CHAPTER 5

SUMMARY

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In the natural environment, the distribution of Fluoride is very uneven which is largely because of the geochemical behavior of this element. Fluorine is conversely enriched in magmas and hydrothermal solutions. Due to this high concentration of Fluorine are found in alkaline volcanic, hydrothermal deposits and plutonic rocks.

Fluoride can occur in sedimentary formations that contain Fluoride-bearing minerals derived from the parent rock and fluorapatite. Dissolved Fluoride levels are usually controlled by the solubility of fluorite (CaF2); thus, high concentrations are often associated with soft, alkaline, and calcium-deficient waters. The health related problems due to ingestion of high Fluoride is persisting in Third World countries. A number of adverse effects of Fluoride in excess on human health includes dental fluorosis, skeletal fluorosis, increased rates of bone fractures, decreased birth rates and increased rates of urolithiasis.

Global water quality and Fluoride-related issues have drawn overall awareness to the problems associated with Fluoride in drinking water. In India, fluorosis has become a serious national problem. The seriously affected areas are villages of Punjab, Haryana, Rajasthan, Andhra Pradesh, Tamil Nadu and Gujarat. As reported by various researchers, North Gujarat and Saurashtra are the two main regions where The Fluoride content in groundwater has increased to as high as 25-35 mg/litre., especially in the summers in North Gujarat, and in parts of Saurashtra and has continued for the last two decades. This causes serious health hazards to the residents of the area. Gradually, awareness of the hazards posed by Fluoride has built and is growing among common people residing in the area. Municipalities in towns like Patan and Sidhpur (North gujarat) have explored a variety of alternatives to provide safe drinking water to their citizenry. However, none of these has proved sustainable.

The government policies for rural drinking water through Swajaldhara and other programs have been mainly focused on ensuring supply of drinking water and the institutional mechanisms needed to sustain the system. However, not much emphasis has been paid towards water quality problems due to biological and chemical contaminations occurring in the Groundwaters of the area.

Keeping the general health point of view, this study was designed to review concentration of Fluoride in groundwater in some districts of North Gujarat and Saurashtra in the year 2009-12., mapping Fluoride in villages of Mehsana, Amreli and Rajkot districts, to select the best suitable plant based Fluoride adsorbent, to optimise these adsorbents with respect to time, dose and initial Fluoride concentration in-vitro and to compare Freundlich and Langmuir isotherm for MBP (*M. oleifera* bark powder) and MSP (*M. oleifera* seed powder) which are selected for the present study as bioadsorbents of Fluoride. The study also involved estimation of various physico-chemical properties of Groundwater of Satlasana, Lilia and Wankaner taluka during pre and post monsoon season of the year 2009-12 and to establish relationship between Fluoride and other water quality parameters. From this, Piper-Hill diagram are plotted which are used to infer hydro-geochemical facies. Thus this research also made use of tri-linear diagrams so as to bring out chemical relationships among groundwater samples in more definite terms. It is always desirable to have a comparative account on in-vivo and in-vitro efficiency of plant based bioadsorbent used for Fluoride removal. Thus the current study also incorporates to evaluate capacity of MBP and MSP to reduce the level of Fluoride in Groundwater of the villages under study. As Fluoride is known to affect general metabolism in plants, various biochemical properties were studied in plants exposed to Fluoride concentration. For this, as Wheat (*Triticum aestivum* L) and Bajra (*Pennisetum glaucum* R.Br.) are main crops of the study area, in-vitro pot experiments were carried out and Pigment, Carbohydrate, Protein and Proline contents were measured in Fluoride treated and control plants. Also, in the treated plants, amount of Fluoride accumulated in grain samples (seeds) of the test plants was estimated. SEM-EDX analysis on grains/seeds treated with 5 mg/l Fluoride was also undertaken to observe alterations/abnormalities that might have occurred on Flouride exposure. The results and their related causes are summarized as under:

The data obtained from GWSSB, revealed that Amreli and Rajkot ,(Saurashtra) and Mehsana,(North Gujarat) recorded Fluoride level much beyond the permissible limit i.e. 1.5 mg/l. The reason behind this is that, the geological set up of North Gujarat region mainly comprises of country rock as charnokites, calc-granites and calc-gneiss formation. On weathering, the fluorine tends to be released preferentially from these

minerals and enrich Fluoride in the groundwaters. In Saurashtra, presence of Basaltic rock, sandstone, Deccan trap lava, supra trappeans, Gaj beds, and Miliolite limestone serve as natural source of contamination of Groundwater Fluoride. Thus, Fluoride contamination in Groundwater in these areas are mainly due to their Hydrogeology.

As Mehsana, Amreli and Rajkot districts, the goundwater shows elevated Fluoride level, Sampling to measure only Fluoride content was carried out in 30 villages of the districts. The results revealed that villages; Nana Kothasana (4.6 ppm), Gundaran (3.0ppm), and Samadhiyala (3.37 ppm) showed very high concentration of Fluoride in groundwater and was found beyond permissible limit prescribed by BIS.

In order to find out best plant based bioadsorbent for reducing the level of Fluoride, different plant materials were screened for their removal efficiency**.** For *Moringa oleifera* - Bark, *Moringa oleifera* – Seed, *Cocos nucifera* - Shell, *Cocos nucifera* - Mature Fruit Fiber and *Oryza sativa* – Husk were used. The order of removal capacity of Fluoride was *M. oleifera* – Bark (16%) > *M. oleifera* – Seed (13.33 %) > *C. nucifera* - Shell (3.33 %) > *O. sativa* – Husk (2.67%) > *C. nucifera* fruit fiber (2.0%). Bark and seeds of *M. oleifera* exhibited maximum Fluoride removal capacity. Though, bioactive component present in Bark and seeds of *M. oleifera* was not investigated in the present study. Bark and seeds of *M. oleifera* help to reduce Fluoride level. Thus, experiment were carried out on *M. oleifera* bark powder (MBP) and Seed powder (MSP) in-vitro. In-vitro optimisation study was done to check Fluoride removal capacity MBP and MSP. In-vitro Fluoride removal efficiency of MBP was 92.75% within 8 hours of contact time at 5 g/l dose with initial concentration of 1 ppm as measured in optimized study whereas for MSP, it was 32.5% within 4 hours of contact time at 5 g/l dose and 1 ppm initial concentration of Fluoride. Though the adsorption data obtained on optimisation study, was found suitable for Freundlich and Langmuir isotherm, it fits Freundlich better than Langmuir isotherm.

To check the Groundwater quality of the study area (Satlasana, Lilia and Wankaner) various physicochemical parameters were estimated in pre as well as in post monsoon seasons and the data was compared with the prescribed limit of BIS. In Satlasana, values of pH and Fluoride were reported beyond permissible limit; In Lilia, pH,

Fluoride, Sodium, Sulphate and TDS were beyond the limit and in Wankaner; pH, Fluoride, TDS, Sodium and Calcium were found beyond limit. Correlation analysis was also performed between Fluoride and other physico-chemical parameters. These were pH, Total alkalinity, TDS, Calcium, Magnesium, Carbonate, Bicarbonate, Sulphate and Sodium as they are responsible for increase or decrease Fluoride concentration in a particular water sample. In Satlasana taluka of Mehsana district, pre and post monsoon correlation analysis showed that Fluoride concentration in groundwater was positively correlated with pH, Total alkalinity, TDS, Carbonate, Bicarbonate and Sodium and negatively correlated with Calcium and Magnesium. The Correlation analysis in pre monsoon of Lilia taluka of Amreli district, Fluoride showed positive correlation with TDS, Carbonate, Sodium, Calcium and Magnesium while negative correlation with pH, Total alkalinity and Bicarbonate. In post monsoon, Fluoride was positively correlated with all the parameters except pH. In Wankaner taluka of Rajkot district, Fluoride showed positive correlation with pH, Total alkalinity, TDS, Carbonate, Bicarbonate and Sodium in pre monsoon season while negatively correlated with Calcium and Magnesium. For post monsoon season, Fluoride showed positive correlation with all parameters except Calcium, Magnesium and Sodium.

Piper diagram plotted for Satlasana taluka revealed that the groundwater of this area is of Magnesium Bicarbonate type in both the seasons-pre and post. In Liliya, in pre-monsoon season groundwater is of both the types; Sodium Chloride and Sodium Bicarbonate type and in post monsoon season it is only of Bicarbonate type. In Wankaner, the Groundwater is of Sodium Bicarbonate and mixed type in both the seasons while is of Sodium Chloride type in post monsoon. Generally, High fluoride occurrence in groundwater is expected from sodium bicarbonate-type water. Because of this, these area suffers from high Fluoride contamination and other related problems.

Experiments on defluridation by MBP and MSP suggested that the defluoridation capacity of MBP and MSP in in-vivo was much lower than in in-vitro condition.

Triticum aestivum L. and *Pennisetum glaucum* R.Br. were selected to investigate the effect of Fluoride concentration on pigment, carbohydrate, protein and proline

contents of the plants (Treated plants) and the data was compared with the control plants. The concentration of Fluoride used for the experiments were 1, 2, 3, 4 and 5 mg/l. No marked increase or decrease in the pigment contents of the treated test plants was noticed when compared with the content in control plants indicated that Fluoride have not posed any inhibitory effect on the pigment content of the plant. Both the plants under study showed no inhibition towards carbohydrate and protein synthesis indicating that Fluoride exposure might have not affected the general metabolism of the test plants. The proline level was highly fluctuated both in Treated as well as in control test plants. This indicated that plants under Fluoride exposure were not under stress. The results on effect of Fluoride ion on biochemical components of the plants relates to amount of Fluoride accumulation in the grains of the test plants; both, treated and control. We found very less accumulation of Fluoride in the grains of both the test plants and therefore it might be not sufficient enough to exert any negative impacts on these properties of the test plant.

The test plants grown in pots were allowed to reach mature stage so as to obtain fruiting and thereafter Grains (seeds) of both the test plants were collected and analysed for estimating concentration of Fluoride. The estimated value of Fluoride in grains of *Triticum aestivum* L. was 0.076, 0.092, 0.128, 0.161 and 0.19 mg/g with the initial Fluoride concentration of 1,2,3,4 and 5mg/l respectively whereas in *Pennisetum glaucum* R.Br it was 0.069, 0.089, 0.114, 0.156 and 0.194 mg/g. Results showed that gradual rise in the Fluoride concentration increased Fluoride accumulation in the grains of both the test plants. There was negligible difference in the accumulation. However as compared to reports on Fluoride accumulation by various researchers, we got very less accumulation in the grains of both the test plants.

SEM micrographs of treated (5 mg/l Fluoride concentration) grains of *Triticum aestivum* L. and *Pennisetum glaucum* R.Br. did not exhibit any alterations or abnormal features. The quantitative analysis using EDX on grains of Fluoride treated *Triticum aestivum* L. plant showed 0.16 % Fluoride ion and in *Pennisetum glaucum* R.Br. treated seeds Fluoride ion concentration was 0.03%, the presence of which was

confirmed by a very small peak. The control grains of both the plants showed absence of Fluoride ion concentration as well as peak. These results clearly stated that because the grains of the test plant had shown little accumulation of Fluoride, no abnormal features were noticed while observing them SEM images.

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