CHAPTER 4

RESULT AND DISCUSSION

4.0 RESULTS AND DISCUSSION

4.1. Fluoride mapping in groundwater of Kheralu Taluka and analysis of Fluoride concentration in soil and plant samples

Fluorine is reported being the most abundant element and a common geogenic problem on our planet. Fluoride ions from the minerals leach into the groundwater and contribute to high fluoride concentrations (Schultheiss and Godley, 1995). High fluoride concentration in drinking causes a disease called fluorosis, known for its detrimental effects on health. The bioavailability of soluble fluoride ingested with water is nearly 100% because soluble fluoride in drinking water is easily absorbed by the gastrointestinal tract (Ekstrand *et al.,* 1978; Whitford, 1996). So, a level of fluoride in water is a primary factor for the cause of fluorosis. In many states of India prevalence of fluorosis is mainly due to the intake of large quantities of fluoride through drinking water (Teotia and Teotia, 1991; Susheela *et al.,* 1993; Karthikeyan *et al.,* 1996). The number of fluoride affected people fluoride endemic areas are steadily increasing ever since the disease was discovered in India during 1930s. The reason for this increase is the population explosion and rapid industrialization, necessitating more and more water, leading to indiscriminate digging for groundwater extraction without responsible management as well as without due attention to quality issues, specifically for fluoride and due to water shortage (Ravindra and Garg, 2007).

One such zone in India is North Gujarat where the ground water table is being continuously emptied due to over-extraction in absence of adequate surface waters. As a result water table has gone down to 200 to 300 meters deep and excessive fluorides are now found in the groundwater of all areas. The Government of Gujarat conducted a survey for fluoride distribution in Mehsana District which had identified Kheralu Taluka as the most affected one. In Kheralu Taluka, groundwater extraction through electrically operated borewells forms a major part of Public Water Supply system to nearby residential communities of rural areas and some urban areas while remaining communities use water brought by Narmada canal provided by WASMO. The residents of the area were found to be totally dependent on groundwater for the domestic purpose including drinking reason being water supplied by WASMO was economically not suitable for them and so to describe health effects groundwater quality for each area has been taken into consideration.

4.1.1. Spatial mapping of Fluoride in Groundwater

To understand spatial distribution pattern of fluoride, mapping for distribution of fluoride concentration in groundwater is a prerequisite step. Fluoride analysis of water samples collected from entire taluka (comprising of 51 villages and 1 town) in the year 2012 and in the year 2013 was performed to obtain a primary data on fluoride concentration in the groundwater. The results are recorded in (Table 10: Figure 3).

The data revealed that average fluoride concentration in groundwater samples for the year 2012 varied from lowest fluoride concentration of 0.31±0.1 mg/l recorded in village Balad to highest fluoride concentration of 4.87±2.39 mg/l reported from the village Malarpura. In the year 2013, it was found to be varied from lowest fluoride concentration of 0.33±0.09 mg/l recorded in village Balad to lowest fluoride concentration of 5.28±2.7 mg/l reported from Malarpura village.

From the data obtained, it is clear that the major problem of the residents is the presence of fluoride in potable groundwater water. According to BIS, for India states 1 ppm of fluoride is considered as the optimal level while 1.5 ppm to be a permissible limit in drinking water. It was envisaged from the result that 23 villages (i.e. 44%) have fluoride concentration above the permissible limit in 2012, hence were found to be unsafe for drinking purpose. The remaining 29 villages i.e. 56% have the value below the permissible limit and thus safe for drinking. In 2013, additional 1 villages from the study area have recorded unsafe drinking water, thus from entire study area total 24 villages (i.e. 46%) were found to have fluoride concentration above the permissible limit. The remaining 28 villages were found to be safe for drinking purpose as their F^- concentration was below 1 ppm.

Henceforth, out of 52 sampling sites, 20 villages were found to have high fluoride concentration i.e. above 2 ppm in both the consecutive years. These villages were Arthi, Chotiya, Dabhoda, Dalisana, Delwada, Fatepura, Gajipur, Gathaman, Gorisana, Lalawada, Mahekubpura, Mahiyal, Malarpura, Malekhpur, Mandropur, Nalu, Rahemanpura, Unad, Vaghvadi and Vithoda.

Table 10: Fluoride Concentration in groundwater

Sr. No.	Villages	Average Fluoride concentration (mg/l)	
		2012	2013
1	Amarpura	0.59±0.05	0.64±0.07
2	Ambavada	1.01±0.37	1.1±0.41
3	Arthi	2.38±0.17	2.57±0.2
4	Balad	0.31±0.1	0.33±0.09
5	Chachariya	0.96±0.25	1.04±0.26
6	Chada	0.91±0.3	0.98±0.31
7	Chansol	1.22±0.25	1.31±0.24
8	Chotiya	2.34±1.86	2.54±2.07
9	Dabhad	1.29±0.13	1.39±0.11
10	Dabhoda	2.67±0.8	2.89±0.92
11	Dalisana	2.34±0.12	2.44±0.13
12	Davol	1.24±0.44	1.33±0.44
13	Dedasana	0.38±0.04	0.41±0.05
14	Delwada	4.63±0.78	4.97±0.72
15	Fatepura	3.9±0.33	4.2±0.29
16	Gajipur	2.34±0.31	2.52±0.35
17	Gathaman	3.08±1.14	3.33±1.28
18	Gorisana	3.19±0.49	3.43±0.49
19	Kheralu	0.75±0.87	0.81±0.94
20	Kuda	0.62±0.2	0.67±0.22
21	Lalawada	2.12±0.83	2.29±0.92
22	Limdi	0.5±0.19	0.54±0.21
23	Lunva	0.49±0.07	0.53±0.06
24	Machhava	1.03±0.38	1.1±0.39
25	Madhasana	1.52±0.3	1.64±0.33
26	Mehkubpura	1.23±0.54	1.32±0.57
27	Mahiyal	1.98±0.37	2.14±0.42
28	Malarpura	4.87±2.39	5.28±2.7
29	Malekhpur	3.2±0.25	3.45±0.34

Sr. No.	Villages	Average Fluoride concentration (mg/l)	
		2012	2013
30	Mandali	1.76±0.54	1.89±0.58
31	Mandropur	2.8±1	3±1.04
32	Moti Hirvani	0.33±0.14	0.36±0.15
33	Nalu	2.14±0.83	2.31±0.92
34	Nandali-Miyasan	0.88±0.09	0.95±0.11
35	Nani Hirvani	0.79±0.52	0.85±0.56
36	Nanivada	0.62±0.32	0.67±0.35
37	Nortol	0.81±0.25	0.88±0.28
38	Pancha	1.21±0.72	1.3±0.78
39	Rehmanpura	3.69±0.33	3.97±0.28
40	Rasalpur	1.57±0.1	1.7±0.11
41	Sadikpur	1.54±0.04	1.66±0.06
42	Sakri	1.45±0.14	1.57±0.13
43	Samoja	1.32±0.18	1.42±0.19
44	Sangthala	0.77±0.3	0.82±0.3
45	Santokpura	1.27±0.23	1.37±0.28
46	Suvariya	1.05±0.43	1.13±0.47
47	Thangana	0.59±0.45	0.63±0.46
48	Unad	2.18±0.88	2.35±0.96
49	Vagvadi	4.49±0.37	4.85±0.5
50	Varitha	1.11±0.13	1.2±0.12
51	Vavdi (khe)	0.75±0.34	0.8±0.34
52	Vithoda	4.03±1.45	4.32±1.48

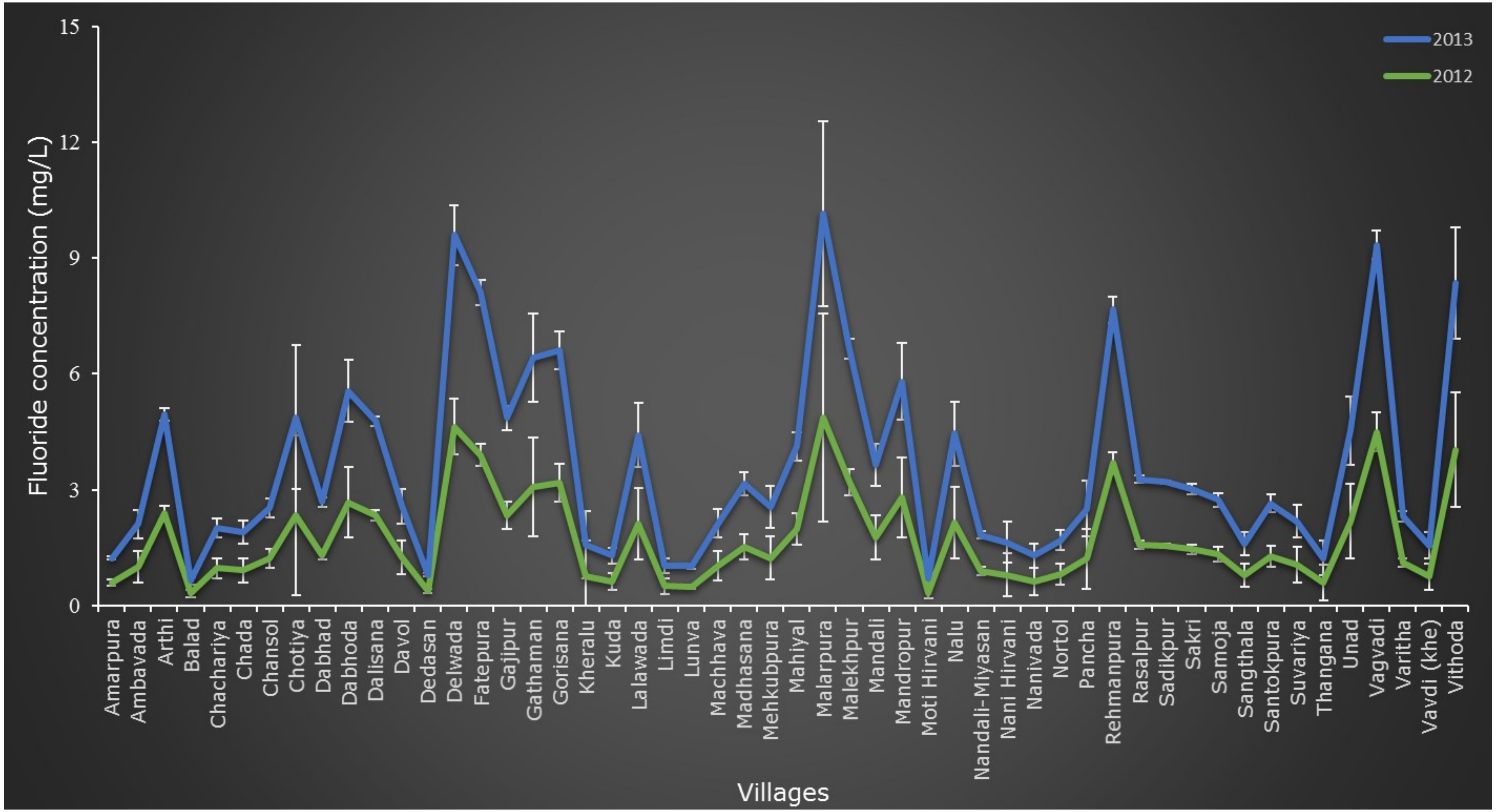
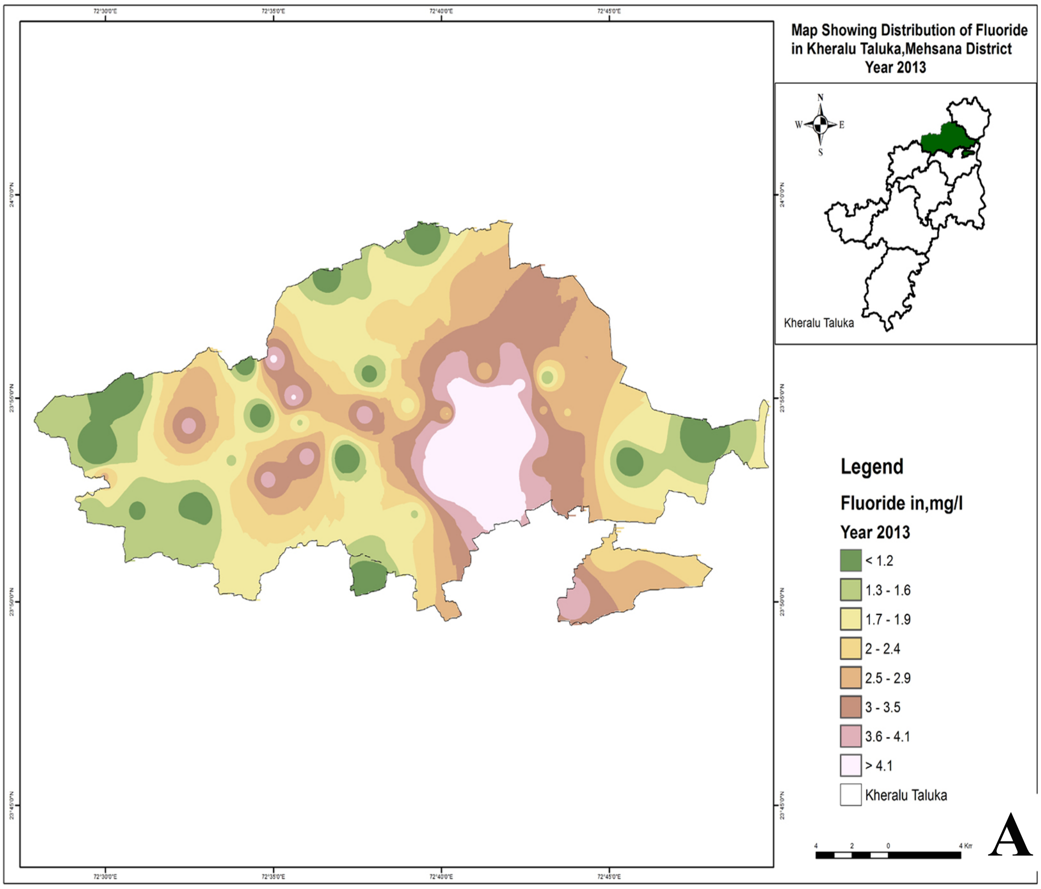


Figure 3: Average seasonal variation in fluoride concentrations of groundwater of Kheralu taluka

From the data collected, a map was generated to understand the spatial distribution of fluoride in the study area. As shown in the map (PLATE 8), areas having fluoride concentration above permissible limit were arranged in two lineages: one lineage initiating from north-eastern border progressing towards the southern border that falls under areas with very high fluoride concentration. These villages were Dabhoda, Arthi, Chotiya, Lalawada, Gathaman, Malarpura, Delwada, Gorisana, Unad and Madhasana. This lineage is overlaying onto the down flow stream of groundwater from the Aravalli ranges. The other lineage that had covered the western border of the map was reported for moderate to high fluoride in the study. These villages were Vithoda, Fatepura, Malekhpur, Mahiyal and Sakri.

According to UPHSE, in semi-arid areas like our study area, water consumption versus environmental temperature is found to change the limit of fluoride intake through drinking water. Thus considering temperature factor, a reference value for computing optimal amount of fluoride intake was necessary. According to the calculation given by Galagan and Vermillon (1957) for our study area, it was found that the optimal fluoride content for drinking water ranged from 0.5 to 0.8 mg/l during the year 2012 and 2013. This indicated that 76% village population in the year 2012 and 81% in the year 2013 were found to consume fluorinated drinking water and were prone to fluorosis.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72°35'0"E
72°40'0"E
72°45'0"E
24°0'0"N
23°55'0"N
23°50'0"N
23°45'0"N
Map Showing Distribution of Fluoride in Kheralu Taluka,Mehsana District Year 2013
N
W
E
S
Kheralu Taluka
Legend
Fluoride in,mg/l
Year 2013
< 1.2
1.3 - 1.6
1.7 - 1.9
2 - 2.4
2.5 - 2.9
3 - 3.5
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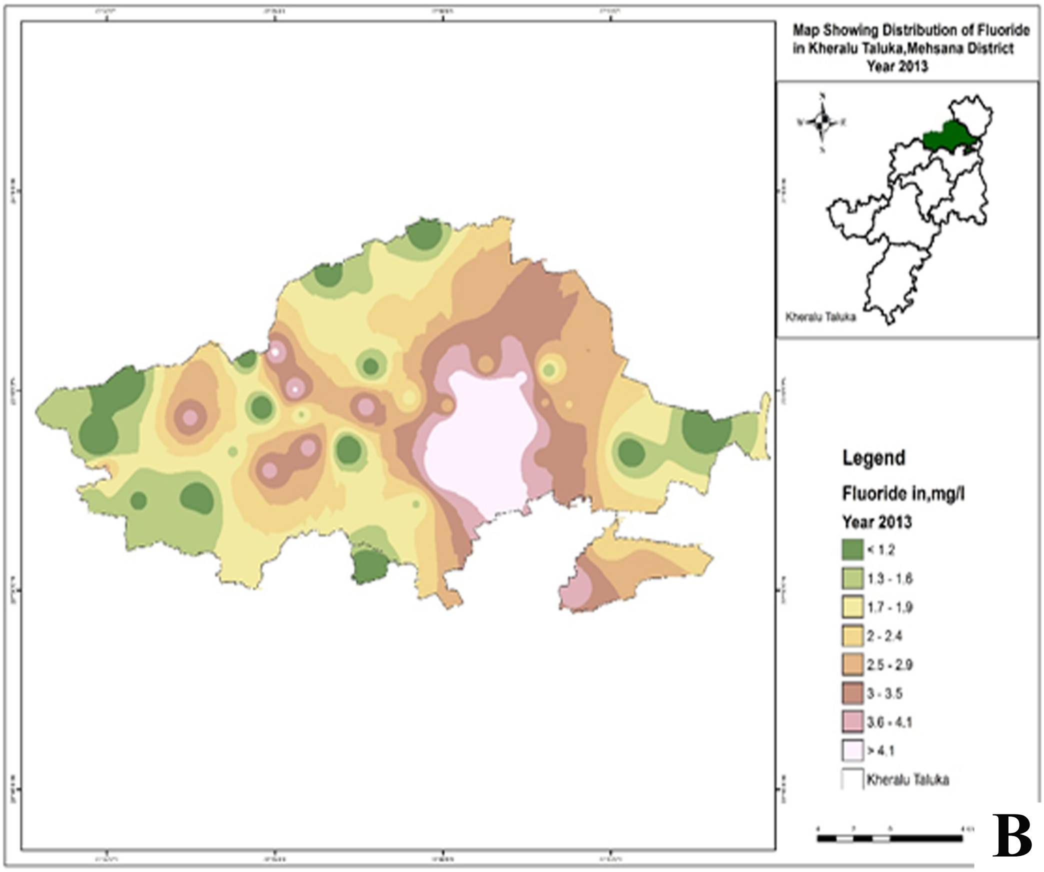

Map Showing Distribution of Fluoride in Kheralu Taluka,Mehsana District Year 2013
N
W
E
S
Kheralu Taluka
Legend
Fluoride in,mg/l
Year 2013
< 1.2
1.3 - 1.6
1.7 - 1.9
2 - 2.4
2.5 - 2.9
3 - 3.5
3.6 - 4.1
> 4.1
Kheralu Taluka
B

PLATE 8

PLATE 8

A: Spatial map of fluoride in Kheralu Taluka (2012)

B: Spatial map of fluoride in Kheralu Taluka (2013)

4.1.2. Influence of fluoride on human health

With such data indicating the villages to be under greater threat for the fluorosis due to much higher intake of fluoride (even more than its optimal level), next step to assess the impact on the area was to assess the village population affected. To check the prevalence of fluorosis in the study area, data from both, primary and secondary sources were collected. Primary source data was collected from officials of public health centres using questionnaire and local population by group interview while secondary data was collected from data available with Public health centres (PHC) and Community health centre (CHC) located in the taluka.

After analysing the data that was generated from primary sources (Table 11, as depicted in Figure 4), it was found that the population affected in the area were directly proportional to the fluoride intake from ground water. It was noted that out of 51 villages, 17 villages had 20-30% of its entire population affected and 16 villages had 30-40% of its total population affected. In 4 villages it was recorded that more than 50% of total population was affected due to fluorosis. In contrast to this, 14 villages were found comparatively safe with only 5 to 10% population affected by fluorosis.

After compiling the above data it was observed that on an average 24-26% of total population residing in Kheralu taluka (as described in Table 11) had developed one or the other symptoms of fluorosis.

In addition to primary data, the secondary data of government records were collected from health centres (PHC and CHC) (Tables 12 & 13). In the year 2012-2013, out of 23,512 population came for check-up at PHC's, 1235 had developed various fluoride related disorders *i.e.* 5% of the total surveyed population were reported to have fluorosis while rest have not developed any visible impact of fluorosis. Majority of affected population were reported by the public health centre situated at Dabhoda which falls in western zone of the taluka. The villages in this zone were located where there is ingress of high fluoride content in groundwater through various sources.

As per the government records, maximum cases were observed in post winter seasons. Also as per public health centre report males of villages under jurisdiction of Dabhoda and Panchha PHC's were found to be affected more than females of same villages.

Table 11: Village wise Status of Population affected in Kheralu taluka

Village Name	Males	Females	Total Persons	% Population affected
Dedasan	543	522	1,065	5
Lunva	2,378	2,193	4,571	5
Moti Hirvani	729	695	1,424	5
Nortol	1134	1054	2,188	5
Samoja	428	421	849	5
Shahpur (Santokpura)	240	216	456	5
Kuda	1,909	1,961	3,870	10 - 20
Limbdi	877	720	1,597	10 - 20
Nandali (Miyasana)	1053	987	2,040	10 - 20
Nani Hirvani	1102	1012	2,114	10 - 20
Nanivada	976	1454	2,430	10 - 20
Sangathala	1148	1070	2,218	10 - 20
Sadikpur	360	346	706	10 - 20
Sakari	1067	966	2,033	10 - 20
Amarpura	178	180	358	20 - 30
Ambavada	958	902	1,860	20 - 30
Balad	1,425	1,317	2,742	20 - 30
Chachariya	495	459	954	20 - 30
Chada	1,140	1087	2,227	20 - 30
Chansol	1,712	1,585	3,297	20 - 30
Dabhad	2,608	2,514	5,122	20 - 30
Davol	989	952	1,941	20 - 30
Machhava	781	748	1,529	20 - 30
Madhasana	991	974	1,965	20 - 30
Mandali	2,545	2,365	4,910	20 - 30
Panchha	1,392	1,315	2,707	20 - 30
Rasulpur	658	653	1,311	20 - 30

Village Name	Males	Females	Total Persons	% Population affected
Thangana	598	537	1,135	20 - 30
Varetha	1074	982	2,056	20 - 30
Vavdi (khe)	1034	967	2,001	20 - 30
Arathi	947	859	1,806	30 - 40
Chotiya	748	677	1,425	30 - 40
Dabhoda	5,164	4,960	10,124	30 - 40
Dalisana	1132	1039	2,171	30 - 40
Gajipur	548	1616	2,164	30 - 40
Gathaman	538	493	1,031	30 - 40
Gorisana	1,426	1,322	2,748	30 - 40
Mahekubpura	546	526	1,072	30 - 40
Mahiyal	769	785	1,554	30 - 40
Malarpura	558	534	1,092	30 - 40
Malekpur (Khe)	2,795	2,556	5,351	30 - 40
Mandropur	1,547	1,473	3,020	30 - 40
Nalu	981	913	1,894	30 - 40
Unad	1,494	1,440	2,934	30 - 40
Vaghvadi	1026	933	1,959	30 - 40
Vithoda	1,552	1,476	3,028	30 - 40
Fattepura(Khe)	400	377	777	40 - 50
Delvada	1194	189	1,383	Above 50
Lalawada	851	833	1,684	Above 50
Rahemanpura	369	270	639	Above 50
Suvariya	184	101	285	Above 50

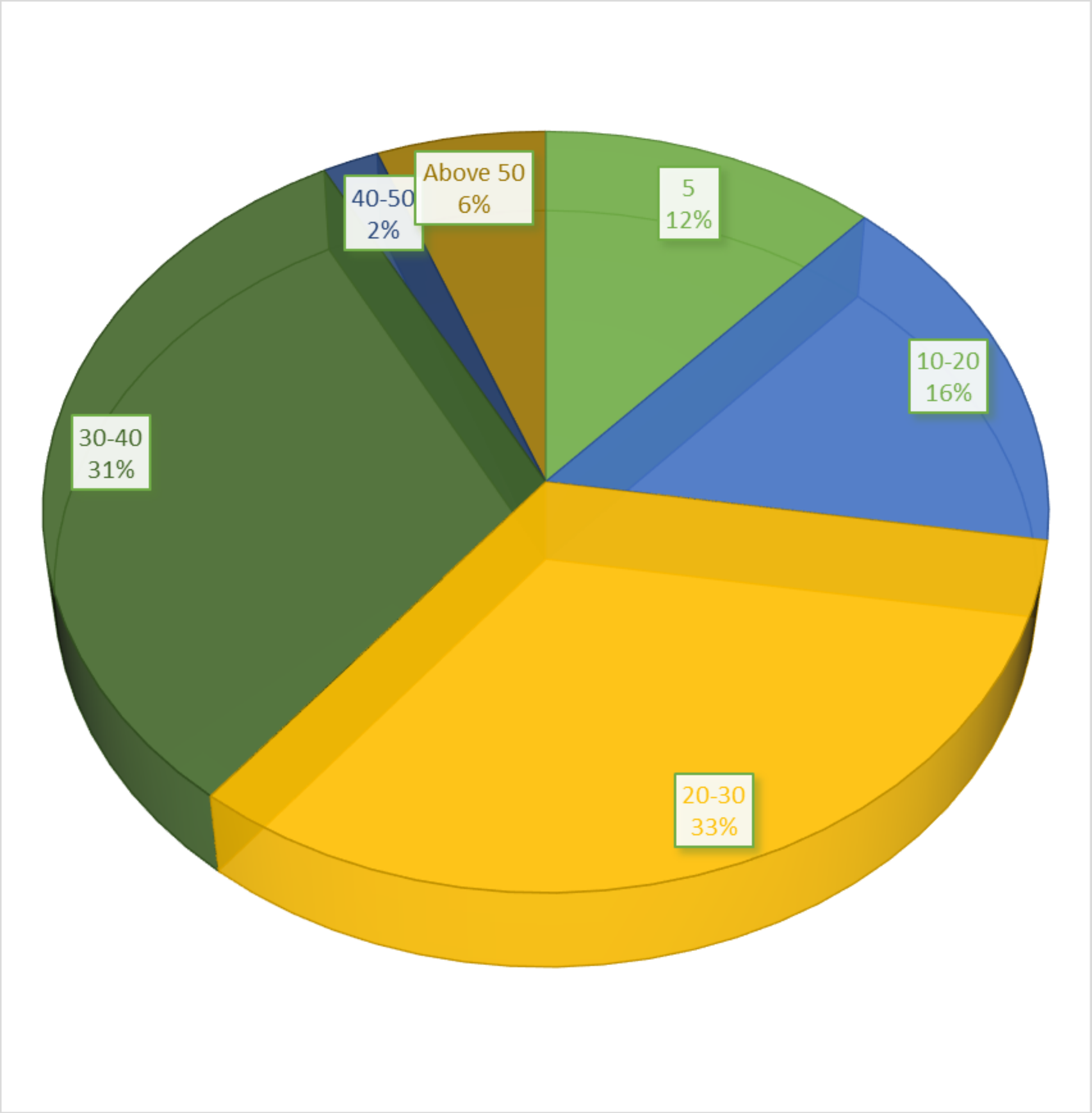


Figure 4: Percent Population affected

Table 12: PHC survey report (Symptom wise)

PHC	Surveyed population	Surveyed Family	Cases of fluorosis				
			Teeth Pain	Waist pain	Spinal Cord Problem	Joint pain	Total
Chansol	9538	1577	37	86	0	143	266
Dabhoda	11540	2350	110	235	83	313	741
Panchha	2434	340	41	43	0	9	93
Total	23512	4267	215	394	74	494	1177

Table 13: PHC survey report (Age group wise)

PHC	Age										
	1 to 10		11 to 21		21 to 30		Above 31		Total		
	M	F	M	F	M	F	M	F	M	F	Total
Chansol	0	0	6	5	19	32	86	118	111	155	266
Dabhoda	90	85	79	62	141	36	142	106	452	289	741
Panchha	10	5	15	12	21	5	12	13	58	35	93
Total	109	92	95	79	197	86	262	257	663	514	1177

4.1.3. Agricultural soil analysis:

To assess the fluoride concentration in the soils of the selected villages of the taluka, the samples were collected during post-harvest season. Sampling was done from total twenty villages. The concentrations of total fluoride in the soil of 0–45 cm depth is presented in Table 14. The mean total fluoride content of surface soil in the villages ranged from 0.3 to 10.98 kg/ha with a mean value of 5.4±3.24. The lowest concentration of fluoride was recorded in the soil samples of Ambavada village while highest concentration was reported from the samples from Delwada village. This village was also reported for the highest population affected due to fluorosis.

The physico-chemical analysis of the soil samples is shown in Tables 15-16 and Figures 5-17. The pH in the soil samples was found to vary from 7.1 to 9.49 (Tables 15 and 16) while cation exchange capacity of the soil samples varied from minimum value, i.e. 0.35 µS/cm to maximum value of 7.65 µS/cm.

Soil organic carbon of the samples varied from 0.27(%) to 0.49 (%). Available phosphorous of soil samples ranged from 16.42 to 125.1 kg/ha and potassium from 205.1 to 1050.18 kg/ha. The content of sodium ranged from 8.96 to 197.12 kg/ha while that of calcium ranged from 67.33 kg/ha to 163.75 kg/ha. Other than this, the micronutrients like zinc, iron, manganese copper and sulphur were also analysed. The values of zinc varied from 0.5 to 7.98 kg/ha, iron from 14.16 to 71.91 kg/ha, manganese from 4.93 to 86.47 mg/ha, copper from 0.68 to 6.77 kg/kg and sulphur from 0 to 53.32 kg/ha.

The correlation analysis was performed between fluoride content and analysed soil quality parameters. The Correlation analysis (Table 17) showed very strong positive correlation between phosphorous-fluoride (r = 0.8) while very strong negative correlation between Calcium-fluoride (r = -0.84). A weak negative correlation is observed between CEC-fluoride (r = -0.38), Iron-fluoride(r = -0.48) and Sodium-fluoride(r = -0.42). Rest all parameters showed very weak negative correlation with fluoride.

Table 14: Fluoride concentration in soil

Sr. No	Village name	Fluoride Concentration (kg/ha)
1	Ambavada	0.3
2	Chotiya	4.26
3	Dabhad	0.9
4	Dalisana	6.72
5	**Fatepura**	**5.83**
6	**Gathaman**	**6.72**
7	**Gorisana**	**3.36**
8	Lalavada	10.76
9	**Malarpura**	**6.37**
10	Malekhpur	6.95
11	Mandali	3.54
12	Mandropur	9.23
13	Nani hirvani	2.02
14	**Delwada**	**10.98**
15	Panchha	1.8
16	Rehmanpura	7.62
17	Suvariya	4.71
18	Vaghvadi	9.64
19	Varetha	6.72
20	Vavdi	0.41

Table 15: Statistical evaluation of other soil parameters

	Min	Max	Mean±SD
pH	7.1	9.49	8.42±0.56
CEC (µS/cm)	0.35	7.65	2.6±1.86
SOC (%)	0.27	0.49	0.34±0.07
P_2O_2 (kg/ha)	16.42	125.1	61.23±29.43
K_2O_2 (kg/ha)	205	1050	410.7±220.08
Zinc (kg/ha)	0.5	7.98	2.3±1.88
Iron (kg/ha)	14.16	71.91	28.43±14.79
Mn (kg/ha)	4.93	86.47	60.3±20.46
Copper (kg/ha)	0.68	6.77	3.09±1.58
Sulphur (kg/ha)	0	53.32	45.59±11.4
Sodium (kg/ha)	8.96	197.12	64.48±43.29
Calcium (kg/ha)	67.33	163.75	104.67±30.12

Figure 5: Fluoride content in agricultural soils

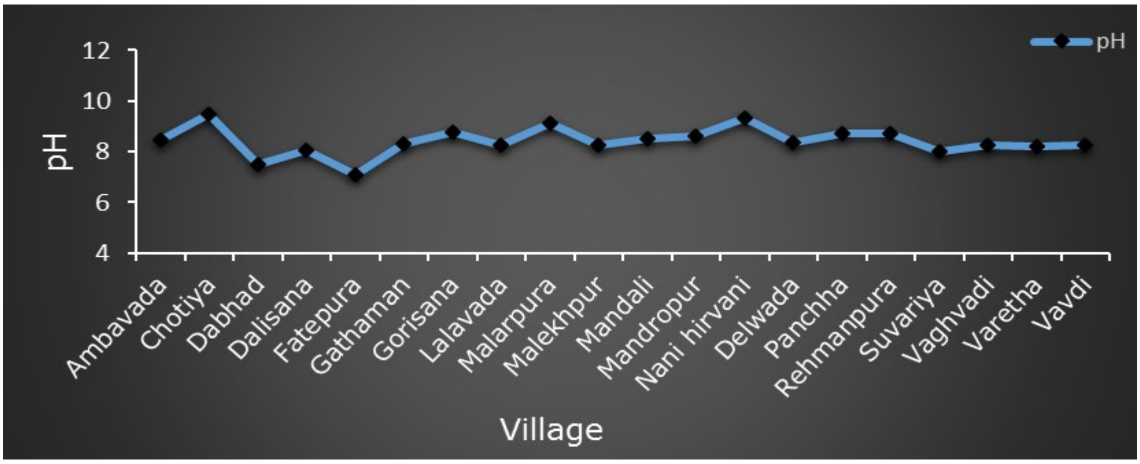


Figure 6: pH of agricultural soil

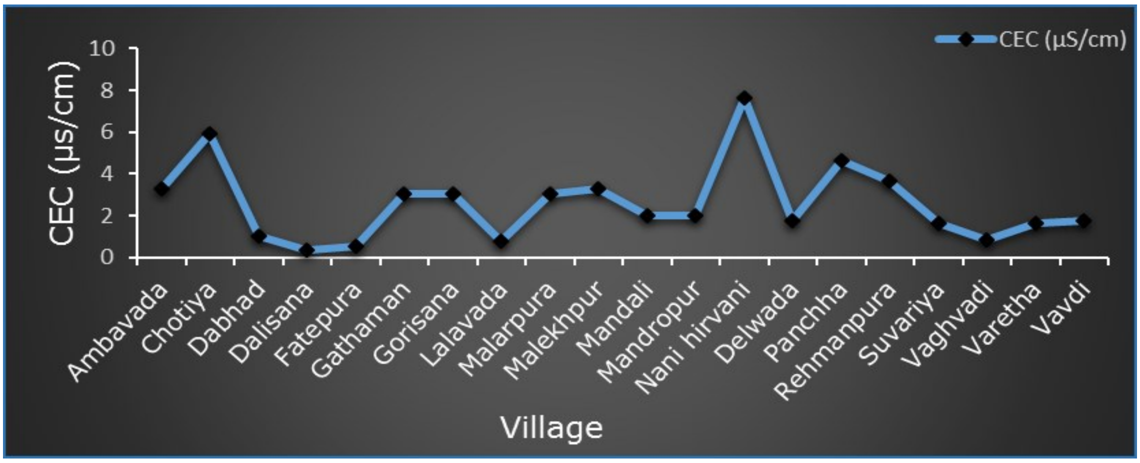


Figure 7: Cation exchange capacity of agricultural soil

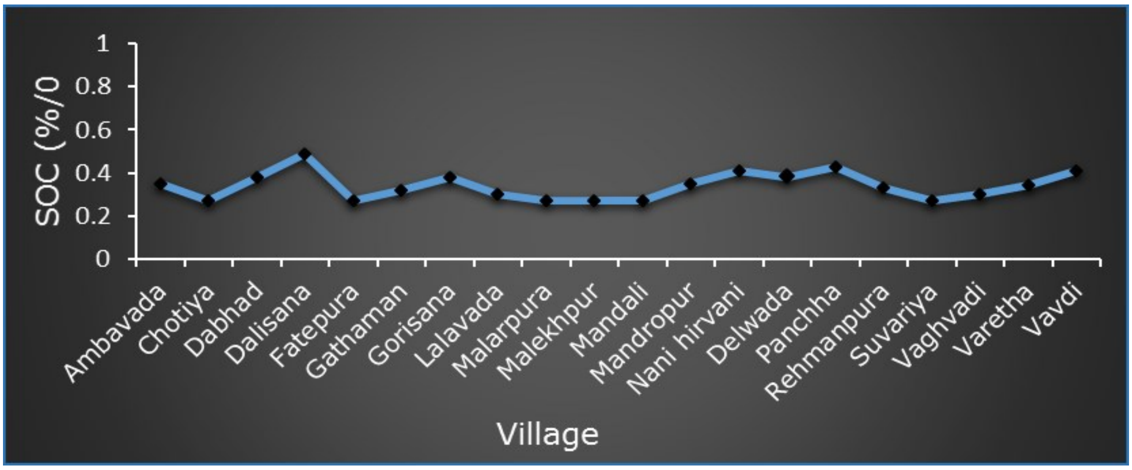


Figure 8: Soil organic carbon of agricultural soil

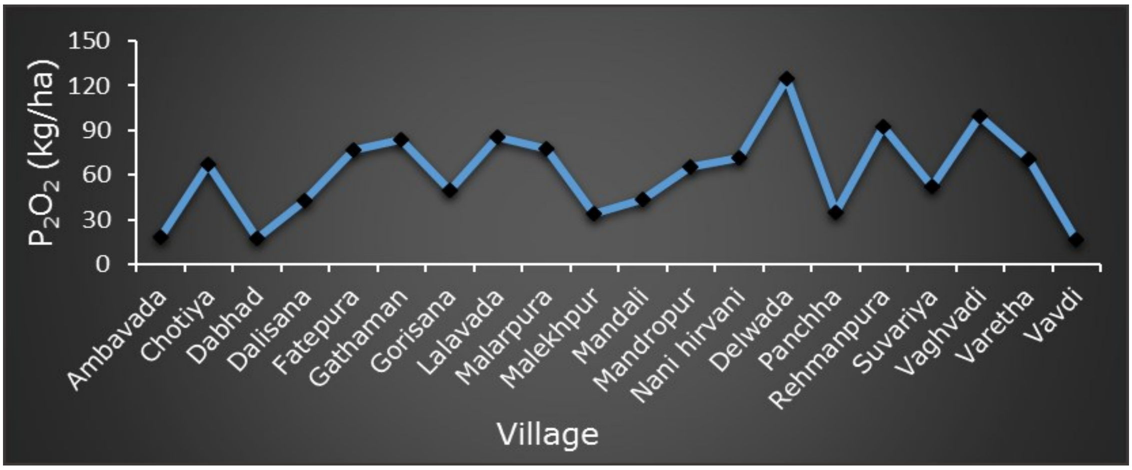


Figure 9: Available phosphorus in agricultural soil

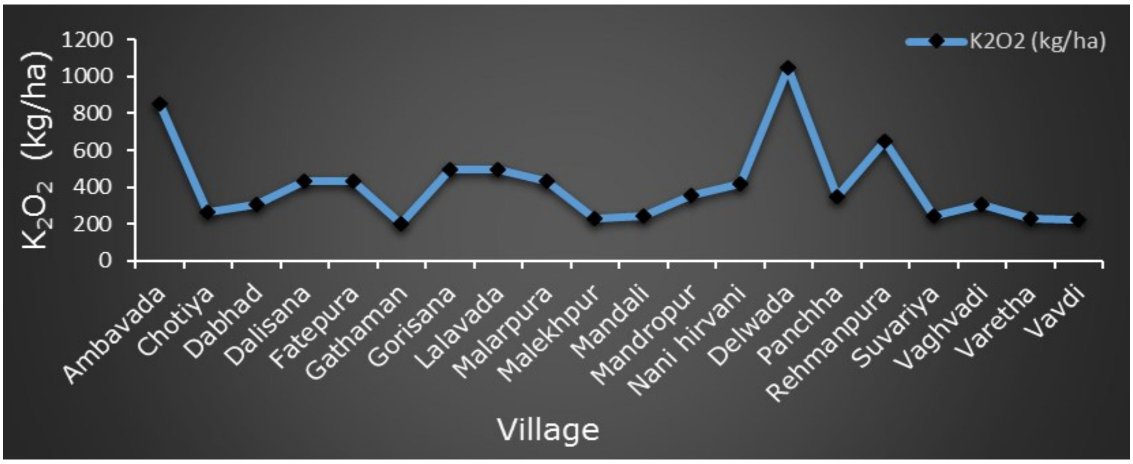


Figure 10: Available potassium in agricultural soil

Figure 11: Zinc content in agricultural soil

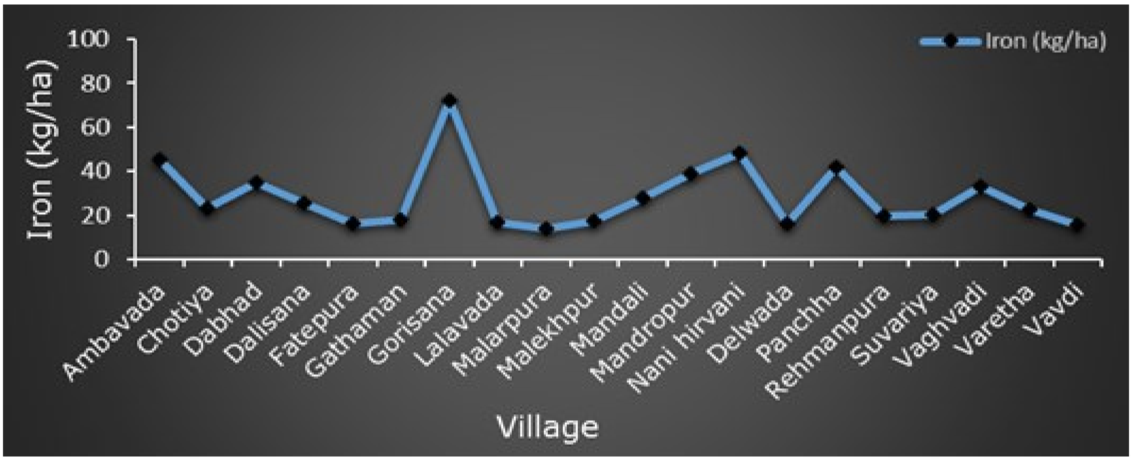


Figure 12: Iron content in agricultural soil

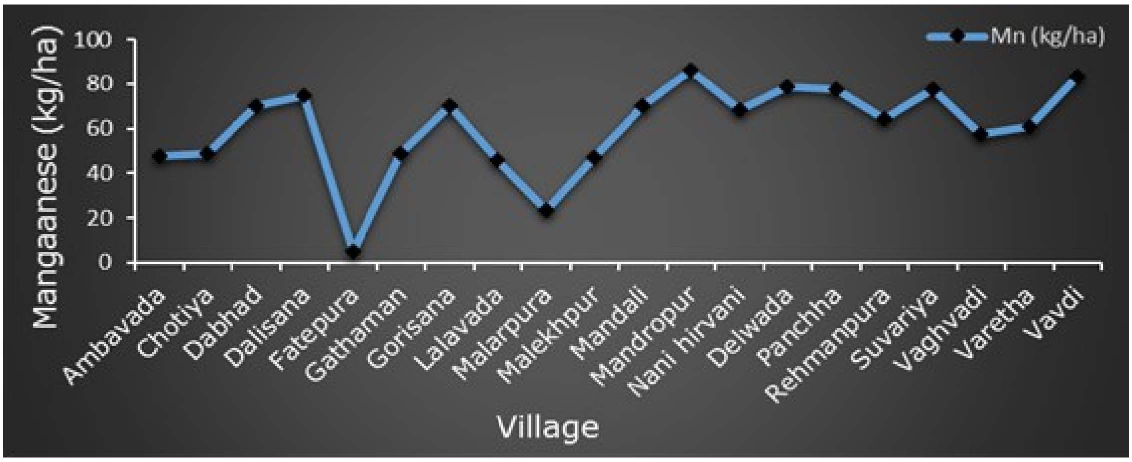


Figure 13: Manganese in agricultural soil

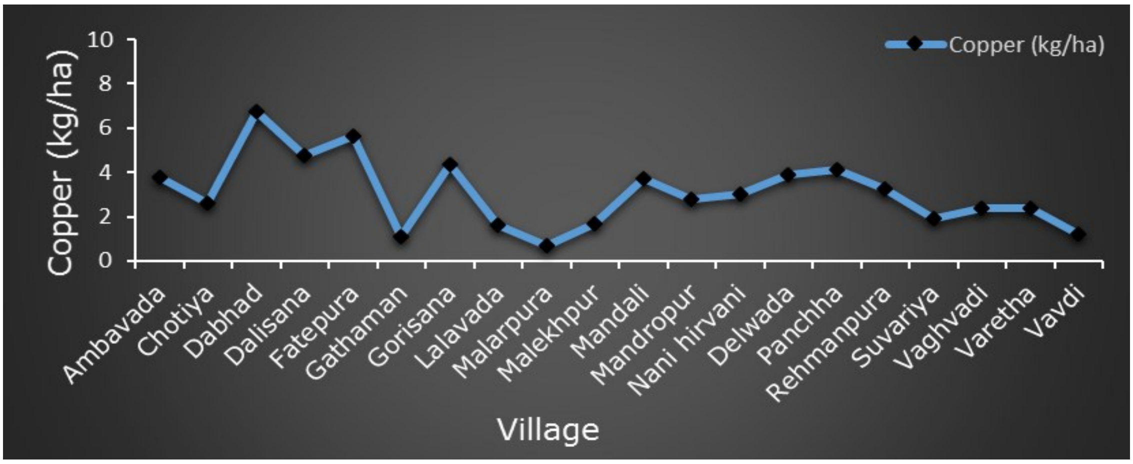


Figure 14: Copper content in agricultural soil

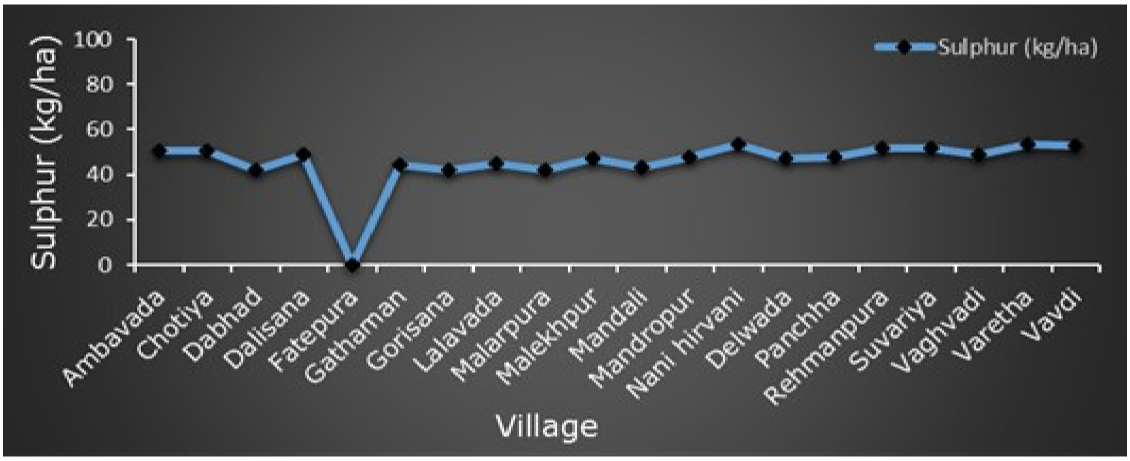


Figure 15: Sulphur content in agricultural soil

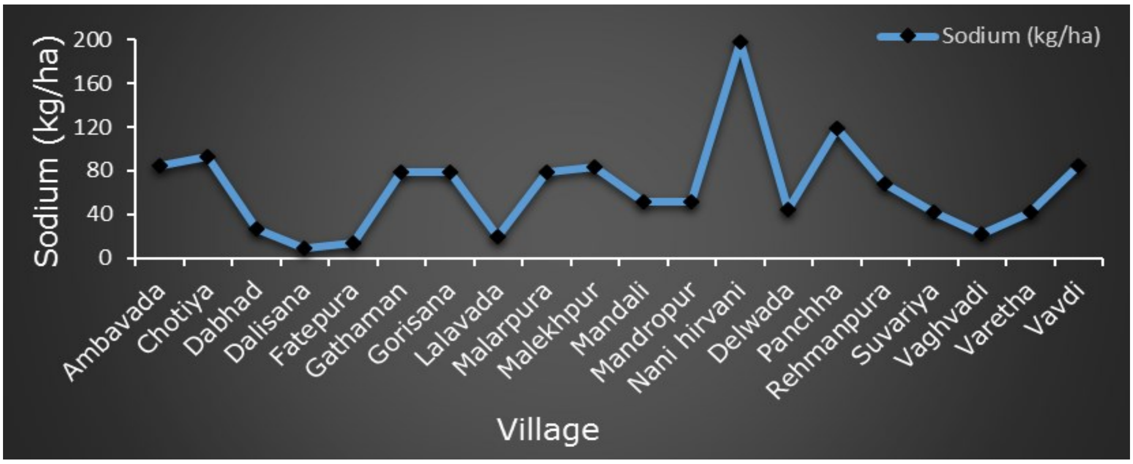


Figure 16: Sodium content in agricultural soil

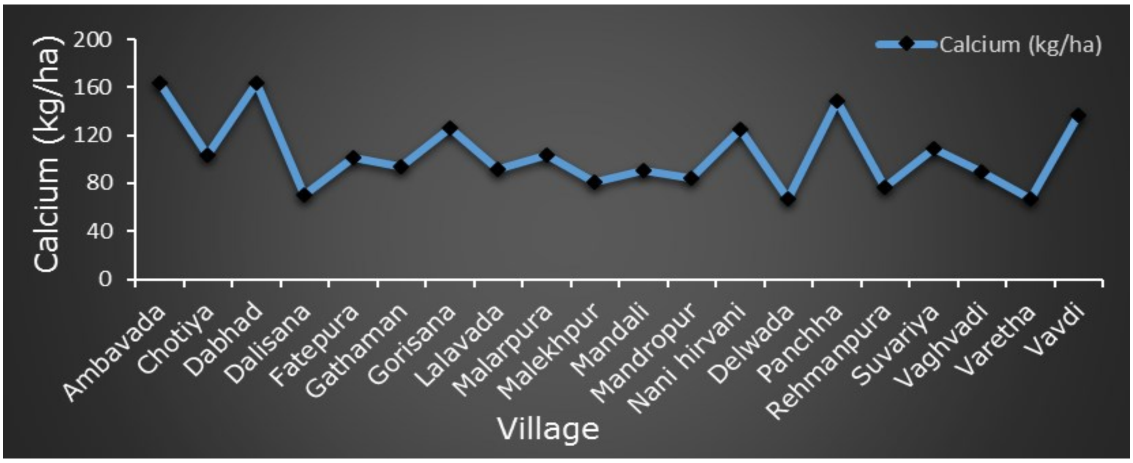


Figure 17: Calcium content in agricultural soil

Table 16: Physico-chemical parameters of agricultural soils

Village name	pH	CEC	SOC (%)	P_2O_2 (kg/ha)	K_2O_2 (kg/ha)	Zn (kg/ha)	Fe (kg/ha)	Mn (kg/ha)	Cu (kg/ha)	S (kg/ha)	Na (kg/ha)	Ca (kg/ha)
Ambavada	8.47	3.3	0.35	18.31	848	1.71	45.25	47.94	3.77	50.85	85.12	163.75
Chotiya	9.49	5.91	0.27	66.96	267	1.75	22.99	48.61	2.6	50.85	92.32	103.88
Dabhad	7.5	1.04	0.38	17.43	309	7.98	34.86	69.89	6.77	42.12	26.88	163.75
Dalisana	8.04	0.35	0.49	43.08	432	2.11	25.76	74.82	4.75	49.06	8.96	70.58
Fatepura	7.1	0.52	0.27	77.1	432	0.99	16.13	4.93	5.65	0	13.44	101.06
Gathaman	8.31	3.04	0.32	83.51	205	0.86	18.15	49.02	1.12	44.13	78.4	94.17
Gorisana	8.77	3.04	0.38	49.77	494	1.93	71.91	69.89	4.35	42.12	78.4	126.42
Lalavada	8.28	0.78	0.3	85.56	494	1.35	17.07	45.7	1.62	45.03	20.16	91.6
Malarpura	9.14	3.04	0.27	77.66	432	0.5	14.16	23.61	0.68	42.12	78.4	103.73
Malekhpur	8.28	3.27	0.27	33.76	230	1.17	17.48	46.96	1.66	47.04	82.88	80.78
Mandali	8.53	2	0.27	43.77	242	1.12	27.78	69.89	3.72	43.24	51.52	90.14
Mandropur	8.61	2	0.35	64.97	358	1.17	39.2	86.47	2.78	47.94	51.52	84.19
Nani hirvani	9.3	7.65	0.41	71.57	415	1.84	48.39	68.1	3.05	53.32	197.12	124.49
Delwada	8.38	1.74	0.38	125.1	1050	3.1	16.36	78.85	3.9	47.27	44.8	67.33
Panchha	8.71	4.61	0.43	34.47	346	3.01	41.67	77.73	4.13	47.94	118.72	148.43
Rehmanpura	8.73	3.63	0.33	92.41	652	2.18	19.94	64.07	3.25	51.52	68.56	77.1
Suvariya	8	1.65	0.27	52.34	247	2.87	20.39	77.51	1.89	51.97	42.56	108.53
Vaghvadi	8.26	0.87	0.3	99.47	309	1.8	32.93	57.57	2.38	49.06	22.4	89.38
Varetha	8.21	1.65	0.34	70.87	230	6.72	22.45	60.93	2.38	53.32	42.56	67.33
Vavdi	8.28	1.74	0.41	16.42	222	1.66	15.68	83.33	1.21	52.87	84.8	136.57

Table 17: Correlation analysis

	pH	CEC	SOC	P	K	Zn	Fe	Mn	Cu	S	Na	Ca	F
pH	1	0.79	0.01	0.15	0.07	-0.34	0.27	0.17	-0.44	0.57	0.7	0	-0.07
CEC		1	0.06	-0.03	0	-0.18	0.34	0.04	-0.18	0.34	0.93	0.27	-0.38
SOC			1	-0.27	0.22	0.28	0.4	0.59	0.38	0.3	0.2	0.24	-0.28
P				1	0.36	-0.2	-0.3	-0.22	-0.23	-0.12	-0.15	-0.66	0.8
K					1	-0.06	0.11	0	0.28	-0.02	-0.03	-0.01	0.21
Zn						1	0.09	0.31	0.45	0.18	-0.2	0.21	-0.21
Fe							1	0.33	0.4	0.14	0.38	0.49	-0.42
Mn								1	0.08	0.67	0.14	0.06	-0.13
Cu									1	-0.42	-0.23	0.31	-0.29
S										1	0.35	0	-0.06
Na											1	0.38	-0.49
Ca												1	-0.84
F													1

4.1.4. Fluoride concentration in crop plants

Fluoride concentration in vegetation depends on fluoride concentration of soil as well as irrigation water. Kheralu taluka is an agricultural zone with around 275 km^2 of area under crop cultivation. It is rich in cultivating many important agricultural crops. *T. aestivum* (*Triticum aestivum* L.) and *P. typhoides* (*Pennisetum typhoides* L.) being the major edible crop of the area. The grains of *T. aestivum* and *P. typhoides* were collected from 5 selected villages.

The fluoride content in *T. aestivum* L. is as shown in Table 18. The mean total fluoride content in *T. aestivum* L. ranged from 17.3 to 46.18 µg/g with a mean value of 25.80±20.24 µg/g. The lowest concentration were estimated in grains collected from Gorisana village while highest concentration was reported from Delwada. The Bio-conentration factor for *T. aestivum* L. was found to range from 0.13 to 0.22.

The fluoride content in *P. typhoides* L. is shown in Table 19. The mean total fluoride content ranged from 8.4 to 92 µg/g with a mean value of 18.53±24.54 µg/g. The Lowest concentration was recorded in the field samples of Gathaman village while highest concentration was reported from Malarpura village. The Bio-concentration factor for *P. typhoides* L. was found to be varied from 0.05 to 0.27.

The Estimated Daily Intake of fluoride was calculated for the two major crops grown in the Kheralu taluka (Table 20). It is evident from the data that except for Malarpura, the EDI for *T. aestivum* was much higher than *P. typhoides*. For children of 4 to 7 years age group, EDI for *T. aestivum* varied from 0.126 to 0.376 mg/kg/day while for *P. typhoides* ranged from 0.029 to 0.320 mg/kg/day. For teenagers, EDI for *T. aestivum* ranged from 0.094 to 0.301 mg/kg/day while for *P. typhoides* it varied from 0.027 to 0.310 mg/kg/day. For adults EDI for *T. aestivum* varied from 0.063 to 0.192 mg/kg/day while for *P. typhoides* it varied from 0.018 to 0.204 mg/kg/day. For all the age groups, it was found that EDI after consumption of grains of *T. aestivum* and *P. typhoides* were above permissible limit i.e. 0.06 mg/kg/day

Table 18: Fluoride content in T. aestivum grains

Sr. No	Villages	*T. aestivum* grain (µg/g)	BCF
1	Fatepura	25±1.97	0.19
2	Gathaman	20±1.4	0.13
3	Gorisana	17.3±0.5	0.22
4	Malarpura	31.15±2.18	0.22
5	Nava Delwada	46.15±2.53	0.19

Table 19: Fluoride content in P. typhoides grains

Sr. No	Villages	*P. typhoides* grain (µg/g)	BCF
1	Fatepura	19.8±1.21	0.15
2	Gathaman	8.4±1.1	0.09
3	Gorisana	17.9±1.12	0.24
4	Malarpura	92±1.53	0.27
5	Nava Delwada	11.1±1.28	0.05

Table 20: EDI for selected villages

		Fatepura	Gathaman	Gorisaana	Malarpura	Delwada
T. aestivum	Children of age group 4 to 7 yrs	0.126	0.138	0.232	0.172	0.376
	Males of age group 10 to 12 yrs	0.101	0.111	0.185	0.138	0.301
	Females of age group 10 to 12 yrs	0.094	0.103	0.172	0.128	0.28
	Adult males	0.064	0.071	0.118	0.088	0.192
	Adult females	0.063	0.069	0.115	0.086	0.187
P. typhoides	Children of age group 4 to 7 yrs	0.069	0.029	0.062	0.320	0.039
	Males of age group 10 to 12 yrs	0.067	0.028	0.060	0.310	0.037
	Females of age group 10 to 12 yrs	0.064	0.027	0.058	0.299	0.036
	Adult males	0.044	0.019	0.040	0.204	0.025
	Adult females	0.041	0.018	0.037	0.191	0.023

4.1.5. Discussion

4.1.5.1. Spatial mapping of fluoride

Fluoride is an essential oligo-element necessary for the development of teeth and bones. From past few decades, fluoride concentration in the groundwater of the study area had increased above the permissible limit. In India, it was previously recorded that of total 26 states were found to have high fluorinated water. A survey conducted by Gupta and Despande (1998), Dhiman and Keshari, (2006) and Patel and Bhatt (2007) reported high fluoride concentration in groundwater of Gujarat. Patel and Bhatt (2007) have earlier reported fluoride concentration in 4 districts of North Gujarat. They investigated that 80% villages from Sabarkantha District, 95% villages from Patan District, 92% villages from Banaskantha District and 95% villages from Mehsana District had fluoride level in groundwater above the permissible limit. Mehsana District which is under groundwater mega-depletion zone is one of the most affected district due to high fluoride in groundwater. Defluoridation camp carried out by the government showed Kheralu taluka as one of the most affected Taluka in Mehsana District.

In the present study, it was investigated that the fluoride concentration in 44 % villages in 2012 and 46% villages in 2013 had fluoride above the permissible limit. The groundwater in Kheralu Taluka is stored in shallow and deep aquifers created by alluvial layers. Gupta *et al.* (2005) reported several high fluoride pockets in cambian zone are aligned along the recharge area. These pockets of high fluoride in the recharge area suggests preferential dissolution of fluoride-bearing minerals present in the Aravalli foothills (Choudhary *et al.*, 1984). According to Handa (1975) high rate of evapo-transpiration, comparatively low rainfall, intensive irrigation, alkaline environment, longer residence time of water in the weathered aquifer zone and low rate of dilution are favourable factors for the dissolution of fluorine-bearing minerals and thereby increase of fluoride concentration in the groundwater as reported in the study area.

In addition, the lineages mapped in the study area with high fluoride concentrations were in the path of subsurface flow of groundwater from Aravalli mountain which brings the water with high fluoride concentration. The North-eastern border of the Mehsana District comprises of degraded gneiss rocks of Delhi supergroup (which acts as fluoride source) in addition to sedimentary rocks of available ranges. All these are responsible for adding fluoride to groundwater of shallow aquifers of the area.

Overall 38% villages in the present study area were reported to have fluoride concentration above 2 ppm in potable groundwater. Our results are in accordance with the study conducted by Gupta and Despande (1998). Salve *et al.,* (2008) had recorded 40% samples in Kadi tehsil of Mehsana that had the fluoride level above permissible limit. In Nalgoda district of Andhra Pradesh, Brindha *et al.,* (2011) reported 30% villages with high fluoride concentration in groundwater. 76.6% and 95% of groundwater samples collected from Rajgarh Tehsil of Churu District (Muralidharan *et al.,* 2002) and Hanumangarh District (Suthar *et al.,* 2008) of Rajasthan respectively were found to have fluoride above permissible limit for drinking purposes.

High concentration of fluoride in drinking water leads to fluorosis (Short *et al.,* 1937; Sarala and Rao, 1993; Mohan *et al.,* 1995). According to Whiteford (1997) on an average 75 – 90% of ingested fluoride is absorbed in an acidic stomach and is converted into hydrogen fluoride (HF). Once absorbed into the blood, fluoride readily distributes throughout the body, with approximately 99% of the body burden of fluoride retained in calcium rich areas of the body such as bones and teeth (dentine and enamel) (WHO, 1997).

Galagan *et al.* (1957), noted that areas with similar fluoride concentration but different temperatures zones have varying cases of fluorosis. They collected data on the drinking habits of children in different temperature conditions. The aggregate data was used to formulate a range (0.7–1.2 ppm) of optimal fluoride concentrations for mean maximum temperatures between 50 and 90°F. The optimal level of fluoride in drinking water has since then universally been calculated by applying the equation of Galagan *et al.* (1957), which permits the calculation of water intake as a function of temperature.

The results of this study indicated that the recommended level of fluoride in drinking water of Kheralu Taluka should be set between 0.5 and 0.8 ppm. The optimal concentration has been calculated to be 0.6 by the modified equation of Galagan and Vermillion (Locker, 1999) and authenticated by the dose–response study, which also indicates a very close cut-off value at 0.6 ppm concentration of fluoride in drinking water. Similar findings were earlier reported for endemic regions of South India (Visvanathan *et al.,* 2009).

4.1.5.2. Human health assessment

Fluorosis is a slow, progressive, crippling malady, which affects every organ, tissue and cell in the body and results in health complaints having overlapping manifestations with several other diseases. Drinking water may not be the only source of fluoride. Olsson (1978) found mild degrees of dental fluorosis in 18% of the population living in areas with as low as 0.2 to 0.3 mg F/litre in the drinking water. Ibrahim *et al.* (1995) found the prevalence of dental fluorosis to be 91% in a study on Sudanese children consuming water with 0.25 mg F/litre. Also in India, dental fluorosis has been reported in areas where the fluoride concentration of the drinking water was well below the indicated maximum limit (Rao and Mahajan, 1990).

On the contrary, data from this study corroborate a number of other recent investigations (Choubisa 1997 Choubisa *et al.* 2001; Gopalakrishnan 2000; Dhar *et al.* 2007) indicating that the rate and extent of fluorosis in Kheralu taluka of Mehsana District increased with an increase of fluoride level in drinking water.

The results of analysis of primary data revealed that on an average 24-26% of the total population residing in Kheralu Taluka has developed one or the other symptoms of Fluorosis. Hussain *et al.* (2010) have found the prevalence of skeletal fluorosis to be 47.5% in a fluorotic area of central Rajasthan. In a study conducted by Kotecha *et al.* (2012) in Gujarat, India, have found the prevalence of dental fluorosis to be 59.31% in areas having high fluoride content in the water while 39.21% in the areas having low fluoride content in water. Choubisa *et al.* (2001) revealed that prevalence of skeletal fluorosis to be 7.4% and 37.7% adults aged more than 21 years in areas having mean water fluoride concentration of 1.7 ppm and 6.1 ppm respectively.

In the current study, males (52%) were found to be more affected than females (48%). Krishnamachari *et al.* (1973) investigated that prevalence of fluorosis among male was higher than female and this difference was more obvious in children than among adolescents and adults. Bharati and Rao (2003) conducted a study in Dharwad district of Karnataka which revealed the prevalence of fluorosis among males (66%) was significantly higher as compared to females (57.94%). In a study in southwestern

China, Watanabe *et al.* (2000) have also found that the prevalence among female (30%) was lesser than among male (66%). In a study from Tanzania, where a ubiquity of juvenile skeletal fluorosis was 4.4% and it was found to be more common in males (Jarvis *et al.,* 2013).

It was observed that the population with the age group of 21-30 and above 31 in our study area were severely affected. Shashi *et al.* (2008) have found the prevalence of skeletal fluorosis was be high in the age groups of 30-40 years and 50-60 years age group. In another study from Rajasthan, India it was revealed that the incidence of skeletal fluorosis was 27.6% in Dungarpur and 12% in Udaipur among people of 21 years age. This study also showed that the maximum incidence of skeletal fluorosis occurred at age of 44 years and the minimum incidence was found in the age group of 21-28 years (Choubisa *et al.,* 2010). A study by Pandey (2010) has revealed that incidences of skeletal fluorosis increased with the age group. Our results are in accordance with these previous reports.

4.1.5.3. Soil fluoride

In the present study, we reported that the fluoride in the surface soil varied from 0.4 kg/ha to 10.98 kg/ha and was found to be lower than the worldwide average of 320mg/kg (Alina and Henryk, 1984). Similar finding was reported by Jha (2012); Madhvan and Subramanium (2002) and Chaudhary *et al.* (2009) for TF of the surface soil from agricultural land. In our study highest fluoride content in the soil had been reported from villages like Lalavada, Mandropur, Malarpura and Nava Delwada. The high concentrations might be associated with geogenic and anthropogenic sources in Kheralu Taluka.

The Geomorphological structure of Kheralu Taluka depicted thick layer of alluvial soil with a clayey fraction. At some source points towards northeastern belt at foothills of the Aravalli mountain weathered rocky layer of Delhi supergroup found to contain granite and other rocks. Weathering of these rocks can add up fluoride in the soil. In addition to the geogenic source high fluoride level might be due to irrigation of soil with fluorinated groundwater and application of phosphate fertilizer. This can be distinctly observed from a high degree of positive relation between phosphorous and fluoride which revealed that high fluoride in soil was due to an addition of phosphate fertilizer to the soil.

The negative relationship between F and SOC showed insignificant biogenic control of fluoride cycle which presents an inactive role of microbes in the mineral cycling of fluoride. In addition to it, the negative relation of the CEC with fluoride revealed the occurrence of non-reactive interaction on clay surface of the soil. Evidently, the high alkalinity results in a larger fraction of fluoride leach at higher pH. Such soils have higher water soluble fluoride caused due to the availability of fluoride in ions form formed by repulsion force that exists between fluoride ions and other ions at higher pH.

As reported in our study, a negative relation between calcium and fluoride indicated the addition of gypsum in the fields as well as limestones present at the depth which decreases the leaching of fluoride by forming CaF at higher pH. Similarly, high sodium had the same impact on soil fluoride. While the negative relation of soil micronutrient with fluoride indicated an increase in fluoride content with decreased micronutrients which can be correlated with the weak interaction of fluoride with other minerals on clay surface of soil caused by alkaline pH.

Thus excess fluoride in the region at some place like Vaghvadi, Varetha and Rehmanpura, might be due to excess fertilizer application, induced weathering of soils and irrigation of cultivated land by fluoride rich groundwater. In the study area, the groundwater fluoride concentrations were beyond permissible limit (> 1.5 mg/l) in the pre-monsoon and monsoon seasons.

4.1.5.4. Fluoride content in major crops

The fluoride concentration of *P. typhoides* varied from 4 to 92 ug/g while fluoride concentration of *T. aestivum* varied from 0.06 to 46.15 ug/g. Previous studies conducted by various researchers obtained similar results of accumulation of fluoride in grains grown on land irrigated with fluorinated water. Earlier reports by Patel and Bhatt (2008) for fluoride accumulation in food crops grown in the fields of North Gujarat and Gautam and Bhardwaj (2010) for crops grown in fields of Nava tehsil of Nagpur district obtained similar results.

Total fluoride concentration in the soil generally do not correlate well with the uptake of fluoride by roots because the fluoride taken up by the plants from soil solution are easily in the form of desorbable fluoride (Brewer, 1965; Cooke *et al.,* 1976; Gisiger, 1968). A number of factors influence the uptake and accumulation of fluoride by plants viz: initial fluoride concentration, solubility of mineral phases such as Ca and P content (Fawell *et al.,* 2003); soil type (Conover and Poole, 1971), and soil reaction (pH) (Stevens *et al.,* 2000). In this regard, we obtained contradictory results. The alkaline pH of the soil of the study area might have converted fluoride complex into free fluoride ion which increased the bioavailability of fluoride further enhancing absorption by plants mainly by passive uptake in root system (Barrow and Ellis, 1986; Wenzel and Blum, 1992). However, Cooke *et.al.* (1978) noted that positively charged AlFx complex are more easily taken up by the roots than free F^- ion due to anion exclusion by the negatively charged cell walls, particularly in the case of acidic soil where F exists as AlFx complex (Elrashidi and Lindsay, 1986). Stevens *et al.* (1997) also reported that F was taken up by the plant in the form of AlF_3 complex from solution culture containing Al and F.

In addition to soil fluoride, continuous use of irrigation water carrying high fluoride concentrations might lead to its accumulation beyond the critical limits and affect the quality of crops (Kanwar and Mehta, 1968; Paliwal *et al.,* 1969; Singh *et al.,* 1987). Most of the applied fluoride is retained on the soil surface and is not leached down even after a considerable period (Tracy *et al.,* 1984; Peek and Volk, 1985; Robbins, 1986). Paliwal *et al.* (1969) reported that on an average 7 mg/l of fluoride along with EC values of 6 mmho/cm were detrimental to the growth of *T. indica*. A safe limit of 10 mg/l of fluoride was proposed for all types of crop plants by Leone *et al.* (1948).

BCF is an important parameter that has been used widely for the assessment of contamination in the soil (Alonso *et al.* 2003; Tome, *et al.,* 2003). Jha *et al.* (2011) used BCF as an indicator of affinity for the accumulation of F in plants. Basically, BCF is a relative uptake of F ion by plants with respect to the presence of F ion in solution. A ratio greater than 1 indicates hyper-accumulation of F in plants while less than 1 is a hypo-accumulation (Gupta and Banerjee, 2009). In our study, it was observed that only the fraction (below 1) of fluoride was accumulated in the grain. Possibly the root retained much of the F and restricted its translocation to different tissue parts. Generally the crops genetic characteristics are also responsible for the differential accumulation (Peris *et al.* 2007). However, Swartjes *et al.* (2007) also reported that BCF values are not always constant in specific vegetables and are largely dependent upon the types of soil and its characteristics on which the vegetables are grown as well as plant factors like type of plant and their growth rate.

In our phonological study during field visits, no phytotoxic symptoms were observed on plants grown in the fields irrigated with fluorinated water. This might be due to F exclusion at the root or detoxifying F at a cellular level in a plant (Jha, *et al.,* 2008). Khandare and Rao (2006) suggested that the occurrence of phytotoxic symptoms due to F varied greatly with plant species and cultivars. Large differences in fluoride concentrations among different plant species and a great variation in the degree of tolerance to fluoride pollution were observed by Haidouti *et al.* (1993). Some accumulator species can concentrate F^{-1} up to 4,000 μg/g dry mass and without any signs of injury, while many others, in contrast, are extremely sensitive to concentrations even <20 μg F/g dry mass like Gladiolus and Freesia (Cronin *et al.,* 2000). In plants, F generally occurs in the range of 1 - 10 mgF/g dry weight in most species. High concentration of F causes various changes in mineral content in plants which are important for physiological and biochemical reactions. Injury to the most sensitive vegetation by HF begins at a concentration <1ppb, or 0.8 mg/m^3, for a 1 to 3 day period, with a long-term threshold concentration of 0.25 - 0.30mg/m^3. The general symptoms of F injury such as a necrotic lesion, chlorosis, and burning first appear in the leaf tips and margins. Afterwards, physiological parameters, viz. root length, shoot length, dry weight, vigor index, chlorophyll content, catalase activity, tolerance index, germination rate, germination relative index, mean daily germination decreases with increasing F. Besides, fluorides have been found to inhibit or stimulate enzymes involved in glycolysis, respiration, photosynthesis, and metabolite transport across membranes and other processes Response of F depends upon factors such as dose, duration of exposure, age, and genotypes of plants.

Though it may not have any impacts on plants, fluoride accumulated grain adds dietary fluoride intake in humans. In absence of any stringent national guidelines with respect to the dose-effect relationship, a dose of 0.06 mg/kg/day body weight as stipulated by USEPA (1992) was taken for comparing the risk of fluoride on humans due to the ingestion of the grain (edible part). The EDI values were found to be higher than the prescribed limits. As the values obtained in the study were only for the dietary intake through the consumption of *T. aestivum* and *P. typhoides* grains, it did not account for total fluoride intake through foodstuff. Malde *et al.* (2004) explained that the F content of prepared food stuffs mainly depends on F content of food, the concentration and amount of water used and retained in the food during its preparation need to be considered. The consumption of edible parts of the plants containing higher fluoride content may lead to a higher dietary fluoride intake. It was investigated that in fluoride endemic area, fluoride ingestion through food constitutes a significant portion of the total daily intake (Kumari *et al.,* 1995; Malde *et al.,* 1997, 2011). In this context, we also reported similar results that *T. aestivum* and *P. typhoides* were found to be the major contributors of EDI.

4.2. Batch biosorption technique using TISP for fluoride removal: Optimization and instrument study

The compendious survey of fluoride concentration in the two major sources water and vegetation preview that part of the study area is highly affected and can become major fluorosis prone area. Keeping in mind the toxic effects of fluoride on human health, taken either through drinking water or through food accumulated from fluoride contaminated irrigated water, there was an urgent need to find out an effective and robust technology to remove excess fluoride in order to cope up from this vicious cycle of fluorosis. Of all the techniques adsorption using Tamarindus indica L. seed powder was chosen to study defluoridation capacity. The plant is easily available in the area and economically cheap.

To assess the defluoridation efficiency, the water affected villages are selected and analysis for various physicochemical properties was being performed. These parameters were considered for optimizing to synthetic water and the resulting protocol is utilized for groundwater defluoridation.

4.2.1. Batch optimization study using TISP

Adsorption of fluoride ions on *Tamarindus indica* L. seed powder was studied through batch mode, considering different factors such as agitation speed, pH of the medium, dosage, agitation time, particle size, an initial concentration of fluoride ions, interference of co-ions and temperature. Experiments were conducted keeping one test parameter varied and remaining parameter constant.

4.2.1.1. Effect of agitation speed

In batch reactions, the shaker speed plays an important role in the rate of distribution of fluoride ions to the surface of the adsorbent. Thus in order to optimize optimum shaker speed for effective adsorption of fluoride on T. indica L. seed powder studies were conducted at different agitation speed ranging from 50 to 250 rpm. The results obtained are shown in Fig. 18. It was found that percentage defluoridation increased from 32 % to 51.28% with an initial increase in agitation speed from 50 to 100 rpm. After 100 rpm the adsorption capacity showed a steep downfall from 51.28% to 13.21%. The maximum adsorption capacity was achieved at an agitator speed of 100 rpm (1.118 mg/g) and maximum percent removal of fluoride at this speed was found to be 51.28%.

4.2.1.2. Effect of pH:

pH is an important factor controlling the process of adsorption. Change of pH affects the adsorptive process through the dissociation of functional groups on the active sites of an adsorptive surface. This subsequently leads to a shift in reaction kinetics and equilibrium characteristics of the adsorption process. Therefore, the effect of ionizing species of adsorbate in aqueous solution on adsorption of fluoride using T. indica L. seed powder was examined at the pH range from 1 to 12 was studied. The results are presented in Figure 19. Removal of fluoride increased with the increase in pH of the aqueous solution upto pH 7. Beyond this pH, the % removal decreased gradually. The optimum range of adsorption was observed to be between pH 5 to 7 where adsorption capacity rapidly increased from 0.94 to 1.11 mg/g. It could be inferred that maximum removal efficiency i.e. 53.18% was obtained at pH 7.

4.2.1.3. Effect of temperature

The influence of temperature in adsorption process is very important because an increase in the temperature induces a decrease in the adsorption capacity of fluoride on the adsorbent surface. To check the same in the present work three temperatures were taken viz: 25°C, 35°C and 45°C at 150 rpm. As shown in Figure 20, the batch study carried out showed that the highest percent sorption was recorded for 25°C which was 55.21% followed by 35°C with 27.40% fluoride removal and lastly 45°C having only 13.50 % fluoride removal. It was observed that the temperature has a greater role in the adsorption of fluoride ions as both percentage of fluoride adsorption and adsorption capacity reduces with the increase in temperature from 303 to 323 K. This result suggests that low temperature favours the removal of fluoride ions by adsorption on TISP. It also proves that the adsorption process is exothermic in nature. Highest removal of fluoride i.e. 55.21% is thus observed at 25 °C.

4.2.1.4. Effect of contact time

The contact time was assessed as a significant parameter affecting the biosorption capacity of biosorbent. The variation of fluoride adsorption was analyzed at varying time duration from 0 to 240 min with a dose of 0.5 g/l TISP at 100 rpm. From the Figure 21, it can be observed that the defluoridation capacity of adsorbate increased rapidly from 0% to 55.21% during first 150 min, and thereafter, there was no significant change in the rate of fluoride adsorption. Highest removal of fluoride i.e. 55.21% was observed after agitating for 150 minutes. Hence 150 minutes of agitation time was considered to be optimal time duration for the further adsorption study.

4.2.1.5. Effect of initial fluoride concentration

The feasibility and efficiency of adsorption process not only depends on the properties of the adsorbent but also on the concentration of the metal ion solution as the initial metal concentration provides an important driving force to overcome all the mass transfer resistances of the metal between aqueous and solid phase. Studies were conducted taking different initial concentrations (5 - 20mg/l) of fluoride solutions. As shown in Fig. 21 with the increase in metal ion concentration from 5 mg/l to 20 mg/l defluoridation capacity increased from 0.54 to 1.44 mg/g but removal efficiency dropped from 55.21% to 39.62%. As mean fluoride concentration of the study area was 7 ppm, 10 ppm was taken for optimization study.

4.2.1.6. Effect of particle size of TISP

The effect of particle size on the fluoride adsorption by *T. indica* L. seed powder was explored by studying the adsorption of fluoride from aqueous solution with the change in the particle size from 0 to 500 μ mesh at optimum conditions. As shown in Figure 22, the removal efficiency decreases steeply from 22.59% to 56.42% on increasing particle size from >50 micron to particle size of 250-500 micron. Highest adsorbate removal of 56.42% was recorded by *T. indica* L. seed powder with particle size >50 μ. Thus the optimum size of the particles of TISP was >50 μ.

4.2.1.7. Effect of adsorbent dosage on adsorption

Biomass dose is an important parameter owing to its effect on efficiency and on the amount of fluoride removed per unit weight of biomass. The effect of sorbent dosage ranging from 0.025 to 2 g/100 ml on the percentage removal of fluoride was studied. As shown in Fig. 23, the removal efficiency of adsorbate increased from 17.27% to 51% with an increase in adsorbent dosage from 0.025 g/100 ml to 2 g/100 ml of adsorbent dosage after which it reached a constant value which still found to be remained constant indicating the attainment of sorption equilibrium. At an adsorbent dosage of 1 g/100 ml, the solution turns turbid while at 0.5g/100 ml the solution was clear with minor variation in defluoridation capacity. Hence 0.5 g/ 100 ml of the biomass was taken as the dose possessing the optimum fluoride removal efficiency and this was fixed as the dose of the material for further experiments.

4.2.1.8. Effect of interfering co-ions

Co-ions present in water along with the fluoride interfere in adsorption due to competition between ions for getting adsorbed at the limited amount of vacant surface area. Groundwater is a good solvent dissolving many minerals from the parent rocks in its periphery. Of this only major ions viz: bicarbonate, chloride, phosphate, sulphate and nitrate were taken under study. The concentration for the co-ion study was determined on the basis of its concentration in groundwater of the study area. Concentration varying from 200 to 1000 ppm in the study was taken for chloride and bicarbonate while for nitrate, sulphate and phosphate concentration ranging from 20 to 100 ppm were taken into consideration. As seen in Fig. 24, removal efficiency decreased from 16.46% to 2.86% and 11.24% to 7.49% with increase in chloride and bicarbonate concentration from 200 to 1000 ppm while defluoridation capacity decreased from 11.58% to 8.85%, 27.66% to 8.34% and 29.12% to 4% respectively with increase in nitrate, sulphate and phosphate concentration from 20 to 100 ppm. The impact of anions on defluoridation in descending fashion is as follow: Nitrates > Phosphates > Sulphates and Chlorides > Bicarbonates. Overall the defluoridation capacity reduced to half or less than half due to the presence of anions in the synthetic aqueous fluoride solution.

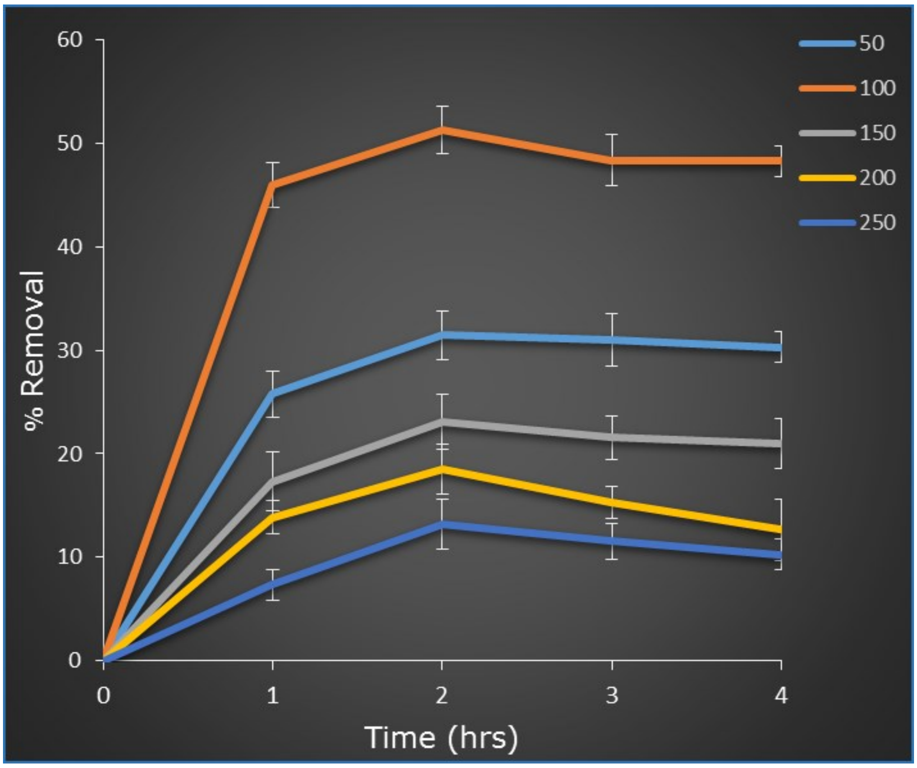


Figure 18: Effect of shaker speed on fluoride ion removal by TISP (Initial fluoride ion concentration = 5 mg/L, TISP dose = 5g/L, time = 0 to 240 min and temperature = 25±2 °C, pH = 7)

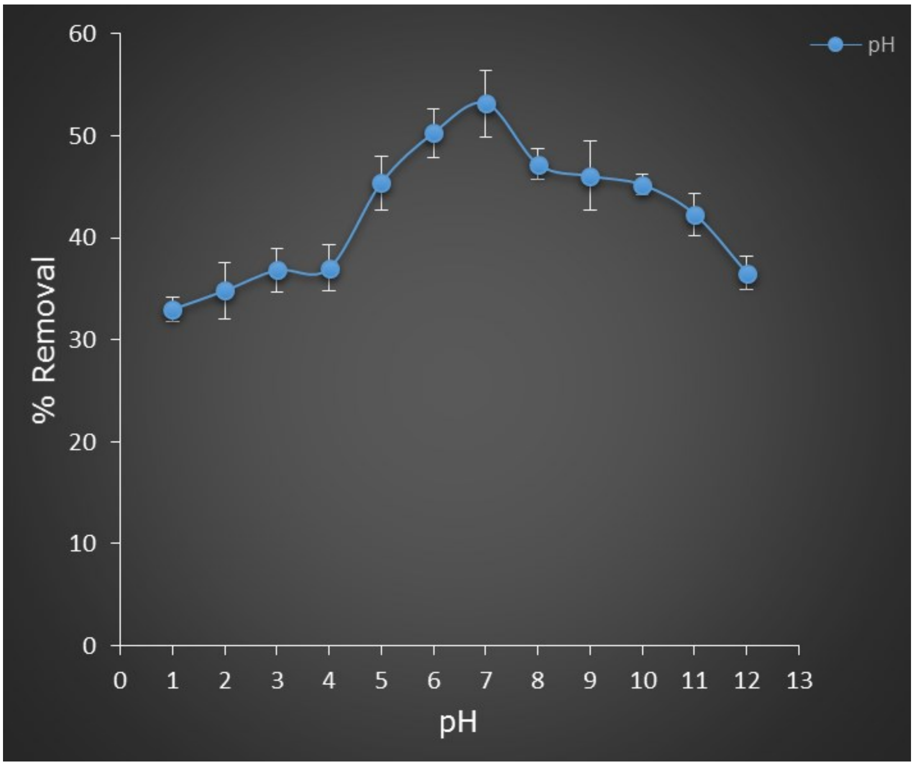


Figure 19: Effect of the solution pH on fluoride ion removal by TISP (Initial fluoride ion concentration = 5 mg/L, TISP dose = 5g/L, time = 120 min and temperature = 25±2 °C)

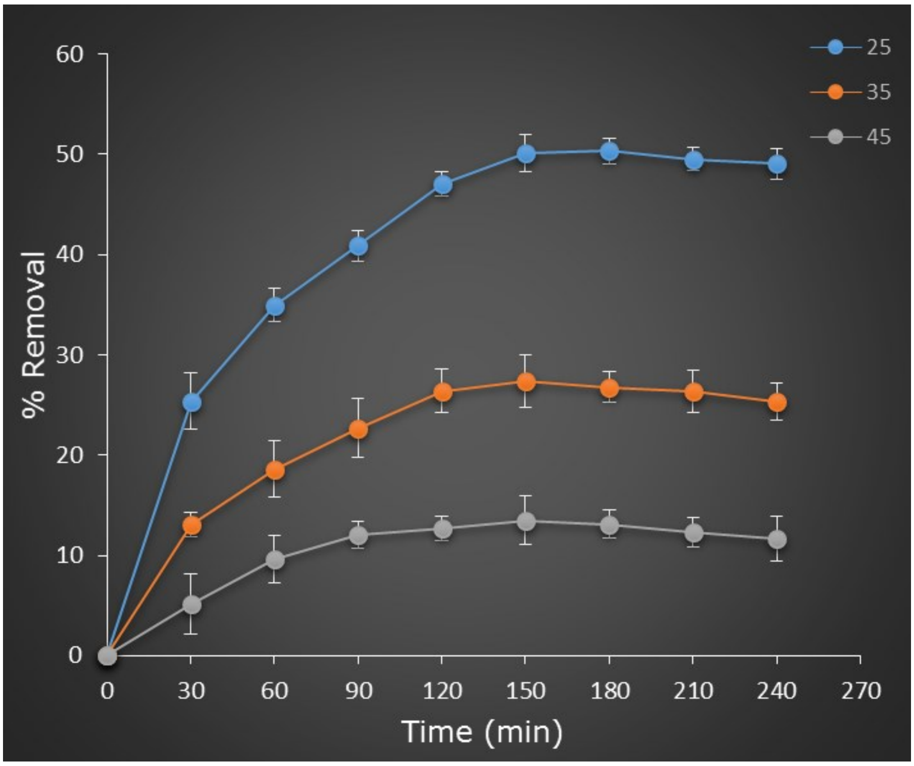


Figure 20: Effect of temperature on fluoride ion removal by TISP (Initial fluoride ion concentration = 5 mg/L, TISP dose = 5g/L, temperature = 25±2 °C)

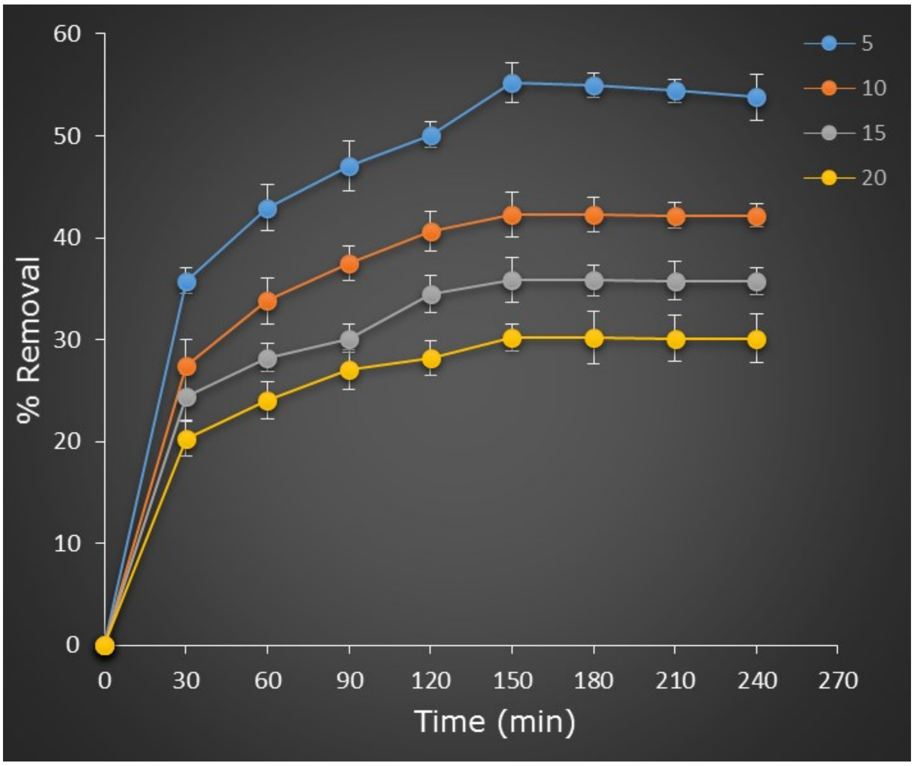


Figure 21: Effect of contact time and Initial fluoride on removal by TISP (Initial fluoride ion concentration = 5 to 20 mg/L, TISP dose=5g/L, Time = 0 - 240 min and temperature = 25±2 °C)

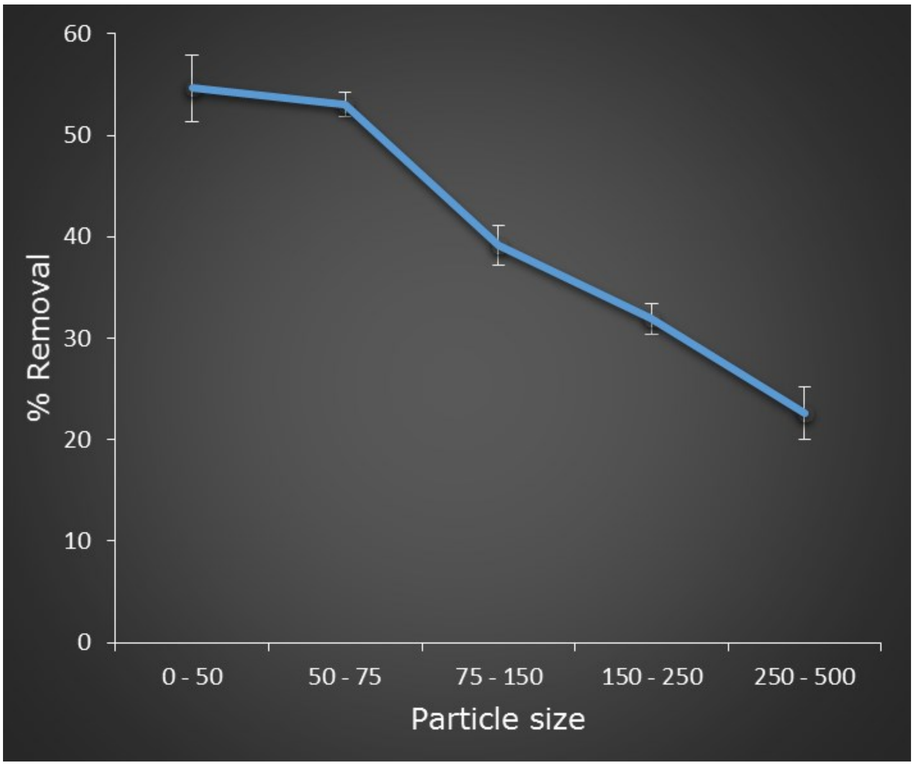


Figure 22: Effect of particle size on fluoride ion removal by TISP (Initial fluoride ion concentration = 5 mg/L, TISP dose = 5g/L, time = 150 min and temperature = 25±2 °C)

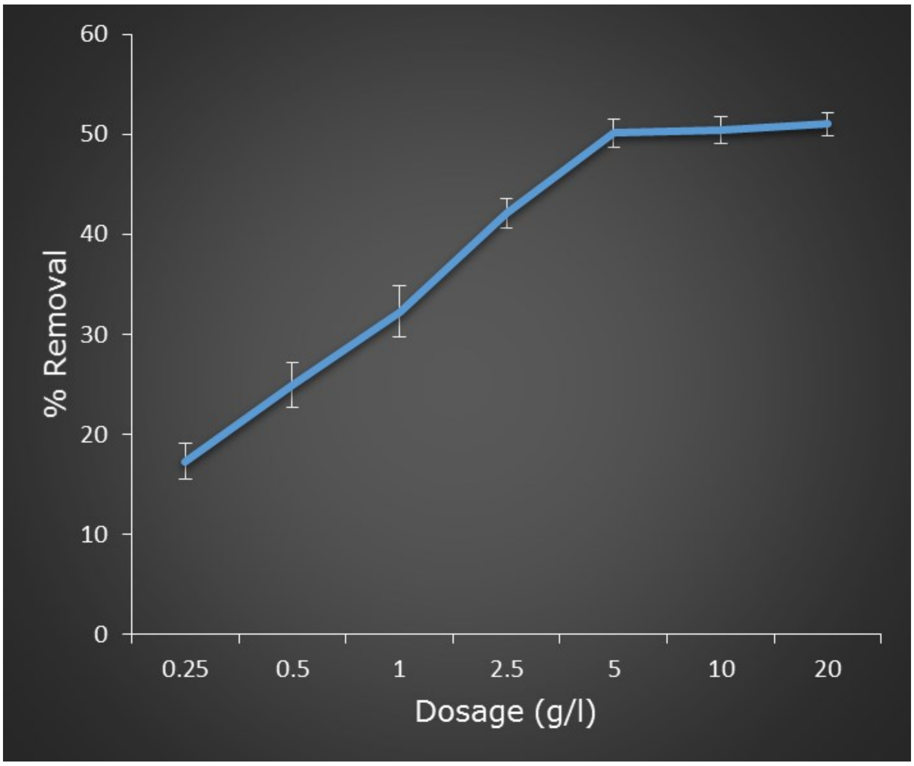


Figure 23: Effect of dosage on fluoride ion removal by TISP (Initial fluoride ion concentration = 5 mg/L, Particle size = 50microns time = 150 min and temperature = 25±2 °C)

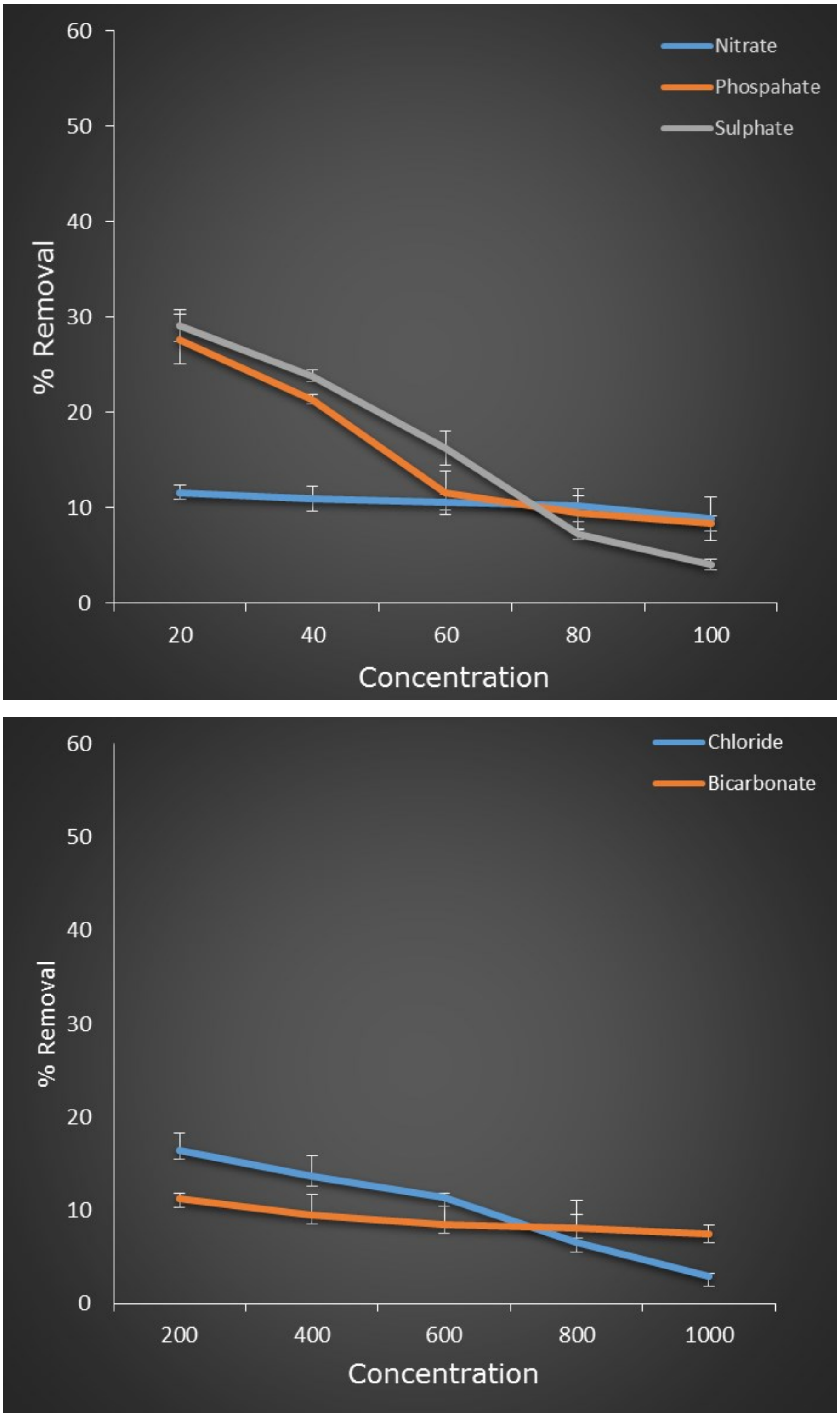


Figure 24: Effect of Co-ions interference in fluoride ion removal (Initial fluoride ion concentration = 5 mg/L, TISP dose = 5g/L, min And temperature = 25±2 °C)

4.2.2. Adsorption isotherms

Adsorption isotherm is a functional expression that correlates the amount of solute adsorbed per unit weight of the adsorbent and the concentration of an adsorbate in bulk solution at a given temperature under equilibrium conditions. It is important to establish the appropriate relationship for the batch equilibrium data using empirical or theoretical equations as it may help in modeling, analyzing and designing adsorption systems. The adsorption isotherms are one of the most useful data to understand the mechanism of the adsorption and the characteristics of isotherms are needed before the interpretation of the kinetics of the adsorption process. Various Adsorption isotherms were applied as follows:

4.2.2.1. Langmuir isotherm

A plot of $\frac{1}{q_e}$ vs $\frac{1}{C_e}$ was drawn (Fig. 25) from the linear equation of Langmuir. The result obtained from the regression correlation was almost unity (R^2 = 0.99) for all the temperature showing the excellent fit of the experimental values to the data. The value of K_L and q_m (as shown in Table 21) the value of K_L and q_m obtained from the slope as well as intercept varied from (0.58 – 0.08 L/mg) and (1.51 to 0.50 mg/g) respectively for temperature ranging from 303 to 323K. In addition to above the value of dimensionless constant separation factor R_L varies from 0.26 to 0.70 for 5 ppm, 0.14 to 0.52 for 10 ppm, 0.1 to 0.42 for 15 ppm and 0.08 to 0.38 for 20 ppm respectively for temperature varying from 303 to 323K. Overall the value lies between 0 to 1 indicating adsorption to be favorable.

4.2.2.2. Freundlich isotherm

In contrast to the isotherm model for homogeneous adsorption on the monolayer, the Freundlich model provides a model for the heterogeneous adsorption. The plot of ln $q_e$vs ln C_e is drawn as shown in Fig. 26. The result disclosing fairly good fit to the experimental data for temperature varying from 303 to 323K. The Value of K_F is decreased from 0.38 to 0.11 for temperature ranging from 303 to 323K. In addition to this the value of heterogeneity factor “n” varies from 2.27 to 2.36 g/l (Table 22)

4.2.2.3. Dubinin–Radushkevich isotherm model

The present data are analyzed according to the linear form of D-R isotherm and the linear plot is shown in Fig. 27. The model generated from the data shows excellent fit to the experimental data as the regression coefficient correlation was close to unity for all the temperatures. As shown in Table 23, the value of β i.e. constant related to the adsorption energy, calculated from the slope of qe versus e^2 of the linear plot of a model, decreases from 2.133 x 10^{-6} to 4.299 x 10^{-6} with the increase in temperature. The value of B is used the calculate value of mean free energy of adsorption (E). Thus 0.484KJ/mol, 0.441KJ/mol and 0.341KJ/mol are the value of free energy changes when 1 mole of fluoride ions are adsorbed on the surface of TISP when temperature increases from 303K to 323K. As the value of mean free energy of adsorption (E) is less than 8 KJ/mol the adsorption is physio-sorption.

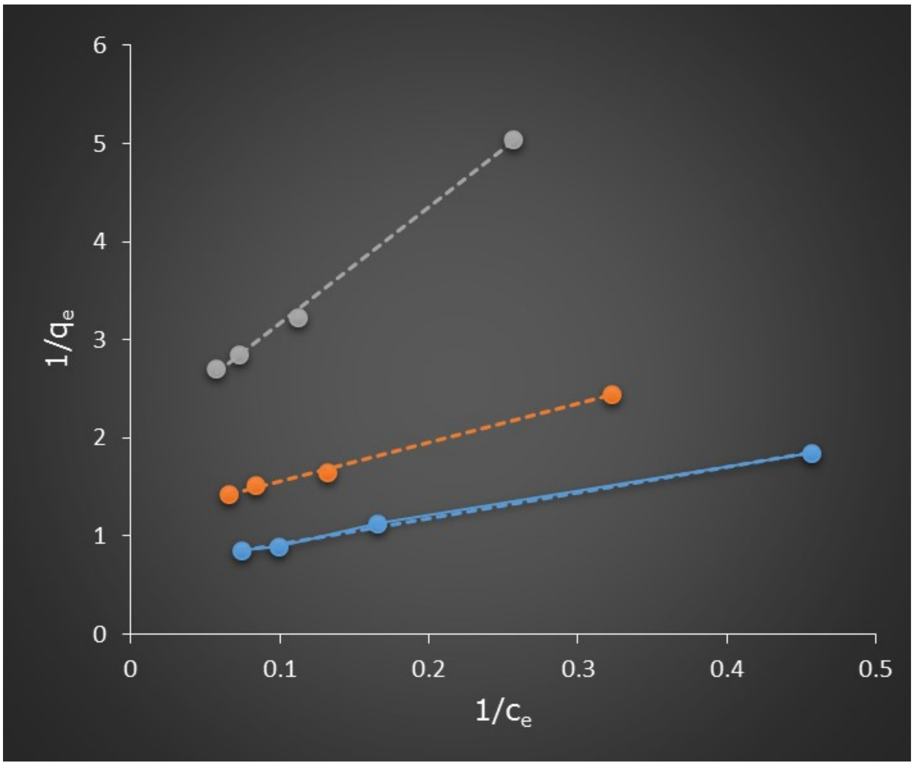


Figure 25: Langmuir adsorption isotherm

Table 21: Langmuir variables

Sr. No.	Temp (K)	q_m	K_L	R_L				R^2
				5	10	15	20	
1	298	1.51	0.57	0.26	0.14	0.09	0.08	0.99
2	308	0.85	0.21	0.48	0.30	0.23	0.19	0.99
3	318	0.50	0.08	0.70	0.52	0.42	0.37	0.99

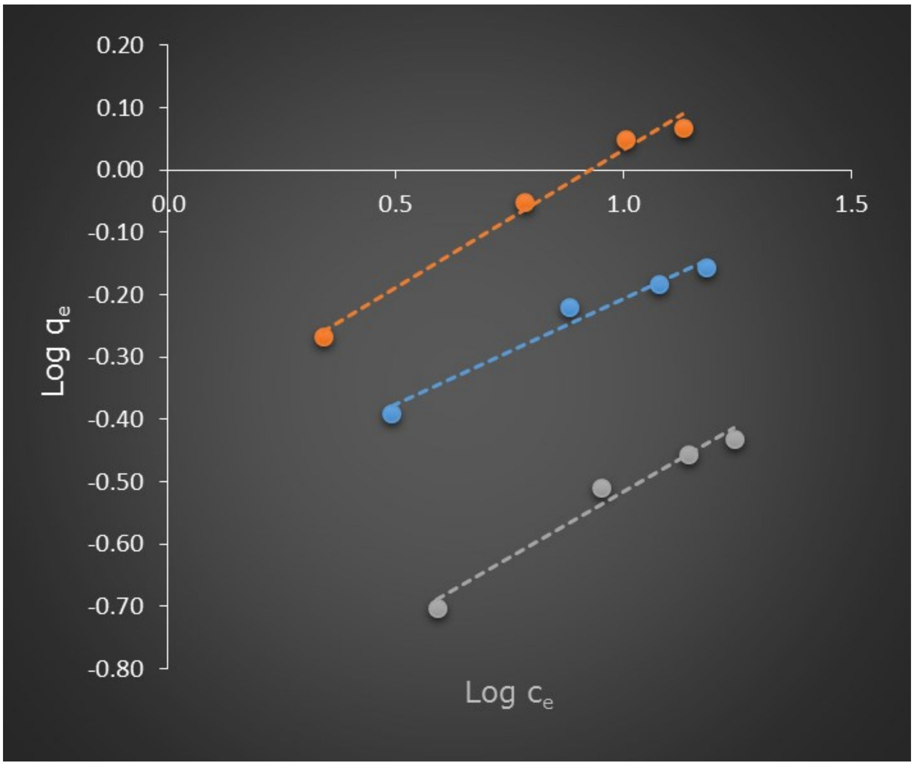


Figure 26: Freundlich adsorption model

Table 22: Freundlich variables

Sr. No.	Temperature (K)	K_F (mg/g)	n	R^2
1	298	0.39	2.27	0.98
2	308	0.29	2.95	0.96
3	318	0.11	2.36	0.97

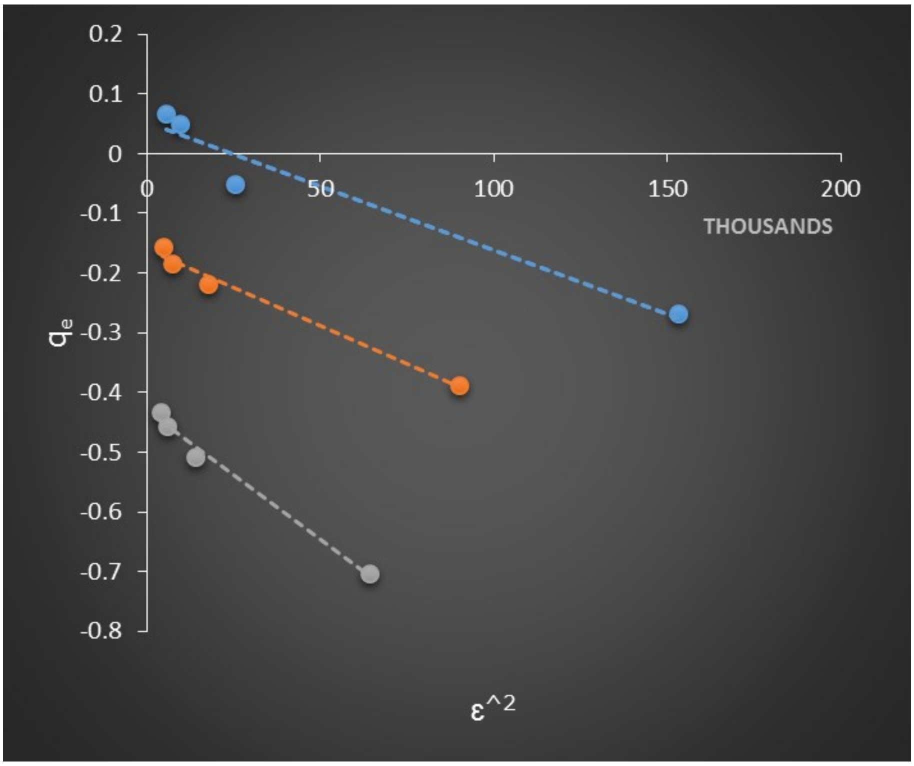


Figure 27: Dubinin–Radushkevich isotherm model

Table 23: Dubinin–Radushkevich variables

Sr. No	Temp (K)	β $(1 * 10^{-6})$	E (KJ/mol)	R^2
1	298	2.13	0.484	0.94
2	308	2.56	0.441	0.98
3	318	4.29	0.341	0.98

Batch Adsorber Design

The adsorption of metal ions onto the adsorbent TISP has been found to proceed by film diffusion. In order to predict the adsorber size and efficiency in the removal of fluoride ions by the adsorbent, an empirical procedure based on the adsorption equilibrium has been designed (McKay *et al.*, 1985). A schematic diagram of single-stage batch adsorption system is shown in Fig.28.

The design objective is to reduce the initial metal ion concentration from Co (mg/L) to Ce (mg/L) of solution volume V (L). The amount of adsorbent is M (g) and the metal ion loading changes from q_o (mg/g) to q_e (mg/g). At time t=0, $q_o=0$ and as time proceeds, the mass balance equates the metal ions removed from the aqueous solution to that picked by the adsorbent.

The mass balance for the single-stage batch adsorption system can be expressed as:

$$V\,(C_o - C_e) = M(q_e - q_o) = Mq_e \qquad \text{…[equation 22]}$$

Since Adsorption follows langmuir equation the equation can be rearranged into:

$$M = \frac{(C_o - C_e)}{\left[\frac{q_{mK_L} C_e}{1 + K_L C_e}\right]} \qquad \text{…[equation 23]}$$

The Fig 29, shows plot between calculated amount of TISP required 55% metal removal from the solution of an initial concentration of 5 mg/L for different solution volumes (1 to 10 L) for a single-stage batch adsorber, for which the design procedure is outlined. The amount of TISP required for 55% removal of fluoride ion from an aqueous solution of 5 mg/L concentration was 2.015, 4.030, 6.045, 8.060, 10.075, 12.090, 14.105, 16.120, -18.135 and 20.150 g for fluoride ion solutions of different volumes (1 to 10 L), respectively.

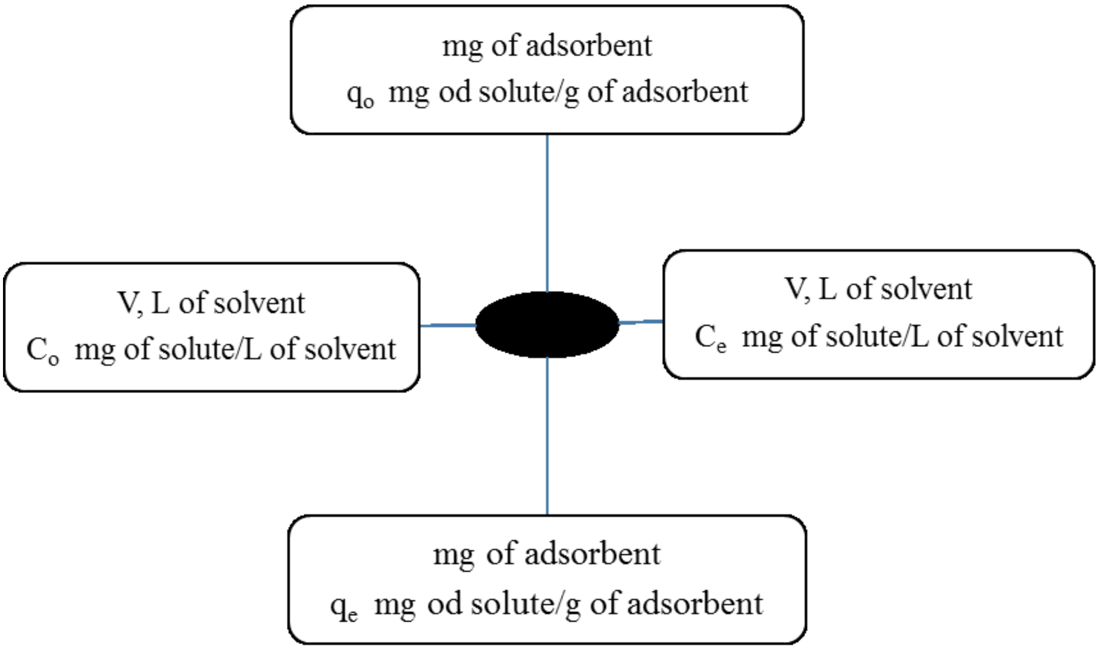


Figure 28: Single stage batch adsorber

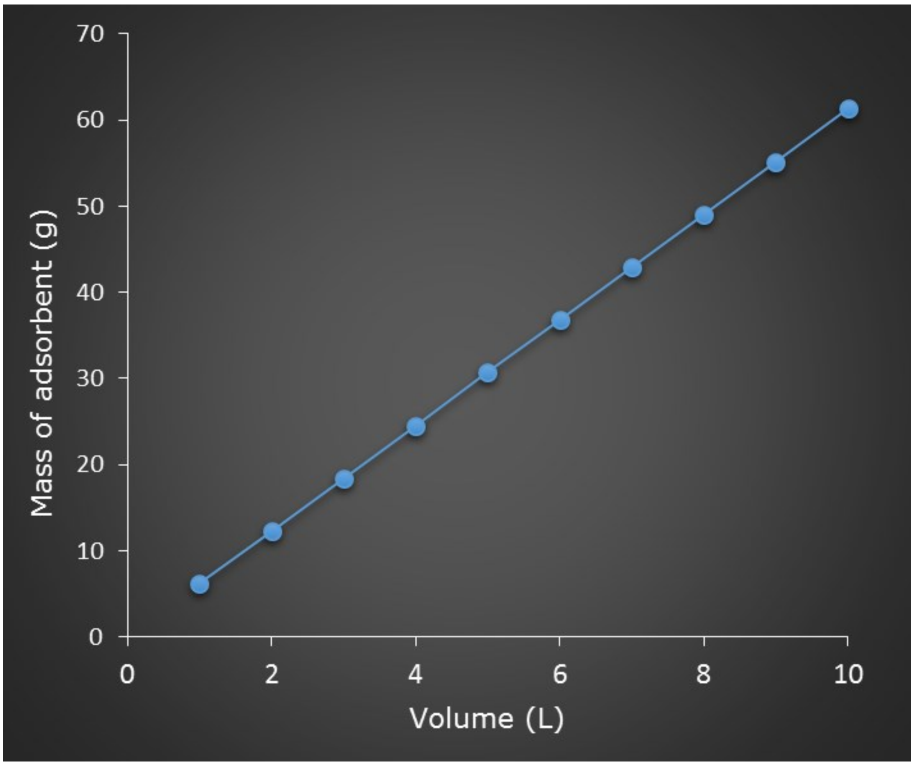


Figure 29: Design plot for the adsorption of fluoride ions onto the TISP

4.2.3. Kinetics

Predicting the rate at which adsorption takes place for a given system is probably the most important factor in adsorption system design, with adsorbate residence time and the reactor dimensions controlled by the system's kinetics. An attempt was made to find a suitable explanation for the mechanisms. In order to investigate the mechanisms of adsorption, various kinetic models have been suggested. In order to investigate the adsorption processes of onto T. indica seed powder, four kinetic models were used.

4.2.3.1. Langregen's pseudo first order kinetics

The adsorption kinetic data of fluoride ions measured on *T. indica* powder was analysed according to the linearized form of Pseudo first-order kinetic model (Lagergren, 1898). The linear plot of log (q_e-q_t) vs t is shown in Fig. 30. As shown in Table 24 the value of K_t i.e. rate constant, calculated from the slope of log (q_e-q_t) versus t of the linear plot of the model, for initial fluoride ranging from 5 to 20 mg/l is 0.004 min^{-1}. The value of rate constant decreases with the increase in initial fluoride concentration. The regression coefficient correlation generated from model varies from 0.98 to 0.99.

4.2.3.2. Ho and Kay's pseudo second order kinetics

The adsorption kinetic data of fluoride ions measured on *T. indica* powder was analysed according to the linearized form of Pseudo second-order kinetic model (Ho and McKay, 1997). The linear plot of t/q_t versus t is shown in Fig. 31. As shown in Table 24 the value of K_t i.e. rate constant, calculated from the slope of t/q_t versus t of the linear plot of the model, for initial fluoride ranging from 5 to 20 mg/l varies from 0.008 to 0.07 min^{-1}. The value of rate constant increases with the increase in initial fluoride concentration. The regression coefficient correlation generated from model is 0.99 for all concentration.

The Regression analysis for sorption reaction kinetics indicates both pseudo first order kinetics and pseudo second order kinetics as the desired model for explaining the mechanism. But the q_m calculated from the model favours pseudo first order kinetics to be an efficient model for explaining the adsorption

4.2.3.3. Weber-morris Intraparticle Diffusion

The present data are analyzed according to the linear form of intra-particle diffusion model (Weber and Morris, 1963). The adsorption data plotted in Fig. 32 shows good linearity for intra particle diffusion model. The equations with correlation coefficients are shown in Table 25. The values of K_{diff} calculated from the slope of q_t versus t/2 of the linear plot of model, for initial fluoride ranging from 5 to 20 mg/l varies from 0.008 to 0.017 min^{-1}. The value of rate constant increased with the increase in initial fluoride concentration. The R^2 values varied from 0.83 to 0.87.

4.2.3.4. Film diffusion kinetics

The present data are analyzed according to the linear form of Pseudo first-order kinetic model (Boyd *et al.,* 1947) and the linear plot is shown in (Fig. 33). The model generated from the data shows excellent fit to the experimental data as the regression coefficient correlation was closed to unity for all the temperatures. As shown in Table 25, the value of K_t i.e. rate constant, calculated from the slope of log (q_e-q_t) versus t of the linear plot of model, for initial fluoride ranging from 5 to 20 mg/l varies from 0.009 to 0.01 min^{-1} The R^2 for all the variants was 0.99.

From the Fig.32, it was observed that the line does not pass from the origin in case of Intraparticle diffusion kinetics hence can’t be utilized to explain but in case of film diffusion it passes through the origin and thus is best fit to explain adsorption process.

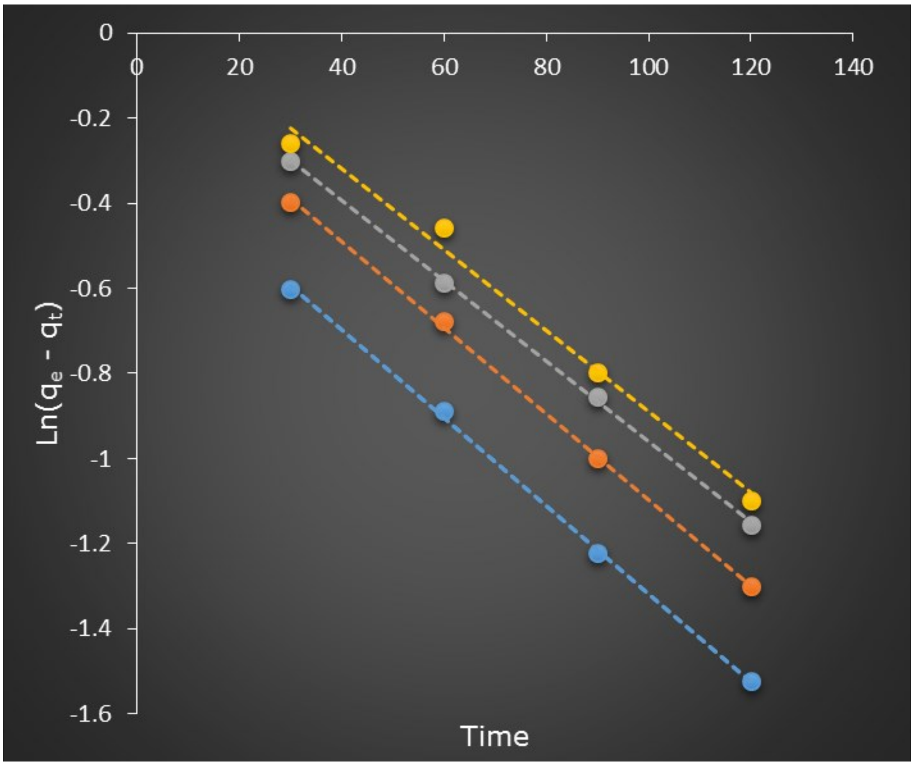


Figure 30: Pseudo first order kinetics

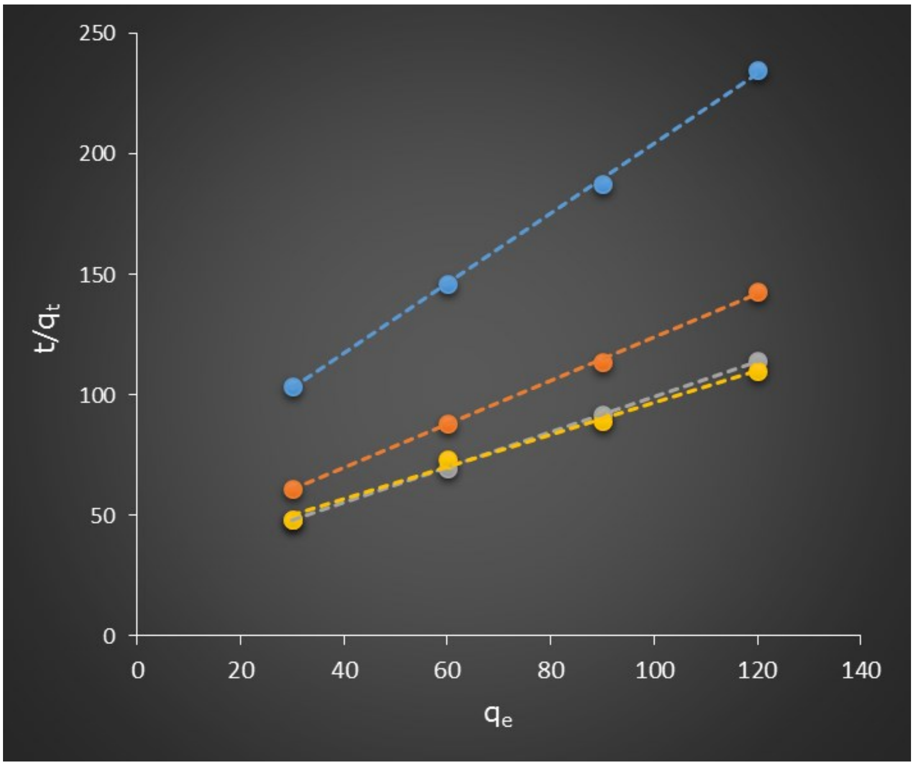


Figure 31: Pseudo second order kinetics

Table 24: Kinetic study for defluoridation

Sr No.	Initial fluoride	Psuedo first order kinetics				Psuedo second order kinetics			
		$q_{e\ exp}$ (mg/g)	$q_{e\ calc}$ (mg/g)	Rate Constant k_1 (min^{-1})	R^2	$q_{e\ exp}$ (mg/g)	$q_{e\ calc}$ (mg/g)	Rate Constant k_2 (g/mg·min)	R^2
1	5	0.54	0.52	0.004	0.99	0.54	0.56	0.008	0.99
2	10	0.89	0.82	0.004	0.99	0.89	0.95	0.03	0.99
3	15	1.12	1.07	0.004	0.99	1.12	1.19	0.07	0.99
4	20	1.17	1.15	0.004	0.98	1.17	1.27	0.07	0.99

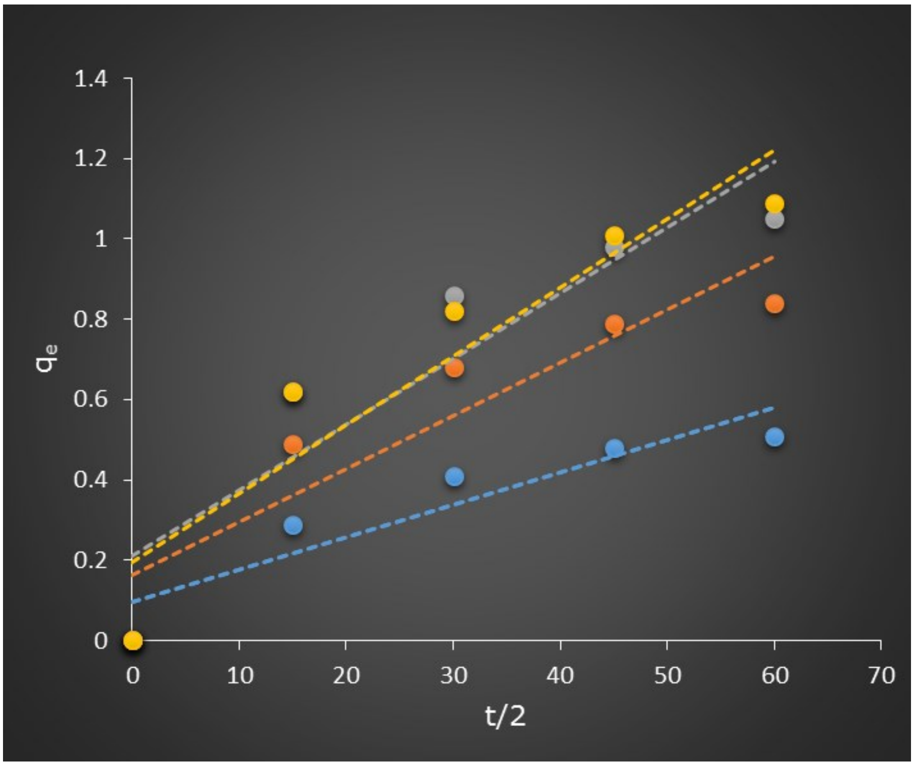


Figure 32: Intraparticle Diffusion kinetic model

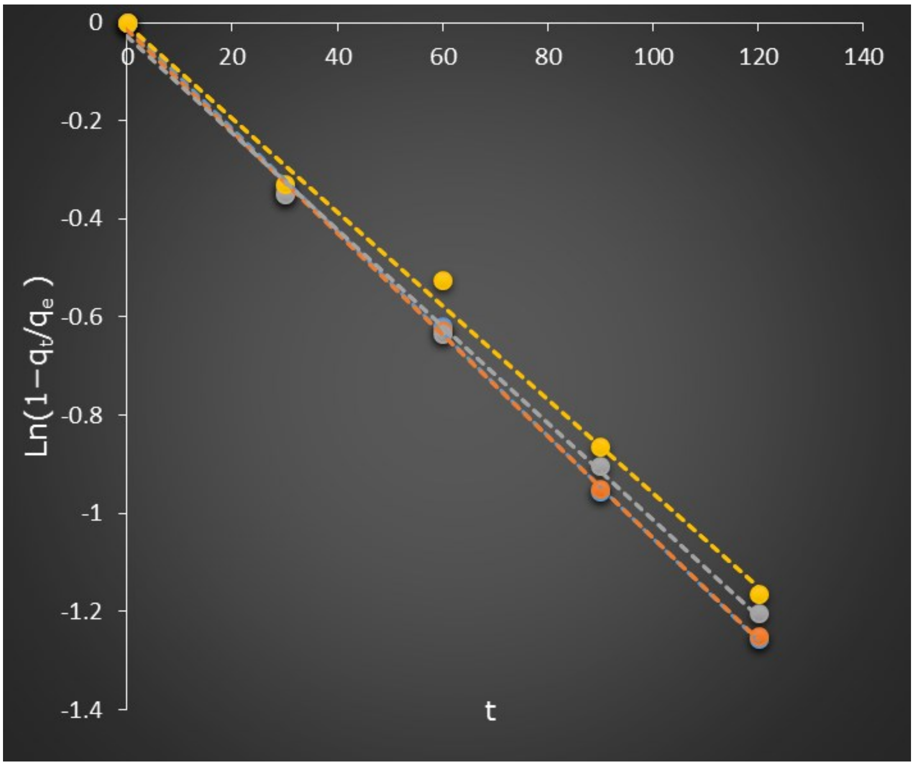


Figure 33: Liquid film diffusion model

Table 25: Diffusion model study for defluoridation

Sr No.	Initial fluoride	Intra particle diffusion kinetics		Liquid film diffusion kinetics	
		Rate Constant K_{diff}	R^2	Rate Constant	R^2
1	5	0.01	0.85	0.009	0.99
2	10	0.01	0.84	0.009	0.99
3	15	0.01	0.83	0.01	0.99
4	20	0.01	0.87	0.01	0.99

4.2.4. Thermodynamics

The effect of temperature on adsorption of fluoride at the adsorbent-adsorbate interface has been studied in the temperature range of 298 – 318K. A plot of K versus 1/T was found to be linear (Fig. 34, Table 26). The standard enthalpy and entropy changes were determined from the slope and intercept of the plot respectively. The standard free energy change was negative for 303K i.e. 25 °C but turns positive as the temperature rises. In addition to the free energy change the value of Enthalpy and entropy are also negative.

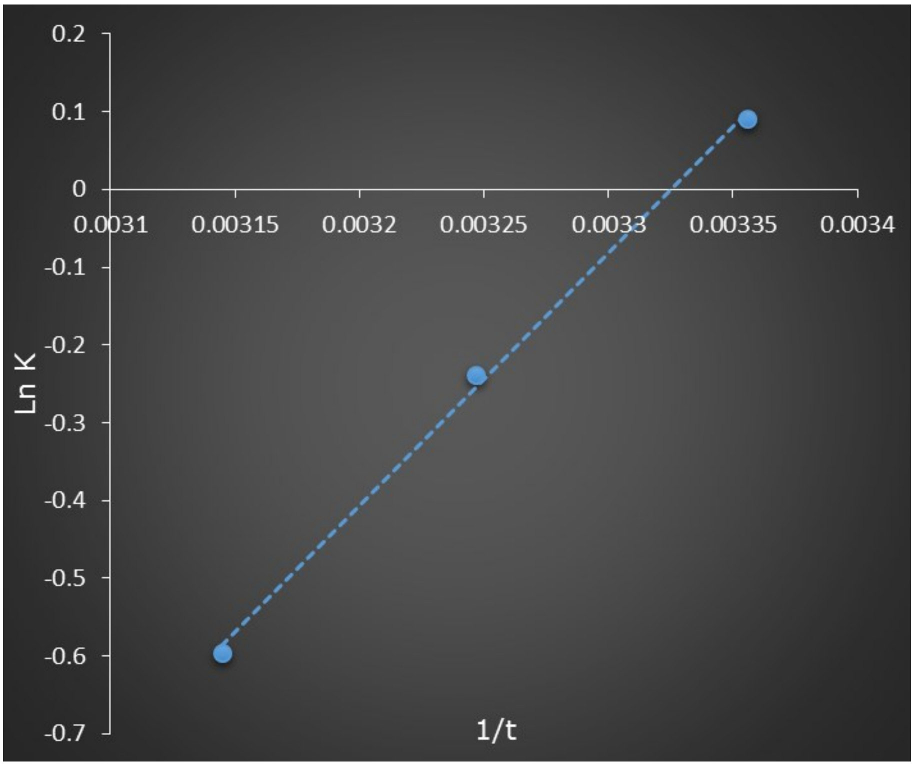


Figure 34: Thermodynamics of adsorbent

Table 26: Thermodynamic variable

Sr. No.	Temperature, K	ΔG, KJ/mole	ΔH, KJ/mole	ΔS, KJ/mole K
1	298	-0.225	-27.01	-89.83
2	308	0.61		
3	318	1.574		

4.2.5. Discussion

Batch adsorption study

The result of agitation speed on adsorption capacity of *T. indica* seed powder indicated that the percent adsorption increased with increased agitation speed from 50 to 100 rpm because low speed could not spread the particles properly in the solution for providing active binding sites for adsorption of fluoride (Hanafiah *et al.,* 2009). The increase in both adsorption rate and uptake capacity at a higher agitation speed could be explained in terms of the reduction of boundary layer thickness around the adsorbent particles and a higher agitation speed also encourages a better mass transfer of fluoride ions from bulk solution to the surface of the adsorbent and shortens the adsorption equilibrium time (Hanafiah *et al.,* 2009). Beyond that, with further increase in agitation speed, some amount of fluoride adsorbed in the surface of seed powder, desorbed due to the centrifugal force, and as a result bound fluoride get desorbed (Crini *et al.* 2007). Similar

The pH is an important parameter influencing the sorption process at the water–adsorbent interfaces (Mahdavi *et al.,* 2015). pH affects surface charge of the adsorbents, the degree of ionization and the species of adsorbate. (Venkateshwarlu *et al.,* 2007). At highly acidic pH fluoride dominantly occurs as HF in aqueous solution which hinders the fluoride adsorption on TSP. It was inferred from the results that maximum defluoridation capacity i.e. 0.986 mg/g obtained at pH 7. Consequently, there is a greater possibility of coulombic interaction between fluoride ion and surface charge on *T. indica* seed powder. This can be explained on the basis of the change in surface charge of the adsorbent, at pH values lower than the pH_{zpc}, functional groups on the surface of mechanically modified tamarind seeds will have net positive charge (Mahdavi *et al.,* 2015) which enhances electrostatic attraction between the fluoride and cations present on the surface (Fufa *et al.,* 2013; Mondal, 2010; Ayoob and Gupta, 2006). However, the percentage of fluoride removal was found to be inhibited at higher pH which might be attributed to the electrostatic repulsion created due to increase of hydroxyl ions leading to formation of aqua-complexes and subsequently adsorbent surface become negative (Andjelkovic *et al.,* 2014). Similar trend was shown by Pandey *et al.* (2012) and Murugan and Subramanian (2006).

Results on optimizing temperature showed that low temperature favours the removal of fluoride ions by adsorption on TISP as well as that the adsorption process is exothermic in nature. The decrease in the removal may be due to the fact that at high temperature the thickness of the boundary layer decreases due to increased tendency of the molecules to escape from the adsorbent surface to the solution phase, resulting in a decrease in the adsorption capacity as temperature is increased (Sadaf and Bhatti, 2014; Sujana and Anand, 2010). Also Loganathan *et al.* (2013) reviewed that increase in thermal energy of fluoride at higher temperature can raise desorption capacity

While optimizing contact time, it was observed that the rate of fluoride adsorption was very rapid during first 150 min, and thereafter, there is a mild decrease of adsorption. Initially, there were large number of vacant active binding sites in TISP, and consequently large amount of fluoride ions was bound rapidly onto the adsorbent (Alagumuthu *et al.* 2011; Kumar *et al.* 2008). The binding site shortly become limited, and the remaining vacant surface sites are difficult to be occupied by fluoride ions due to the formation of repulsive forces between the adsorbate on the solid surface and the liquid phase (Bhaumik and Mondal 2016; Bhaumik *et al.* 2012). Besides the mesopores become saturated at the initial stage of adsorption where the metal ions are adsorbed as a result the driving force of mass transfer between liquid and solid phase of an aqueous adsorption system decreases with time elapse further the metal ions have to pass through the deeper surface of the pores for binding and encounter much larger resistance which slowing down the adsorption during latter phase of adsorption (Srivastava *et al.* 2006).

The results illustrated decreased fluoride removal efficiency with increasing initial concentration. Lower concentration causes more interaction of fluoride ions with the binding sites, and at higher concentration, increase in the number of ions is responsible for competition in availability of binding sites on the adsorbent surface (Murugan and Subramanian, 2006). Moreover, for fixed TISP dose, the total available adsorption sites were limited, which became saturated at high concentration (Bhaumik and Mondal, 2016; Namasivayam and Kavitha, 2002). Due to increasing concentration gradient, fluoride acts as increasing driving force to overcome all mass transfer resistances of the fluoride between the aqueous and solid phase, leading to an increasing uptake capacity until sorbent saturation is achieved. Similar trend has been reported for fluoride removal by Sujana *et al.* (2009), Mondal *et al.* (2013), Chakrabarty and Sarma (2012) Saha *et al.* (2010) and Mondal *et al.* (2012).

During optimization of particle size, it was observed that smaller the particle size more was the removal efficiency. This may be due to with decrease in biosorbent size, surface area of the biosorbent increases and the number of active sites on the biosorbent are better exposed to the biosorbate. This is mainly due to the fact that a larger mass of adsorbent could adsorb larger amount of adsorbate due to the availability of more vacant pores on the surface area of adsorbent.

It can be observed that removal efficiency of the adsorbent generally improved by increasing its dosage. This is expected due to the fact that the higher dose of adsorbents in the solution, the greater availability of exchangeable sites for the ions. This fact is supported by Kumar *et al.* (2009) and Yadav *et al.* (2012). Results showed no further increase in adsorption after a certain amount of adsorbent was added. This might be due to overlapping of adsorption sites as a result of overcrowding of adsorption particles, thus reducing of the net surface area (Brown *et al.,* 2000; Killedar and Bhargava, 1993). This was also reported by various authors Vardhan and Karthkeyan (2011) and Kumar *et al.* (2009).

It is expected that the presence of anions in solution would enhance coulombic forces between the anions and fluoride or would compete with fluoride for the activities (Onyango *et al.,* 2004). Tor (2006) reported that chloride formed outer-sphere surface complexes, while sulphate formed both outer-sphere and inner-sphere surface complexes. Thus expected impact of sulphate is more in comparision to chloride which supports present study. He *et al.,* (1997) reported phosphate replaces water and hydroxyl groups from the surface thus decreasing the fluoride adsorption. Kumar *et al.* (2009) reported that for dosage of 5 mg/l reduced the adsorption of fluoride in presence of 100 mg/l of phosphate, carbonate and sulphate. Similar results of anion competition were reported for nitrate and sulphate by Sujana *et al.* (1998) for fluoride adsorption on alum sludge. In the present study the fluoride adsorption is govern by non-specific mechanism. Findings of Loganathan *et al.* (2013) that when F is adsorbed by non-specific adsorption the non-specifically adsorbing anions can compete with F supported the present work.

Isotherm

Adsorption isotherms describe the equilibrium relationships between adsorbent and adsorbate and also indicate how the adsorbate particles distribute between the liquid and the solid phases when the adsorption process reaches the equilibrium state (Athar *et al.* 2014). Of the two isotherm model studied, Langmuir for adsorption on the homogeneous surface of adsorbate and Freundlich for adsorption on the heterogeneous surface of adsorbate, the regression analysis shows Langmuir model to be fit for understanding the sorption system at equilibrium. Similar results are reported by Huang *et al.* (2011), Pandey *et al.* (2012), Shyam and Kalwania (2013) and Bhaumik (2015) for adsorption of fluoride on various adsorbents.

The result follows the empirical model of Langmuir. Langmuir model considers that the sorption energy of each molecule is the same, independently of the surface of the material; the sorption takes place only on some sites and there are no interactions between the molecules (Teutli-Sequeira *et al.*, 2012). Therefore, it is assumed that homogeneous biosorption plays an important role in the removal of fluoride by T. indica seed powder.

The calculated value for the magnitude of the Langmuir constant K_L was small indicating a low heat of adsorption capacity (Pandey and Prasad, 1984; Dongan, 2004). The value of K_L and q_m decreases with the increase in temperature which shows the process to be exothermic in nature. The feasibility of the isotherm was tested by calculating the dimensionless constant separation factor or equilibrium parameter, R_L (Weber and Chakravorti, 1974). The R_L values at different temperatures were lying between 0 and 1 representing favorable conditions for adsorption (Langmuir, 1918). D-R model was used to confirm the nature of adsorption. From the result obtained a value of Ea < 8 kJ/mol, thus it can be inferred from the results that the adsorption process is of a physical nature (Rieman and Walton, 1970; Onyango *et al.*, 2006).

Kinetics

The kinetics of any sorption process is a function of different parameters, such as the structural properties of adsorbent, nature, and concentration of adsorbate and adsorbent–adsorbate interactions (Mondal and George, 2015; Sadaf and Bhatti, 2014). Adsorption kinetics not only describes the adsorption mechanism of fluoride ions on adsorbents but also describes the fluoride ions adsorption rate which checks the residence time of the sorbate at the solid-liquid interface (Chouchene *et al.*, 2014; Ho *et al.*, 2000). Moreover, it is important to predict the rate-determining step for the purpose of scaling up of the process.

The result for sorbent based kinetics indicates that the regression correlation of both the pseudo first order model and Pseudo-second order model, the data fits more to pseudo first-order kinetics. In addition to the regression analysis, the adsorption efficiency calculated from the model favors pseudo first order kinetics. Similar results are reported by Sinha *et al.* (2003), Liao and Shi (2005), Bansiwal *et al.* (2009), Swain *et al.* (2009) for fluoride adsorption on various absorbents. Following of pseudo first order kinetics shows that the process is governed only by a single mechanism. The reaction based kinetic model shows the liquid film diffusion is best fit to describe the adsorption mechanism in comparison to intraparticle diffusion based on the obtained data.

Thermodynamics

From the results obtained, the decreasing value of K and negative value of ΔH° represents the reaction to be exothermic in nature. The entropy value is negative indicating that during the fluoride adsorption process, the solid–solution interface approaches a more organized structure (decrease of randomness). (Bhaumik and Mondal, 2015) and also it suggests no significant change occur in the internal structure of TISP during the adsorption (Gupta *et al.*, 2005). The sorption process causes an increase in the order of the system. The small and negative value of ΔG° at lower temperature indicates the feasibility of the process and the spontaneous nature of adsorption especially at a lower temperature, i.e. the adsorptive forces are strong enough to overcome the potential barrier (Chaturvedi and Pathak, 1988; Bhaumik *et al.* 2012). But at a higher temperature, the Gibbs free energy decreases indicating the process to be non-spontaneous.

4.3. Characterization of Adsorbent:

4.3.1. Material study

The Zero charge potential study of TISP powder indicated that the pH^0_{ZPC} of TISP is 7.42. The fluoride analysis of T. indica seed powder revealed that 40µg/g of fluoride concentration has been assimilated by the seed collected from tree in Malekhpura villages of the study area. This may be the possible reason for comparatively low absorption in accordance to its previous study by Murugun and Subramanium (2006).

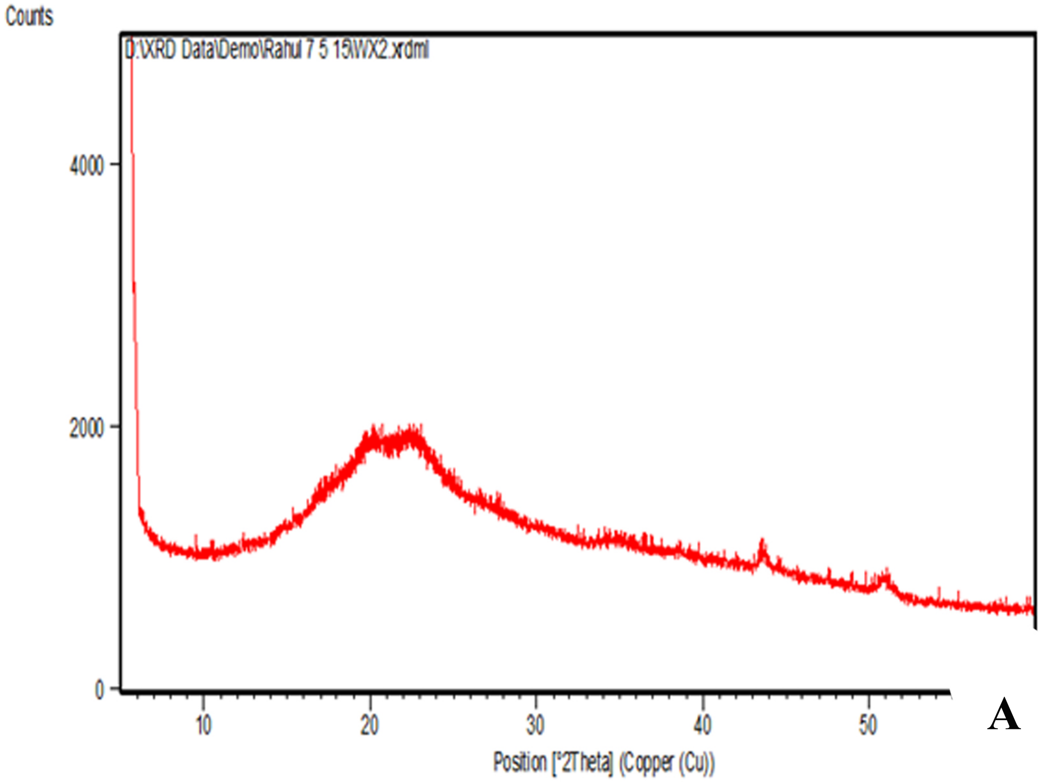
4.3.2. Instrument study

XRD:

XRD is an instrument important to study the chemical interaction of the material as well as identification of mineral present in the material. The XRD study was carried out for TISP powder to study before and after changes in functional group on surface. As shown in (PLATE 9), in XRD for image of TISP was a bit amorphous in nature as no such crystalline peak were seen. The result of before and after adsorption of the fluoride on TISP shows shows depression in intensity from 4000 to 2000 between ϴ position of 10 to 30. This depression might be due to adsorption of film over the surface of the powder of whole seed after adsorption. No new distinct peak was formed after adsorption of fluoride indicating the adsorption to be physical in nature.

FTIR:

FTIR is an important instrument detects vibration between bonds of the functional groups presents on the surface. Knowledge of surface functional groups would give an insight to the adsorption capability of the TISP. The FT-IR spectrums of the TISP are shown in (PLATE 10). From the figure, it was found that OH and NH are stretching between 3100 and 3500 cm-1, C–H aromatic stretching between 3000 and 3100 cm^{-1}. The spectrum shows a broad band near 3399 cm^{-1}, which indicates the presence of hydroxyl groups on the TISP surface. The stretching was attributed to the absorbed water on the surface of TISP. Several bands peaks of stretching appeared between 1500 to 1800cm^{-1} showing aromatic alkenes C=C before adsorption which disappeared after adsorption. Also, a distinct peak was observed at 848cm^{-1} showing possible C-F bond favoring fluoride adsorption.


Counts
D:\XRD Data\Demo\Rahul 7 5 15\WX2.xrdml
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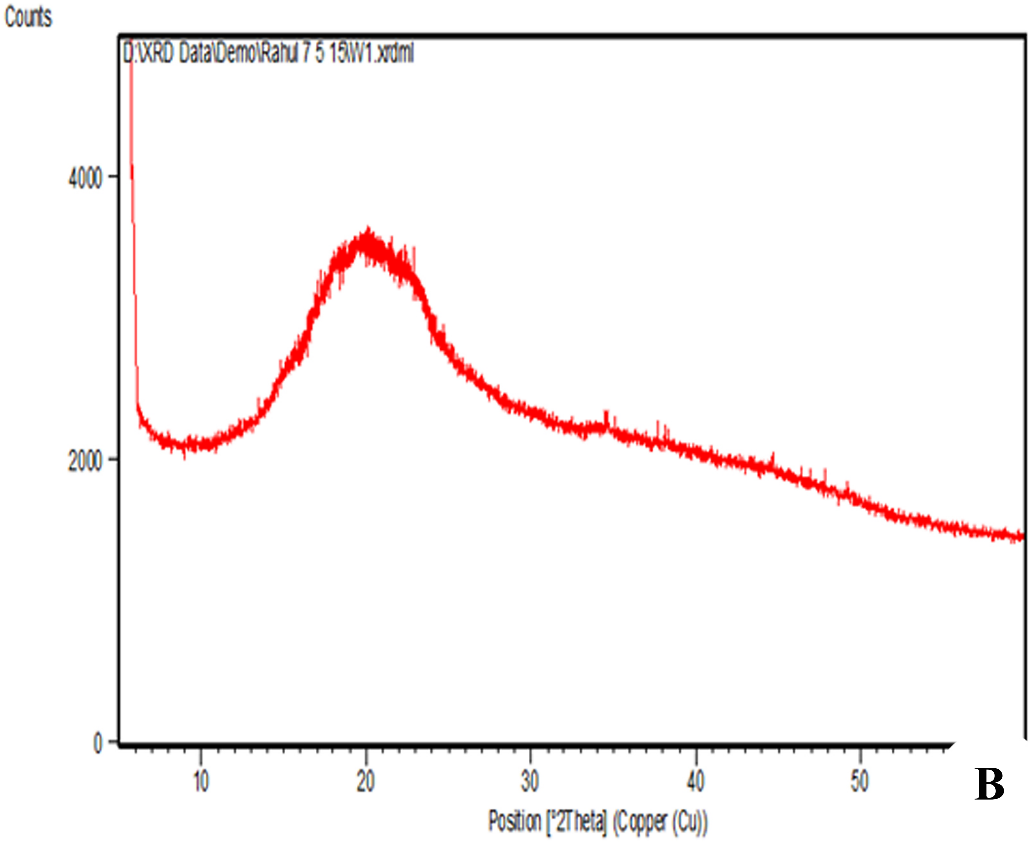
2000
0
10
20
30
40
50
Position [°2Theta] (Copper (Cu))

A


Counts
D:\XRD Data\Demo\Rahul 7 5 15\W1.xrdml
4000
2000
0
10
20
30
40
50
Position [°2Theta] (Copper (Cu))

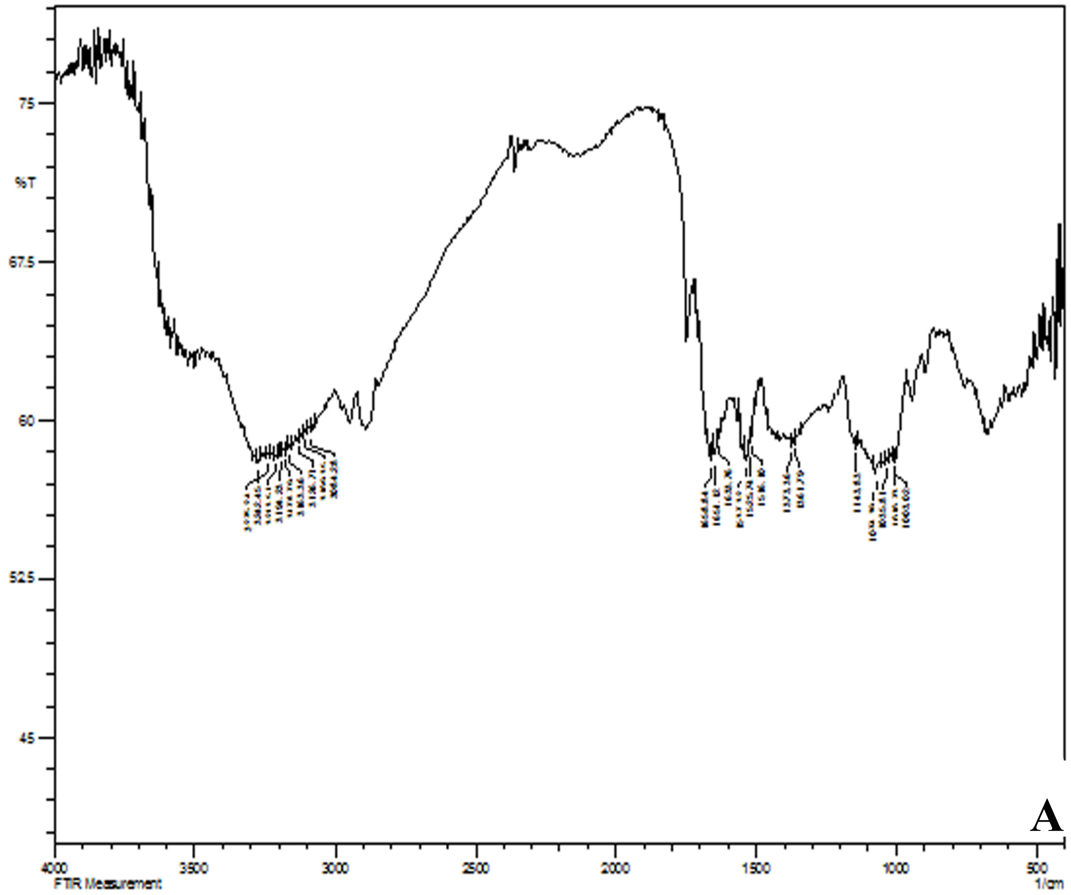
B

PLATE 9

PLATE 9

A: XRD image of TISP before adsorption

B: XRD image of TISP after adsorption


75
%T
67.5
60
52.5
45
A
4000
3500
3000
2500
2000
1500
1000
500
FTIR Measurement
1/cm

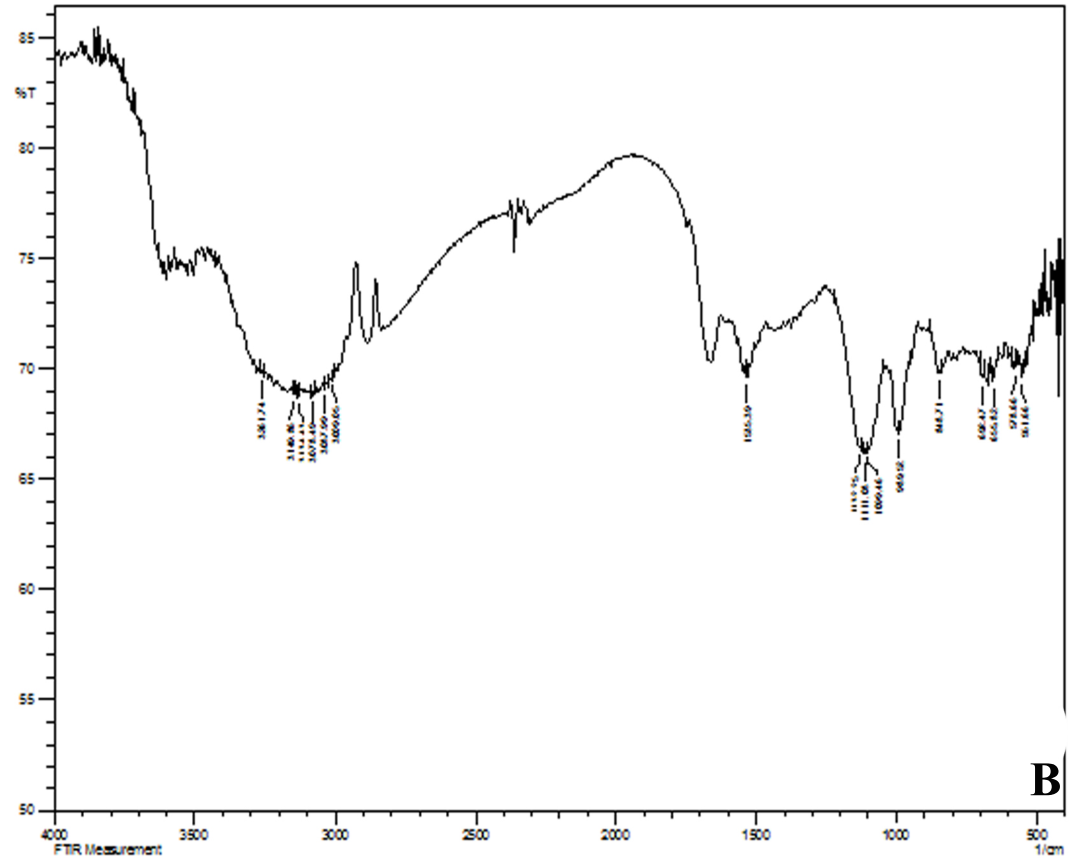

85
%T
80
75
70
65
60
55
50
B
4000
3500
3000
2500
2000
1500
1000
500
FTIR Measurement
1/cm

PlATE 10

PLATE 10

A: FT-IR image of TISP before adsorption

B: FT-IR image of TISP after adsorption

4.3.3. Comparative account of fluoride Adsorption by biochemical Parts and their respective residue

Batch defluoridation study has shown that TISP could adsorb the fluoride ion, and the extent of adsorption depends on several parameters. In this part of the work, an effort was made to analyze and compare the adsorption abilities of biochemical parts viz: carbohydrates, proteins and lipid along with the residual powder of T. indica seeds separately using synthetic fluoride solution as model adsorbate (Tables 27 and, Fig 35-37). In each study synthetic fluoride solution having concentration 10 mg/L was treated with 0.5 mg of the adsorbent for 150 minutes.

The fluoride removal efficiencies of crude extracts of carbohydrates, lipids and proteins were found to be 75.05%, 42.38% and 21.33% respectively while their adsorption capacities were 1.58mg/g, 0.89mg/g and 0.45mg/g respectively. Among the studied biochemical components the adsorption capacity of carbohydrate was found to be maximum followed by protein and then lipids (carbohydrate > protein > lipids).

The experiments carried for defluoridation of residual seed powder after each extract showed following result: The defluoridation efficiency of seed powder after lipid extract elevated from 55.21% to 67.38% while defluoridation capacity decreased from 1.01 to 0.76mg/g. The experiment carried out further with the residue of seed powder without lipid and protein and residue of seed powder without lipid and carbohydrate showed a steep decline in removal efficiency from 55.21% to 33.14% and from 55.21 to 24.57 respectively while defluoridation capacity from 1.01 to 0.69mg/g and from 1.01 to 0.52mg/g respectively.

Table 27: Defluoridation by pure extracts

	Time	IF	FF	Diff	% removal	Qe (mg/g)
Carbohydrate	1	10.5	5.99	4.51	42.95	0.902
	2		2.62	7.88	75.05	1.576
	3		2.98	7.52	71.62	1.504
	4		3.46	7.04	67.05	1.408
	Time	IF	FF	Diff	% removal	Qe (mg/g)
Protein	1	10.5	8.27	2.23	21.24	0.446
	2		6.05	4.45	42.38	0.89
	3		6.08	4.42	42.10	0.884
	4		6.2	4.3	40.95	0.86
	Time	IF	FF	Diff	% removal	Qe (mg/g)
Lipid	1	10.5	9.59	0.91	8.67	0.182
	2		8.26	2.24	21.33	0.448
	3		8.7	1.8	17.14	0.36
	4		8.87	1.63	15.52	0.326

Table 28: Defluoridation by residue

	Time	**IF**	**FF**	**Diff**	**% removal**	**Qe (mg/g)**
Seed powder w/o lipid*	1	10.5	8.25	2.25	40.11	0.45
	2		7.49	3.01	53.65	0.602
	3		6.72	3.78	67.38	0.756
	4		7.13	3.37	60.07	0.674
	Time	**IF**	**FF**	**Diff**	**% removal**	**Qe (mg/g)**
Seed powder w/o lipid and Protein*	1	10.5	8.25	2.25	21.43	0.45
	2		7.67	2.83	26.95	0.566
	3		7.02	3.48	33.14	0.696
	4		7.45	3.05	29.05	0.61
	Time	**IF**	**FF**	**Diff**	**% removal**	**Qe (mg/g)**
Seed powder w/o lipid and carbohydrate*	1	10.5	8.48	2.02	19.24	0.40
	2		8.12	2.38	22.67	0.48
	3		7.92	2.58	24.57	0.52
	4		8.24	2.26	21.52	0.45

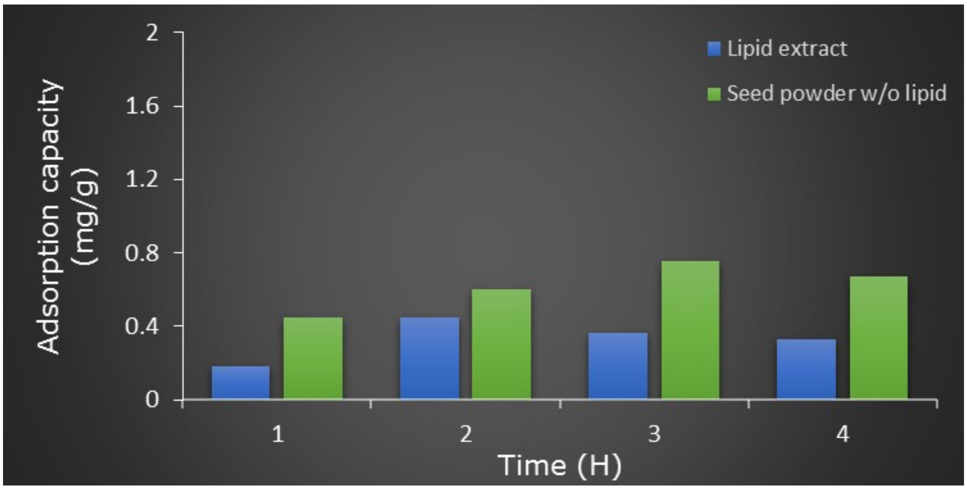


Figure 35: Effect of lipids on defluoridation by TISP

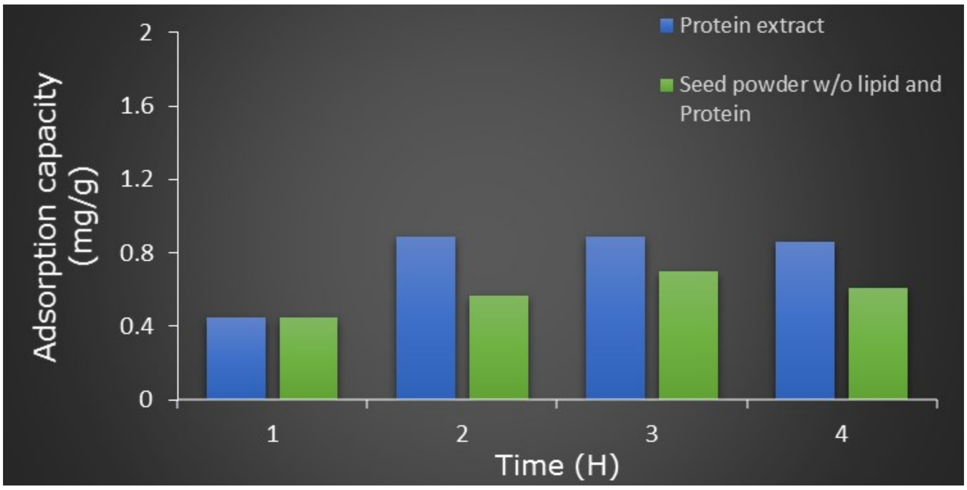


Figure 36: Effect of proteins on defluoridation by TISP

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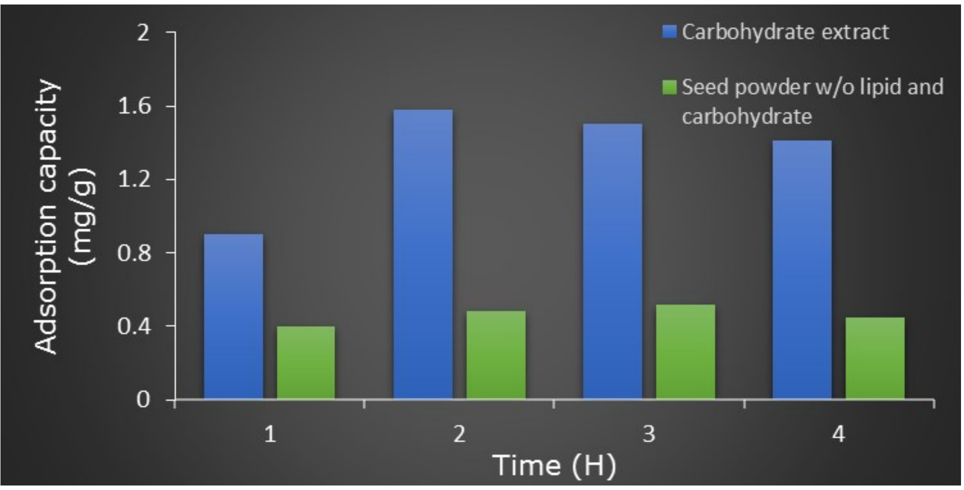

Figure 37: Effect of carbohydrates on defluoridation by TISP

4.3.4. Mechanism of Adsorption

The adsorption process of fluoride onto the surface of TISP is following Langmuir isotherm as evaluated from the isotherm study, thus is monolayer adsorption occurring between the fluoride ion and the surface of TISP. The R_L value calculated from the linear equation of Langmuir shows a favourable reaction. The decrease in value of Langmuir rate constant demonstrates the process to be an exothermic reaction. The value of n obtained from the Freundlich isotherm was between 1 and 10 showing an involvement of weak bonding like vander-waal forces. The value of E calculated from D-R model was less than 8 KJ/mol showing the model to be physical adsorption

The reaction followed pseudo first order kinetics. The diffusion kinetics studies show the process to be governed by film diffusion kinetics. The film diffusion supports the acceptance of Langmuir isotherm as the film constructed over the surface of the adsorbent is a monolayer. The polysaccharide leaching from the seed powder can possibly make a thin film like coating around the particle.

The study of thermodynamics shows the value of enthalpy that verifies the assumption of the process to be exothermic in nature. Also, the negative value of entropy suggests a lower degree of disorderliness at the adsorbate-adsorbent interface during adsorption of fluoride on TISP supporting the Langmuir isotherm. The value of "ΔG" is negative at at lower (room) temperature which represents the reaction is spontaneous in nature.

The observation made from the experiments performed for characterization of adsorbent shows that the adsorption process on whole seed powder is governed maximum by carbohydrate content followed by protein and then lipids, fibers, etc. The XRD and FTIR study showed only lowering in the intensity of diffraction of IR transmittance. This characteristic supports the mechanism of physical adsorption.

4.4. Defluoridation

To check the adsorption efficiency of *T. indica* seed powder in *In-vivo* conditions experiments were set for batch adsorption of fluoride from the groundwater as selected in previous chapter. The intention of this work was to move out of the lab, back into the field, and begin to explore the efficiency for removal of fluoride by TISP in a natural environment, as well as to compare the behaviour of impact on fluoride removal across a range of various physico-chemical parameter like pH, TA, TH, TDS, etc.

4.4.1. Selection of fluoride affected areas

To study the defluoridation capacity of the adsorbent in the field affected areas were selected. These fluoride affected areas were selected based on two main criteria

1) Villages with groundwater fluoride above 2 ppm
2) Villages with more than 30% of its population affected due to fluorosis

Taking into consideration the above two criteria, from the data obtained, we selected twenty villages for defluoridation study.

4.4.2. Groundwater study of the selected villages

The seasonal physico-chemical analysis of groundwater is presented in Tables 29-31; Fig. 38-50 Groundwater analysis was carried out for pH, total alkalinity, total dissolved solids, total hardness, bicarbonate, carbonate, calcium, magnesium, sodium, potassium, fluoride, chloride, and sulphate.

The pH of groundwater was found to vary from 7.38 to 8.56 in pre-monsoon and 7.2 to 8.1 in post monsoon. Total alkalinity ranged from 525 and 1470 mg/l (mean: 801 mg/l) in pre-monsoon and 500 to 1200 (mean: 709 mg/l) in post-monsoon periods. Concentration of salinity (TDS) ranged from 1000 to 3200 mg/l with a mean of 1940 mg/l in pre-monsoon while 1000 to 2800 mg/l, with a mean of 1731 mg/l in post-monsoon. Higher concentration of TDS was observed in the western part while lower TDS in the remaining area. TDS levels were recorded to be highest in pre-monsoon groundwater samples. The Total hardness ranged from 270 to 1,100 mg/l in pre-monsoon mean: 577 mg/l) and 240 to 916 mg/l in post-monsoon (mean: 512 mg/l).

Among the cations, calcium and magnesium varied from 64 to 328 mg/l and 0 to 148 mg/l with a mean of 183 mg/l and 29 mg/l in pre-monsoon while 94 to 334 mg/l and 0 to 77 mg/l with a mean of 177 mg/l and 17mg/l in post-monsoon. Similarly, Sodium and Potassium varied from 82 to 815 mg/l and 0 to 6 mg/l with a mean of 373 mg/l and 2 mg/l in pre-monsoon while 78 to 766 mg/l and 0 to 4 mg/l with a mean of 300 mg/l and 1.14 mg/l in post-monsoon.

Dissolved anions, Carbonate and Bicarbonate in the villages varied from 0 to 220 mg/l and 641 to 1659 mg/l with a mean of 41 mg/l and 927 mg/l in pre-monsoon while 0 to 132 mg/l and 598 to 1330 mg/l and with a mean of 17 mg/l and 830 mg/l in post-monsoon. Similarly, Chloride and sulphate varied from 71 to 880 mg/l and 0 to 30 with a mean of 294 mg/l and 12 mg/l in pre-monsoon while 42 to 800 mg/l and 0 to 35 with a mean of 256 mg/l and 15 in post-monsoon. The fluoride concentration of the area varied from 1.79 to 13.6 mg/l with a mean of 3 mg/l in pre-monsoon while 1.45 to 5.71 mg/l with a mean of 2.45 mg/l in post-monsoon.

Geochemical evaluation

Major cations and anions such as Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, CO_3^{2-}, HCO_3^{-}, SO_4^{2-} and Cl^{-} (in meq/l) were plotted in piper trilinear diagram (Piper 1944) to evaluate the hydrochemistry of groundwater of study area(Fig. 51 & 52). The plot shows that most of the groundwater samples fall in the field of alkaline earth metals (Ca^{2+}, Mg^{2+}) dominating over the alkalies (Na^{+}, K^{+}) and weak acid (CO_3^{2-}, HCO_3^{-}) exceed the strong acid (SO_4^{2-}, Cl^{-}). The plot shows that majority of chemical composition obtained of groundwater fall in the field of Ca-Mg-HCO_3, Ca–Mg–Cl and Na-HCO_3 type.

In addition, to understand the mechanism of ion interaction Gibbs diagram was plotted (Fig. 53 and 54). It is clearly seen that the geochemistry in groundwater is governed by combination of rock water interaction along with evapotranpiration.

Table 29: Statistical analysis for groundwater

Water quality parameter	Post-monsoon analysis				Pre-monsoon analysis			
	Minimum	Maximum	Mean	Standard Deviation	Minimum	Maximun	Mean	Standard Deviation
pH	7.2	8.1	7.52	0.31	7.38	8.56	7.89	0.31
TA (mg/l)	500	1200	764.25	207.16	525	1470	876.75	233.61
TDS (mg/l)	1000	2800	1950	480.68	1000	3200	2160	492.47
HCO_3 (mg/l)	598	1330	883.89	210.62	641	1659	1009.24	250.68
CO_3 (mg/l)	0	132	23.1	38.75	0	220	49.5	75.5
TH (mg/l)	240	916	517.05	172.20	270	1100	591	201.28
Ca (mg/l)	94	334	175.72	62.54	64	328	178.42	67.02
Mg (mg/l)	0	77	19.64	23.67	0	148	35.37	39.18
Na (mg/l)	78	766	407.75	206.92	82	815	479.45	221.59
K (mg/l)	0	4	1.1	1.34	0	6	1.9	1.52
F (mg/l)	1.45	5.71	3.40	1.30	1.79	13.6	4.02	2.51
Cl (mg/l)	42	800	301.49	224.03	71	880	345.85	237.82
SO_4 (mg/l)	0	35	10.9	8.17	0	30	9.2	7.20

Table 30: Physicochemical analysis of groundwater in post-monsoon season

Village	pH	TA (mg/l)	TDS (mg/l)	HCO_3 (mg/l)	CO_3 (mg/l)	TH (mg/l)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)	F (mg/l)	Cl (mg/l)	SO_4 (mg/l)
Arthi	8	800	2000	976	0	240	94.12	1.22	526	3	2.24	171	4
Chotiya	7.5	800	2000	841.8	66	415	166.21	0.00	560	0	2.2	264	11
Dabhoda	7.8	900	1600	1098	0	540	212.27	2.43	124	2	4.48	113.9	9
Dalisana	7.2	500	1000	610	0	430	168.21	2.43	78	2	5.41	120.7	2
Fatepura	7.4	675	2000	823.5	0	400	150.19	6.08	550	0	4.2	250	11
Gajipur	7.2	700	1800	854	0	370	144.18	2.43	524	0	2.14	76	0
Gathaman	7.4	500	2000	610	0	410	144.18	12.16	440	0	2	697	5
Gorisana	7.2	1135	2400	1250.5	66	800	302.38	10.94	120	4	3	412	20
Lalawad	7.6	600	2000	732	0	530	200.25	7.29	656	1	2	277.5	12
Mahekubpura	8	725	1800	884.5	0	530	130.16	49.84	409	1	4.61	292.3	10
Mahiyal	7.2	600	1200	732	0	430	170.21	1.22	86	1	3.06	134.9	3
Malarpura	7.4	1200	2400	1329.8	66	415	160.20	3.65	550	0	4	125	9
Malekhpur	7.4	550	1400	640.5	0	520	116.15	55.91	311	3	2	170.4	14
Mandropur	7.2	700	2400	854	0	916	334.42	19.69	300	0	3.1	656	13
Nalu	7.5	600	1200	732	0	600	240.30	0.00	120	0	2.7	42	10
Nava Delwada	7.2	1100	2200	1073.6	132	425	140.18	18.23	470	0	5	196	4
Rahemanpura	7.4	600	2000	597.8	66	530	128.16	63.21	530	0	5.71	421	20
Unad	7.8	800	2200	976	0	360	98.12	27.96	766	2	2.04	205	6
Vaghvadi	8.1	850	2800	1037	0	630	200.25	31.60	585	3	4.5	800	35
Vithoda	7.9	950	2600	1024.8	66	850	214.27	76.58	450	0	4.22	605	20

Table 31: Physicochemical analysis of groundwater in pre-monsoon season

Village	pH	TA (mg/l)	TDS (mg/l)	HCO_3 (mg/l)	CO_3 (mg/l)	TH (mg/l)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)	F (mg/l)	Cl (mg/l)	SO_4 (mg/l)
Arthi	7.99	892.5	2200	954.65	110	270	108.14	0.00	615	3	2.42	220.1	4
Chotiya	7.64	840	2200	890.6	110	500	200.25	0.00	600	1	5.26	320.92	10
Dabhoda	8.03	1050	2000	1281	0	650	260.33	0.00	168	2	3.84	156.5	6
Dalisana	7.85	525	1000	640.5	0	450	160.20	12.16	82	1	2	106.5	0
Fatepura	7.77	787.5	2000	960.75	0	460	172.22	7.29	580	1	4.26	262.7	12
Gajipur	8.26	787.5	1800	960.75	0	400	156.20	2.43	570	4	3.85	78.1	0
Gathaman	8.35	787.5	2600	960.75	0	480	148.19	26.74	575	2	5.1	724.2	5
Gorisana	7.5	1155	2400	1409.1	0	930	300.38	43.76	148	6	3.35	461.5	12
Lalawad	7.47	525	2200	640.5	0	570	220.28	4.86	770	1	2.35	362.1	11
Mahekubpura	7.59	892.5	2200	1088.85	0	650	140.18	72.93	430	1	2	355	11
Mahiyal	7.61	735	1600	896.7	0	550	200.25	12.16	166	1	2.3	191.7	1
Malarpura	7.96	1470	2800	1659.2	110	500	172.22	17.02	665	0	13.6	156.2	9
Malekhpur	8.15	630	1800	768.6	0	600	120.15	72.93	400	2	3.75	276.9	12
Mandropur	7.85	787.5	2600	960.75	0	1100	328.41	68.07	475	3	4.2	745.5	11
Nalu	7.71	735	1400	896.7	0	610	244.31	0.00	155	1	4.24	71	7
Nava Delwada	7.96	1207.5	2400	1204.75	220	420	132.17	21.88	545	0	5.76	220.1	4
Rahemanpura	8.01	735	2200	762.5	110	580	112.14	72.93	620	1	2.84	454.4	19
Unad	8.1	892.5	2200	954.65	110	450	64.08	70.50	815	3	3.75	213	3
Vaghvadi	7.38	997.5	3200	1216.95	0	720	200.25	53.48	670	4	3.18	880.4	30
Vithoda	8.56	1102.5	2400	1076.65	220	930	128.16	148.29	540	1	2.6	660.3	17

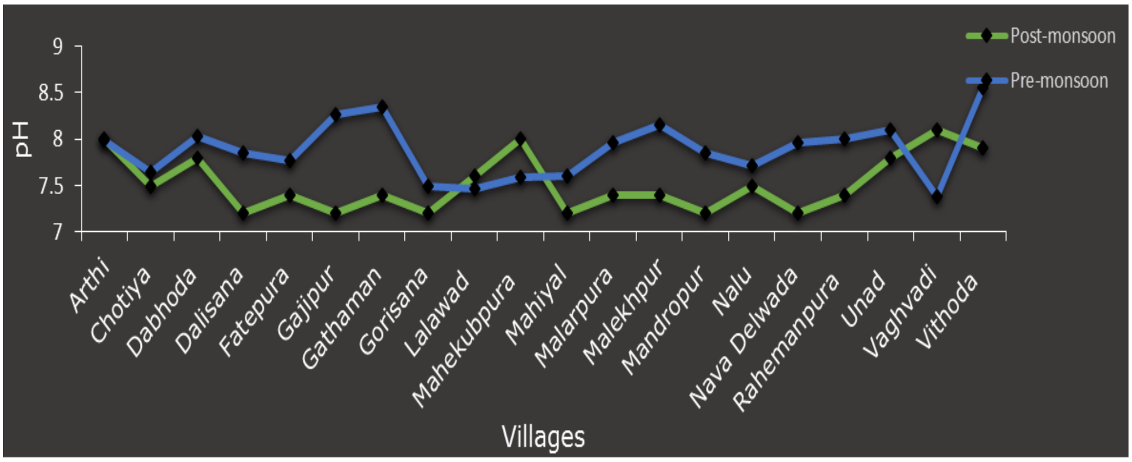

Figure 38: Seasonal variation in pH

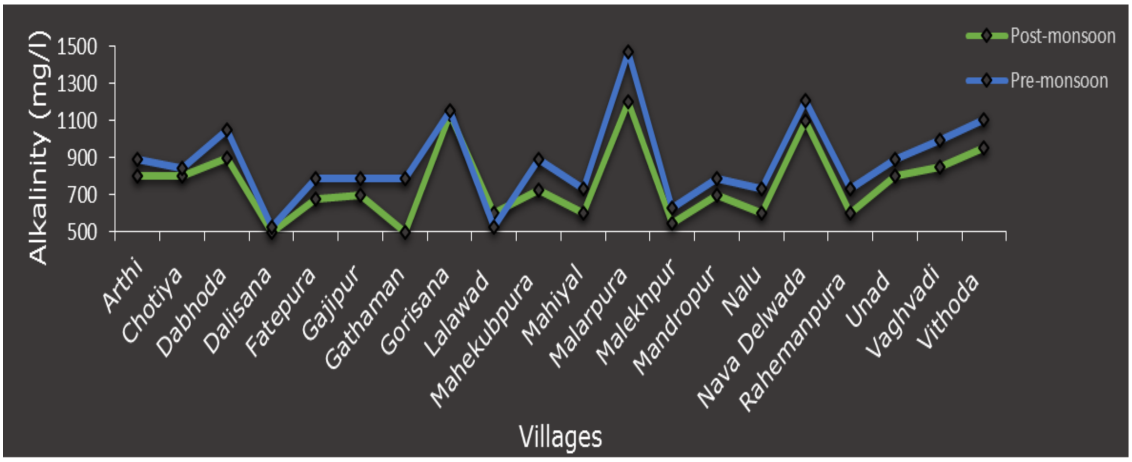

Figure 39: Seasonal variation in Total Alkalinity

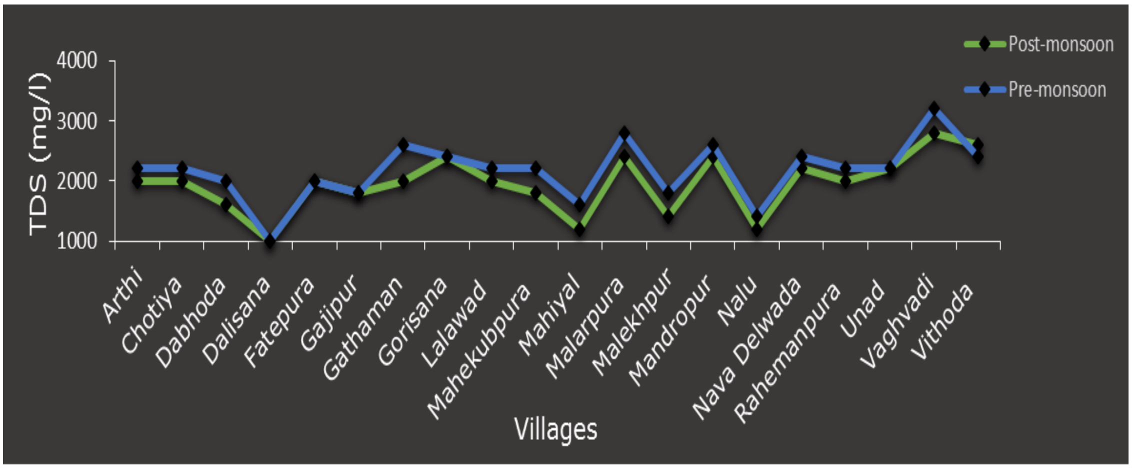

Figure 40: Seasonal variation in TDS

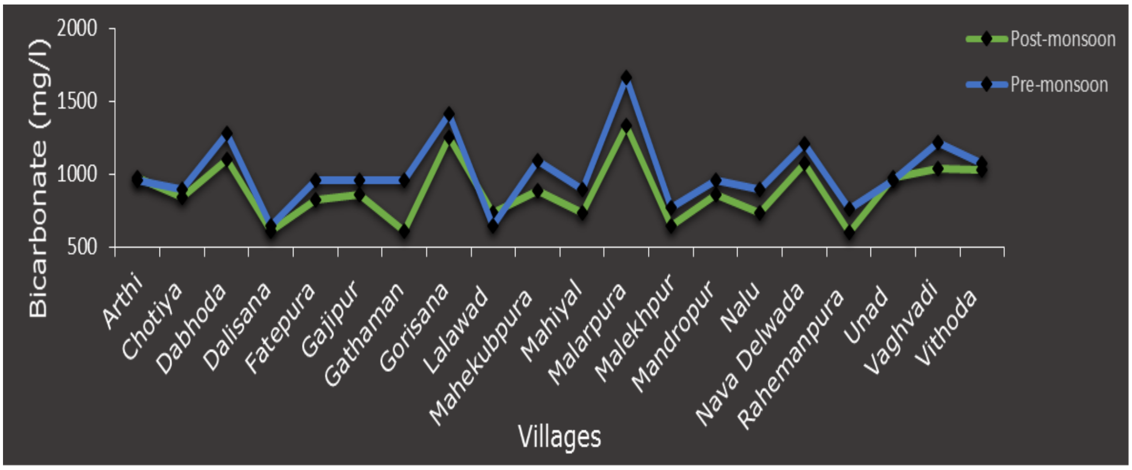

Figure 41: Seasonal variation in bicarbonate

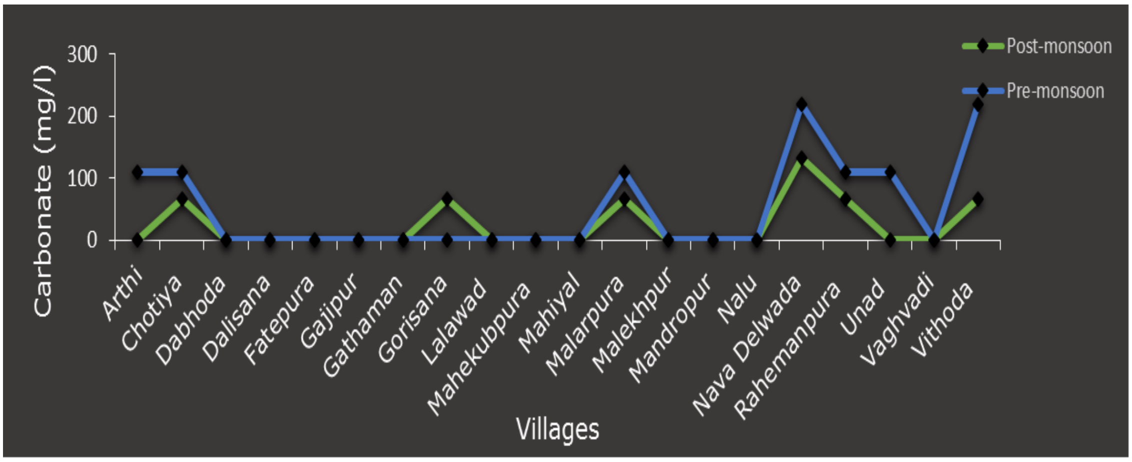

Figure 42: Seasonal variation in carbonate

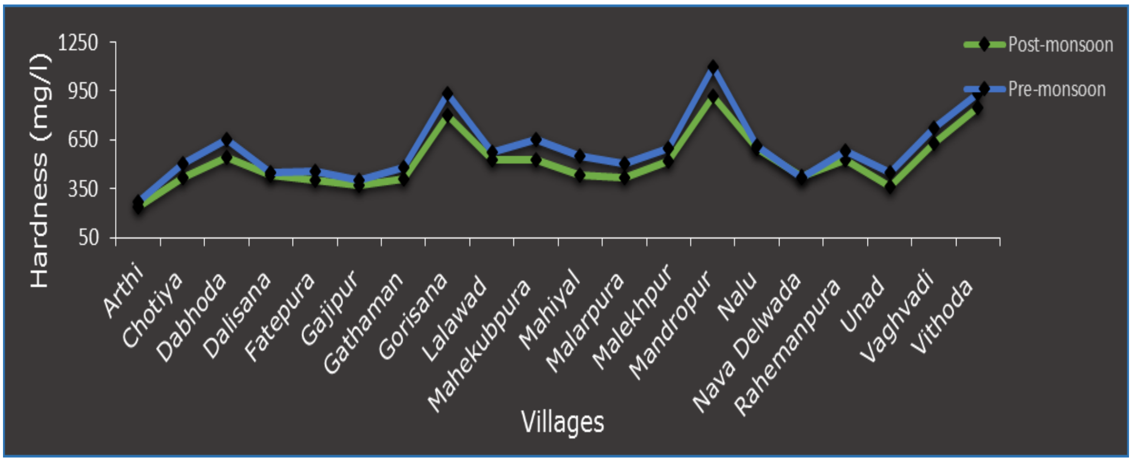

Figure 43: Seasonal variation in Hardness

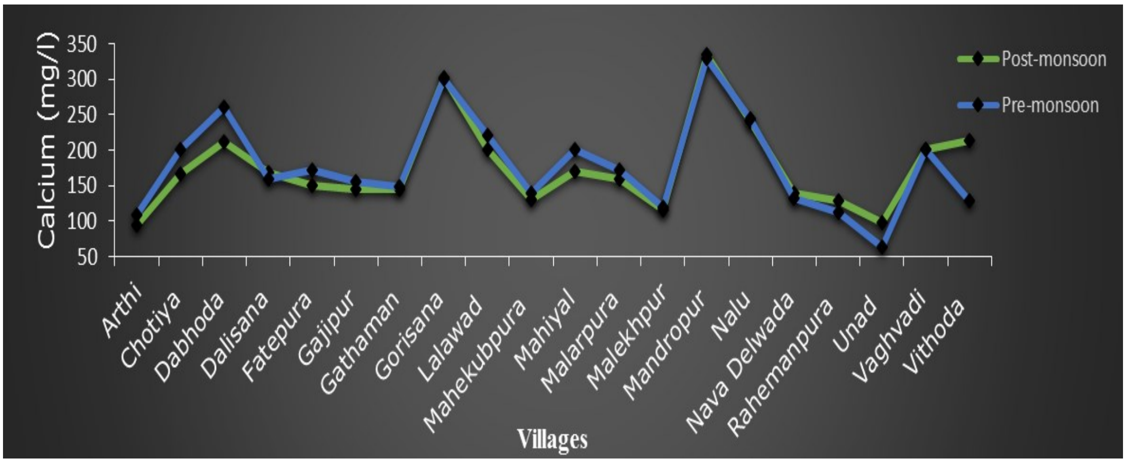

Figure 44: Seasonal variation in Calcium

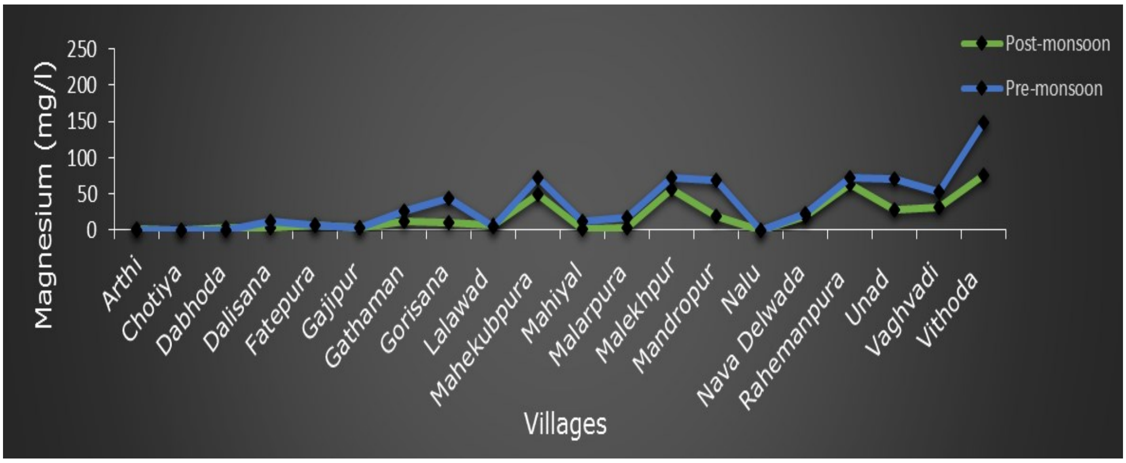

Figure 45: Seasonal variation in Magnesium

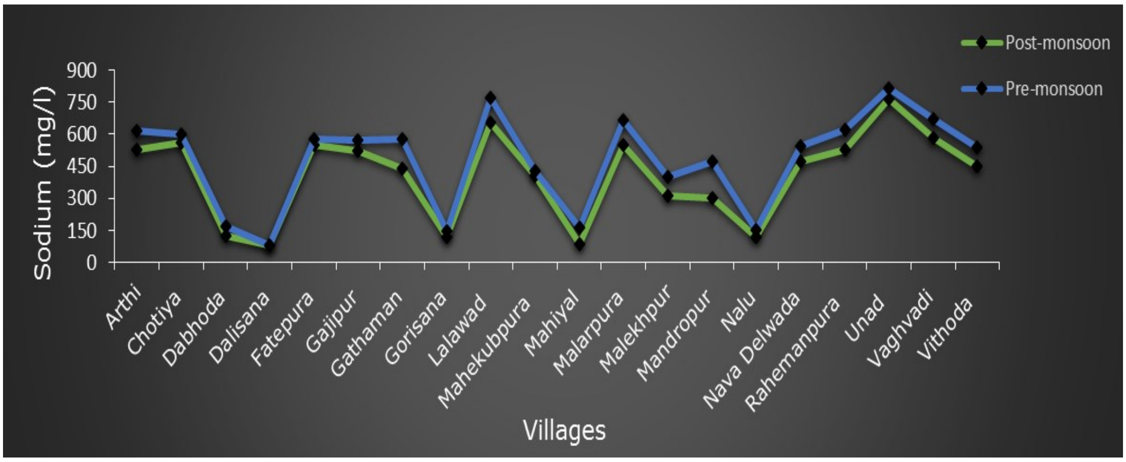

Figure 46: Seasonal variation in Sodium

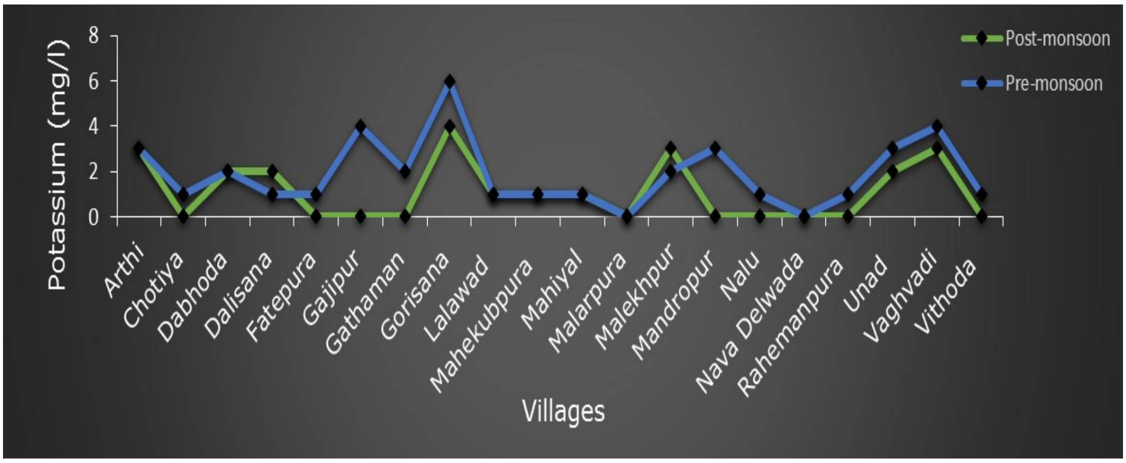

Figure 47: Seasonal variation in Potassium

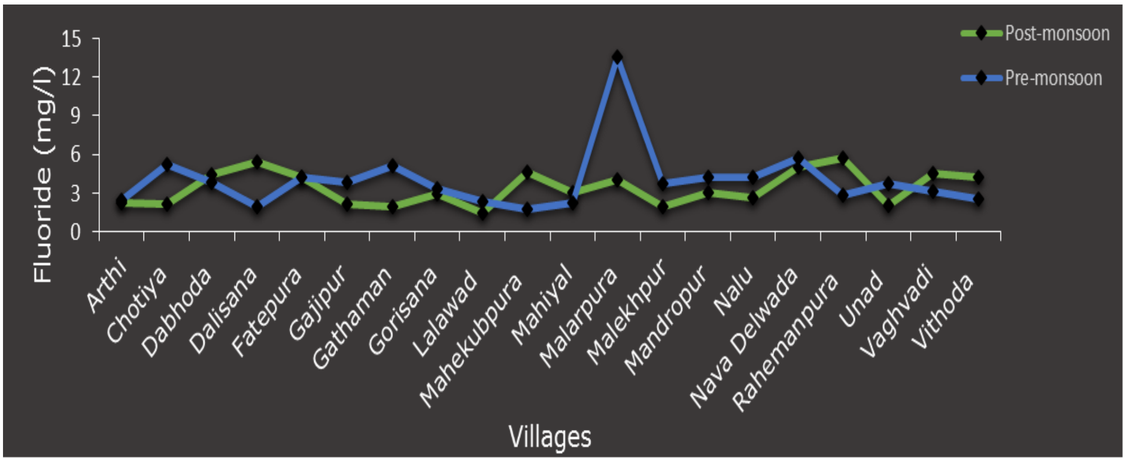

Figure 48: Seasonal variation in Fluoride

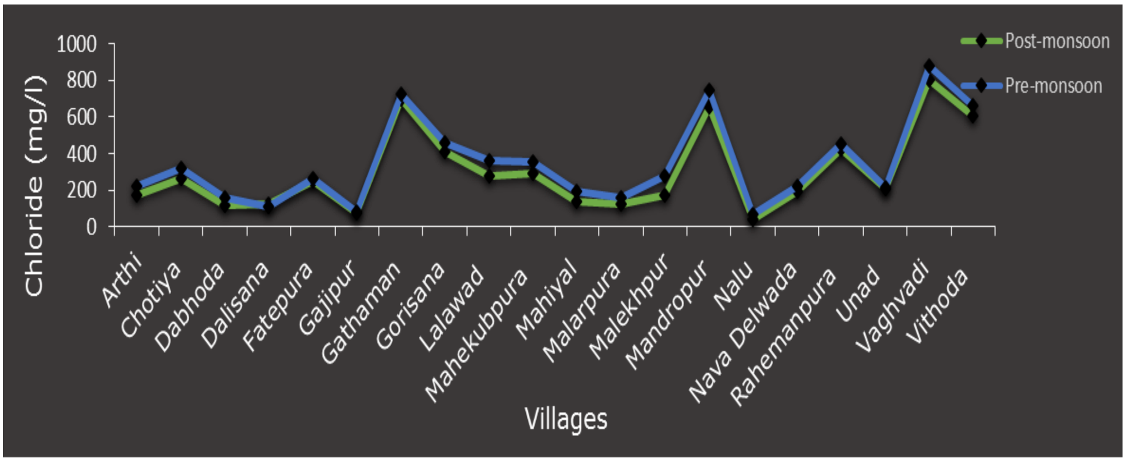

Figure 49: Seasonal variation in Chloride

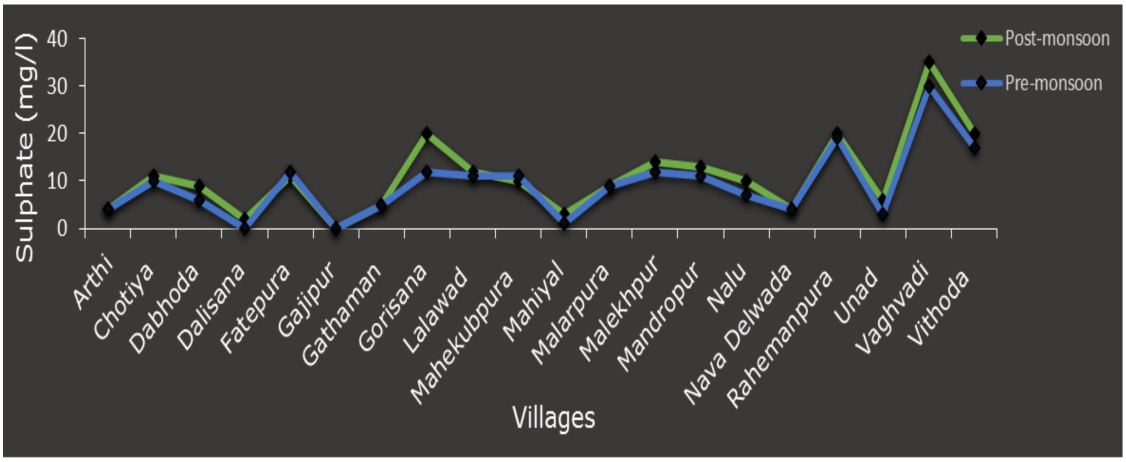

Figure 50: Seasonal variation in Sulphate

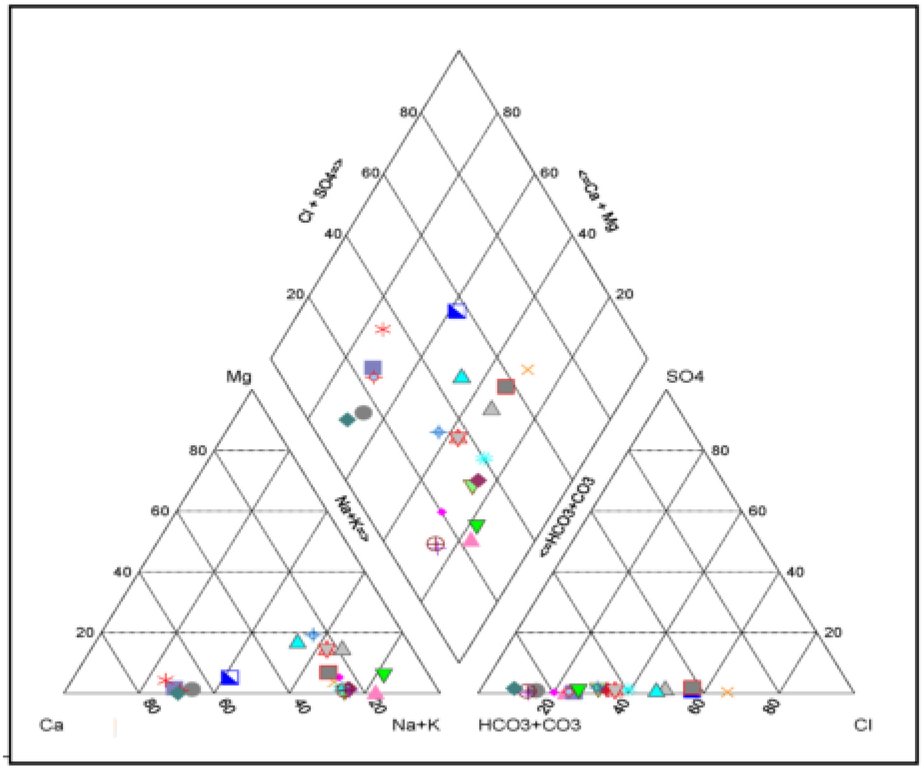

Figure 51: Piper Diagram for Post Monsoon

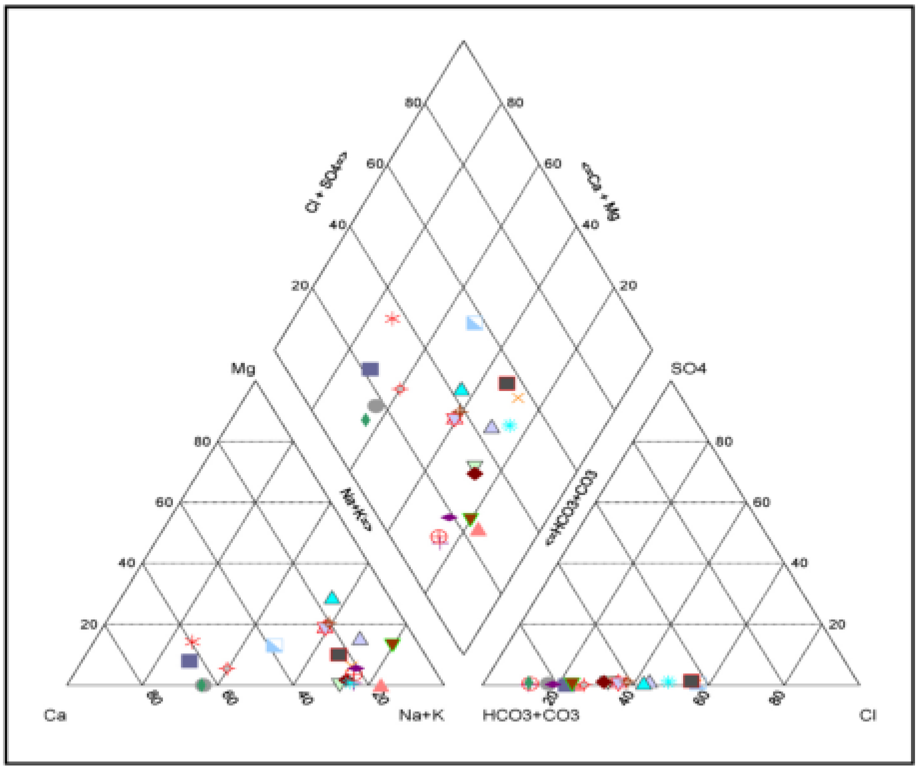

Figure 52: Piper Diagram for Pre Monsoon

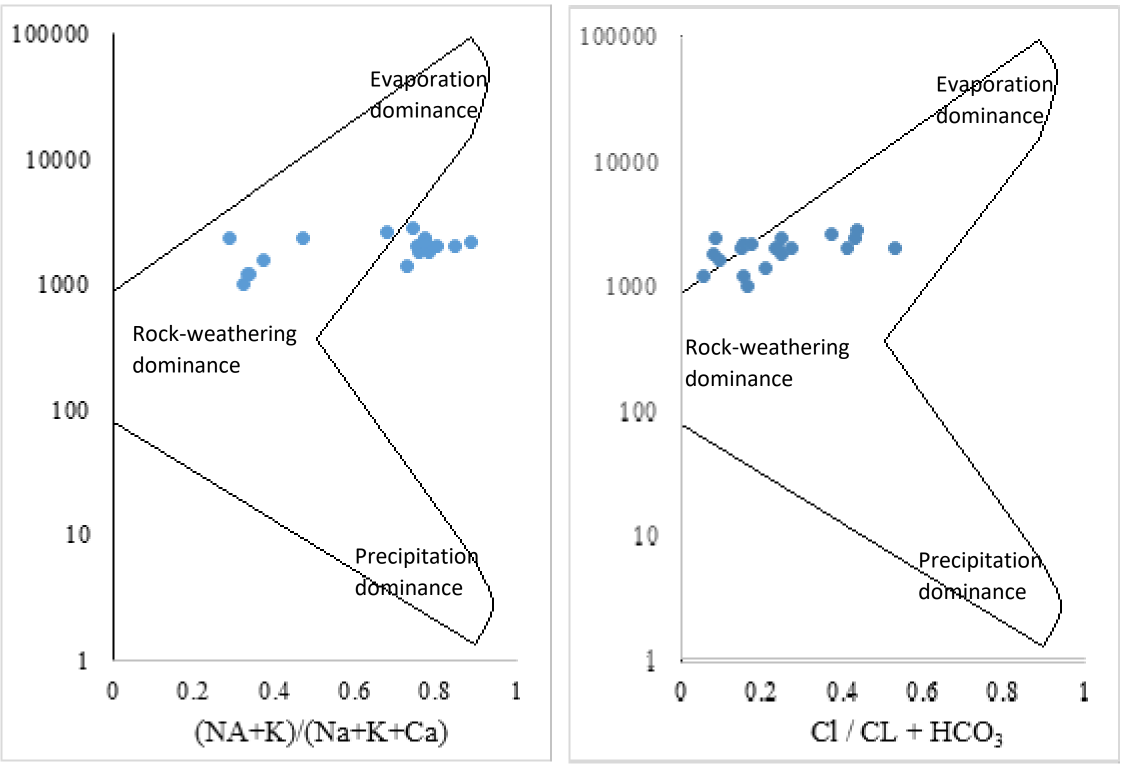

Figure 53: Gibbs Diagram for Post Monsoon

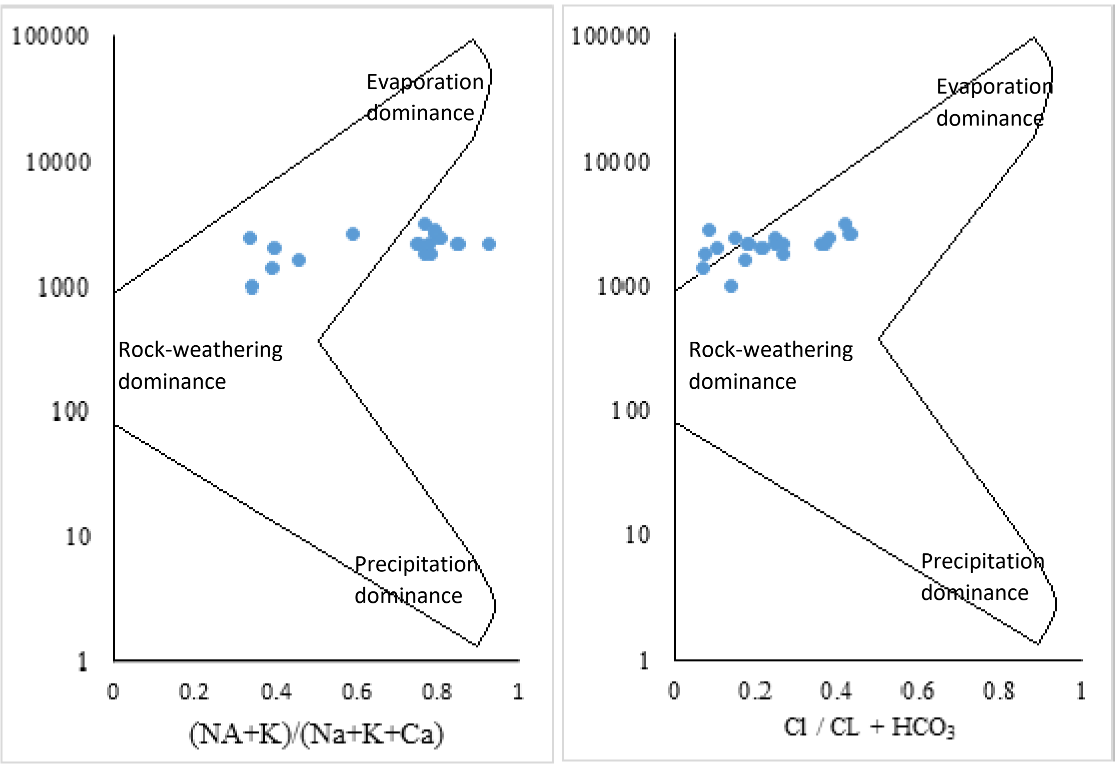

Figure 54: Gibbs Diagram for Pre-Monsoon

4.4.3. Assessment of Drinking water Quality

To assess drinking water quality of the selected villages following parameters were taken into consideration viz: Fluoride, Total Dissolved Solids, Total Hardness, Chloride and Sulphate because these are the major parameters responsible for altering drinking water quality when groundwater fluoride is high. The data was compared with the standard guideline values as recommended by the BIS (1993) for drinking and public health purposes (Table 18).

4.4.3.1. pH

pH is an important piece of information used as first measure to evaluated the applicability of groundwater for drinking purpose. The pH of all the 20 samples in both post-monsoon (2012) and pre-monsoon (2013) from study area showed value within the limits permitted my BIS (Table 32). Overall the pH of the study area were slightly alkaline

4.4.3.2. Total alkalinity

Alkalinity is due to various ionic species of bicarbonate, hydroxide, phosphate, borate and organic acids. Total alkalinity of 65% samples (i.e. 13 samples) in post-monsoon season (2012) and 90% (i.e. 18 samples) in pre-monsoon season (2013) respectively were found to be above permissible limit. Rest samples were below the permissible limit. High amount of total alkalinity can be correlated with the alkaline nature of pH in the groundwater of sample locations in study area.

4.4.3.3. Total dissolved solids

Total dissolved solids are the concentrations of all dissolved minerals mainly inorganic salts in water which indicate the general nature of salinity of water. As shown in Table 32, the test samples in post-monsoon (2012) 16 villages while in pre-monsoon (2013) 18 villages were reported to have TDS value above the permissible limit. Rest of the samples were within the permissible range for drinking. According to the classification of groundwater given by (Davis and De Wiest, 1966) 90% of samples in post-monsoon (2012) and 95% samples in pre-monsoon (2013) (Table 33) were found unsafe for drinking purpose.

Table 32: Drinking water quality assessment

Water quality Paramenters	BIS standard		Post monsoon analysis			Pre monsoon analysis		
	Most Desirable Limits	Most allowable limit	>PL	<PL >DL	<DL	>PL	<PL >DL	<DL
pH	6.5 - 8.5	--	0	20	0	0	20	0
TA (mg/l)	200	600	13	7	0	18	2	0
TDS (mg/l)	500	1500	16	4	0	18	2	0
TH (mg/l)	300	600	5	14	1	8	11	1
Ca (mg/l)	75	200	7	13	0	8	11	1
Mg (mg/l)	25	600	6	0	14	9	0	11
Na (mg/l)	200	-	15	5	0	15	5	0
F (mg/l)	1	1.5	20	0	0	20	0	0
Cl (mg/l)	250	1000	0	16	4	0	17	3
SO_4 (mg/l)	200	400	0	0	20	0	0	20

Table 33: Davis and De Wiest classification of TDS for groundwater samples

TDS (mg/l)	Water Class	Total no. of wells	
		Pre-monsoon	Post-monsoon
<500	Desirable for drinking	0	0
500-1000	Permissible for drinking	1	1
1000-3000	Useful in irrigation	19	18
>3000	Unfit for irrigation and drinking	0	1

Table 34: McCarty classification of TH for groundwater samples

TH as $CaCO_3$ (mg/l)	Water Class	Total no. of wells	
		Pre-monsoon	Post-monsoon
<75	Soft	0	0
75-150	Moderately hard	0	0
150-300	Hard	1	1
>300	Very hard	19	19

4.4.3.4. Total Hardness

Total Hardness of water is caused by the presence of the multivalent cations and is largely due to calcium and magnesium ions. In post-monsoon season (2012) 5 samples while in post-monsoon season (2013) were reported to have total hardness of groundwater above maximum permissible limit (Table 32). Of remaining, 14 villages (post monsoon) and 11 villages (pre-monsoon) had hardness above desirable limit but below permissible limit. Only 1 in both pre and post monsoon season village had hardness below desirable limit (Table 32). As per classification given by Sawyer and McCartly, (1967) 95 % samples were not suitable for drinking purpose as far as hardness is concerned (Table 34). In addition to total hardness, Calcium and Magnesium ions values were also recorded. As shown values of calcium ions in 7 villages for post monsoon and 8 villages for pre-monsoon were above permissible limit while rest were in permissible range. Similarly magnesium content of 6 villages in post-monsoon and 9 villages in pre monsoon were above permissible range while rest were below the desirable range.

4.4.3.5. Sodium

Sodium is one of the major inorganic cation of water. It is the sixth most abundant element in the Earth’s crust. The sodium content of around 75% groundwater samples i.e. 15 samples were above limit in both pre-monsoon and post-monsoon season. High sodium can cause many problems related to blood pressure.

4.4.3.6. Fluorine

Fluorine is one of the most common geogenic problem that occurs in natural water. Excess of fluorine is reported to cause fluorosis and many relating disorders. All the groundwater samples (i.e. 20 samples) in post-monsoon season (2012) and in pre-monsoon season (2013) were above permissible limit (1.0-1.5 mg/l) prescribed by BIS (1991) (Table 32).

4.4.3.7. Sulphate

Sulphate is unstable and causes a laxative effect on human system with the excess magnesium in groundwater. All the samples in post-monsoon season (2012) and pre-monsoon season (2013) of the selected sampling sites were within the desirable limit (Table 32).

4.4.3.8. Chloride

Chloride is one of the major inorganic anion of water. Chloride concentration of 16 samples in post-monsoon season (2012) and 17 samples in pre-monsoon season (2013) were found to be above the maximum desirable limit but below maximum permissible limit while rest of the samples had chloride were below the desirable limit (Table 32).

4.4.4. Water Quality Index

The BIS listed limits for the important parameters described above for analysing usability of drinking water. In order to club the whole data with their limits into consideration and to evaluate the drinking water portability Weight arithmetic index was calculated using the values of parameters like pH, total dissolved solids, total alkalinity (carbonate and bicarbonates), total hardness (calcium and magnesium), fluoride, chloride, sulphate and sodium and potassium. As seen in the Tables 35 and 36, all the samples are very bad to unfit for drinking purposes.

Table 35: Weigh Arithematic Index for drinking water assessment

Sr. No.	Village	WQI value for post-monsoon season	WQI value for pre-monsoon season
1	Arthi	157	167
2	Chotiya	117	311
3	Dabhoda	272	245
4	Dalisana	303	136
5	Fatepura	245	261
6	Gajipur	126	254
7	Gathaman	97	326
8	Gorisana	172	201
9	Lalawad	102	147
10	Mahekubpura	287	119
11	Mahiyal	175	147
12	Malarpura	234	778
13	Malekhpur	97	245
14	Mandropur	178	260
15	Nalu	165	256
16	Nava Delwada	282	349
17	Rahemanpura	328	191
18	Unad	141	244
19	Vaghvadi	285	189
20	Vithoda	263	196

Table 36: Interpretation of WQI-WQI

Criteria	Post-monsoon season		Pre-monsoon	
	WQI value	%	WQI value	%
Excellent water	0	0	0	0
Good Water	0	0	0	0
Poor Water	0	0	0	0
Very Poor water	2	10	0	0
Water unsuitable for drinking	18	90	20	100

4.4.5. In-vivo defluorination experiment:

A defluorination experiment was carried out with groundwater samples from selected twenty villages. The results revealed that defluoridation capacity of plant material in ground water samples is lesser than that of synthetic water used in vitro possibly due to the presence of cations and anions. As shown in Table 37 & 38, the highest defluoridation was observed in the samples of Dabhoda (24.48%) followed by Rehmanpura (24.29%) and Mandropur (24.28%) and least was observed Nalu (10.37%). The efficiency of fluoride removal in natural water decreased to more than half the efficiency with synthetic water. Fluoride removal was favoured in water having higher calcium and sodium in the water while alkalinity severely affected fluoride scavenging capacity. In addition to fluoride other water quality parameters also were found to get decreased. As the defluoridation was too low the process was repeated thrice which resulted in lowering of fluoride concentration upto desirable range in 50% samples (Table 39). The water obtained after defluoridation was found colourless and odourless. The water contained few amount of polysaccharide gel might be due to leaching from the powder.

Table 37: Defluoridation in groundwater

Sr. No.	Village	Fluoride (mg/l)			
		Initial	Final	Difference	% removal
1	Arthi	2.42	2.1	0.32	13.22
2	Chotiya	5.26	4.5	0.76	14.45
3	Dabhoda	3.84	2.9	0.94	24.48
4	Dalisana	1.96	1.54	0.42	21.43
5	Delwada (Nava)	5.76	5.1	0.66	11.46
6	Fatepura	4.26	3.7	0.56	13.15
7	Gajipur	3.85	3.3	0.55	14.29
8	Gathaman	5.1	4.3	0.8	15.69
9	Gorisana	3.35	2.7	0.65	19.4
10	Lalawada	2.35	1.9	0.45	19.15
11	Mahekubpura	1.79	1.49	0.3	16.76
12	Mahiyal	2.3	2	0.3	13.04
13	Malarpura	13.6	11.67	1.93	14.19
14	Malekhpur	3.75	3.1	0.65	17.33
15	Mandropur	4.2	3.18	1.02	24.29
16	Nalu	4.24	3.8	0.44	10.38
17	Rahemanpura	2.84	2.15	0.69	24.3
18	Unad	3.75	3.2	0.55	14.67
19	Vaghvadi	3.18	2.76	0.42	13.21
20	Vithoda	2.6	2.3	0.3	11.54

Table 38: Adsorption of ions by TISP

Sr. No.	Village	pH		T. Alkalinity (mg/l)		TDS (mg/l)		T. Hardness (mg/l)		Sodium (mg/l)		Chloride (mg/l)		Sulphate (mg/l)	
		Ini	Fin	Ini	Fin	Ini	Fin	Ini	Fin	Ini	Fin	Ini	Fin	Ini	Fin
1	Arthi	7.99	7.69	893	853	2200	1540	270	208	615	474	220	169	4	0
2	Chotiya	7.64	7.67	840	835	2200	1650	500	385	600	462	321	247	10	0
3	Dabhoda	8.03	7.71	1050	995	2000	1350	650	501	168	129	157	121	6	0
4	Dalisana	7.96	7.69	1208	1000	2400	1680	420	323	545	420	220	169	4	0
5	Delwada	7.85	7.68	525	500	1000	700	450	347	82	63	107	82	0	0
6	Fatepura	7.77	7.7	788	756	2000	1400	460	354	580	447	263	202	12	0
7	Gajipur	8.26	7.79	788	740	1800	1200	400	308	570	439	78	60	0	0
8	Gathaman	8.35	7.8	788	743	2600	1800	480	370	575	443	724	558	5	0
9	Gorisana	7.5	7.59	1155	820	2400	1600	930	716	148	114	462	355	12	0
10	Lalawada	7.47	7.55	525	519	2200	1400	570	439	770	593	362	279	11	0
11	Mahekubpura	7.59	7.6	893	826	2200	1400	650	501	430	331	355	273	11	0
12	Mahiyal	7.61	7.64	735	708	1600	1200	550	424	166	128	192	148	1	0
13	Malarpura	7.96	7.69	1470	983	2800	2000	500	385	665	512	156	120	9	0
14	Malekhpur	8.15	7.8	630	601	1800	1200	600	462	400	308	277	213	12	0
15	Mandropur	7.85	7.69	788	730	2600	1800	1100	847	475	366	746	574	11	0
16	Nalu	7.71	7.65	735	701	1400	980	610	470	155	119	71	55	7	0
17	Rahemanpura	8.01	7.7	735	706	2200	1600	580	447	620	477	454	350	19	0
18	Unad	8.1	7.8	893	725	2200	1600	450	347	815	628	213	164	3	0
19	Vaghvadi	7.38	7.61	998	752	3200	2200	720	554	670	516	880	678	30	0
20	Vithoda	8.56	7.9	1103	814	2400	1600	930	716	540	416	660	508	17	0

Table 39: Defluoridation runs for groundwater

Sr. No.	Villages	First run			Second run		Third run	
		Initial	Final	Diff.	Final	Diff.	Final	Diff.
1	Arthi	2.42	2.1	0.32	1.78	0.64	1.46	0.96
2	Chotiya	5.26	4.5	0.76	3.74	1.52	2.98	2.28
3	Dabhoda	3.84	2.9	0.94	1.96	1.88	1.02	2.82
4	Dalisana	1.96	1.54	0.42	1.12	0.84	0.7	1.26
5	Delwada (Nava)	5.76	5.1	0.66	4.44	1.32	3.78	1.98
6	Fatepura	4.26	3.7	0.56	3.14	1.12	2.58	1.68
7	Gajipur	3.85	3.3	0.55	2.75	1.1	2.2	1.65
8	Gathaman	5.1	4.3	0.8	3.5	1.6	2.7	2.4
9	Gorisana	3.35	2.7	0.65	2.05	1.3	1.4	1.95
10	Lalawada	2.35	1.9	0.45	1.45	0.9	1	1.35
11	Mahekubpura	1.79	1.49	0.3	1.19	0.6	0.89	0.9
12	Mahiyal	2.3	2	0.3	1.7	0.6	1.4	0.9
13	Malarpura	13.6	11.67	1.93	9.74	3.86	7.81	5.79
14	Malekhpur	3.75	3.1	0.65	2.45	1.3	1.3	1.95
15	Mandropur	4.2	3.18	1.02	2.16	2.04	1.14	3.06
16	Nalu	4.24	3.8	0.44	3.36	0.88	2.92	1.32
17	Rahemanpura	2.84	2.15	0.69	1.46	1.38	0.77	2.07
18	Unad	3.75	3.2	0.55	2.65	1.1	2.1	1.65
19	Vaghvadi	3.18	2.76	0.42	2.34	0.84	1.46	1.26
20	Vithoda	2.6	2.3	0.3	2	0.6	1.7	0.9

4.4.1. Discussion

Groundwater quality

The result for study of groundwater quality of selected villages depicted that the samples of the selected locations were unfit for drinking not only due to fluoride but also due to concentration of various other parameters like total alkalinity, total dissolved solids, total hardness and sodium were above the permissible limit set by BIS (1993).

pH is considered as an important ecological factor and provides an important piece of information in many types of geochemical equilibrium or solubility calculation (Shyamala *et al.*, 2008). The mean pH measured for the samples was 7.52 ± 0.31 in post-monsoon and 7.89 ± 0.31. The results clearly indicate that the groundwater sample was slightly alkaline.

The mean alkalinity of the study area was 764.25 ± 207.16 in post-monsoon and 876.75 ± 233.61 in pre-monsoon. The alkalinity of the water is mainly due to the excess presence of bicarbonate and carbonate salts in the water. The mean bicarbonates in water were 883.89 ± 210.63 in post-monsoon and 1009.24 ± 250.68. Results revealed that around 13 villages in post-monsoon and 18 villages in pre-monsoon were having total alkalinity above the permissible limit. The high alkalinity imparts water with unpleasant taste and may be deleterious to human health. Increased alkalinity shows an increase in bicarbonate salts. Generally, bicarbonates are associated with hardness or sodicity of water

Total hardness of the samples relates to the presence of calcium, magnesium and salts of heavy metals. The mean total hardness of the area was 510.05 ± 172.2 in post-monsoon and 591 ± 201.28 in pre-monsoon. Calcium ions and magnesium ions present in the water were recorded to be 175.72 ± 62.54 and 19.64 ± 23.67 in post-monsoon and 178.42 ± 67.02 and 35.37 ± 39.18 in pre-monsoon respectively. Ca^{2+} is usually associated with carbonate mineral, viz., calcite and dolomite, which commonly occur in veins and secondary minerals in granite while the higher concentrations of Mg^{2+} may be due to the specificity of the minerals at the sampling site. Increased hardness is possibly due to the dedolomization process occurring in Mehsana district at certain places. The study area shows very hard water for drinking purpose. There is some suggestive evidence that long term consumption of extremely hard water might lead to an increased incidence of urolithiasis, anencephaly, prenatal mortality, some types of cancer and cardiovascular disorders (Agrawal and Jagetai 1997; Durvey *et al.,* 1991).

Sodicity of water is related to the Sodium content in the water. The sodium content of the study area was found to be 407 ± 206.92 in post-monsoon and 479.45 ± 221.59 in pre-monsoon. The result shows a presence of high amount of sodium ions in the groundwater samples. The higher concentration of Na^+ may pose a risk to the persons suffering from cardiac, renal and circulatory diseases.

Chloride concentrations higher than permissible limit are considered to be at risk for human health and may cause unpleasant taste of water. High consumption of Chloride may be crucial for the development of essential hypertension, a risk for stroke, left ventricular hypertrophy, osteoporosis, renal stones and asthma (McCarthy 2004). The Chloride content of the area was 301.49 ± 224.03 in post-monsoon and 345.85 ± 237.82 in pre-monsoon. Similarly, sulphate was 10.9 ± 8.17 and 9.2 ± 7.2 in post-monsoon and pre-monsoon respectively. None of the samples studied reported higher chloride or sulphate. No addition of these salts due to anthropogenic sources like fertilizers or other non-point source was observed.

As selected, all the villages were having fluoride concentration above 2 ppm. High fluoride causes a crippling disease called fluorosis. The fluoride concentration was 3.4 ± 1.3 and 4.02 ± 2.51 in a post and pre monsoon respectively. Deficiency or low concentration in drinking water (<0.5 mg/l; therefore, low intake dose) leads to dental caries (Edmunds and Smedley1996). High intake of fluoride (over 1.5 mg/l) results in physiological disorders, skeletal and dental fluorosis (Latha *et al.* 1999; ISI1983). The dissolution of fluoride due to alkaline water, from fluoride bearing granite and gneiss rocks in north-eastern recharge area, to be the main source of high concentration of fluoride in these areas (Handa, 1975). The Piper diagram indicates the Sodium bicarbonate type of water in the study area supporting to fluoride dissolution. In addition, the Gibbs diagram clearly indicates the rock water interaction along with the evapotranspiration in the area for major ionic concentration present in the groundwater.

The high concentration of all these salts increases the total dissolved solids. High solids relate to a high amount of cations and anions dissolved in water. The TDS of the samples were 1950 ± 480.68 in post monsoon and 2160 ± 492.47 in pre-monsoon. The results revealed 16 villages in post-monsoon and 18 villages in pre-monsoon were having very high TDS. Higher concentrations of TDS decrease the palatability and may cause gastrointestinal irritation in human and may also have a laxative effect particularly upon transits. Classification by Davis and De Wiest showed water from all the samples were unfit for drinking.

The WQI varies from 97 to 328 in post-monsoon season and 119 to 778 in pre-monsoon season. The high value of WQI in study area specially Malarpura has been found mainly due to higher values of fluoride along with that of pH, total dissolved solids, total alkalinity (carbonate and bicarbonates), total hardness (calcium and magnesium), fluoride, chloride, sulphate and sodium and potassium in some cases. All these factors may pose health hazard on a long term and can degrade the quality of drinking water, therefore require to be treated before using for drinking purpose. Research carried out by Rupal *et al.* (2010) which concluded that groundwater quality in some of the area of Surat City it has been found within the range of very poor water. Similarly, research has been carried out by Shah *et al.* (2008) and Bhattachariya *et al.* (2012) showing poor quality index value for groundwater of Gandhinagar Taluka and Anand District, Gujarat, respectively. Thus, the presents study shows that the overall ground water quality is poor to very poor and require some pre-treatments before use.

Defluoridation:

The defluoridation experiments with the groundwater showed that the adsorption capacity of the adsorbent in In-vitro condition is less in comparison to In-vivo conditions. Overall the results indicated that the highest defluoridation was observed in Mandropur and Dabhoda. The fluoride scavenging capacity of the adsorbent is affected greatly by the ions. Calcium and magnesium salts in water improved fluoride scavenging efficiency of the salts while bicarbonate salts mainly sodium bicarbonate reduced the scavenging efficiency of the salts. Similar results are observed by Sivasankar (2012).

4.5. Recommendation

In the semi-arid regions like our study area, the geogenic sources are found to serve as the main source of Fluoride contamination in groundwater. Therefore, the residents have to face various health problems due to ingestion of Fluorinated water and there is no permanent solution to bring down the enhanced Fluoride level in drinking water.

From the experiments conducted in the present research, we conclude that *T. indica* seed powder helps to reduce Fluoride concentration in groundwater; though 100% achievement in defluoridation with this adsorbent is not possible. But continuous use of the seed powder lowers the risk of Fluorosis in the population of Fluoride endemic areas. Thus the study recommends the use of *T. indica* seed powder as bio-adsorbent for removal of fluoride is feasible.