्मात काही बदल केला तर ते रूपतत्व विस्कळीत होईल. पं. वि.रा. आठवले यांनी भक्तीसंगीत व शास्त्रीयसंगीत हया लेखामध्ये एक आठवण सांगीतली आहे. सं. क. विहार जुलै–१९८२ "आकाशवाणीवरील त्यांच्या एका संगीत निर्मात्या मित्राने तुकारामबुवांच्या एका अभंगाला गझलच्या सुरावटीत निबध्द केले. हे संगीत कसे काय वाटेल". हे त्याने दुसऱ्या एका बुजुर्ग दिग्दर्शकाला विचारले ते "दिग्दर्शक म्हणाले तुमची ही चाल चांगली आहे पण तो अभंग ऐकताना असे वाटले, की तुकारामबुवांच्या मांडीवर बसुन बेगम अख्तर गात आहे". अशाच प्रकारे एखादा पारंपारिक अभंग ख्यालाच्या शैलीने म्हटला तर मराठी आहे की हिंदी बोलीभाषेत आहे हे ओळखणे काही क्षण अवघड जाईल. सारांश हा की बंदिश याचा आनखी एक अर्थ व अमूर्त अशी काल्पनिक आधार चौकट असा आहे. दुसऱ्या शब्दात बंदीश म्हणजे चाल असा अर्थ येथे गश्हीत धरलेला नाही.

३. बंदिश म्हणजे चाल नव्हे अस म्हणण्याचं कारण हे की, भावगीत, गझल, भजन, नाटयगीत यांच्या चाली ख्याल, ठुमरी, दादरा यांच्या तुलनेत कितीतरी मुक्त व स्वैर असतात. तेथे शब्दाला उठान दयायचा असतो. विशिष्ट भाव समुर्त करायचा असतो त्या करीता संगीतकार स्वररचनेला वाटेल तसे वळवीत असतो, तो रागाच्या बंधनात अडकवून राहणे पसंत करीत नाही. या उलट धृपद, ख्याल इत्यादीच्या स्वर रचनेतील प्रत्येक कण संगीताच्या सिध्दीसाठी वेचलेला असतो. त्यातील सम, वियम मुक्काम हे सर्व

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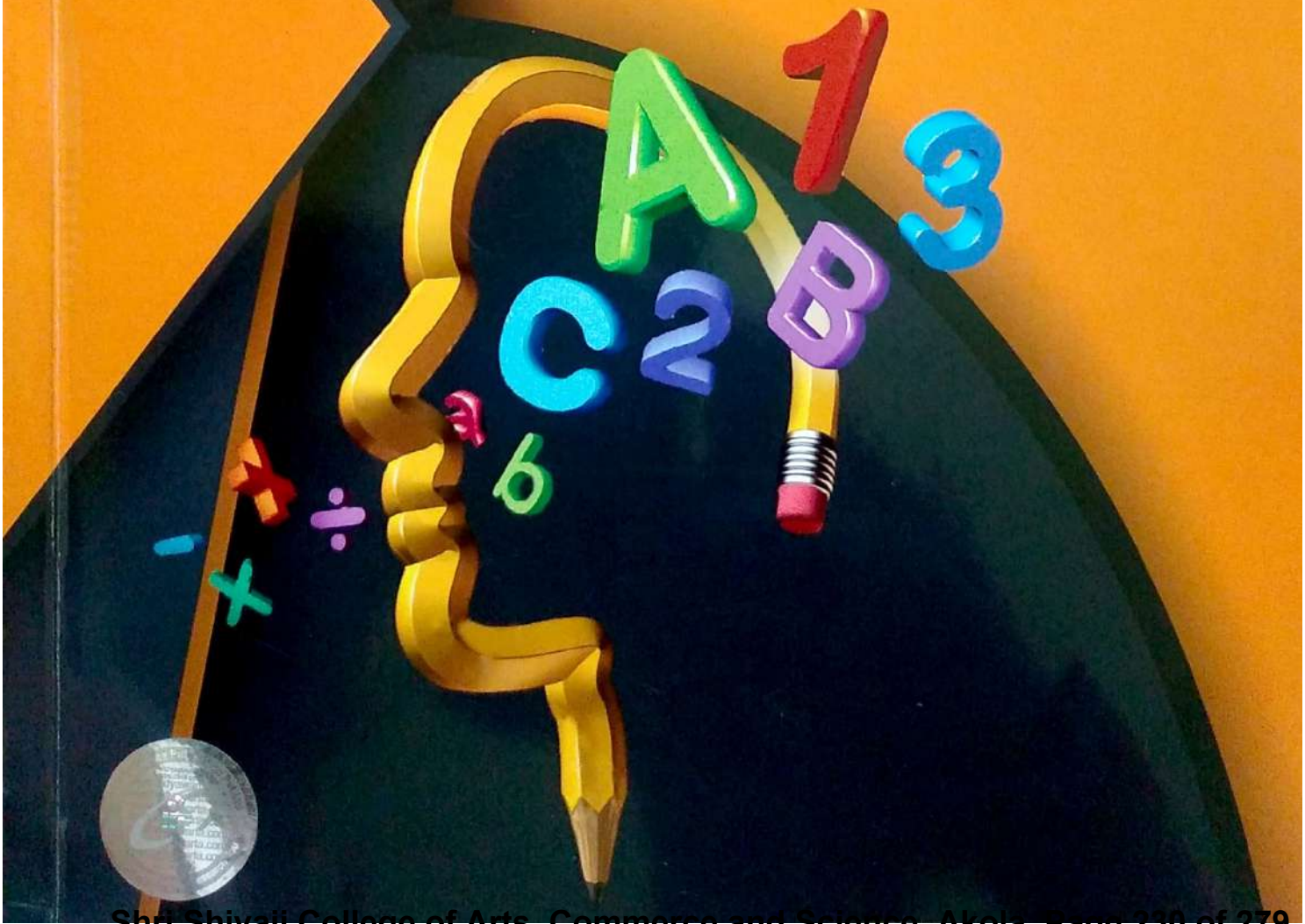

If should be the mitigation of flood control and water management.

To lift up proper step for connecting rivers plan.

Implementation of employed oriented plans.

The above mentioned suggestions can be accepted for minimizing urban population pressure and broken down being migration towards urban area. The present travelling government, for creating self employment there are many plans underlying as well as for this action ton system also implementing.

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08

THE ROLE OF FOLK MUSIC IN CULTURAL & TRADITIONAL DEVELOPMENT

Dr. SOPAN SITABRAO WATARE
SHRI SHIVAJI COLLEGE OF ARTS, COMMERCE & SCIENCE, AKOLA

Traditional folk music has been defined in several ways, as music transmitted by mouth, as music of the lower classes and as music with unknown composers. It has been contrasted with commercial and classical styles. One meaning often gives is that of old songs, with no known composers, another music is that has been transmitted and evolved by a process of oral transmission or performed by custom over a long period of time.

Indian folk music is diverse because of India's vast culture diversity. Though it might be started with devotional song later it covered each and every part of contemporary human life including psychology,philosophy,anotomy socio-economic condition, love, day to day living etc. and in many of them you will find deep insight into life. There are numerous eminent bards/ saints or fakirs who had contributed a lot in this field. Few of them are kabir,Moinuddin Chishti,Lalon,fakir and many more. Main classification can be done based on the regional languages. It has many forms including Bhangra,Lawni Dandiya and Rajasthani.The arrival of movies and pop music,weekened folk musics popularity,but saints and poets to have large musical libraries and tradition to their name, often sung in thumri seme the folk music of India is dance oriented. Folk music includes both traditional music and general evolved from it during the 20 th century folk revival. The term originated in the 19 th century but it often ap-

plied to music that is order than that. Some types of folk music are also called world music.

Starting in the mid 20 th century a new form of popular folk music evolved from traditional folk music. This process an period is called the second folk revival and reached a zenith in the 1960. This form of music sometime called contemporary folk music or folk revival music to distinguish it from earlier folk form smaller similar revivals have occurred elsewhere in the world at other times, but the term folk music has typically not been applied to the new music created during those revivals. This type of folk music also includes fusions genres such as a folk rock, folk metal, electric folk and others. While contemporary folk music is a genre generally distinct from traditional folk music, in English it shares the same name and, and it often shares the same performance and venues and traditional folk music. Even individual songs may be a blend of the two, there are many different contents include folk music as like Bhawgeet,Bhangra and Giddha Bihugeet, Lavani, Uttarkhandi music, Dandiya, Pandavani, Bauls,Bhatiali, Garba, Dollu kunita, kolata/ Kolattam, Veergase,Naatupura Pattu etc.

Bhangra and Giddha: Bhangra is not a form of dance oriented folk music of Punjab. The present musical style is derived from nontraditional musical accompaniment to the riffs of Punjab called by the same name. The female dance of Punjab region is known as Giddha.

Bihugeet: Bihugeet is a traditional folk music of Assam performed through Bihu dance in the festival of Bihu.The song has themes of romance, love nature and incidents. The dance is celebrates in group by young girls and boys.

Dandiya: Dandiya is a dance oriented folk music that has also been adapted for pop music worldwide popular in Western India, especially during nawratri.The present musical style is derived from the traditional musical accompaniment to the folk dance of Dandiya called by the same name.

Pandavani: Pandavani is a folk singing style of musical narration of tales from ancient epic Mahabharata with musical accompaniment to the folk dance of Dandira called by the same.

Bauls: The Bauls of Bengal were an order of musicians in 18 th,19 th and early 20 th century. India who played a form of music using a khamak,ektara and dotara.The world baul comes from Sanskrit meaning divinely inspired insanity. They are a group of Hindu mystic minstrels. They are through to have been influence breathy by the Hindu tantric sect of the kartabhajas as well as by Sufi sects.Bauls travel in search of the internal ideal.

Bhatiali: This type of music was cultured mainly by the oarsmen and fishermen of eartwhile Bengal. There are many opinions regarding the origin of the term Bhatiyali.

Garba: Garba(song) is sung in honor of Hindu goddesses god during Nawratri.They are sung in the honors of god Krishna, Hanuman ,Ram etc.

Lavani: Lavani is a popular folk from of Maharashtra.Traditionaly,the songs are sung by female artists, male artists may occasionally sing lavanis.The dance format associated with Lavani is knows as Tamasha.This dance format contains the dancer, the helping dancer maavshi,The Drummer-Dholkiwala and the flute Boy.

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भारतीय संगीत के विकास और वैश्विकरण में नई तकनिकों की उपयोगीता

प्रा. नेहा मानकर (सोलव)
श्री शिवाजी कला वाणिज्य व विज्ञान महाविद्यालय, अकोला

Abstract

उद्देश : *इस लेख लेखन के द्वारा हम यह जानने का प्रयत्न करेंगे कि भारतीय संगीत के प्रचार एवं प्रसार में इन नए वैज्ञानिक उपकरणों एवं नई नई तकनिकों का कितना महत्वपूर्ण योगदान रहा है।*

शोध पद्धती : *प्रस्तुत शोध लेख के लिखने के लिए विवरणात्मक, इतिहास जन्य, अवलोकनात्मक तरीकों का उपयोग किया गया है।*

प्रस्तावना :

संगीत कला एक प्रस्तुतीकरण का श्रेष्ठ कला माना जाता है। इसके अमूर्त रूपसे मानव के अंतर्मन पर लोकेजाला प्रभाव इस कला को श्रेष्ठता को दर्शाता है। विश्व का सांस्कृतिक परिचय से भारत सर्वश्रेष्ठ अंगणा है। भारतीय संगीत की परंपरा उन उन को चिरजीवन देने वाली श्रुतपरंपरा की तरह प्राचीन काल से ही एक वेगवती धारा के रूप में अखंड प्रवाहित होती हुई वर्तमान समय तक पहुँचा है। आज संगीत का जो रूप हमारे समक्ष उपस्थित है वह एकाएक किसी स्रोत या बौद्धिक उपज द्वारा निर्माण नहीं हुआ। इसके मूल रूप से विकास वृद्धि और परिवर्तन होते होते इस का वर्तमान स्वरूप निश्चित हुआ है। भारतीय संगीत एक अत्यंत विशेषज्ञ और सुदृढ़ परंपरा को लेकर चलने वाला और उज्ज्वल है।

मानव निसर्गतः ही अत्यंत बुद्धिमान कलाकार और प्रतिभा है। अपने जिवन को विकसित और प्रतिभाशाली बनाने के लिए उसने जैसे अन्न वस्त्र, निवास इन जिन मूलभूत आवश्यकताओं का शोध लगाया वैसे ही संगीत का शोध लगाकर उसका दिन ब दिन विकास किया।

संगीत घरानों का संगोपन था और गुरुओं द्वारा शिष्यों को विद्या के साथ सिखाने के अलावा अनेक उदाहरण मिलते है। जिससे प्रतीत होता है कि शिक्षण पद्धतियां और अभ्यास पद्धतियां में वैज्ञानिक उपकरणों का उपयोग किसी भी रूप में चला होगा था किंतु घरानेदार जैसे वैज्ञानिक उपकरण के माध्यम से ये कलाकार अब अपनी सीमाओं से बाहर निकलने लगे थे। ग्रामोफोन के आने से विभिन्न ग्रामोफोन कंपनियाँ उनके रेकॉर्डिंग बनाने लगा थी। इसमें H.M.V. निकोल Twine, Bulbul इत्यादि कंपनियों ने उस समय के प्रसिद्ध गायक—गायकों के Records बनाए। जिन कलाकारों के रेकॉर्डिंग बने उनमें फैयाजखान आग्रावाले, अल्लादियाखान, भेंडीबाजार घराने, फैयाजहुसेन, अब्दुलकरीम खां, उ बिलायत खां इत्यादी के नाम लिये जा सकते है। लेकिन ग्रामोफोन का प्रयोग सिर्फ—सुनाने के लिए नहीं किया जाता था। परन्तु भातखंडे जी ने ग्रामोफोन का प्रयोग सिखने की पद्धति में किया।

घरानेदार कलाकारों को इसके उपरांत अन्य घरानों का गायकी से दूर रखते थे। ताकि उनका अपना घरानेदार गायकी की व दूसरे घराने वाले सुर सजे और व उनका स्वर उनकी अपनी गायकी पर पड़े। इन कलाकारों को अपनी रिसायों से बाहर निकलने का यह बहुत बड़ा आत्मविश्वास था। जिसका प्रभाव भारत में २० जुलाई

१९८७ में हुई। जिसमें शास्त्रीय संगीत को विशेष महत्व दिया। इसमें संगीत परंपरा के विभिन्न आयामों से निकलकर आकाशवाणी के माध्यम से सर्वसामान्य लोगों तक पहुँचा। शास्त्रीय तथा उपशास्त्रीय इन सभी प्रकार के संगीत के प्रचार एवं प्रसार के लिए आकाशवाणी एक सशक्त माध्यम रहा है। वैसे तो अब संगीत के विविध प्रकारों का प्रसारण अनेकानेक कार्यक्रमों में होता जा रहा है। आजतक कई संगीत कलाकारों ने आकाशवाणी केंद्र पर कार्यक्रम अधिकारी के रूप में कार्य किया है। जिसके फलस्वरूप उत्तम दर्जे के संगीत के विविध कार्यक्रम प्रसारित हुए है। भारतीय संगीत का जतन करने में आकाशवाणी का महत्वपूर्ण योगदान रहा है।

आज सर्वाधिक महत्वपूर्ण पद जो हमारे सामने है वह है कम्प्यूटर। कम्प्यूटर द्वारा प्रभावी रिकॉर्डिंग लिप्यंकिंग, संपादन जैसे काम हलके रूप से किया जा सकते है। कई सॉफ्टवेयर प्रोफेशनल संगीतकार इसके लिए उपलब्ध है। एक ही समय कई वाद्य यंत्रों का ध्वनियों को सुना जा सकता है। इंटरनेट, वेबसाईट आदि इस प्रौद्योगिकी युग के अत्यन्त उपयोगी उपकरण है। संगीत के क्षेत्र में 'कम्प्यूटर' से वाद्यवृंद को जोड़ना और उन्हें संचालित करना पूरी तरह से तकनीकी दृष्टिकोण है। इस कम्प्यूटर भाषा को संगीतज्ञों के लिए एक सरल प्रोटोकॉल विकसित किया गया है। जिसे 'म्यूजिकल इन्स्ट्रूमेंट डिजिटल इन्टरफेस' यानि से इसे 'मिडी' भी कहते है। इसके द्वारा गुरु से गुरु वाद्य यंत्रों का नाप लिया जाता है और संचालन स्वतः नाप कर लिया जाता है।

कम्प्यूटर और इंटरनेट शास्त्रीय संगीत के लिए उपयोगी है। कम्प्यूटर और इंटरनेट के आगे से एक जगह बैठकर ही बहुत सारे लोगों को शास्त्रीय संगीत का प्रशिक्षण दिया जा सकता है।

आज के युग में इलेक्ट्रॉनिक टेक्नोलॉजी के विविध नये एवं अत्याधुनिक इलेक्ट्रॉनिक वाद्यवृंद उपकरणों संगीत को अपार सहायता की है। आज हम इन्हीं उपकरणों की सहायता से अपने संगीत को सहेजकर रख सकते है और पुनः पुनः जब चाहे तब सुन भी सकते है। आज इलेक्ट्रॉनिक तकनीक के माध्यम से तानपुरा और तबला जैसे वाद्यों की सजीव आवाज भी उपलब्ध हो गई है। सिंथेसाइजर ने तो सैकड़ों वाद्यवृंदों को एक ही की—बोर्ड पर संभव बनाकर चमत्कार कर दिया है। जहाँ तक संगीत का प्रश्न है तो इसे कोई रोक नहीं सकता। संगीत एक ऐसा भाषा है। जो सच्चे अर्थों में सर्वोत्तम है।

आधुनिक युग के आरंभ से ही संगीत का भी आधुनिकीकरण किया है। आज शास्त्रीय संगीत अथवा सुगम संगीत के भी कई ई—सेल और कैसेटस है। जिसमें देश के कई नामी गिरामी शास्त्रीय संगीतज्ञ जुड़े हुए है। तकनीकी सुलभ साधनों द्वारा भारतीय संगीत जिसका स्वरूप ही विशेषता संगीत, आध्यात्मिकता एवं स्वरात्मकता जिससे विश्व भर के समस्त संगीत प्रेमी भारतीय संगीत की ओर खिंचे है और इसे आत्मसात कर रहे है।

निष्कर्ष :

आज के इस प्रौद्योगिकी युग में तकनीकद्वारा संगीत को विभिन्न विधाओं में उपयोगी प्रयोग किया जा सकता है। तथा इन सुलभ साधनों के माध्यम से कई गिरी अपनी सांगीतिक जिज्ञासा एवं जिज्ञासा की पूर्ति कर आजीविका का भी निर्वहन कर सकता है। इस नई Technology ने कलाकारों और श्रोताओं को कलाकारों आज एक दौर से अधिक पुलवा दी गई है। और इन सभी बातों की चर्चा मैं यहाँ जरूरी नहीं समझती हूँ। क्योंकि इसकी चर्चा हुई है। जिससे संगीत का प्रचार और प्रसार आज लोगों तक हुआ है। इसलिए निश्चय ही भारतीय शास्त्रीय संगीत कला अंतर्राष्ट्रीय स्तर पर अपना विशेष स्थान निर्माण कर चुका है।

संदर्भग्रंथ सूची :

भारतीय समाज में देवदासी [illegible]
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वैश्वीकरण और संगीत के विकास में आधुनिक तकनिक का योगदान

प्रा. डॉ. वनिता तुकारामजी भोपत (केतकर)

श्री शिवाजी कला, वाणिज्य व विज्ञान महाविद्यालय, अकोला, महाराष्ट्र, भारत

Abstract

संगीत कला है जिसे इंद्रियों के माध्यम से महसूस किया जाता है। यह मन को शांति देता है इसे सिर्फ सुनकर ही मन खुश हो जाता है। यह मन को शांति पहुंचाता है। इसी लिए संगीत अन्य सभी विषयों से अलग है। इसे सुनकर ही मन को आनंद की अनुभूति होती है। इसे समझने के लिए किसी भाषा की आवश्यकता नहीं होती है। यह एक सार्वभौमिक भाषा है। यह सभी को समझ में आती है। यह एक ऐसी कला है जो मनुष्य को ईश्वर से जोड़ती है। संगीत के द्वारा ही मनुष्य ईश्वर की भक्ति कर सकता है। यह एक ऐसा माध्यम है जो मनुष्य को ईश्वर से जोड़ता है। इसी लिए संगीत को ईश्वरीय कला का दर्जा दिया गया है। आज संगीत ने बहुत विस्तृत स्वरूप ले लिया है। संगीत ऐसा है जो सभी को आकर्षित करता है। यह एक ऐसा माध्यम है जो मनुष्य को ईश्वर से जोड़ता है। इसी लिए संगीत को ईश्वरीय कला का दर्जा दिया गया है। आज संगीत ने बहुत विस्तृत स्वरूप ले लिया है। संगीत ऐसा है जो सभी को आकर्षित करता है।

प्रस्तावना :

हमारे देश में प्राचीन काल से संगीत – संस्कृति का अत्यंत महत्व बताया गया है। भारतीय संगीत अत्यंत प्राचीन काल से ही धर्म से अनुप्राणित है। अपनी आध्यात्मिकता के कारण ही यह विश्व संगीत में अपना विशिष्ट स्थान रखता है। संगीत का यह परिवर्तन रूप ही आनंददायी है। विश्व का सबसे प्राचीन ग्रन्थ 'वेद' है और सबसे प्राचीन संगीत सामगान है, जिसमें स्वर का बहुत महत्वपूर्ण स्थान है। ब्रह्म ब्रह्म एवं वासुदेवों की सहजतम अभिव्यक्ति की जैसी आकांक्षा और उपासना भारतीय ऋषियों ने की वह विश्व के इतिहास में विलक्षण है। सृजनात्मक चाक के अनादायक स्वरूप को ही सृष्टि सामवेद या साम संगीत ने जैसे गीत से आत्मवत् का साक्षात् स्वरूप कहा है।

भारतीय ही नहीं अपितु समग्र विश्व में विभिन्न उत्सवों तथा धार्मिक अनुष्ठानों पर गीत–वृत्य की परम्परा का प्रमाण मिलता है। देवी देवताओं की स्तुति में विभिन्न संस्कारों के साथ रूप में अभिव्यक्ति साथ संज्ञा से ही अभिहित है। विशिष्ट मासों का सम्बन्ध ऋतु–विशेष से रहा है।

संगीत सम्बन्धित प्रयोगात्मक परीक्षण करता है। जिसका मुख्य उद्देश्य आत्म सन्तुष्टि है जहां एक ओर संगीत आध्यात्मिक साधना का सशक्त माध्यम है वहां दूसरी ओर वैज्ञानिक शोध का इसका विशेषता रहा है वैदिक युग से चलकर युग तक संगीत अपने दोनों स्वरूपों में मानवीय जीवन से जुड़ता है।

संगीत एक परिभाषित शब्द है जिसमें गाना बजाना एवं नृत्य जैसी विधाओं का समावेश होता है। गाना बजाना तथा नृत्य त्रय संगीत कहलाता। संगीत में मनुष्य के मन को आकर्षित करने की अद्भुत शक्ति होती है। संपूर्ण विश्व में आज संगीत का प्रचार और प्रसार हुआ है इसमें निश्चित इलेक्ट्रॉनिक उपकरणों ने इस प्रसार माध्यमों बहुत बड़ा योगदान है।

यह परिवर्तन समय का अनिवार्य नियम है जिसके अनुसार सामाजिक सांस्कृतिक राजनैतिक वातावरण भी बदलता रहा है अतः परिवर्तन संगीत में विविध रूपों में भी परिवर्तन लाना अत्यन्त आवश्यकता समझा गया है। भारतीय

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THE SIGNIFICANCE OF MUSIC EDUCATION IN INDIA

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Abstract

This paper highlights the importance of music education to the Indian educational system. It identifies the prospects, problems and proffered possible solutions to them. In achieving its objectives, the study uses ethnographic and qualitative methods with simple percentages for eliciting and collation of data. The paper suggests that the society, the curriculum planners, and the government have much to do so music education is appreciated in India. It proposes as part of its recommendations that the government provide necessary facilities and personnel for music to thrive as a vocational subject; and that parents and the larger society must become educated on the usefulness of music as a career subject worth pursuing by pupils.

Keywords: *Music Education*

Introduction: Music education is a field of study associated with teaching and learning music. It touches on all learning domains, including the psychomotor domain, the cognitive domain and in particular and significant ways, the affective domain including music appreciation and sensitivity. Music training from preschool through post-secondary education is common in most nations because involvement with music is considered a fundamental component of human culture and behavior. Music, like language, is an accomplishment that distinguishes us as humans.[1]

In schools in European countries, children often learn to play instruments such as keyboards or recorders, sing in small choirs, and learn about the elements of music and history of music. In countries such as India, the harmonium is used in schools, but instruments like keyboards and violin are also common. Students are normally taught basics of Indian Raga music. In primary and secondary schools, students may often have the opportunity to perform in some type of musical ensemble, such as a choir, orchestra, or school band: concert band, marching band, or jazz band. In some secondary schools, additional music classes may also be available. In junior high school or its equivalent, music usually continues to be a required part of the curriculum.[2] At the university level, students in most arts and humanities programs receive academic credit for music courses such as music history, typically of Western art music, or music appreciation, which focuses on listening and learning about

different musical. Most universities also offer degree programs in music education, certifying students as primary and secondary music educators. Advanced degrees such as the M.A. or the Ph.D can lead to university employment. These degrees are awarded upon completion of music theory, music history, technique classes, private instruction with a specific instrument, ensemble participation, and in depth observations of experienced educators. Music education departments in North American and European universities also support interdisciplinary research in such areas as music psychologfy, music education historiography, educational ethnomusicology, socio-musicology, and philosophy of education.

Music Education in India:

Institutional Music education was started in colonial India by Rabindranath Tagore after he founded the Visva-Bharati University. At present, most universities have a faculty of music with some universities specially dedicated to fine arts such as Indira Kala Sangeet University, Swathi Thirunal College of Music or Rabindra Bharati University. Indian classical music is based on the gurushyshya-parampara system. The teacher known as Guru, transmit the musical knowledge to the student, or shyshya. This is still the main system used in India to transmit musical knowledge. Some schools and organizations promote integration of arts classes, such as music, with other subjects, such as math, science, or English. It is thought that by integrating the different curricula will help each subject to build off of one another, enhancing the overall quality of education. Music education can play a vital role in the development of the whole child and their scholastic journey.

Significance:

It has been argued that studying music enhances academic achievement.[3] The research was brought to the attention of mainstream America with the assertion that listening to Mozart improved spatial reasoning skills.[4] The human brain has been shown to be "hard-wired" for music; there is a biological basis for music being an important part of human experience. Music and the Arts surround daily life in our present day culture. Most present day artists, architects, and musicians acquired their interests during public school Fine Arts classes... Education without the Fine Arts is fundamentally impoverished and subsequently leads to an impoverished society." William Earhart, former president of the Music Educators National Conference, said that "Music enhances knowledge in the areas of mathematics, science, geography, history, foreign language, physical education, and vocational training." Music not

only inspires creativity and performance, but academic performance over all is seriously impacted. A research study produced by the Harris Poll has shown that 9 out of 10 individuals with post graduate degrees participated in music education. The National Report of SAT test takers study indicated students with music performance experience scored higher on the SAT: 57 points higher on verbal and 41 points higher on math. The Texas Commission on Drugs and Alcohol Abuse Report noted that students who participated in band or orchestra reported the lowest lifetime and current use of all substances including alcohol, tobacco, and illicit drugs. Playing music increases overall brain activity. In experiments done at the University of Wisconsin students with piano or keyboard experience performed 34% higher on tests that measure spatial-temporal lobe activity, which is the part of the brain that is used when doing mathematics, science, and engineering.Music aids in text recall. Wallace (1994) studied setting text to a melody. The repetitive music produced the highest amount of text recall; therefore, music serves as a mnemonic device. Smith (1985) studied background music with word lists. A 2011 study conducted by Kathleen M. Kerstetter for the Journal of Band Research found that increased non-musical graduation requirements, block scheduling, increased number of non-traditional programs such as magnet schools, and the testing emphases created by the No Child Left Behind Act are only some of the concerns facing music educators. Both teachers and students are under increased time restrictions". Unfortunately, music in our schools are being cut at a drastic rate due to budget cuts being forced upon the schools. What some school boards do not know is that cutting music might cause test scores to fall due to the positive effect on everything from academics to citizenship and even personal hygiene.

Music makes students more successful in school. Skills learned through the discipline of music, transfer to study skills, communication skills, and cognitive skills useful in every part of the school curriculum. It also makes students become successful is participation in ensembles. This helps students learn to work effectively in the school environment and cuts down on resorting to violent or inappropriate behavior. Studies have found that some measure of a child's intelligence is indeed increased with music instruction. What is new however, is a combination of tightly controlled behavioral studies and groundbreaking neurological research that show how music study can actively contribute to brain development. Researchers at the University of Montreal used various brain imaging techniques to investigate brain activity during musical tasks and found that sight-reading musical scores and playing music both

activate regions in all four of the cortex's lobes; and that parts of the cerebellum are also activated during those tasks. Other studies show that music also helps with reasoning. Music makes students better learners and better thinkers.

Contemporary Problems Facing Music Education in India:

We made an attempt to find out the major problems facing the study of music in Indian secondary schools and tertiary institutions and the perceptions of the society about Music as school courses. This study was conducted in Arts faculty of Shri. Shivaji Arts, Commerce and Science College, Akola, Maharashtra, India which offers music as one of the career options. Seven hundred had opted for Arts faculty of which 250 had chosen music as career option. This consisted of 96 females and 154 males with ages ranging from 16-24 years. The questionnaire consist of

a. Why they choose music as a career?
b. Whether they encountered any objections from their parents for choosing music?
c. Did they choose music as the last resort after failure to make entry requirements for other courses?
d. Whether they did music in their secondary schools;
e. What was their musical background; whether they sang in the church choir, came from a family of musicians, participated in any form of communal musical activities, etc.
f. What was their role model in music?
g. What the public perception of school music and music scholars is?
h. Whether the traditional stigma attached to music and music practitioners has reduced? What they intend to achieve with their music education, (e.g. to be a pop star? to promote serious music?)
i. Whether the training given to them in Indian institutions prepares them to compete and fit properly into the saturated labor market; and also compete favorably with their peers studying other disciplines and on the global stage? And
j. Students were asked to comment on the provision of facilities and education structures and availability of competent instructors. We distributed the questionnaire to the respondents who were guided on how to properly answer them. After completion and collation, the responses were analyzed and the frequencies were then used as percentages.

Findings:

The study group comprised of 250 candidates who enrolled for music. Of those 250 candida 61.6% (154) were males and 38.4% (96) were females.

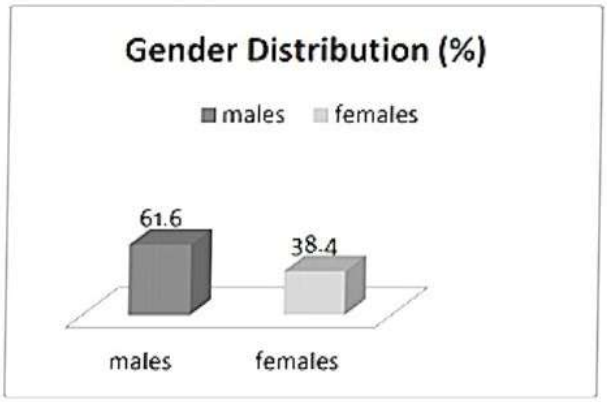

Fig: I Gender Distribution of enrolled Students

As per the questionnaire reason for choosing music as a career were broadly categorized i following reasons:

Table no. I: Reasons for choosing Music

Reason for choosing Music	n	Percent (%)
Passion for Music	42	16.8
More scoring subject	67	26.8
Low qualifying percentage for music	83	33.2
Background in Music	38	15.2
Other	20	8
Total	250	100

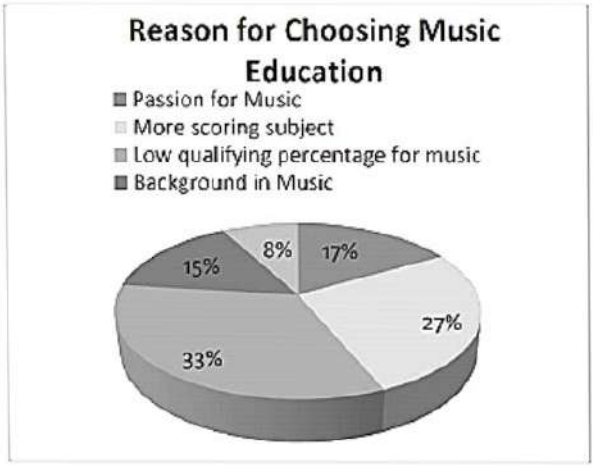

Fig: II Reasons for choosing Music in enrolled student

a. Students had problems convincing their parents about their choice of music as a career. 69% of the population said their parents disliked music as a career for their wards. It was particular visible in the responses of the female respondents whose parents felt it is a profession for men not women, while others had problems drawing lines between music as vocation and avocation.

b. The findings also indicated that most respondents choose music out of frustration of not making the required grades for their first choice courses and their attempt to get admission to the university in any other available courses with a lower requirement.

c. The age-long stigma attached to music is still quite prevalent in contemporary times, as undergraduates still encountered derogatory remarks from the society on their choice of music as a course and profession.

d. As a follow-up to the aforementioned, most of the respondents generally chose pop icons, both local and international, as their role models and would rather chart and pursue their career in popular music because of the immediate financial rewards rather than a career in classical music.

e. Students showed total disappoint regarding the training, facilities, and instructors in most Indian institutions. A total of 75% of the respondents were of the opinion that facilities used for instruction were inadequate and obsolete; 39% opined that more competent and well-trained instructors should be employed; and 40% expressed that

the curriculum should be broadened to cater for and accommodate different areas of interest of students as some would like to specialize in areas, such as, studio management, entrepreneurial or music business, music therapy, and other specializations that were not currently offered in most Indian institutions.

Recommendations:

In this paper, we have looked at the problems confronting music education in India. We found out about problems of supporting music education. Some ways these problems can be adequately tackled are by the tripartite parties of parents-society-government. We recommended that parents should be properly enlightened about the usefulness of music education and should allow gifted pupils to pursue a career in music. We also propose that the mass media should do more to promote music education by offering programs that will show the ideals of music education. Likewise, guidance counselors must double their efforts in giving proper advice to pupils and parents on career choice and paths. The society should be educated on the usefulness of music education and its benefits to the society. Finally, government should not neglect the arts and should do more to fund it for "art they say is life." The curriculum planner should also look at the contents of music curriculum and include local content that would make music education more relevant and meaningful to the society. we should respect the contributors for the developments of music education in India.

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Performance of PMFBY Crop Insurance Scheme in India

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Research Paper - Commerce

Introduction :

Agriculture is livelihood for majority of the population and can never be underestimated,but agriculture and perils both are synonymous in Indian context due to many reasons such as increasing population, increasing number of marginal land holdings, dependency on climatic situation for farming,etc. Crop insurance is to use as risks management policy in agriculture sector. Hence Indian governments introduce the various agriculture insurances schemes in India from time to time. In 2016, PradhanMantriFasalBimaYojana(PMFBY) introduced under government flagship.It avails to offer financial support to farmers suffering crop loss or damage arising out of various risks and to protects farmers from production risks. It took overNational Agricultural Insurance Scheme (NAIS) and Modified National Agricultural Insurance Scheme (MNAIS). To take technology assistance for implementing the scheme efficiently, National Crop Insurance Portal (NCIP) developed. It provides cover to food crops i.e., cereals, millets and pulses, oilseeds, annual commercial and annual horticultural crops.It covers prevented planting situations up-to post harvesting losses risks. From the implementation of this scheme, it provided assurance to 1,49,87,948 average numbers of farmer's applications in kharif seasonsand 63,28,446 in rabi seasons as per agriculture insurance company report. 2,93,24,109 total numbers of farmers benefitted against approved claims

got from this scheme. The research study is to review and analyse performance of PMFBY crop insurance scheme in India.

Need of Study:

Every agriculture insurance scheme is provided by the government for the betterment of farming society of country by providing insurance cover to the various farming risks. The PMFBY scheme also avails to aim at supporting sustainable production in agriculture sector by protecting risks in this sector. Although scheme is efficient, review of the scheme is needed for effectively implementation scheme which provides better coverage of area, crops, farmers and risks. Hence there is need of study to review and analyse the performance of PMFBY crop insurance scheme.

Review of Literature:

Rai, R. (2019) studied the PradhanMantriFasalBimaYojana (PMFBY). In his study, he assessed the PMFBY on secondary data. The study highlighted that the rationale of crop insurance with features of said scheme. It provided comparisons among NAIS, MNAIS & PMFBY schemes. It analysed data related to insured farmers, claims paid, gross premium area insured, and farmers benefited. The study expressed need that failure of some fundamental issues must be discussed that mitigates risks in agriculture for farmers and food security.

Singh., R. S. (2018) evaluated the PMFBY scheme in Uttar Pradesh. It was found non loanee farmers were insured lower than loanee farmers. The coverage of area insured in hectors was limited in rabi seasons than kharif seasons. The premium amount per insured farmers was slightly higher in rabi 2017 as compared to kharif 2016. It was found that the amount paid of premium also higher than compensation amount paid to the farmers.

Gulati, A.; Terway, P., Hussain, S. (2018) had studied key issues in crop insurance in India. The study is review of PMFBY scheme. It was found that the scheme has faced several challenges during its first year of implementation which affect to extension of cut off dates for registration resulting in high premium rates; delay in submission of yield data; lack of trust in the quality of such data as they are not being video recorded and delay in payment of premium subsidy by the state governments to the insurance companies, etc.

The study suggested use of high technology and a portal with linking Core Banking Solution (CBS).

Objectives of Study:

1. To review the PMFBY scheme of crop insurance.
2. To analyse the performance of PMFBY crop insurance scheme.

Data Collection& Analysis:

The Proposed study is based on secondary data related to PMFBY crop insurance scheme. Secondary data are collected from web portal of Agriculture Insurance Company. Tools and techniques used for study for the analysis of data are data descriptors, percentage and various charts.

Descriptive Statistical Analysis of PMFBY Crop Insurance Scheme Data:

Table no. 1 Total Number of Applications for PMFBY Season Kharif and Rabi from 2016-2020

Year	Total No. of Applications for PMFBY Season Kharif	Total No. of Applications for PMFBY Season Rabbi
2016	1,74,40,964	79,71,001
2017	1,20,89,763	33,39,186
2018	65,92,830	35,25,736
2019	2,03,26,191	63,33,568
2020	1,84,89,990	1,04,72,738

The table no. 1showed thattotal number of applications for PMFBY season kharif and rabi from 2016-2020. It showed gradual decline in total number of applications for PMFBY in both seasons up to 2018. Then in 2019 has hike in 2019 but year 2020 has showed decline in it.

Chart No. 1 Total Number of Applications for PMFBY Season Kharif and Rabi from 2016-2020

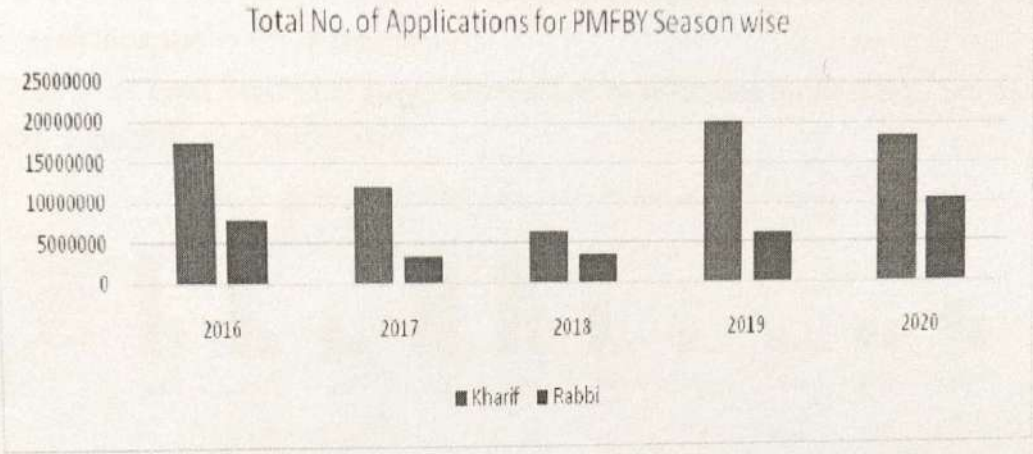


Chart no.1 pictured thatthattotal number of applications for PMFBY season kharif in 2016, 2019, 2020 had better growth of assured farmers. The total number of applications for PMFBY season Rabi in 2017 was lowest. The total number of applications for PMFBY season Rabi in every year was near about halves of kharif seasons.

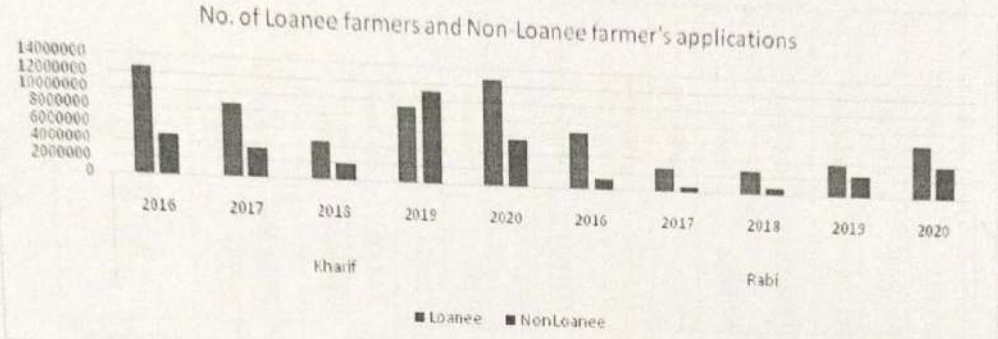
Table no. 2 Total Number of Lonee farmers and Non-Loanee for PMFBY - Seasons Kharif and Rabi from 2016-2020

Season	Year	Loanee	Non Loanee
Kharif	2016	1,27,11,506	47,29,458
	2017	86,53,539	34,36,224
	2018	45,19,827	20,73,003
	2019	91,75,678	1,11,50,513
	2020	1,28,59,414	5630576
Rabi	2016	67,88,201	11,82,800
	2017	27,56,643	5,82,543
	2018	28,08,858	7,16,878
	2019	38,60,596	24,72,972
	2020	64,74,106	39,98,632

The above table showed thattotal number of lonee farmers and non-loanee for pmfby scheme in seasons kharif and rabi from 2016-2020. In 2016 and 2020, loanee

farmers crossed the one crore number in kharif seasons as well as in 2019 only this year crossed the same by non-loanee farmers.

Chart no. 2 Total Number of Lonee farmers and Non-Loanee for PMFBY -Seasons Kharif and Rabi from 2016-2020



The above charts no.2 showed that Loanee farmer s application are approximate 'U' shape curve in kharif seasons and platy 'U' shaped curve in rabi seasons. The non-loanee farmer's application showed the gradual negative slop till 2018 then has piked in 2019in kharif season but again showed decline in rabi seasons except 2019 and 2020.

Table No.3 Descriptive Statistics of Loanee and Non-Loanee farmer's Applications

Name of Technique	Mean	Median	Maximum	Minimum	Std. Deviation	Skewness	Kurtosis	Co-efficient of Variation
Loanee	7060837	6631154	12859414	2756643	3745888	0.483238	-1.02117	53.05161241
Non-Loanee	3597359.9	2954598	11150513	582543	3152724.19	1.6420147	3.3173249	87.63994358

The above table no.3 shows the descriptive statistics of Loanee and Non-Loanee farmer's applications for PMFBY during 2016 to 2020. The mean value represents the average of aggregate of the applications during the four years period. The co-efficient of skewness is found low (0.483238) for loanee which imply that the applications for a given period have very minimumvariation in the applying for pmfby insurance as compared to the non-loanee farmer's applications. The value of The co-efficient of kurtosis (3.3173249) higher than three indicate that distribution is leptokurtic for non-loanee farmers as compared to the loanee farmer's applications (-1.02117). The value of co-efficient of

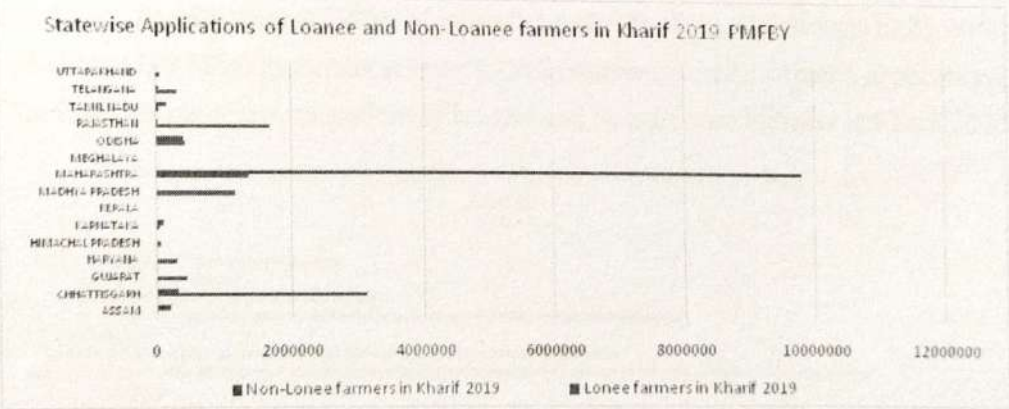
variations show that there is found more variation in the applying for pmfby scheme by non-loanee farmer than the loanee farmers.

Table No. 4State wise Applications of Loanee and Non-Loanee Farmers in Kharif 2019

State	Assam	Chhattisgarh	Gujrat	Haryana	Himachal	Karnataka	Kerala	Madhya Pradesh	Maharashtra	Meghalaya	Odisha	Rajasthan	Tamil Nādu	Telangana	Uttarakhand
Lonee farmers in Kharif 2019	18201	3132095	460883	305380	69773	60782	7665	1161891	1377976	607	440687	1690804	63726	313801	71407
Non-Lonee farmers in Kharif 2019	212223	313325	6695	7419	958	116498	350	9833	9788010	0	416173	34674	170797	55003	18555

The above table no 4 showed that the Maharashtra has greatest percentage (87.78%) of loanee as well as non-loanee farmer's applications in number in Kharif 2019.Meghalaya is the lowest in percentage of application in number

Chart No.3 State wise Applications of Loanee and Non-Loanee Farmers in Kharif 2019



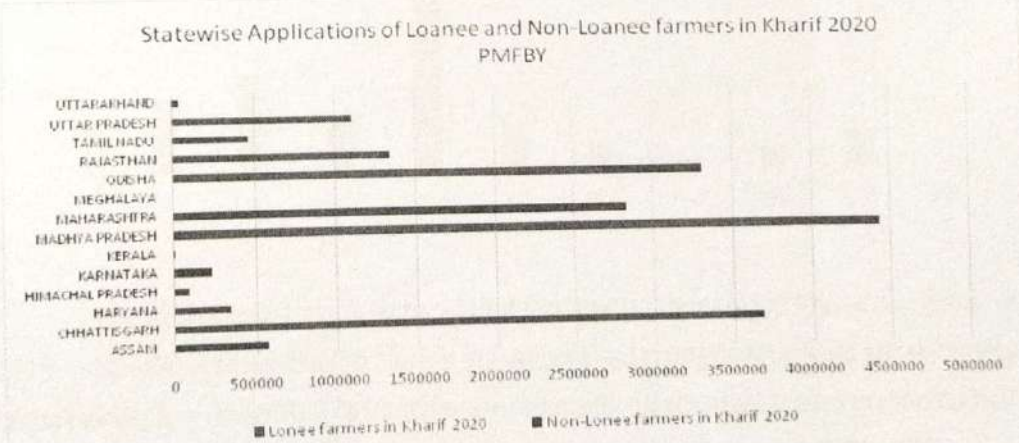
The above table no. 3 depicted that the Maharashtra has greatest percentage (87.78%) of loanee as well as non-loanee farmer's applications in number in Kharif 2019. Chhattisgarh state has greatest loanee farmer's applications among all states.

Table No.5 State wise Applications of Loanee and Non-Loanee Farmers in Kharif 2020

State	Assam	Chhattisgarh	Haryana	Himachal	Karnataka	Kerala	Madhya Pradesh	Maharashtra	Meghalaya	Odisha	Rajasthan	Tamil Nādu	Uttar Pradesh	Uttarakhand
Lonee farmers in Kharif 2020	9334	3459259	317294	85480	28436	10473	3790934	59675	129	2685647	1282192	40422	1062236	27903
Non-Lonee farmers in Kharif 2020	560991	226584	30526	383	207645	3530	641332	2774582	1	628783	57541	432655	45379	20644

The above table no. 5 showed that the Maharashtra has near about half of total no. of number of non-loanee farmer's applications in number in Kharif 2020. Meghalaya is the lowest in percentage of application in number in 2020 also. It is also depicted that the Maharashtra has greatest percentage (49.28%) of non-loanee farmer's applications in number in Kharif 2020 followed by Madhya Pradesh (11.39%), Odisha (11.16%) and Assam (9.96%) states. While Madhya Pradesh (29.48%), Chhattisgarh (26.90%) and Odisha (20.88%) had greatest share in total number of loanee farmer's applications.

Chart No.4 State wise Applications of Loanee and Non-Loanee Farmers in Kharif 2020



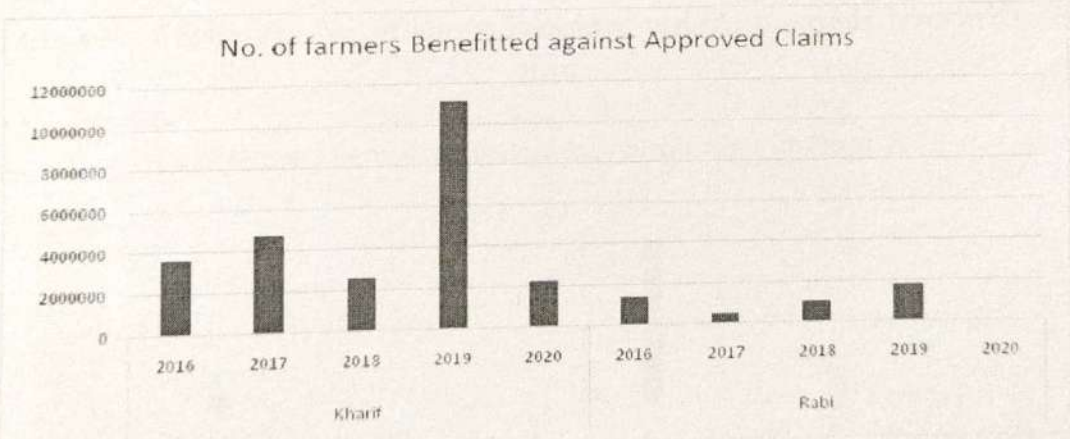
The above chart no.4 depicted that the Maharashtra shared near about half of in non-loanee farmer's applications while Madhya Pradesh, Chhattisgarh and Odisha shared highest loanee farmer's applications of total applications.

Table no.6Number of Farmers Benefitted against Approved Claims

Season	year	No. of Farmers Benefitted against Approved Claims	Total No. of Applications	Percentage of No. of Farmers Benefitted against Approved Claims to number of Farmer's applications
Kharif	2016	3665672	17440964	21.02
	2017	4769542	12089763	39.45
	2018	2583834	6592830	39.19
	2019	11179163	20326191	55.00
	2020	2320602	18489990	12.55
Rabi	2016	1388482	7971001	17.42
	2017	500779	3339186	15.00
	2018	1082860	3525736	30.71
	2019	1833175	6333568	28.94
	2020	NA	10472738	0.00

The above table no. 6 showed that in kharif season in every year farmers got benefitted rather than rabiseasons. In 2019 kharif season,no. of farmers benefitted against approved claims has highest in numbers where is 2017 rabi season has lowest in numbers of benefitted farmers.

Chart No. No. 5 of farmers Benefitted against Approved Claims



The above chart no. 5 showed that farmers got benefitted above one crore in 2019's kharif season having the highest in numbers and they got benefitted above twenty lakhs having lowest in 2020's kharif seasons among all seasons. It also presented that

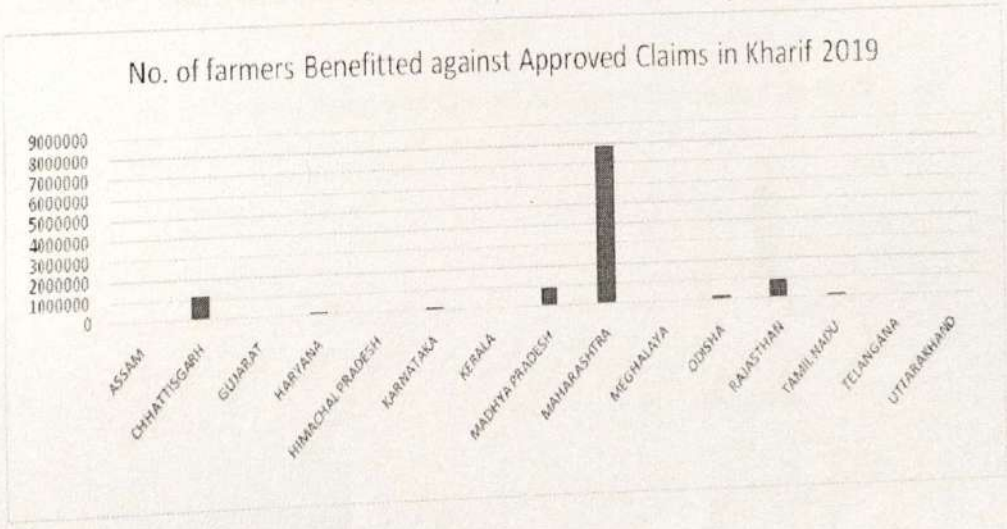
they got benefitted the highest in numbers in 2019's rabi season and they got benefitted lowest in numbers in 2017's rabi season.

Table No. 7 State-wise No. of farmers Benefitted against Approved Claims in Kharif 2019

State	Assam	Chhattisgarh	Gujrat	Haryana	Himachal Pradesh	Karnataka	Kerala	Madhya Pradesh	Maharashtra	Meghalaya	Odisha	Rajasthan	Tamil Nâdu	Telangana	Uttarakhand	
No. of farmers Benefitted against Approved Claims in Kharif 2019	0	1165434	3976	109055	37060	106905	5558	842745	7852621	544	141386	803314	90219	0	20346	Median of data = 90219

Table No. 7 State-wise No. of farmers Benefitted against Approved Claims in Kharif 2019In the above table Maharashtra showed the highest no. of farmers benefitted against approved claims in kharif 2019 while Meghalaya showed the lowest no. of farmers for same followed Assam and Telangana had no one. Benefitted farmers in seven states i.e. Assam, Gujrat, Himachal Pradesh, Kerala, Meghalaya, Telangana and Uttarakhand were having less than median numbers but in remaining seven states were having more than median numbers while Tamil Nâdu was having zero deviation from median.

Chart No. 6 State-wise No. of farmers Benefitted against Approved Claims in Kharif 2019



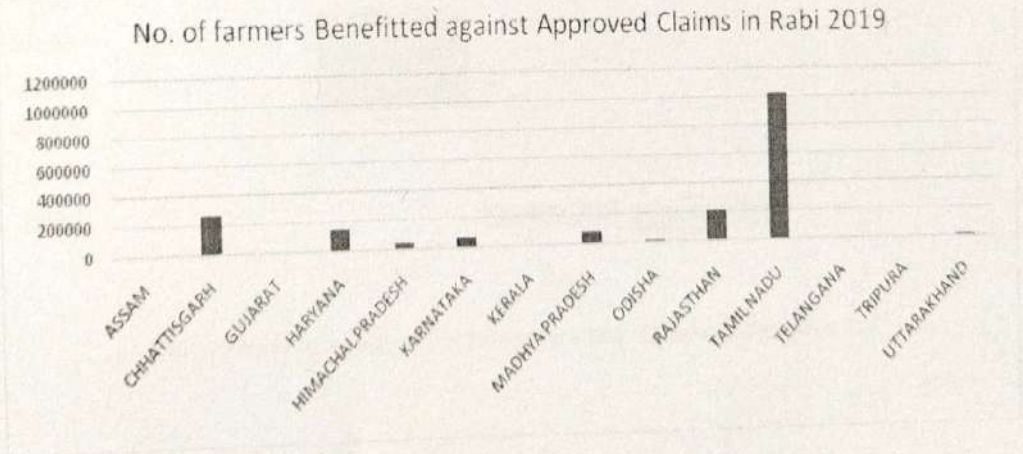
The chart no. 6 showed that Chhattisgarh, Madya Pradesh Maharashtra and Rajasthan were having significant numbers of benefitted farmers specially Maharashtra in Kharif 2019.

Table no. 8 State-wise No. of farmers Benefitted against Approved Claims in Rabi 2019

State	Assam	Chhattisgarh	Gujrat	Haryana	Himachal Pradesh	Karnataka	Kerala	Madhya Pradesh	Odisha	Rajasthan	Tamil Nadu	Telangana	Tripura	Uttarakhand	
No. of farmers Benefitted against Approved Claims in Rabi 2019	0	258143	146	142455	34185	64011	493	74374	9406	211473	1026731	0	2516	9242	Median of data = 21796

In the above tableno. 8 showed that Tamil Nâduthe highest no. of farmers benefitted against approved claims in rabi 2019 while Gujrat showed the lowest no. of farmers for same followed Assam and Telangana had no one. Benefitted farmers in seven states were having less than median numbers but in remaining seven states were having more than median numbers.

Chart No. 7 State-wise No. of farmers Benefitted against Approved Claims in Rabi 2019



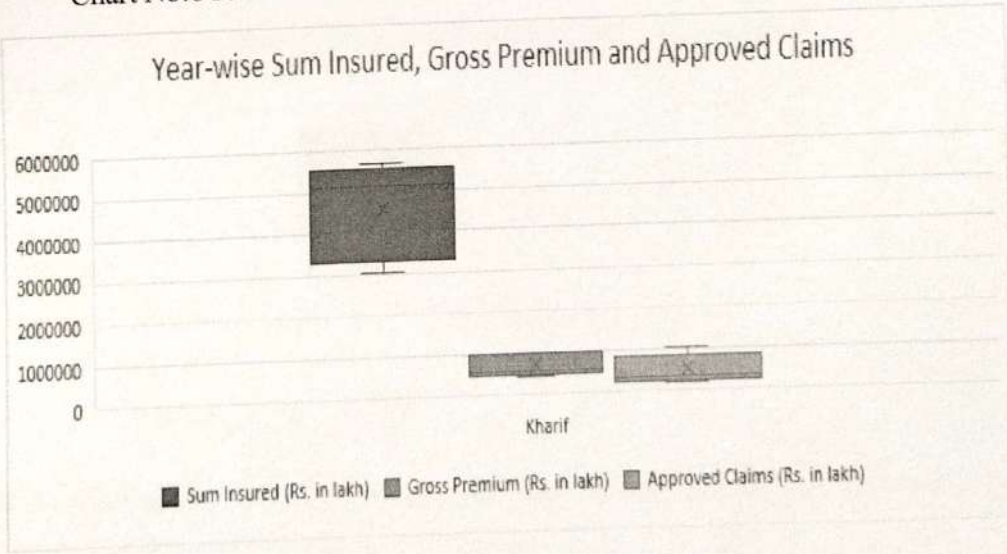
The chart no. 7 showed that Chhattisgarh, Haryana, Rajasthan and Tamil Nâdu were having significant numbers of benefitted farmers specially Tamil Nâdu in Rabi 2019.

Table No. 9 Year-wise Sum Insured, Gross Premium and Approved Claims

Year	Season Name	Sum Insured (Rs. in lakh)	Gross Premium (Rs. in lakh)	Approved Claims (Rs. in lakh)
2016	Kharif	5095204.2	587706.59	325146.72
2017	Kharif	3622643.21	540402.38	677951.17
2018	Kharif	3036687.95	448138.12	365614.15
2019	Kharif	5379540.3	966144.13	1028674.66
2020	Kharif	5686170.64	985828.72	220781.01
Comparison with percentage 2016 to 2020	Increase (+) or decrease (-)	+89.61%	+59.62%	-32.10%

The above table no. 9 showed that Year-wise Sum Insured, Gross Premium and Approved Claims in kharif seasons. Sum insured and gross premium were increased 89.61% and 59.62% respectively as compared with the 2016 data while approved claims was not for same data.

Chart No.8 Year-wise Sum Insured, Gross Premium and Approved Claims



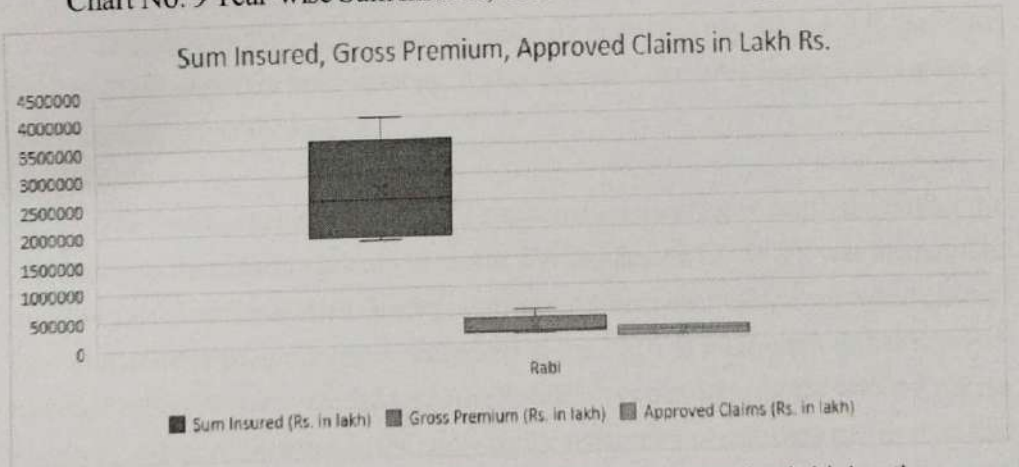
The above chart no. 8 showed thatyear-wise sum insured's median is higher than gross premium and approved claims in kharif seasons.

Table No. 10 Year-wise Sum Insured, Gross Premium and Approved Claims

Year	Season Name	Sum Insured (Rs. in lakh)	Gross Premium (Rs. in lakh)	Approved Claims (Rs. in lakh)
2016	Rabi	3215488.44	202725.04	221533.62
2017	Rabi	1855862.28	147638.34	88129.51
2018	Rabi	1944295.13	168568.88	173660.02
2019	Rabi	2559347.22	276958.91	194913.96
2020	Rabi	4022938.62	555935.36	Awaited
Comparison with percentage 2016 to 2020	Increase (+) or decrease (-)	+79.93	+36.47	-12.02

The above table no. 10 showed thatYear-wise Sum Insured, Gross Premium and Approved Claims in rabi seasons. Sum insured and gross premium were increased 79.93% and 36.47% respectively as compared with the 2016 data while approved claims was not for same data.

Chart No. 9 Year-wise Sum Insured, Gross Premium and Approved Claims



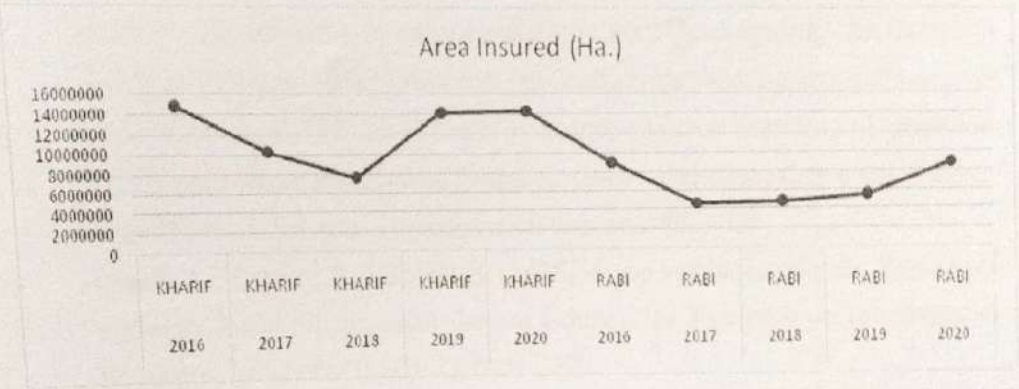
The above chart no. 9 showed thatyear-wise sum insured's median is higher than gross premium and approved claims in rabi seasons.

Table No.11 Year-wise Area Insured

Year	Season Name	Area Insured (Ha.)	Year	Season Name	Area Insured (Ha.)
2016	KHARIF	14855991.96	2016	RABI	9013693.02
2017	KHARIF	10260850.07	2017	RABI	4683936.01
2018	KHARIF	7658062.51	2018	RABI	4872425.09
2019	KHARIF	14214705	2019	RABI	5577775.78
2020	KHARIF	14321254.02	2020	RABI	8848553.92

In the above table no. 11 showed that area insured under pmfby scheme. Area insured under pmfby was highest in 2016 then lowest in 2018 in kharif season while it was highest in 2016 and lowest in 2017.

Chart No. 10 Year-wise Area Insured



The above chart no. 10 showed that only in 2016, area insured is higher than 2017 to 2020 period in both seasons. It also depicted that area insured was more in kharif seasons than rabi seasons.

Conclusion:

The study concludes that PMFBY scheme is providing cover to the farmer for combating to the risks in agriculture sector. Performance of PMFBY was analysed in study by the data of benefitted farmers, sum insured, area insured and approved claims. The total number of applications increased in the 2016 to 2020 period that showed insurance cover is also increased. Due to the PMFBY's compulsion for the loanee farmers, there is found more variation in the applying for scheme by non-loanee farmer than the loanee farmers. Percentage of number of farmers benefitted against approved claims to number of farmer's applications is not more than 50 percent in during period except

2019 kharif season. While the performance of the scheme (farmers benefitted against approved claims) in some states including Maharashtra, Rajasthan, Tamil Nadu, Madhya Pradesh, Chhattisgarh, Haryana is greater than the other states. Sum insured and gross premium's comparison with percentages of 2016 to 2020 showed growth while approved claims showed negative growth. Area insured in hectors declined during the 2016 to 2020. The above finding showed that some modifications are needed in pmfby scheme. After making modifications, it will be proved great scheme for combating with the risks in agriculture sector.

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1

Crypto Currency :- A New Money

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Research Paper - Commerce

ABSTRACT

In recent times following dynamic development of various forms of e-business, dematerialized money has emerged however, in costantly changing conditions it is very difficult to grap the essence of the called e-money or crypto gerreney.From few year onwards cryptocurrencies grab a hot topic in the financial world. cryptocurrency is a digital or internet or virtual currency that uses cryptography for security.concept of cryptocurrency is alittlehrd to accept, but it is easy to use it is considereddifficult because it is entirely different from our conventional currencies that we people are using since 2008. This paper investigate about cryptocurrency present legal as well as future government moves impact on these currencies the paper also analysis investment risks in both bitcoin and gold

Key Words : Cryptocurrency, opportunities, government future more on crypto currency, RBI.

Introduction:

Digital currencies are capable of developing existing payment systems and financial institutions, as they represent a new understanding of the form of money and the security

of transaction for example. The united states has been actively conducting research and actions to introduce crypto currencies into the internal payment system since 2019. At the it end of 2019 the US congress passed a bill for consideration called the "Crypto - Currency Act of 2020"

It reviewed the procedure for the recognition, licensing and registration of digital currencies as a form of payment and also established a list of state institutions responsible for the regulation and control of the new currency. The introduction of crypto currencies has revolutionized the international payment system in a scale that just few year ago were unimaginable in1983, the American crypto graphic is a digital David chaum conceived an anonymous cryptographic electronic money called e-cash, later in 1995, he implemented it through digi cash, an early form of cryptopgraphic electronic payments which required uses software in order to withdraw notes from a bank designate specific encrypted keys before it can be sent to a recipient. This allowed the digital currency to be untraceable by the issuing bank the government, or any third party. A cryptocurrency is difficult to counterfeit because of its security feature.A defining feature of a crypto currency is that it is not issued by central authority. It is completely decentralized.

Now a days many countries in the world have following towards digital currency.

OBJECTIVE OF THE STUDY:

* To understand the concept of crypto currency it types &its working process.
* To Analysis legal status, and opportunities of Bitcoin in India.
* To compare investment Risk between Bitcon &Gold.

RESEARCH methodo logy:

The Secondary data necessary for completing the investigation will be collecting from the published sources in the academic libraries, websites, books journals, magazines, etc.

HYPOTHESIS:

Ho : - There is no difference in the volatility of values of gold's and Bit coins in India.

H1 :- There is difference in the volatility of values of gold and bit coins in India.

Meaning of Crypto Currency:

Crypto currency is decentralized digital money based on blockchain technology.

we may be familiar with the most popular versions, BitcoinEthereum, but there are more than 5000 different crypto currencies in circulation. You can use crypto to buy regular goods and services although many people invest in crypto currencies as they would in other assets like stock or precious metals.

Types of crypto currencies:

Crypto currency is designed to work as a medium of exchange. The number of crypto currencies available over the internet and also growing. A new currency can be created at any time. By market capitalization, Bitcoin is the largest block chain network

Following are the 10 largest trading crypto currencies by market capitalization as a tracked by coin market cap., a crypto currency data.

Global Table:

Name of crypto currency	Market capitalization
Bit coin	$ 1.2 trellion
Ethereum	$ 485.2 billion
Binance Coin	$ 80 bill
Cardano	$ 71.7 bill
Solana	$ 64.2 bill
XRP	$ 51.8 bill
Porkadot	$ 45.1 bill
USD Coin	$ 32.4 bill
Doge Coin	$ 32.1 bill

Data current as 18 Oct. 2021

The Bitcoin has maximum dominance in the crypto currency market with around 45 % of market share& market capitalization. And other crypto currencies are also available in market as namely Ripple (XRP) pioneers unicoin, zebpay, coinex, Bitcoin India etc.

How does Bitcoinwork ?

Each Bitcoin is basically a computer like which is stored in a "digital wallet" app

on a smart phone or computer.

People can send Bit coins or a part of one to your digital wallet and you coin send Bit coin to other people. Every single transaction is recorded in a public list called the block chain. This make to it possible to trace the history of Bitcoins to stop people from spending coins they do not own, making copies or undoing transactions.

Introduction of Bitcoin:

One of the most popular crypto currency wallet using is Bit Coin which was invested by as unknown person or group of people using the name Satoshi Nakamoto in 2008. Bit coin is crypto currency a form of electronic cash. It is decentralized digital currency that can be sent from used to user on the peer to peer Bit coin network without the need for intermediaries, where transaction happen through public ledger called blockchain, handling users data anonymously. Ten years since its introduction.

Bit coin is today the most widely used and accepted digital currency although. Bit coin is commonly referred to as a crypto currency.Bit coin is a system for electronic transactions without relying on trust. But other electronic payments required a trusted intermediary, such as bank or electronic unit in order to verity a transaction. Instead of relying on a single system relies upon a large number of computing miners to very transaction. Bit coin regulate and generate units of currency using the rules of cryptography. Bit coin are completely virtual coins designed to be self contained you their value. There is no need you bank to move and store money. Bit coins are not physically present, so that only balance are kept on a public wallet in the cloud.

All Bit coin transaction is verified by a massive amount of computer power. A personal database that you can store on your computer drive, on your smart phone on your table and personal wallet to another.

Features of Bit coin:

Features of Bit coin is as below.

Control against fraud :-

It provides users with top level of protection against most common frauds like charge back or unwanted charges. Because the security of users can encrpt their wallet and have complete control over their money. So their is no chance of any type of fraud.

Transparency :-

All Bitcoin transaction are public and transparent to all users. The Block chain stores all transaction details. were users can be any time very.

Globally accessible :-

Bitcoin allows any banks business or individual to securely send and receive payment anywere at any time in few minutes. All types of payments in the world are acceptable.

Cast efficient :-

With Bit coin transactions can be possible directly without any mid person.

Legal Status of cryptocurrency in India:

The legal status of Bitcoin and related crypto instrumentvaries substantially from. Country to country and is still under defined or changing in many of them. Where as the majority of countries do not make the usage of Bitcoin it self illegal. Its status as money varies with differing regulatory implications. With the exponential development and unprecedented advancements in the field to technology in India.especially with the emergence of coivd-19, the fintech sector has been on a path of constant rise with the gaining popularity and awareness amongst the people of India with respect to crypto currency. In India apex financialauthority you example, The Reserve Bank of India, has understood cryptocurrency as a for of digital / virtual currency generated through Series of computer codes, that rely on cryptography which is encryption and is thus independent of any central issuing authority person.

Being an untapped, unregulated market with a capability of over a trillion dollars. India also saw a massive surge of crypto currency exchanges. Witnessing the massive popularity of the crypto market. Its usage within a year and potential revenue loss the Government of India the regulators and authorities began to take notice and as a consequence is 2013 the RBI issued a press release cautioning the public against dealing in virtual currencies including Bitcoin. In November 2017 the Government of India constituted a high-level Inter - ministerial committee to report on various issues pertaining to the use of virtual currency and subsequently in July 2019 this committee submitted its report recommending a blanket ban on private crypto currencies in India. Despite the fact

that report from the inter ministerial committee was pending at the beginning of April 2018 the RBI issued a circular preventing all commercial and co-operative banks,small financial banks payment banks and NBFC from Not only dealing in virtual currencies but also directing them to stop providing services to all entities.

In 2021 The Indian government is now considering the introduction of a new bill titled "Crypto currency and Regulation of official Digital currency Bill - 2021" ("New Bill") Which is similar in spirit to its previous version how ever intends to ban privatecryptocurrencies in Indian with certain exceptions to promote the underlying technology and trading of creating an official digital currency which will be issued by the RBI

The following table showing trends of Bit coin value in respect of Indian Rupes.

Gold Value

Gold value (10 grams)			Bitcoin value		
Date	Price	Change %	Date	Price	Change %
Jan 2021	34,692.79	-1.71%	Jan21	26,37,105	24.64%
Dec 2020	35,914.04	6.41%	Dec-20	21,15,850	45.18%
Nov 2020	31,716.05	-5.63%	Nov-20	14,57,389	41.63%
Oct 2020	35,615.24	-0.81%	Oct-20	10,28,993	29.89%
Sep 2020	36,198.87	-4.22%	Sep20	7,92,221	-7.18%
Aug 2020	39,461.82	-0.46%	Aug-20	8,53,531	0.62%
Jul 2020	39,824.19	9.20%	Jul-20	8,48,261	22.87%
Jun 2020	33,397.56	3.23%	Jun-20	6,90,369	-3.49%
May 2020	31,339.62	3.75%	May-20	7,15,323	10.30%
Apr 2020	29,114.60	6.74%	Apr-20	6,48,529	34.20%
Mar 2020	25,555.22	0.73%	Mar-20	4,83,270	-21.91%
Feb 2020	25,185.69	-1.68%	Feb20	6,18,838	-7.53%
Jan 2020	26,053.19	3.79%	Jan20	6,69,214	30.35%
Dec 2019	24,186.47	3.62%	Dec-19	5,13,407	-5.16%
Nov 2019	22,524.01	-3.03%	Nov-19	5,41,312	-16.66%
Oct 2019	23,953.75	2.77%	Oct-19	6,49,510	10.86%
Sep 2019	22,680.36	-3.49%	Sep19	5,85,865	-14.52%
Aug 2019	24,348.48	6.15%	Aug-19	6,85,360	-1.32%
Jul 2019	21,609.00	1.36%	Jul-19	6,94,522	-6.68%
Jun 2019	21,033.70	7.14%	Jun-19	7,44,275	25.36%
May 2019	18,322.33	0.98%	May-19	5,93,713	52.46%
Apr 2019	17,966.72	-0.74%	Apr-19	3,89,434	34.57%
Mar 2019	18,235.80	-1.81%	Mar-19	2,89,395	4.89%
Feb 2019	18,914.50	-0.63%	Feb19	2,75,899	10.61%
Jan 2019	19,154.56	2.74%	Jan19	2,49,431	-6.63%
Dec 2018	18,146.78	4.21%	Dec-18	2,67,136	-5.19%
Nov 2018	16,710.73	0.35%	Nov-18	2,81,748	-40.28%
Oct 2018	16,594.59	1.54%	Oct-18	4,71,799	-1.70%
Sep 2018	16,096.00	-0.70%	Sep18	4,79,973	-3.62%
Aug 2018	16,325.17	-2.45%	Aug-18	4,97,978	-6.15%
Jul 2018	17,155.76	-2.52%	Jul-18	5,30,589	21.29%
Jun 2018	18,055.30	-3.68%	Jun-18	4,37,470	-13.36%
May 2018	19,460.25	-1.70%	May-18	5,04,930	-17.63%
Apr 2018	20,138.45	-0.48%	Apr-18	6,13,004	36.06%
Mar 2018	20,334.76	0.48%	Mar-18	4,50,550	-33.03%
Mean	24457.61			694462.66	
Std deviation	7321.635818			484932.45	
Co-Variance	0.299360233			0.6982844	
Correlation coefficient	0.640122673				

Inference :-

In above table on tail test T value (7.79) is greater than table value of+ (1.6909) so alternative hypothesis have been accepted that means there is adifference between is changing in the value of gold & Bit coin. But as per two tailed test calculated "T" Value (1.55909) is lesser than table value of (2.0322) so null hypothesis has been accepted that means there is no significant difference between in changing in the value of gold & Bitcoin.

Conclusion:

The dynamically growing interest in cryptocurrencies is due to many reasons including transaction anonymity, crypto currency offers a new effective and attractive model of payment methods that can boost companies and operators revenues.

Almost a clear picture of the size of crypto currency use has been drawn from my analysis of the conducted study although the pilot study has been conducted with relatively small sample but the result showed one a preliminary perception about the use, the growth, the trust of using and future expectations of crypto currency.Crypto currency is bring more positive changes to e-Business and e-payment sector, However crypto currency doesnt get that much trust yet. many concerns, challenges and issues are existing is many cryptocurrency platform.

Until crypto currency is being will regulated and controlled, users need to take extra precautions of using such a virtual money.In 2021 Indian government is exploring the creation of state backed digital currency issued by the RBI. While banning private ones dike Bitcoin. Hence trading in cryptocurrency is dangerous.

Change in the value of gold was two in now 2020. It was 5.63 % and it was very high month of July 2020. It was 9.20%.

Volatility of gold value from March 2018 to 2021 is very less (means changes in value of gold is consistent)

Volatility of Bitcoin value from March 2018 to 2021 is very high (means changes in the value of Bit coin is inconsistent).

Is comparing to changes Bitcoin and gold here researcher found that there is significant changes in their value.

Hence investing in gold is better than investing Bitcoin. The Cryptocurrency field creates a lot of research opportunities and many studies need to be done in order to provide scientific contents.

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Synthesis, Characterization and Hyperthermic Evaluation of PEGylated Superparamagnetic $MnFe_2O_4$ Ferrite Nanoparticles for Cancer Therapeutics Applications

Prashant B. Kharat, Sandeep B. Somvanshi,* Saurabh B. Somwanshi, and Anuja M. Mopari*

Poly(ethylene glycol) (PEG)-coated superparamagnetic $MnFe_2O_4$ ferrite nanoparticles are of great interest for application in magnetic fluid hyperthermia (MFH) due to their heat generation capability in an external alternating magnetic field, besides biocompatibility, and surface properties. MFH has emerged as a promising therapeutic approach for cancer treatment and is based on controlled heating tumor tissue through the accumulation of $MnFe_2O_4$ ferrite nanoparticles within cancer cells. In the present work, $MnFe_2O_4$ superparamagnetic ferrite nanoparticles via the chemical combustion method are synthesized. The preparation of PEGylated $MnFe_2O_4$ ferrite nanoparticles, which involves the attachment of such molecules at the surface, without the need for coupling agents or prior modification on the species involved. The conjugation of folate onto $MnFe_2O_4$ ferrite nanoparticles is confirmed by FTIR spectroscopy. The $MnFe_2O_4$ ferrite nanoparticles are colloidal stable. The obtained targeted PEGylated $MnFe_2O_4$ ferrite nanoparticles show superparamagnetic behavior with a saturation magnetization of 78.68 emu·g^{-1} at 300 K. Their specific absorption rate (SAR) ranged from 43.2 to 19.5 W g^{-1} in an alternating magnetic field of 5—20 kA m^{-1}. The heat generated is sufficient to raise the sample temperature to the therapeutic range used in MFH establishing this system as promising candidates for use in MFH treatment.

1. Introduction

The field of nanomedicine is improving vastly with the new advancements in the area of nanoscience and nanotechnologies.[1,2] The nanoscale materials are promising for various kinds of bioapplications due to their smaller size, superior physicochemical properties, improved performances, etc.[3,4] Recently, cancer nanomedicine is advanced by the different kinds of diagnosis and treatment approaches. Among these approaches, magnetic nanofluid hyperthermia (MNH) is promising, as it involves non-destructive tools for the treatment of malignant tumors.[5] Primarily, nanoscale magnetic particles (NMPs) are being used in the MNH to produce the inductive heat by the different kinds of hysteresis and relaxations losses. In the last decades, the spinel nano ferrites (SNFs) such as $MnFe_2O_4$,[6] $ZnFe_2O_4$,[7,8] $MgFe_2O_4$,[9] $CoFe_2O_4$,[10] etc., have been widely studied for the MNH applications. Among these SNFs, the $MnFe_2O_4$ are promising due to their superior properties such as moderate magnetization, easy preparation, chemical stability, etc.[11] The surface modification of the nanomaterials plays an important role in their fruitful use in biomedical applications. The solution combustion method has been proven to be an efficient route for the different kinds of nanoscale materials.[12,13] Recently, various kinds of surface coating agents such as oleic acid, ethylene glycol, polyethylene glycol (PEG), etc., were studied by the researchers. The coating of PEG on the core of SNFs may provide enhanced dipersion ability and biocompatibilty. Thus, the present work aims at the preparation and surface modification of $MnFe_2O_4$ nanoferrite by combustion method. The structural, morphological, infrared, magnetic, and inductive properties of the PEGylated $MnFe_2O_4$ nanoferrites were studied by the standard techiques.

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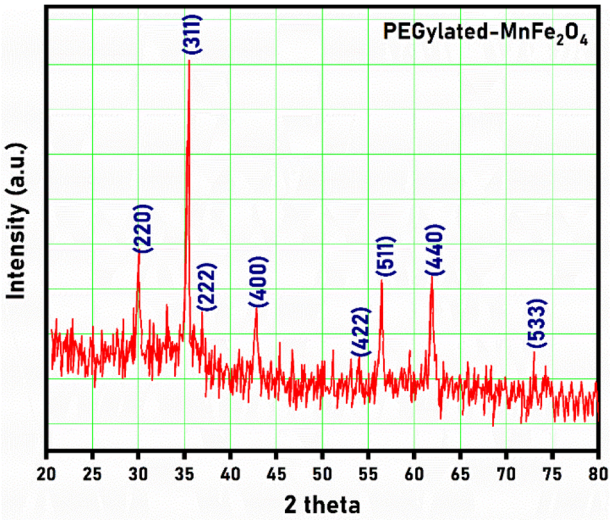

Figure 1. XRD pattern of PEGylated $MnFe_2O_4$ nano ferrites.

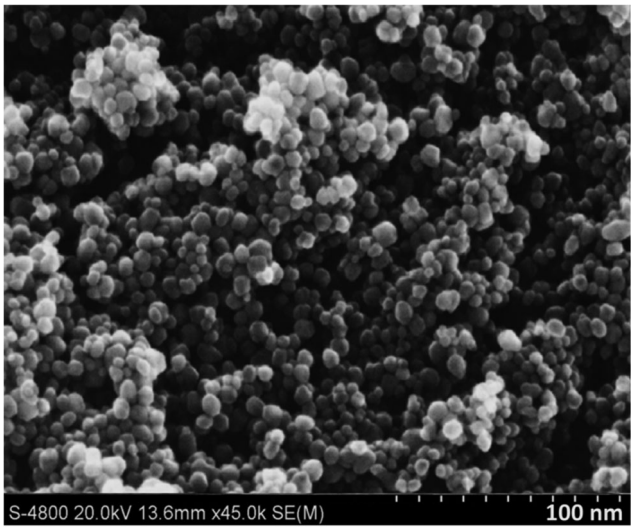

Figure 2. FE-SEM image of PEGylated $MnFe_2O_4$ nano ferrites.

2. Result and Discussion

2.1. Structural Analysis

The singular-phase form and nano-crystalline nature of the PEGylated $MnFe_2O_4$ nano ferrites were studied by XRD analysis. The XRD pattern of the prepared nano ferrites is displayed in **Figure 1**.

It is observed from Figure 1 that, PEGylated $MnFe_2O_4$ nano ferrites possess Bragg planes equivalent to the FCC spinel structure corresponding to the $Fd-3m(Oh^7)$ space-group. All the observed planes are well agreed with that are reported in the literature . The most concentrated peak (311) was utilized to determine the crystallite size by using the Debye-Scherrer's relation [14,15] and it was evaluated as 12 nm. The lattice parameter was determined by interplanar spacing and (h k l) values and is found to be 8.473 Å. Some surroundings noises were recorded in Figure 1, which is attributed to the PEG modification with amorphous nature. It discloses that the surface modification does not affect the pristine structure of $MnFe_2O_4$ nano ferrites so the noise in x-ray data can be seen from Figure 1, which reveals the existence of an amorphous layer of PEG over the $MnFe_2O_4$ ferrites nanoparticles.

2.2. Morphological Analysis

The morphology of the PEGylated $MnFe_2O_4$ nano ferrites was visualized through FE-SEM. **Figure 2** shows the FE-SEM image of the PEGylated $MnFe_2O_4$ nano ferrites. The nano-shape spherical grains with some aggregations are particularly observed in Figure 2. The aggregations in the grain were noted due to the magnetic exchanges among the Fe and Mn ions. The presence of PEG over the core of $MnFe_2O_4$ nano ferrites can be visualized from the FE-SEM image. The average grain size was determined from the FE-SEM image and is found to be around 15 nm.

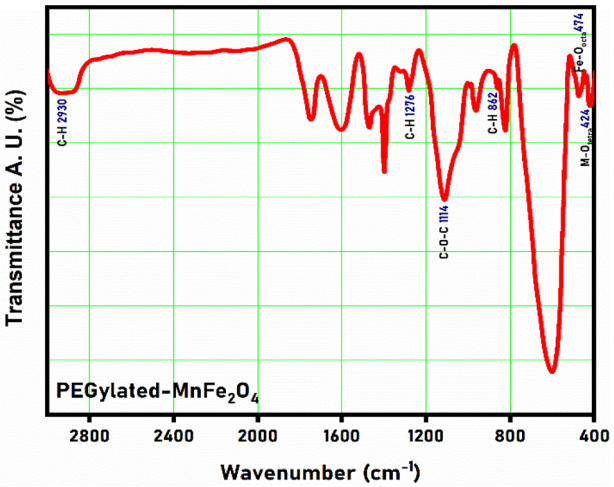

Figure 3. FT-IR spectrum of PEGylated $MnFe_2O_4$ nano ferrites.

2.3. Infrared Analysis

To confirm the functional group present over the surface of $MnFe_2O_4$ nano ferrites, FT-IR spectroscopy was utilized. **Figure 3** depicts the FT-IR spectrum of the PEGylated $MnFe_2O_4$ nano ferrites. The vibrating mode at ~2930, 1276, 1114, 862, 474, and 424 cm^{-1} confirmed the pure phasic spinel formation and surface modifications of $MnFe_2O_4$ nano ferrites. The vibrating mode at 2930 cm^{-1} is analogous to the C-H bonding. The vibrating mode at 1276 and 1114 cm^{-1} is analogous to the stretchings of C-H and C-O, respectively, and it affirmed the successful surface modification over the core of $MnFe_2O_4$ nano ferrites. The vibrating mode at 862 cm^{-1} is analogous to the stretchings of C-H bonds. The vibrating mode noted at 474 and 424 cm^{-1} is analogous to the spinel structure of the ferrites. The FT-IR analysis demonstrates the successful surface modifications of PEGylated $MnFe_2O_4$ nano ferrites.

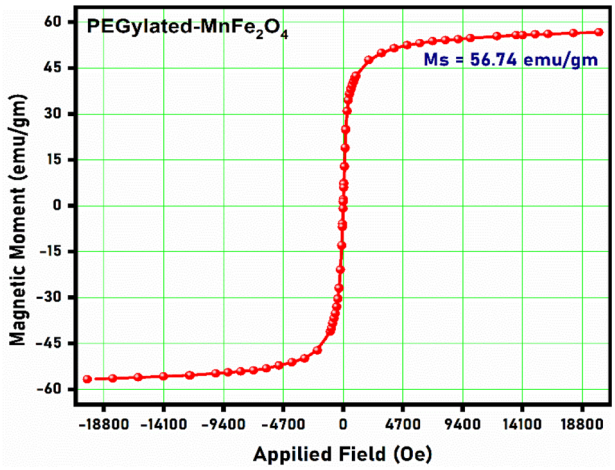

Figure 4. M-H hysteresis curve of PEGylated $MnFe_2O_4$ nano ferrites.

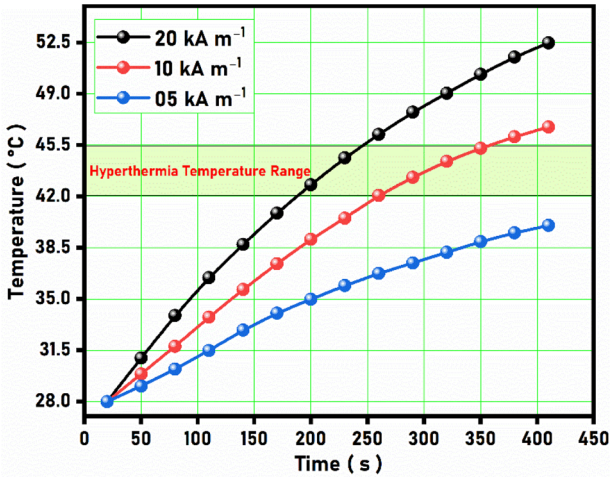

Figure 5. Hyperthermia curves of PEGylated $MnFe_2O_4$ nano ferrites.

2.4. Magnetic Analysis

The magnetic properties of the PEGylated $MnFe_2O_4$ nano ferrites were investigated by VSM. The M-H hysteresis curve of the PEGylated $MnFe_2O_4$ nano ferrites is depicted in **Figure 4**.

It is noted from Figure 4 that, PEGylated $MnFe_2O_4$ nano ferrites possess superparamagnetic gestures. The saturation and remanence magnetization values are determined from Figure 4 and are found to be 56.74 and 0.0092emu g^{-1}, respectively. Whereas, the coercivity value is almost negligible (~0 Oe). The insignificant values of coercivity and remanence show the importance of PEGylated $MnFe_2O_4$ nano ferrites in bio-applications, as these superparamagnetic PEGylated $MnFe_2O_4$ nano ferrites do not conserve the magnetic performance before applying and after the elimination of the exterior magnetic field.

2.5. Hyperthermia Analysis

It is requisite that, the prepared nanoparticles should be capable to produce the hyperthermic heat of the order of 42°C – 45°C for its use in magnetic hyperthermia treatments for malignant tumors. For this purpose, the magnetically inductive heat technique is the significantly employed technique for the evaluation of the hyperthermic ability of prepared nanoparticles which should be dispersed in some suitable fluid like water. In the present case, the different fields viz. 5, 10, and 20 kAm^{-1} were taken to estimate the hyperthermic capability of the PEGylated $MnFe_2O_4$ nano ferrites. In initial stage, the rapid temperature rise is due to the Neel relaxations and Brownian relaxations as eddy current losses are negligible for high resistivity ferrites. The magnetic inductive heating performance of the PEGylated $MnFe_2O_4$ nano ferrites is displayed in **Figure 5**.

The magnetic inductive heating at 5 kA m^{-1} field has been increased slowly saturating at 39°C, which does not attain the required hyperthermic temperature. Likewise, the inductive heating at 10 kA m^{-1} field produces hyperthermic heating saturating at around 46°C. This field was found to be appropriate for the magnetic fluid hyperthermia treatment of cancer, as it generates the hyperthermic temperature up to 46°C. Higher field, i.e., 20 kA m^{-1} may destroy the normal tissues close to the tumor,

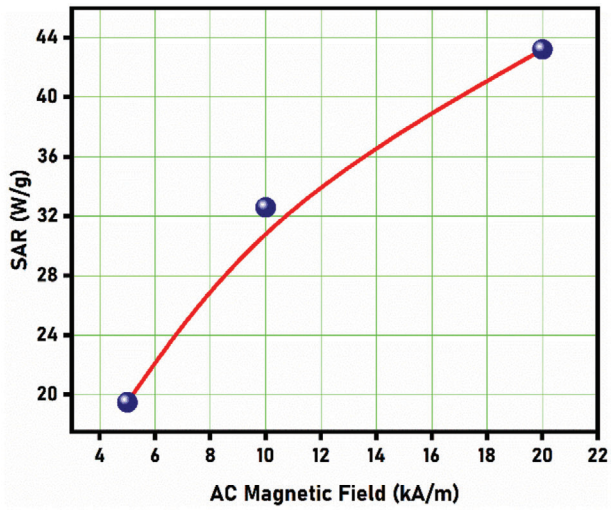

Figure 6. SAR plot of PEGylated $MnFe_2O_4$ nano ferrites.

so it is not appropriate for the MFH. In addition to the heating analysis, the SAR analysis was performed for the PEGylated $MnFe_2O_4$ nano ferrites and the SAR plot is depicted in **Figure 6**. It is observed from Figure 6 that, with an increase in the alternating magnetic field, the SAR value gets increased. The SAR values observed in the present case are high as compared to other magnetic nanoparticles. The highest SAR value was obtained as 43 W g^{-1}, which is in good agreement with that reported in the literature. The material to be used for hyperthermia therapy is superior when SAR value is high and high SAR value minimizes the amount of magnetic material applied for hyperthermia.[16]

3. Conclusion

The PEGylated $MnFe_2O_4$ nano ferrites were successfully prepared via a combustion route. Single-phase cubic formation of PEGylated $MnFe_2O_4$ nano ferrites without any impurity peaks was confirmed by XRD analysis. FT-IR spectrum exposed the occurrence of vibrating modes analogous to the cubic-spinel ferrite structure with a successful modification of PEGylated

$MnFe_2O_4$ nano ferrites. The magnetic hysteresis curve displayed the superparamagnetic nature of the PEGylated $MnFe_2O_4$ nano ferrites. The magnetic inductive heating results demonstrate that PEGylated $MnFe_2O_4$ nano ferrites are capable to attain desired hyperthermic temperature at the permissible field of 10 kA m^{-1}. All the outcomes signify that the PEGylated $MnFe_2O_4$ nano ferrites are desired candidate for MFH therapy of malignant tumors.

4. Experimental Section

Materials: The precursor materials for the relevant metal ion (Manganese(II) nitrate tetrahydrate ($Mn(NO_3)_2$*$4H_2O$) and Ferric nitrate nonahydrate ($Fe(NO_3)_3$*9 H_2O)) of AR grade (~99.8% purity) in the nitrates form, glycine, polyethylene glycol, distilled water (H_2O), and liquid ammonia were used for the synthesis of PEGylated $MnFe_2O_4$ nano ferrite. Chemicals were of analytical reagent (AR) grade and purchased from Merck Millipore.

Synthesis: The easy and cost-efficient combustion preparation route was utilized for the preparation of PEGylated $MnFe_2O_4$ nano ferrite. In brief, the relevant metal ion (Mn and Fe) with proper stoichiometry was dissolved in distilled water and stirred for 1 h. In the stirred solution, the glycine and polyethylene glycol was added with metal nitrate: glycine: polyethylene glycol ratio as 1: 4.4: 3. Further, the pH of the solution was adjusted to ~7 by adding the ammonia solution. The pH changed solution was then rigorously stirred and heated at 85°C until it gets converted to viscous gel. Further, the heat increment (~110°C) turns into the combustion of viscous gel, and the products in the form of loosed powders were acquired. The collected loose powder was then ground and sintered at 550°C for 2 h and further used for characterizations.

Characterizations: The structural analysis of the prepared sample was studied by an X-ray Diffractometer (Model Miniflex, Rigaku International Corporation, Japan) at Kavayitri Bahinabai Chaudhari North Maharashtra University, Jalgaon. The morphology of the prepared sample was visualized via FE-SEM (JEOL-JSM). The FT-IR spectrum was recorded in the wavenumber range of 400 to 4000 cm^{-1} by FTIR Spectrometer (Model Nicolet 380). The M-H hysteresis plot was recorded through a vibrating sample magnetometer (VSM) at TIFR, Mumbai. Hyperthermia analysis was done by measuring the time-dependent heating curves through an indigenous induction heating system.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

FT-IR, modifications, morphology, nanoparticles

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Investigation of Super-Capacitive Properties of Nanocrystalline Copper-Zinc ($Cu_{0.5}Zn_{0.5}Fe_2O_4$) Ferrite Nanoparticles

Prashant B. Kharat, Sandeep B. Somvanshi,* Saurabh B. Somwanshi, and Anuja M. Mopari*

A comparative study is made between the structure and electrochemical properties of Copper-Zinc ($Cu_{0.5}Zn_{0.5}Fe_2O_4$) ferrite nanoparticles prepared by chemical co-precipitation. The obtained ferrites are characterized by FT-IR, XRD, BET, and SEM techniques. The single-phase cubic formation of $Cu_{0.5}Zn_{0.5}Fe_2O_4$ nano ferrites without any impurity peaks is confirmed by XRD analysis. FT-IR spectrum exposes the occurrence of vibrating modes analogous to the cubic-spinel ferrite structure of $Cu_{0.5}Zn_{0.5}Fe_2O_4$ nano ferrites. The magnetic hysteresis curve displays the superparamagnetic nature of the $Cu_{0.5}Zn_{0.5}Fe_2O_4$ nano ferrites. The electrochemical properties of obtained ferrites are studied using cyclic voltammetry, charge-discharge, and electrochemical impedance spectroscopy. The as-synthesized $Cu_{0.5}Zn_{0.5}Fe_2O_4$ sample acts as an excellent electrode material in a supercapacitor with a high specific capacitance energy density and a power density.

1. Introduction

Energy generation and storage devices are demanding in today's era and nanotechnology is moving towards capturing this field with great potentiality.[1] The energy storage devices concerning the generation are parallelly needed to fulfill the ever-growing demand of the energy sector. Recently, various nanoscale devices are being developed for energy storage, and it is still advancing day by day.[2,3] Electrochemical devices such as supercapacitors are one of the potential candidates which gaining much attention from nanoscale scientists and technologists.[4] Supercapacitors are appealing due to their energy storage ability along with their superior stability over many cycles. Recently, spinel class magnetic ferrite materials have been extensively applied in different areas such as magnetic hyperthermia,[5–8] drug delivery, catalysis, photocatalysis, microwave absorption, nanofluids,[9–11] biomedicine,[12] bioseparation,[13] and supercapacitors.[14,15] The spinel ferrite is promising over other magnetic materials due to its versatile nature, chemical stability, easy preparation, cost-effectiveness, etc.[16] Among the spinel ferrite, copper and zinc have their own merits in physicochemical and properties. The copper ferrite is inverse structured, whereas zinc spinel ferrite possesses normal spinel behavior. The combination of these both normal and spinel structured ferrites offers enhanced properties as compared to their individual counterparts. Spinel ferrites have been fabricated my various wet chemical routes, including chemical coprecipitation,[17] hydrothermal,[18] microemulsion,[19] thermal decomposition,[20] sol-gel auto combustion, etc. The chemical co-precipitation is a promising low-temperature synthesis route for the preparation of stable and homogeneous spinel ferrite nanoparticles with a superior yield and cost-effective nature. In the present work, we have opted for chemical coprecipitation synthesis of copper-zinc nano ferrite with composition as $Cu_{0.5}Zn_{0.5}Fe_2O_4$. The prepared $Cu_{0.5}Zn_{0.5}Fe_2O_4$ nano ferrites were characterized by the standard tool to study the structure, morphology, surface, magnetic, and supercapacitive properties.

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2. Result and Discussion

2.1. Structural Analysis

The single phasic formation and nanoscale behavior of the $Cu_{0.5}Zn_{0.5}Fe_2O_4$ nano ferrites was studied by XRD analysis. The XRD pattern of the prepared $Cu_{0.5}Zn_{0.5}Fe_2O_4$ nano ferrites is displayed in **Figure 1**.

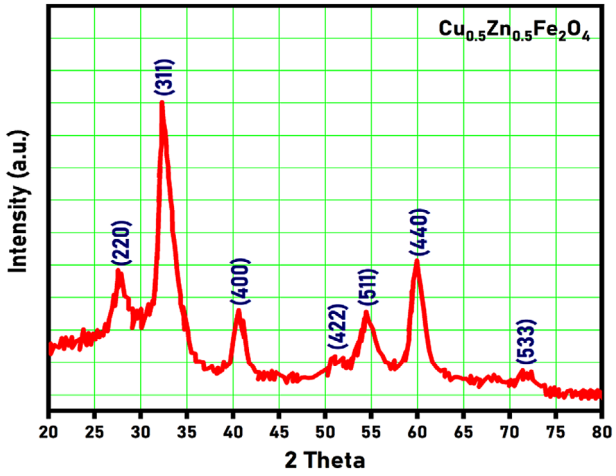

Figure 1. XRD pattern of $Cu_{0.5}Zn_{0.5}Fe_2O_4$ nano ferrites.

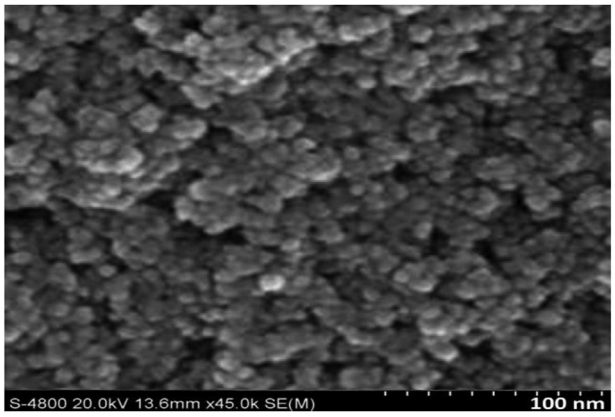

Figure 2. FE-SEM image of $Cu_{0.5}Zn_{0.5}Fe_2O_4$ nano ferrites.

It is observed from Figure 1 that, $Cu_{0.5}Zn_{0.5}Fe_2O_4$ nano ferrites possess Bragg planes equivalent to the spinel FCC structure equivalent to the $Fd-3m(Oh^7)$ space grouping. The most intense peak (311) was used to evaluate the crystallite size by using the Debye-Scherrer's relation[21,22] and it was calculated as 19 nm. The lattice constant was evaluated by interplanar spacing and (h k l) value and is found to be 8.409 Å.

2.2. Morphological Analysis

The morphology of the $Cu_{0.5}Zn_{0.5}Fe_2O_4$ nano ferrites was studied through SEM. **Figure 2** displays the SEM image of the $Cu_{0.5}Zn_{0.5}Fe_2O_4$ nano ferrites. The nano-scaled spherical grains with agglomerations to some extent were mainly visualized in Figure 2. The agglomerations in the grains were observed due to the magnetic superexchange among the ferric ions. The average grain size of the $Cu_{0.5}Zn_{0.5}Fe_2O_4$ nano ferrites was determined from the SEM image and it is found to be 23 nm.

2.3. Infrared Analysis

To confirm the spinel structure formation of $Cu_{0.5}Zn_{0.5}Fe_2O_4$ nano ferrites, FT-IR spectroscopy opted.

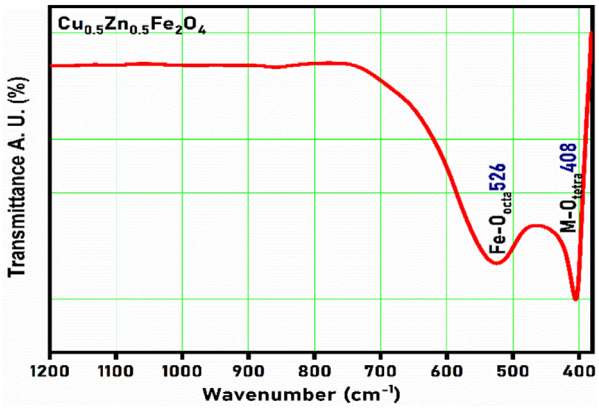

Figure 3. FT-IR spectrum of $Cu_{0.5}Zn_{0.5}Fe_2O_4$ nano ferrites.

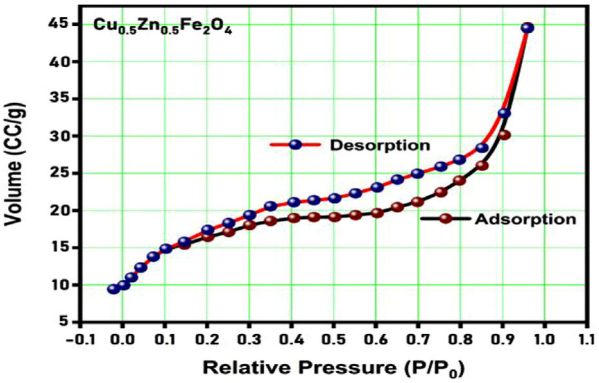

Figure 4. N_2 adsorption-desorption curve of $Cu_{0.5}Zn_{0.5}Fe_2O_4$ nano ferrites.

Figure 3 depicts the FT-IR spectrum of the $Cu_{0.5}Zn_{0.5}Fe_2O_4$ nano ferrites. The vibrating mode noted at 526 and 408 cm^{-1} is analogous to the spinel structure and corresponds to the tetrahedral (A) and octahedral [B] interstitial stretchings of the $Cu_{0.5}Zn_{0.5}Fe_2O_4$ nano ferrites.[23] The FT-IR analysis revealed that the successful spinel phase formation of the $Cu_{0.5}Zn_{0.5}Fe_2O_4$ nano ferrites.

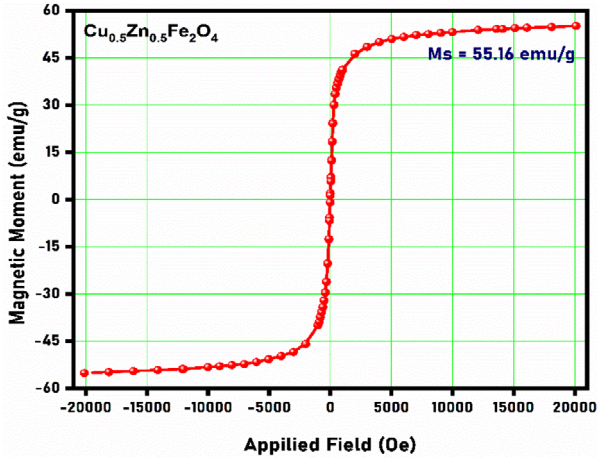

Figure 5. M-H hysteresis curve of $Cu_{0.5}Zn_{0.5}Fe_2O_4$ nano ferrites.

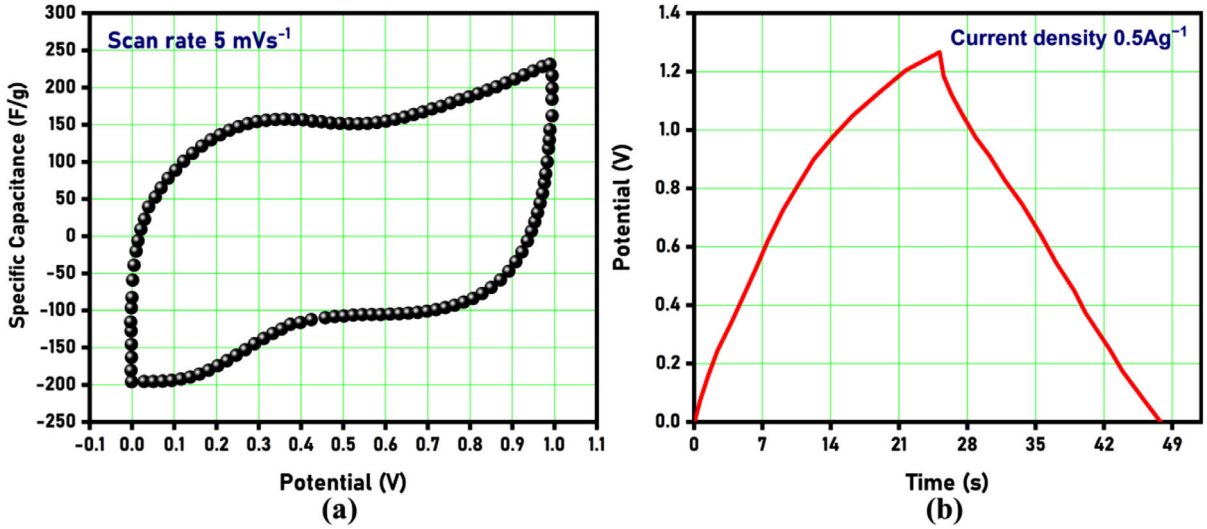

Figure 6. Cyclic voltammetry plot (a) and Galvanostatic charge-discharge plot (b) of $Cu_{0.5}Zn_{0.5}Fe_2O_4$ nano ferrites.

2.4. Surface Area Analysis

The evaluation of specific surface area is a prerequisite in utilizing the nano-scale platforms in super capacitive applications. The surface area measurement was investigated by recording the N_2 adsorption-desorption curve and BET analysis. **Figure 4** depicts the N_2 adsorption-desorption curve of $Cu_{0.5}Zn_{0.5}Fe_2O_4$ nano ferrites. Figure 4 denotes the well-formed hysteresis curve and matches well with that reported in the literature. The specific surface area estimated from BET analysis was found to be 36.77 $m^2\ g^{-1}$ and is superior to that reported in the literature for the other nano ferrites.

2.5. Magnetic Analysis

The magnetic properties of the $Cu_{0.5}Zn_{0.5}Fe_2O_4$ nano ferrites were investigated by VSM at room temperature.

The M-H hysteresis curve of the $Cu_{0.5}Zn_{0.5}Fe_2O_4$ nano ferrites is displayed in **Figure 5**. It is noted from Figure 5 that, $Cu_{0.5}Zn_{0.5}Fe_2O_4$ nano ferrites possess superparamagnetic nature. The saturation and remanence magnetization values are determined from Figure 5 and are found to be 55.16 and 21.42 emu g^{-1}, respectively. Whereas, the coercivity value is almost zero.

2.6. Supercapacitive Analysis

The supercapacitive evaluation of the prepared $Cu_{0.5}Zn_{0.5}Fe_2O_4$ nano ferrites was studied by measuring the specific capacitance through the C—H instrument. The cyclic plot of $Cu_{0.5}Zn_{0.5}Fe_2O_4$ nano ferrites is shown in **Figure 6**a,b. It shows the well-developed CV curve as desired for the supercapacitor applications.

The other plots such as the variation of capacitance with current density and Nyquist of for the $Cu_{0.5}Zn_{0.5}Fe_2O_4$ nano ferrites were recorded and depicted in **Figure 7**a,b, respectively.

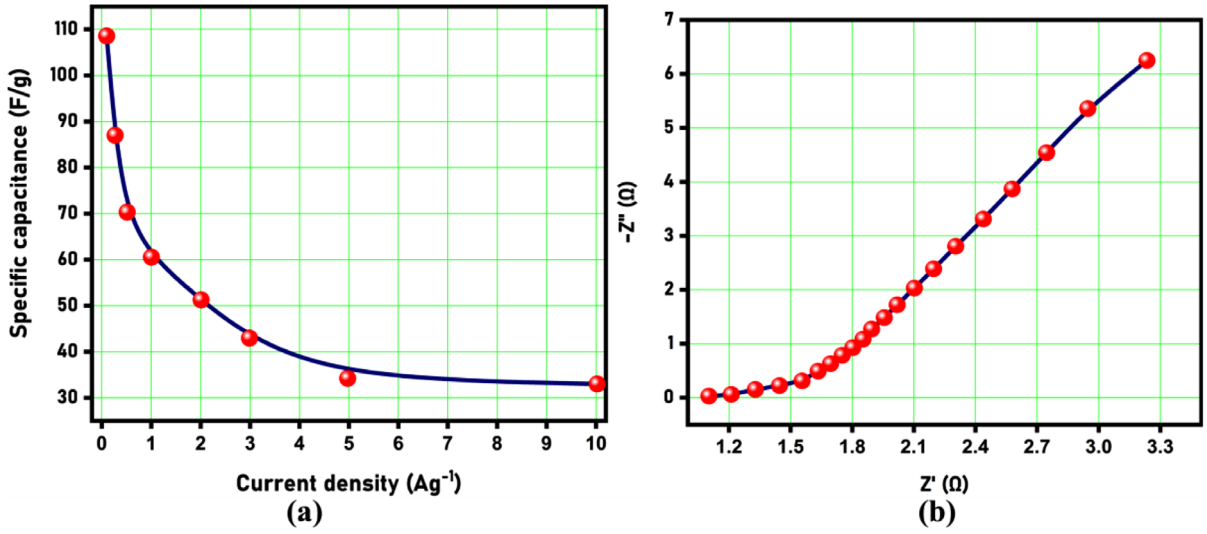

Figure 7. Variation of capacitance with a current density (a) and Nyquist plot (b) of $Cu_{0.5}Zn_{0.5}Fe_2O_4$ nano ferrites.

All these plots show that $Cu_{0.5}Zn_{0.5}Fe_2O_4$ nano ferrites act as excellent electrode material in supercapacitor with a high specific capacitance of 162 F g^{-1}, an energy density of 21.2 Wh kg^{-1}, and a power density of 480 Wkg^{-1} at 1 Ag^{-1}, and a good retention value of 91.25% after 500 cycles at 1 Ag^{-1}.

3. Conclusion

The nanocrystalline $Cu_{0.5}Zn_{0.5}Fe_2O_4$ nano ferrites were successfully prepared via the coprecipitation route. Single-phase cubic formation of $Cu_{0.5}Zn_{0.5}Fe_2O_4$ nano ferrites without any impurity peaks was confirmed by XRD analysis. FT-IR spectrum exposed the occurrence of vibrating modes analogous to the cubic-spinel ferrite structure of $Cu_{0.5}Zn_{0.5}Fe_2O_4$ nano ferrites. The magnetic hysteresis curve displayed the superparamagnetic nature of the $Cu_{0.5}Zn_{0.5}Fe_2O_4$ nano ferrites. The $Cu_{0.5}Zn_{0.5}Fe_2O_4$ nano ferrites act as excellent electrode material in supercapacitor with a high specific capacitance of 162 F g^{-1}, an energy density of 21.2 Wh kg^{-1}, and a power density of 480 Wkg^{-1} at 1 Ag^{-1} and a good retention value of 91.25% after 500 cycles at 1 Ag^{-1}.

4. Experimental Section

Materials: Zinc nitrate hexahydrate ($Zn(NO_3)_2$*$6H_2O$), Copper(II) nitrate trihydrate ($Cu(NO_3)_2$*3 H_2O), Ferric nitrate nonahydrate ($Fe(NO_3)_3$*9 H_2O), Acetone (C_3H_6O), Distilled water (H_2O), and Ammonia (NH_3) chemicals of AR grade (99% purity) were purchased from Merck Millipore and used for the synthesis of $Cu_{0.5}Zn_{0.5}Fe_2O_4$ nano ferrites without any further purification.

Synthesis: The easy and economically cheaper coprecipitation route was utilized for the preparation of $Cu_{0.5}Zn_{0.5}Fe_2O_4$ nano ferrites. The detailed synthesis procedure was reported in our previous articles.[24] In brief, the corresponding metal ions (Cu, Zn, and Fe) with predefined stoichiometry were dissolved in distilled water and continuously stirred for 1.5 h. Further, the precipitates were formed by the addition of the ammonium hydroxide. The formed precipitates were then filtered and washed several times by ethanol. The filtered precipitates in the powder form than dry in the air atmosphere. The dried powder then sintered a 550 °C for 3 h to attain superior crystalline nature and further used for characterizations.

Characterizations: The structural analysis of the prepared sample was studied by an X-ray Diffractometer (Model Miniflex, Rigaku International Corporation, Japan) at Kavayitri Bahinabai Chaudhari North Maharashtra University, Jalgaon. The morphology of the prepared sample was investigated via FE-SEM (Bruker). The FT-IR spectrum was recorded in the wavenumber range of 400–4000 cm^{-1} using FTIR Spectrometer (Model Nicolet 380). The surface area was determined by BET analysis by BET Surface Area Analyser (CAD Instruments, France). The super-capacitive evaluation was done by the C—H instrument (CH Instruments; 660C, 1120) at Dr. Babasaheb Ambedkar Marathwada University, Aurangabad.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

nanoparticles, morphology, FT-IR, X-ray

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Low-cost Fabrication of Zn-doped $MnFe_2O_4$ ($Mn_{0.5}Zn_{0.5}Fe_2O_4$) Film for H_2S Gas Sensing Applications

Prashant B. Kharat, Sandeep B. Somvanshi,* Saurabh B. Somwanshi, and Anuja M. Mopari*

Multicomponent spinel ferrites are essential to be used in high-performance gas-sensing materials. In the present work, $Mn_{0.5}Zn_{0.5}Fe_2O_4$ spinel ferrite thin film is prepared via spray printing technique. The prepared film can be easily retrieved and utilized for multiple cycles due to its magnetic properties. The morphology, composition, and crystal structure of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ spinel ferrite thin film are examined using scanning electron microscopy, infrared spectroscopy, and X-ray diffraction. The produced films are in the range of around 20 nm and manifest spinel cubic structure. The prepared film is tested for its sensitivity to NO_2, NH_3, H_2, and H_2S gases, and the $Mn_{0.5}Zn_{0.5}Fe_2O_4$ spinel ferrite thin film is found the most sensitive and selective to H_2S gas. The prepared $Mn_{0.5}Zn_{0.5}Fe_2O_4$ spinel ferrite thin film shows enhanced sensing performance functional at low temperatures, and consequently, they need low operational power. They are also simple to fabricate at the appropriate cost.

1. Introduction

Recently, the area of nanoscale technologies have been advanced extensively in different areas such as electronics,[1] catalysis,[2] photocatalysis,[3] gas sensing,[4] biomedicine,[5,6] microwave industries, nanofluid,[7–9] etc. Among the class of nanoscale magnetic materials (NMMs), nanoscale spinel ferrites (NSFs) have been showing great promise towards different applications, including magnetic hyperthermia,[10,11] photocatalytic dye degradation, nanocatalyst, and high-frequency applications.[12] The NSFs have been extensively explored in the nanoparticle as well as thin-film form by many researchers . The NSFs in the thin-film form are much appealing in the area of gas sensing due to their easy preparation, superior chemical stability, better response, and recovery time.[13] Among the NSF's, manganese ferrites (MNFs) are studied broadly due to their extraordinary physicochemical properties. The incorporation of guest ions such as zinc in the matrix of MNFs may offer synergistic properties and may show improved properties for gas sensing. In the past, NSF has been fabricated by various methods in the thin film form.[14,15] Among these methods, the spray printing method has some advantages like simple and cost-effective experimental setup, uniform deposition, and better homogeneity over the other deposition techniques . In the present work, we report the simple and cheap fabrication of the $Mn_{0.5}Zn_{0.5}Fe_2O_4$ spinel ferrite thin film via spray printing technique. The structural, morphological, elemental, magnetic, etc., properties and gas sensing towards H_2S was studied by standard techniques.

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2. Result and Discussion

2.1. Structural Analysis

The monophase formation and nanocrystalline nature of the $Mn_{0.5}Zn_{0.5}Fe_2O_4$ thin film were verified by XRD analysis. The XRD pattern of the prepared $Mn_{0.5}Zn_{0.5}Fe_2O_4$ thin film is displayed in **Figure 1**. It is observed from Figure 1 that, $Mn_{0.5}Zn_{0.5}Fe_2O_4$ thin-film possesses Bragg planes equivalent to the cubic spinel structure. The most concentrated peak was utilized to determine the crystallite size by using the Debye-Scherrer's relation[16,17] and it was evaluated as 14.2 nm. The lattice parameter was determined by interplanar spacing and (h k l) values and is found to be 8.472 Å. Some background noises are recorded in Figure 1, which is attributed

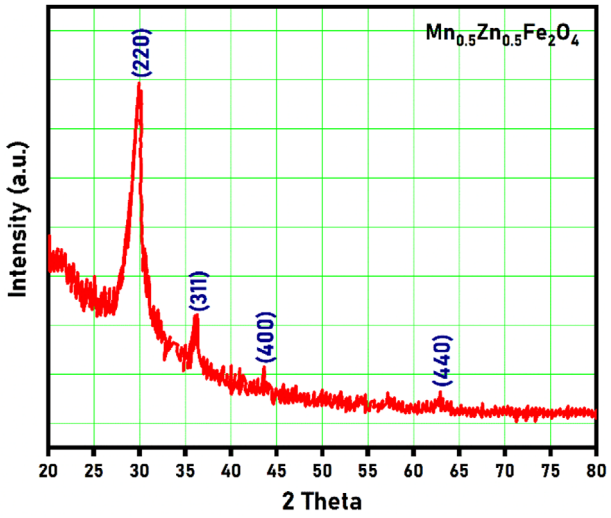

Figure 1. XRD pattern of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ thin film.

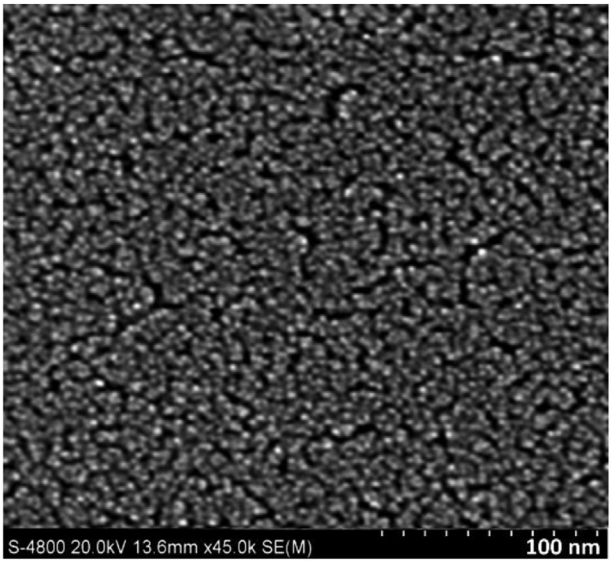

Figure 2. FE-SEM image of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ thin film.

to the amorphous nature of the glass substrate. It discloses the successful preparation of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ thin film.

2.2. Morphological Analysis

The morphology of the $Mn_{0.5}Zn_{0.5}Fe_2O_4$ thin film was visualized through FE-SEM. **Figure 2** shows the FE-SEM image of the $Mn_{0.5}Zn_{0.5}Fe_2O_4$ thin film. The sphere-type grains having nano-shape with some agglomeration were broadly noted from Figure 2. The agglomerations in the spherical grains appeared due to the magnetic exchanging in between the Fe^{3+} ions. The denser morphology with some cracks can be observed from the FE-SEM image of the $Mn_{0.5}Zn_{0.5}Fe_2O_4$ thin film. The average grain size was determined from the FE-SEM image and is found to be 17 nm.

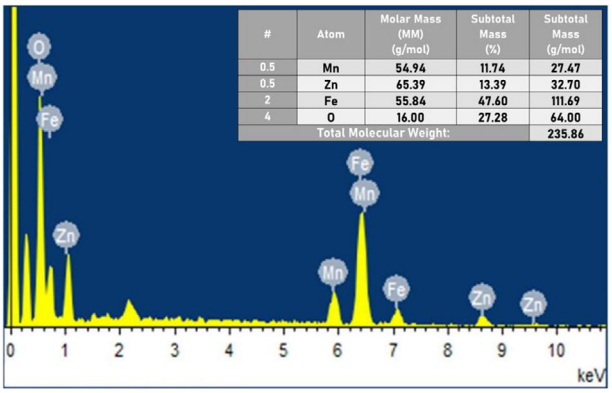

Figure 3. EDAX spectrum of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ thin film.

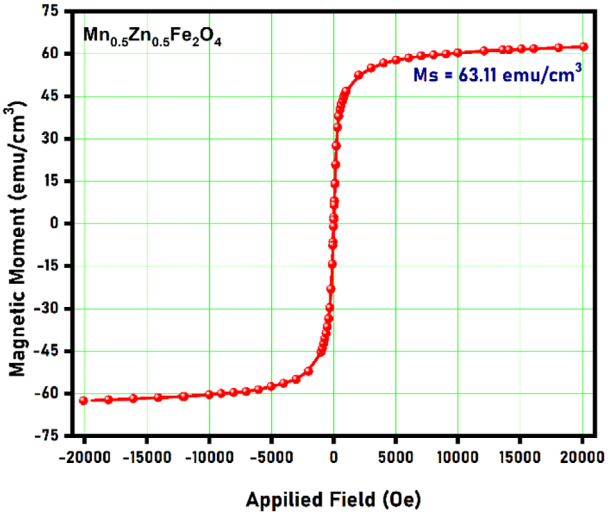

Figure 4. M-H hysteresis curve of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ thin film.

2.3. Elemental Analysis

To confirm the pure phase formation and stoichiometric proportions of the $Mn_{0.5}Zn_{0.5}Fe_2O_4$ thin film, the EDAX spectrum was recorded. **Figure 3** shows the EDAX spectrum of the prepared $Mn_{0.5}Zn_{0.5}Fe_2O_4$ thin film. It is observed from Figure 3 that, the prepared $Mn_{0.5}Zn_{0.5}Fe_2O_4$ thin film contains desired metal ions viz. Mn, Zn, Fe, and O with proper composition. The absence of any other metal ions confirms the elemental purity of the $Mn_{0.5}Zn_{0.5}Fe_2O_4$ thin film.

2.4. Magnetic Analysis

The magnetic properties of the $Mn_{0.5}Zn_{0.5}Fe_2O_4$ thin film were investigated by VSM at 300 K. The M-H hysteresis curve of the $Mn_{0.5}Zn_{0.5}Fe_2O_4$ thin film is shown in **Figure 4**. It is noted from Figure 4 that, $Mn_{0.5}Zn_{0.5}Fe_2O_4$ thin-film displays superparamagnetic behavior. The saturation and remanence magnetization values were evaluated from Figure 4 and are found to be 63.11 and 26.44 emu g^{-1}, respectively. Whereas, the coercivity value is almost insignificant (~0 Oe).

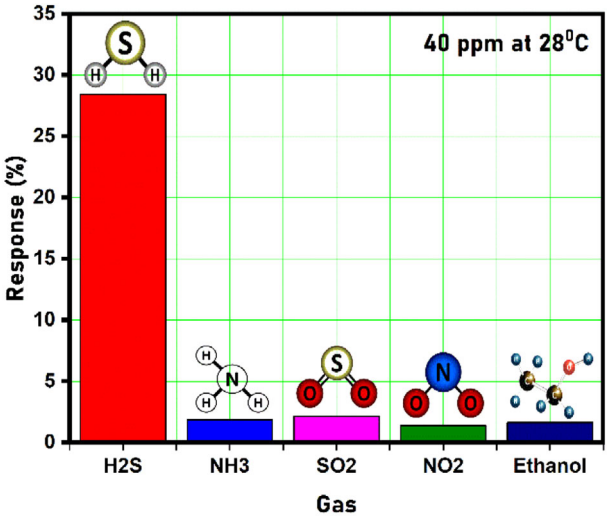

Figure 5. Selectivity plot of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ thin film.

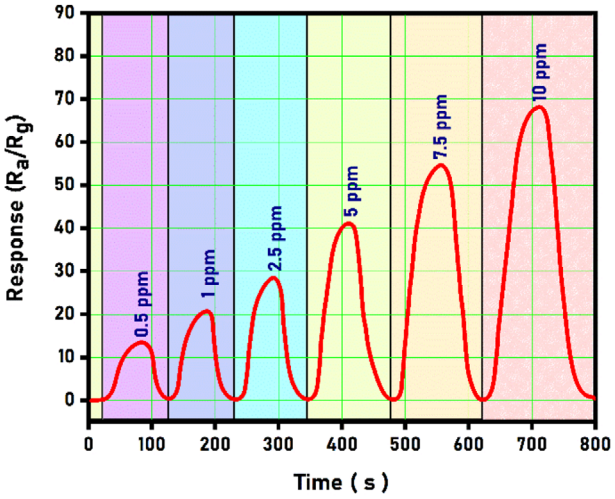

Figure 6. H_2S gas sensing curves of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ thin film.

2.5. Gas Sensing Analysis

In addition to the response and recovery time, the selectivity of the gas sensor is an important parameter for the application in specific gas sensing. In the present study, the selectivity of the prepared $Mn_{0.5}Zn_{0.5}Fe_2O_4$ thin film was determined by exposing it to the different gases viz. H_2S, NH_3, SO_2, NO_2, and Ethanol with 40 ppm concentration. The selectivity plot of the $Mn_{0.5}Zn_{0.5}Fe_2O_4$ thin film is shown in **Figure 6**. It is noted from Figure 6 that, $Mn_{0.5}Zn_{0.5}Fe_2O_4$ thin film shows a higher response to the H_2S gas as compared to the other gases. The response to the other gases (NH_3, SO_2, NO_2, and Ethanol) is very much low as compared to the H_2S, which shows that the prepared $Mn_{0.5}Zn_{0.5}Fe_2O_4$ thin film is more specific to the H_2S gas sensing.

To apply the prepared thin film in the area of the gas sensor, it should show a higher response, low recovery time, and greater cross selectivity. In the present study, the H_2S gas sensing response of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ thin film was studied for different gas concentrations viz. 0.5, 1.0, 2.5, 5.0, 7.5, and 10 ppm. The H_2S gas sensing curves of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ thin film are shown in **Figure 5**. It is observed from Figure 5 that, with an increase in gas concentration, the $Mn_{0.5}Zn_{0.5}Fe_2O_4$ thin film shows a better response. Response of the prepared thin films was increasing linearly for increasing gas concentration.[18,19] The enhanced response and recovery time of the $Mn_{0.5}Zn_{0.5}Fe_2O_4$ thin film is observed from Figure 5.

3. Conclusion

The $Mn_{0.5}Zn_{0.5}Fe_2O_4$ thin film was successfully prepared via the spray printing technique. Single-phase cubic formation of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ thin film without any impurity peaks was confirmed by XRD analysis. The magnetic hysteresis curve displayed the superparamagnetic nature of the $Mn_{0.5}Zn_{0.5}Fe_2O_4$ thin film. The enhanced response time and recovery time of the $Mn_{0.5}Zn_{0.5}Fe_2O_4$ thin film were observed. The response to the other gases (NH_3, SO_2, NO_2, and Ethanol) is very much low as compared to the H_2S, which shows that the prepared $Mn_{0.5}Zn_{0.5}Fe_2O_4$ thin film is more specific to the H_2S gas sensing. The prepared $Mn_{0.5}Zn_{0.5}Fe_2O_4$ spinel ferrite thin film shows enhanced sensing performance functional at low temperatures, and consequently, they need low operational power. They are also simple to fabricate at the appropriate cost.

4. Experimental Section

Materials: Manganese(II) nitrate tetrahydrate ($Mn(NO_3)_2{*}4H_2O$), Zinc nitrate hexahydrate ($Zn(NO_3)_2{*}6H_2O$), Ferric nitrate nonahydrate ($Fe(NO_3)_3{*}9\ H_2O$), Acetone (C_3H_6O), and Distilled water (H_2O) chemicals of AR grade (99% purity) were purchased from Merck Millipore and glass substrates used for the synthesis of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ spinel ferrite thin film without any further purification.

Synthesis: The spray printing as a simple and cheap fabrication route was employed for the preparation of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ spinel ferrite thin film. In brief, the respective metal ions (Zn, Mn, and Fe) with proper stoichiometric proportion were dissolved in distilled water and stirred for 1 h. The stirred solution was then filled in the vacuum cleaned spray nozzle. The glass substrates used for deposition were super cleaned by distilled water and ultrasonicator. The cleaned substrate was then kept under the spray nozzle on the hot plate. The temperature of the hot plate was kept as 300°C. Further, the precursor solution was sprayed onto the substrates with optimized parameters as reported in our previous report. The sprayed thin film was then cooled and annealed at 550°C for 4 h to get better crystallite and used for further characterizations.

Characterizations: The structure of the prepared thin film sample was studied by an X-ray Diffractometer (Bruker D8 Advance). The morphology of the prepared sample was visualized via FE-SEM (JEOL-JSM). The FT-IR spectrum was recorded in the wavenumber range of 400–4000 cm^{-1} by FTIR Spectrometer (Model Nicolet 380). The M-H hysteresis plot was recorded through a vibrating sample magnetometer (VSM) at TIFR, Mumbai. The gas sensing properties were investigated through an indigenously developed Gas sensing unit.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

morphology, sensors, thin films, X-ray

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