CHAPTER 5

SUMMARY AND CONCLUSION

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5.1. SUMMARY

Kheralu taluka is located in the North-Eastern part of the Mehsana District of Gujarat at the foothills of Aravalli range between 23.82N to 23.98N latitude and 72.48E to 72.79E longitude. The Geological setup of the district comprises of thick alluvium over sandstone, conglomerate and shale of Himmatnagar formation covering granite and gneiss rocks from Ajabgarh in the North eastern area. These rocks naturally contain Fluoride bearing minerals such as Apatite and Hornblende. Dissolution of these minerals and their mixing with water from Aravalli ranges at recharge area serve as major sources of the Fluoride in the area. Groundwater when exposed for long periods to such minerals leaches out some minerals, Fluoride being one of them. Fluoride is highly toxic substance that can cause a range of adverse health effects. Kheralu taluka comprises of many rural areas where hand-pumps and tube-wells are the only source of safe drinking water, Fluoride has emerged to cause a serious crisis threatening public health. Over-exploitation of groundwater without responsible management has led to contamination of fluoride in the Groundwater. High fluoride intake causes a slow crippling disease known as fluorosis mainly affects dental and skeletal structures. Fluorosis lead to calcified spinal ligaments or softened bones and degenerative conditions of spinal cord in the advance stage. Such conditions have very serious impacts on the socio-economic aspect of the population especially in the region like Mehsana region a where majority of population are farmers or workers.

Many Talukas of the entire Mehsana district had been earlier reported for high Fluoride content in groundwater and also prevalence of Fluorosis in the region. But till date no such study on Kheralu taluka of Mehsana district has been carried out. Hence, the current study was undertaken to find out Fluoride concentration in the villages of Kheralu taluka

in pre and post monsoon seasons of the year 2012 and 2013 respectively, to characterize physicochemical properties of the collected Groundwater samples and to map Fluoride affected population that was based on the visual symptoms of different types of Fluorosis in the residents of villages under study. Thus, percent population affected in these areas has been evaluated. Also, the district is mainly known for growing many important agricultural crops, it was assumed that there might be chances of Fluoride entering into the food chain via consumption of grains. Thus this study also reports Fluoride concentration in agricultural soils and its bioaccumulation in selected crop plants viz. *Triticum aestivum* L. and *Pennisetum typhoides* L.

The main goal of the current research was to lower/reduce Fluoride concentration in the Groundwater by suitable untreated natural bioadsorbent. *Tamarindus indica* L. seeds has been chosen in the present study to reduce the level of Fluoride in groundwater samples. For this, in vitro optimization study using synthetic fluorinated water was done taking into consideration parameters like agitation speed, pH, temperature, initial fluoride concentration, particle size of the bioadsorbent and time of agitation. The optimised model of in vitro study was then applied to natural fluorinated Groundwater samples of the study area to know the efficiency of *T.indica* seeds towards removal of Fluoride in Groundwater samples.

The results of spatial mapping of Fluoride in Groundwater of the Taluka indicated that out of 51 villages and 1 town, Fluoride content in groundwater of 23 villages (44 % villages) in 2012 and 24 villages in (46% villages) in 2013 was found to be above permissible limit, i.e. 1.5 ppm. From the study it was investigated that 20 villages in study area villages viz: Arthi, Chotiya, Dabhoda, Dalisana, Delwada, Fatepura, Gajipur, Gathaman, Gorisana, Lalawad, Mahekubpura, Mahiyal, Malarpura, Malekhpur,

Mandropur, Nalu, Rahemanpura, Unad, Vaghvadi and Vithoda showed high fluoride concentration (>2 ppm) in both the years. Also, out of total 51 villages surveyed, 14 villages (27%) showed moderately high Fluoride concentration i.e. 2 ppm to 4ppm in both the years while 4 villages (8%) in the year 2012 and 5 villages (10%) in 2013 showed very high Fluoride concentration (> 4 ppm). The Optimal Fluoride intake in the residents of the study area was calculated with reference to temperature. From the calculated value we established that Fluoride intake of 0.5-0.7mg/l to be appropriate for the population of the area. In relation to this value, it was also envisaged that 80% population was exposed to high fluoride containing water. Based on this, we tried to generate a map to identify fluoride prone areas in the Taluka. It showed two lineages of affected area. One starts from north-eastern border (Base of Aravalli Mountain) to the southern border and the other covers the western part of an area.

The data of high Fluoride concentration in the Groundwater of selected villages were then linked with the percentage population affected due to various types of Fluorosis. For this primary data was collected through group interviews of the local people and secondary data was obtained from health centres. 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. Data obtained from health centres indicated that maximum cases of Fluorosis were reported in post winter season. In addition to this, males of villages under the jurisdiction of villages Dabhoda and Panchha PHC's were found to be affected more than females of same villages.

In the present research, efforts have been made to evaluate Fluoride content in soil samples of selected villages and its accumulation in major crops like *Triticum aestivum* L. and *Pennisetum typhoides* L. By this, Fluoride ingestion through food was calculated.

Soil analysis of selected field samples showed that mean total Fluoride content of surface soil 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 sample of Ambavada village while highest concentration was reported in Delwada (10.98 mg/g), village. Also, the samples of Vaghvadi and Mandropur (9.64 mg/g and 9.23 mg/g respectively) were found to contain high Fluoride concentration. These villages were also reported for the maximum population affected due to fluorosis in our study. To check bioaccumulation, Fluoride content in two crops namely *T. aestivum* L and *P. typhoides* L, grown over fields from selected 5 villages were carried out. 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 of Fluoride was estimated in grains collected from Gorisana village while highest concentration was reported from Delwada. The Bio-concentration factor for *T. aestivum* L. was found to range from 0.13 to 0.22. While the mean total fluoride content of *P. typhoides* L.ranged from 8.4 to 92 μg/g with a mean value of 18.53±24.54 μg/g. The lowest concentration of Fluoride in grains of *P. typhoides* L. was recorded in the samples from Gathaman village and 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. From the data obtained, estimated daily intake (EDI) for 3 age groups *i.e.* Children, Teenagers (male and female) and Adults (male and female) was calculated. For all the age groups, it was found that EDI after consuming grains of *T. aestivum* and *P. typhoides* were found to be above permissible limit i.e. 0.06 mg/kg/day.

Physicochemical analysis for pH, total dissolved solids (TDS), total alkalinity (bicarbonates and carbonates), total hardness (calcium and magnesium), sodium, potassium, chloride, Fluoride and sulphate of groundwater samples under study was carried out. The pH of all the samples was found to be alkaline. 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) were found to be above permissible limit. In the test samples, 16 villages in post-monsoon (2012) and 18 villages in pre-monsoon (2013) were reported to have TDS value above the permissible limit. 14 villages (post monsoon) and 11 villages (pre-monsoon) showed hardness above the desirable limit but below permissible limit. As per Sawyer and McCartly classification (1967), 95 % samples from the study area were found very hard and thus not suitable for drinking purpose. The sodium content of 15 samples (75%) were above the permissible limit in both pre-monsoon and post-monsoon season. Chloride and Sulphate contents of all the samples were found below permissible limit for drinking purpose. To find out Water Quality Index (WQI for drinking purpose) of the Ground water samples, Weight arithmetic index calculated using parameters like pH, total dissolved solids, total alkalinity (carbonate and bicarbonates), total hardness (calcium and magnesium), Fluoride, chloride, sulphate and sodium and potassium. The WQI value obtained proved that all the groundwater samples were under the category of unfit and thus unsafe for drinking purpose.

Thus, in the study area, the water resources are found not only unsafe for human consumption but also for irrigation and industrial wants. Therefore, the study focused attention on the long term impact of water resources and development taking into consideration all the associated problems. This can be achieved through Eco friendly technologies to reduce the level of Fluoride in the Groundwater samples of the study area. The best option was to defluorinate these samples using plant based adsorption technique. The plant selected as an adsorbent for the study was *Tamarindus indica L.* The seed powder (TISP) was used in the present study.

To optimize the experiment, a batch study for defluoridation was carried out for synthetic fluorinated water considering pH, temperature, agitation speed, particle size, initial fluoride, dosage, time and ionic interferences as important parameters for study. The optimization experiments showed following results.

The maximum adsorption capacity was achieved at shaker speed of 100 rpm (1.118 mg/g) and the highest percent removal of fluoride at this speed was found to be 51.28%. pH optimization study inferred that maximum removal efficiency of TISP i.e. 53.18% was obtained at pH 7. Temperature study suggests that low temperature favours the removal of fluoride ions by adsorption on *T. indica* seed powder. It also proves that the adsorption process is exothermic in nature. Time study revealed that maximum adsorption is achieved after continuous shaking for 150 minutes. Initial Fluoride and dosage goes hand in hand, increasing initial fluoride requires increased dosage. Best results for 5mg/l fluoride in 100ml were observed with 0.5mg of the adsorbate. The fluoride scavenging capacity of TISP was highly affected by ions in a decreasing order is as follow: Bicarbonate > Chloride > Sulphate > Nitrate > Phosphate. Overall the optimized model generated for 100 ml is 0.5g/l of 75-150 micron size adsorbent added in adsorbate and agitated at speed of 100 rpm for 150 min in neutral water and room temperature.

Isotherm study indicated that the Langmuir Isotherm, *i.e.* monolayer adsorption of adsorbent on adsorbate, is perfectly fit for a process in comparison to the Freundlich model. The value of R_L lies between 0 to 1 indicating adsorption to be favourable. The value of K_L (0.58 – 0.08 L/mg) and q_m and (1.51 to 0.50 mg/g) obtained from the slope as well as intercept decreased respectively with increasing temperature from 25 to 45 °C. From D-R model, it was proved that the mean free energy of adsorption (E) is less than 8 KJ/mol, the adsorption is physio-sorption. Kinetics study indicated that the reaction

follows pseudo first order kinetics. The diffusion kinetics studies reveal that 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 thermodynamics study showed that negative value of ΔH° represents the reaction to be exothermic in nature. The entropy ΔS° value is negative indicating that during the Fluoride adsorption process, the solid–solution interface approaches a more organized structure (decrease of randomness). The sorption process causes an increase in the order of the system. The negative value of ΔG° at lower temperature indicates the feasibility of the process and the spontaneous nature of adsorption especially at a lower temperature but as the temperature rises the Gibbs free energy decreases indicating the process to become non-spontaneous at higher temperature.

XRD and FTIR studies were conducted to understand the mechanism of adsorption on adsorbent i.e. TISP powder. The FTIR image showed depression in intensity from 4000 to 2000 between Θ positions of 10 to 30. As no new distinct peak was formed after adsorption of fluoride, it indicated that the adsorption process is physical in nature. XRD image showed a distinct peak at 848cm^{-1} showing possible C-F bond that might have favoured Fluoride adsorption.

In the current research, efforts were made to analyze and compare the adsorption abilities of biochemical contents along with the residual seed powder viz: carbohydrates, lipids and proteins separately using synthetic Fluoride solution as model adsorbate. The % defluoridation 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. The % defluoridation of residual powder without lipids, residual

powder without lipid and protein and residual powder without lipid and carbohydrate were 67.38%, 33.14% and 24.67% respectively while their adsorption capacities were found to be 0.76mg/g, 0.69 mg/g and 0.52 mg/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).

Defluoridation experiment on groundwaters samples using TISP of the test villages was carried out. 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 Fluoride scavenging capacity of TISP in groundwater samples was found to get decrease to more than half the efficiency with synthetic water. When the experiment was repeated, it was recorded that Fluoride concentration in 50% groundwater samples had come down to desirable limit of 1.5 ppm. The adsorbent is found to be beneficial in both the ways; the seed powder defluorinates the water and the gum from the adsorbent leaches out in water that can be helpful in the eradication of Fluoride from the body.

5.2. CONCLUSION

- Fluoride concentration in Groundwater of 51 villages of Kheralu taluka of Mehsana district was estimated in the year 2012 and 2013 in both; Pre and Post-monsoon seasons. In 2012, 23 villages and in 2013, 24 villages recorded Fluoride level above the permissible limit. The geological set up of the study area (north-eastern border to the southern border and the western part) comprises of granite and gneiss rocks has served as the main and natural source of Fluoride contamination in Groundwater of the area.

- The range of percent population affected due to ingestion of fluorinated water in the residents of the study area was about 24-26%. Also, the data procured from Public Health Centers depicted that male population in villages Dabhoda and Panchha were more affected than the Female population of the same villages.

- Soil Fluoride content in Delwada village was maximum (10.98 mg/g), followed by Vaghvadi (9.64 mg/g) and Mandropur (9.23 mg/g). A positive correlation was found between the soil Fluoride and Fluorosis affected population in these villages.

- *T. aestivum* L. grains accumulated Fluoride in the range of 17.3 to 46.18 µg/g. The samples of village Delwada showed maximum accumulation of Fluoride while the samples from Gorisana accumulated the least.

- In *P. typhoides* L. the estimated range of Fluoride accumulation was 8.4 to 92 µg/g; the sample from Malarpura being maximum and Gathaman the least.

- The calculated value of Estimated Daily Intake in the residents after consuming grains of *T. aestivum* and *P. typhoides* was found to be above permissible limit i.e. 0.06 mg/kg/day.

- The pH of all the samples was alkaline. TDS value of 16 villages in post-monsoon (2012) and 18 villages in pre-monsoon (2013) were above the permissible limit. 14 villages (post monsoon) and 11 villages (pre-monsoon) showed Hardness above the desirable limit but below permissible limit. The Sodium content of 15 samples (75%) were above the permissible limit in both pre-monsoon and post-monsoon season. Chloride and Sulphate contents of all the Groundwater samples were found below permissible limit for drinking purpose.

- The WQI value calculated to check its suitability for drinking purpose. The result proved that all the groundwater samples were under the category of unfit and thus unsafe for drinking purpose.

- The optimization experiment for defluoridation shows maximum of 55% removal of fluoride from synthetic water. The optimized model of TISP using synthetic water showed that maximum adsorption had occurred with 0.5mg/l dosage of TISP powder of particle size of 75-150µm agitated at 100 rpm with synthetic solution of 10mg/l of synthetic solution at neutral pH in room temperature.

- Isotherm of Langmuir (monolayer) was found to be fit for the adsorption process of fluoride on TISP in comparison to the Freundlich mode. Kinetics study proved the reaction followed pseudo first order kinetics.

- The surface and sorption characteristics of TISP were analysed using SEM and FTIR techniques. The presence of distinct peak at 848cm^{-1} in XRD image of

Fluoride treated TISP have suggested the possibility of C-F bond that had favoured Fluoride adsorption on TISP. The FTIR studies have proved that the process to be of physical nature.

- The Fluoride adsorption capacity of carbohydrate component of TISP was found to be maximum followed by protein and then lipids (carbohydrate > protein > lipids).

- TISP treated ground water samples of the villages of Kheralu taluka showed highest defluoridation capacity in Dabhoda ground water sample (24.48%) followed by Rehmanpura (24.29%) and Mandropur (24.28%) and least in Nalu (10.37%). The Fluoride scavenging capacity of TISP in groundwater samples reduced to half as compared to synthetic fluorinated water.