Defluoridation of drinking water from Public water supply system using Natural materials and Nano hydroxyapatites

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Abstract

Field samples were collected with the fluoride containing water sample from the study area (fluoride endemic area) in order to test the suitability of nano and natural material as a defluoridating agent at field condition. The De-F of water has been carried out in the region where several villages entirely depended on ground water enriched in Fluoride (> 3 mg l^{-1} to 8 mg l^{-1}) for their drinking water needs. Defluoridation of groundwater has been attempted using natural materials like serpentine mineral, brick powder, flyash etc., as an adsorbent and studied in batch process, besides adsorption Fluoride using the nano materials. The hydroxy apatite used for the reduction of fluoride ion. Apatite a calcium phosphate material (Ca_{10} $(PO_4)_6$ $(OH)_2$) prepared in lab using different methods. High concentration of fluoride and its effective reduction observed in Hydroxy Apatites prepared using hydrothermal + microwave and hydrothermal method. But in general, the rate of adsorption is found to be higher in the hydrothermal+ microwave samples followed by microwave ones. Few natural materials like locally available soil material were also used and it was found that the red soil was effective in fluoride removal. Different parameters of adsorption, viz. effect of pH, effect of dose and contact time were selected and optimized for the study. Feasible optimum conditions were applied to groundwater samples collected from region of high fluoride concentration to study the suitability of adsorbent in field conditions. Fluoride removal was found to be high for groundwater samples with high fluoride content under the optimized conditions.

Keywords: Fluoride removal, Natural material, Hydroxy Apatite, Natural materials.

Introduction

Fluoride is beneficial, when present in concentration of 0.8-1.0mg/l. The interest of fluoride content in public water supply lies in its ability to prevent dental caries. Absorbed fluoride is distributed rapidly throughout the body and is retained mainly in the skeleton with a small portion in the teeth. Removal of excess fluoride from the natural water supply is still a challenging task. Fluoride removal was done by passing through columns, as earlier studies on stirring methods had confirmed that an increase in stirring rate increase the fluoride for a given temperature.(Killader and Bhargava, 1993). In general aluminum compounds are found to be good fluoride removers because of reaction between Al and F molecules, several fluoride removal methods were carried out using the aluminum based compounds (Bulusu and Nawlakhe, 1992). Strong base anions exchange resins fluorides either on hydroxyl cycle or chloride cycle along with other anions. Both fluoride and phosphate are adsorbed by variable charge surfaces such as iron and aluminum oxides. (McKee and Johnson, 1934) investigated powdered activated carbon for fluoride removal and showed that good results are obtained only at pH 3 or less. Activated carbons prepared by other workers from cotton waste, coffee waste and coconut were tried for defluoridation but all these materials proved to be of academic interest only. He has listed about 20 readily available materials of defluoridation by using magnesium, calcium phosphate and aluminum oxide were reported effective media among the substance reported to have been examined (viz) calcium carbonate lime ($CaCO_3$) heated to 950°C (Viswanathan, et al. 1974). Few studies have been attempted on the possibility of using clay vessels for water defluoridation (Agarwal et al 2003).Such vessels, usually made up of clay-dominated soil, are quite common in rural India and are used for storing water, especially during summers. On account of their porous nature, the clay vessels facilitate water evaporation and thereby act as effective water coolants. Such vessels, having a high F sorption ability, are also expected to effectively defluoridate the stored water. In addition, reports of Street el (1983) and Elrashidi et al (1986) indicate the results on F(NaF) sorption by the soil of Agra (India) and its two fractions. Silty clay (C) fraction exhibiting maximum F sorption was further amended chemically to enhance its potential for water defluoridation—a method when extrapolated to fabrication of vessels would have enhanced potential of utilizing vast naturally occurring adsorbent (i.e. C) for defluoridation of water. Yadav et al (2006) proved that Adsorption of fluoride on Brick powder (BP) from aqueous solution was found to be first order reaction and mechanism of fluoride removal on adsorbent

was found to be complex. The surface adsorption as well as intra-particle diffusion contributes to the rate-determining step. Deflouridation capacity of BP can be explained on the basis of the chemical interaction of fluoride with the metal oxides under suitable pH conditions. The optimum pH was found to be in range of 6.0–8.0 for maximum adsorption of fluoride, which makes it very suitable for use in drinking water treatment, especially in rural areas. The fluoride removal capacity of the medium is 600 mg of fluoride per litre and regenerated with 1.5% sodium hydroxide solution. (Babovich, 1840, 1957). Ion exchanges of F^- for OH^- have also been reported by (Chidambaram, et al. 2003). Hence $(OH)^-$ dominant hydroxyl apatite was selected for defluoridation studies. These hydroxy apatites were prepared by different methods and their variations in the fluoride removal capacities were studied. Fluoride removing capacity of hydroxy apatite was reported to vary widely apparently in this gravity method. Keeping all these factors in mind red soil of silt size fraction mixed with sand which are locally available was used for the present study as the chief fluoride removal agent in the Fluoride Removal Tank (FRT).
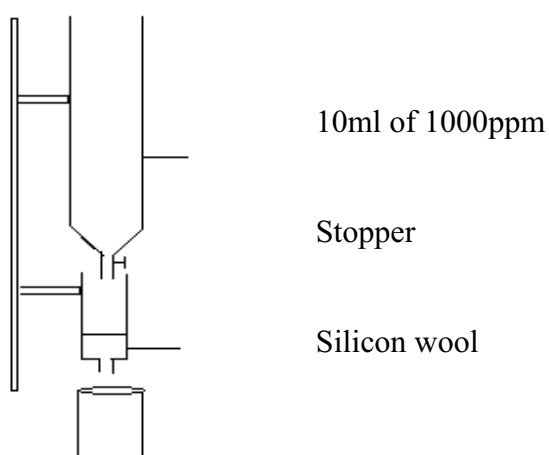

Fig. 1 Experimental setup for fluoride removal study

An accurately measured 0.200 mg of hydroxy apatite was taken in 100ml syringe filled with small amount of silicon wool. Then 10ppm of fluoride solution was allowed to pass through the syringe. The samples were collected in three intervals (sec) and analysed for fluoride fig.1
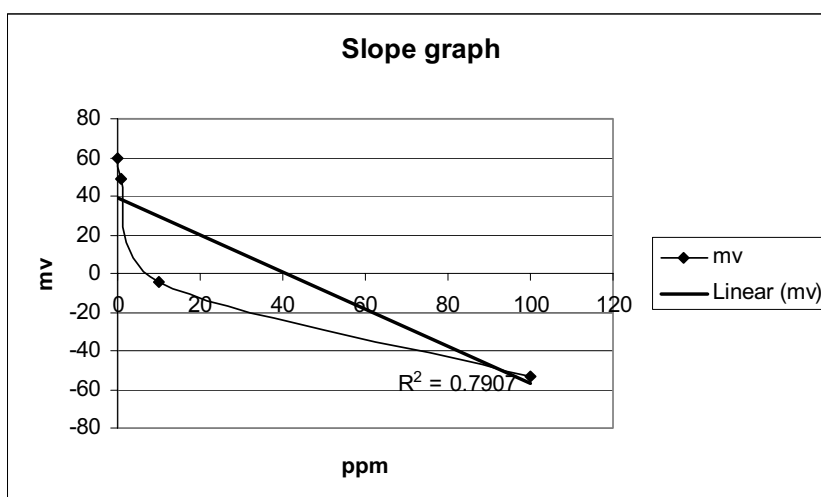
Fig.2 Fluoride analysis methodology

Equal amounts of Fluoride ISA solutions were added to the samples and the standard. Analysis was made by using Eutech electrode and the slope was checked with standards 0.1ppm, 1ppm, 10 ppm, and 100ppm. The slope gave a regression value of 0.79 (Fig. 2). This analysis was carried out for the samples, the values were now then cross checked with the standards. Each value of different types of hydroxy apatite were plotted in the graph.

The apatites used for defluoridation are prepared by the following methods;
1. Solution method
2. Hydro thermal method
3. Gel method
4. Microwave method
5. Hydrothermal + Microwave method

Results

The present work concerns defluoridation of laboratory samples of aqueous the fluoride solutions of 10 ppm and different methods of hydroxyl apatite. Previously a study undergone through defluoridation by stibnite, natrolite and apophylite has been investigated for laboratory samples of aqueous fluoride solution, which results Ca-type Zeolite more effective than Na-type Zeolite for fluoride removal. (Marimuthu and Sivasamy, 1994). Fluoride removal through hydroxyl apatite by gravity method was increased in the initial stage by the force and then it decrease at the end. A process that can be lead to very high

concentration of fluoride in waters (values up to c30mg/l and which is little understood is anion exchange ((OH)⁻for F⁻) involving various types of clay minerals. (Apambire, et al. 1997) The process invariably follows Base Exchange softening (Ca and Mg for Na) where the pH is progressively driven to quite high alkaline values (pH 9.0-10.5). Anion exchange can occur in sedimentary basins (Boyle 1992; Boyle and Chagnon, 1995) or igneous terrains, but is most dominant in the former environment. Apatite, micas and amphiboles have much lower solublites than fluorite; the dissolution of fluoride from these mineral is most pronounced in at low pH values.

Defluoridation was carried out by different methods and the results of these are discussed below

1. Solution method

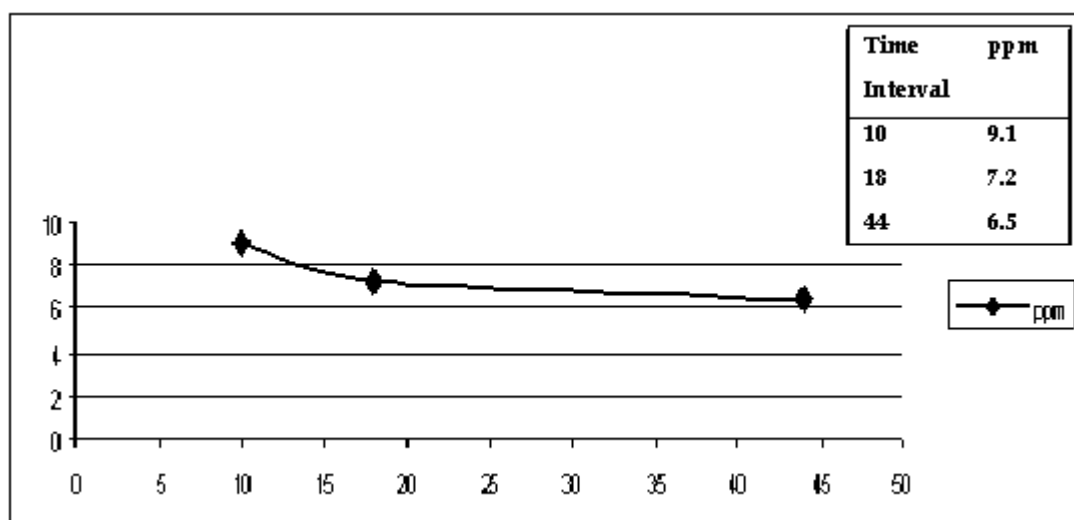| Time Interval	ppm
10	9.1
18	7.2
44	6.5

Fig.3 Fluoride adsorption level in different time interval
(Solution method)

In this method, the fluoride absorbing rates is higher at the initial stage and gets decreased at the end. So, the concentration has decreased in this method. This might be due to the saturation of the fluoride exchange sites in the material. More over it is noted that the rate of flow through this medium becomes lesser with time (Fig.3). It may be because of swelling of the material and filling up of the available pore spaces with time or decrease of hydrostatic pressure.
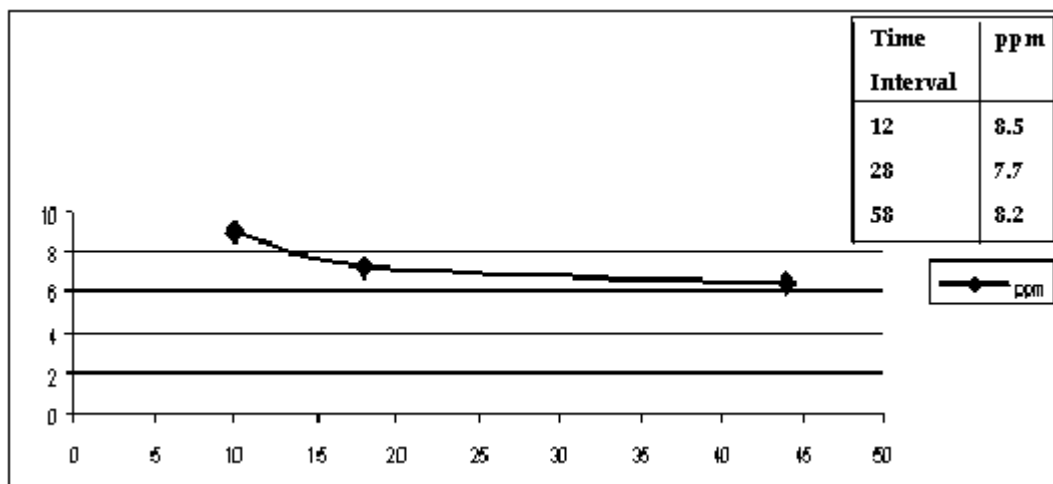
2. Hydrothermal method

Fig.4 Fluoride adsorption level in different time interval
(Hydrothermal method)

In this method, the effective fluoride removal is lesser than the previous method and the rate of adsorption is lesser. It is very interesting to note that the concentration of fluoride increases at the third interval(Fig.4). This may be due to the saturation of the ion exchange sites, hence the fluoride removal capacity becomes lesser and gradually the concentration of the fluoride in the sample gets increased.
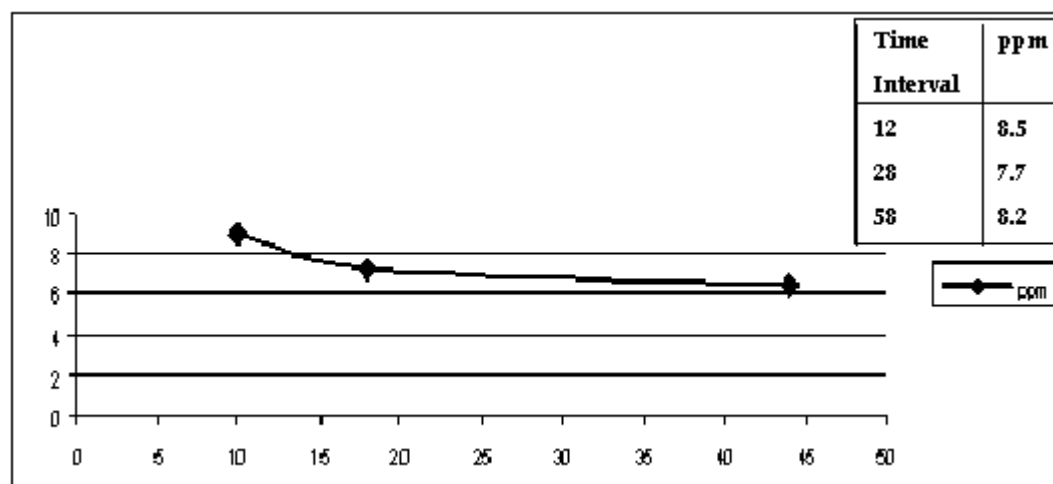
3. Gel method

Fig.5 Fluoride adsorption level in different time interval
(n-Hap by Gel method)

The removal of fluoride by this method is almost similar to that of the solution method (Fig.5). But the rate of flow is slightly higher, hence the rate of adsorption of fluoride is also

lesser. But the rate of decrease of fluoride is higher at the first interval and very low at the third interval.

4. Microwave method

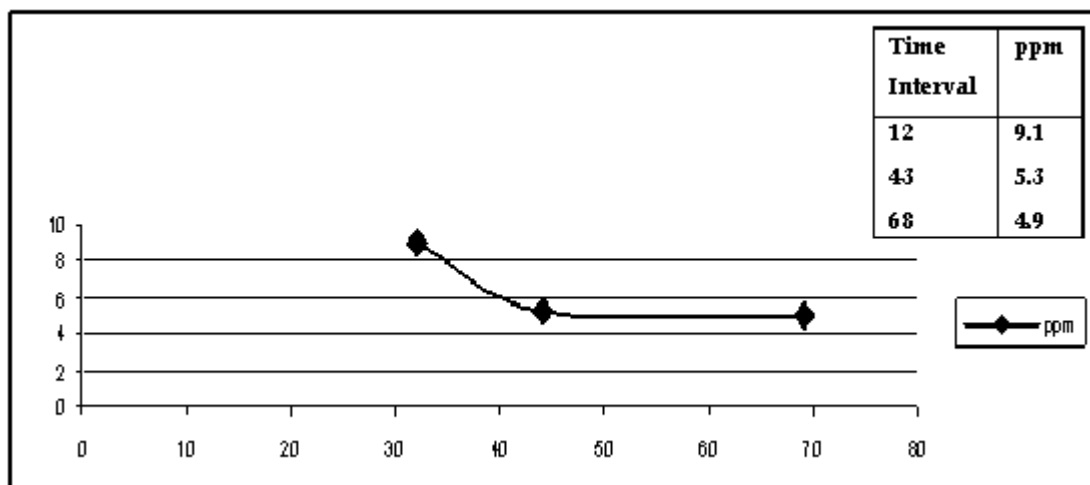| Time Interval	ppm
12	9.1
43	5.3
68	4.9

Fig.6   Fluoride adsorption level in different time interval
(n-Hap by microwave method)

The rate of flow of samples through this medium was slow and the rate of removal at the first interval is lesser (Fig.6). But subsequently the rate of removal has increased with time and it shows effective removal of fluoride even at the second and third intervals.

5. Microwave + Hydrothermal method

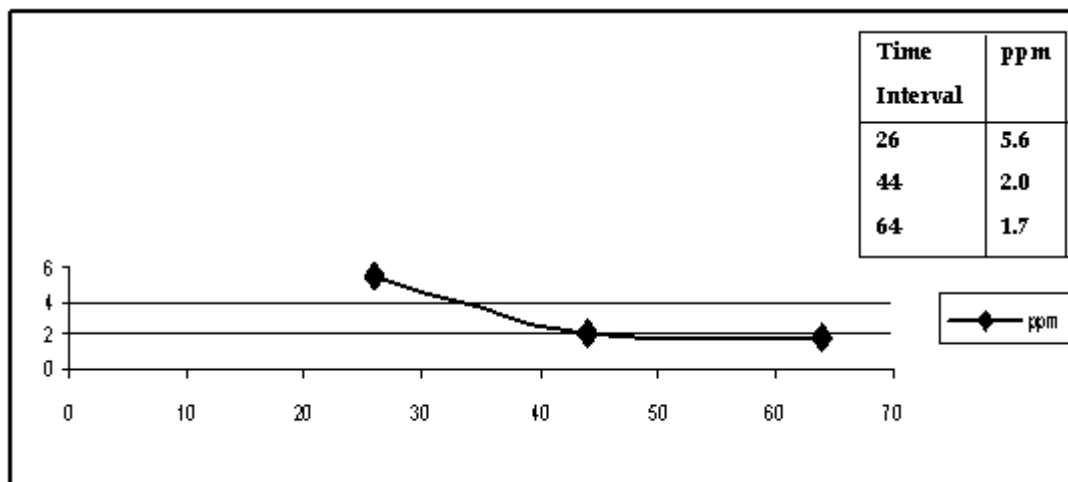| Time Interval	ppm
26	5.6
44	2.0
64	1.7

Fig.7 Fluoride adsorption in different time interval
(n-Hap by Microwave + Hydrothermal method)

The rate of flow through the medium is slow and the samples collected at the first interval and at the third interval shows high rate of fluoride adsorption due to the lesser saturation of the exchange sites (Fig.7).

Natural materials

Every solids material is a potential adsorbent. it is also reasonable to utilize the occurring fluoride-seeking minerals since the mineral can provide a number of fluoride-seeking cation such as Ca (II), Mg (II), Al (II), etc. besides these cations, exchangeable anions such as OH are present in many minerals and the proxy of F for OH would serve as one of the principal contributing factors for defluoridation due to the similar charge and size of defluoride concentration in the natural freshwater and were found to be effective.

Untreated charcoal seems (Table.1) to have no effect on the concentrations of fluoride with time and it adsorbs 0.5 mgl^{-1} of fluoride. The brick and fly-ash show typically a sudden removal of fluoride from 10 mgl^{-1} to 5 mgl^{-1}. 50% reduction of concentration takes place within 30 min. Red soil absorbs 9 mg l^{-1} of fluoride immediately after 15 min. After 30 min the fluoride decreases from 1.0 to 0.1mg l^{-1}and keeps on reducing with time up to 0.02 mg l^{-1} in 90 to 120 min. In serpentine the fluoride removal is maximal 0 to 15 min, i.e.3.7 mg l^{-1} later the defluoridation capacity increases to 5.8 mg -190 to 120 min gradually. But the defluoridation Capacity is less when compared to red soil.

Time	Red soil	Charcoal	Fly-ash	Brick	Serpentine
15	0.64	9.05	3.4	4.7	3.7
30	0.09	9.05	3.7	4	4.1
60	0.06	9.1	4.7	3.7	4.6
90	0.035	9.05	6	4	4.8
120	0.029	9	7.1	3.9	5.8

Table.1 Fluoride in time intervals

The study reveals that of the five materials used for defluoridation red soil has a good defluoridation capacity followed by brick, serpentine, fly-ash and charcoal. Near equilibrium is attained after about 30 min of the experiment. Maximum defluoridation occurs immediately after the experiment has started. The morality of fluoride removed per gram is more in red soil when compared to the other materials Red lateritic soil has the highest fluoride removal capacity because it has oxide of aluminium and iron as its major components. Both are good removers of fluoride but the red soil is found to be very effective. The column study reveals that use of the amount of materials according to fluoride removal

capacity seems to be very effective. This study lacked detailed monitoring of data over a periodic time interval of 1 min, where sequential changes can occur rapidly; further, the soils are not studied in detail for textural character and are not penetrated.

The observation reveals that after a period 30min removal of fluoride is reduced. Perhaps due to saturation of the anion-exchange sites and hence the concentration of fluoride shoots up. This is also evident in the increase of the HCO_3 content in water, which increases along with pH (Kulkarani et al 1974).The removal of fluoride ion with pH variation was found to be very effective by various workers (Bulusu and Nawlakhe,1992) at lower ranges. As a decrease of fluoride of pH probably results in the reduction of negative charges which are more at the surface of the material adsorption is enhanced. It is interesting to note that red soil has the highest capacity to remove fluoride. The main factors here are, the dominance of very fine clays, organic matter and rich in iron aluminum oxide in composition and has good anion exchange capacity. In general aluminum compounds are found to be good fluoride removers because of reaction between Al and F molecules.

Earlier experiments were tried with following options : 1) red soil + sand mixture, 2) pebbles and red soil + sand mixture , 3) Pebbles + Red soil + Sand mixture and Charcoal, 4)Pebbles + Red soil + Sand mixture + Charcoal and Brick powder. These are experimented to avoid clogging, prevention of color in the treated water, prevention of movement of red soil materials from the FRT along the supply line and to optimize the flow in the FRT. Among all these mixture the fourth sequence was found to be fruitful. The defluoridation tank erected was 6' height and 1.5' diameter rubber coated and the sequence of the material filled in is given in the fig.9.The water flows against gravity first flows through pebbles, followed by charcoal, then through red soil then by brick and then goes to the supply. The size fraction arrangements are in such a way that the charcoal and brick powder are sand sized and red soil was silty sand. The red soil was comparatively finer than the other two fractions which increase the retention time to the water passing through the medium. It is also observed that after the introduction of the FRT, of water supply along the normal distribution pipe line reduces the pressure, hence the consumers at the far end of the water supply line receives a lesser quantity of water and a few places dependent people at the end of the are even devoid of water supply .
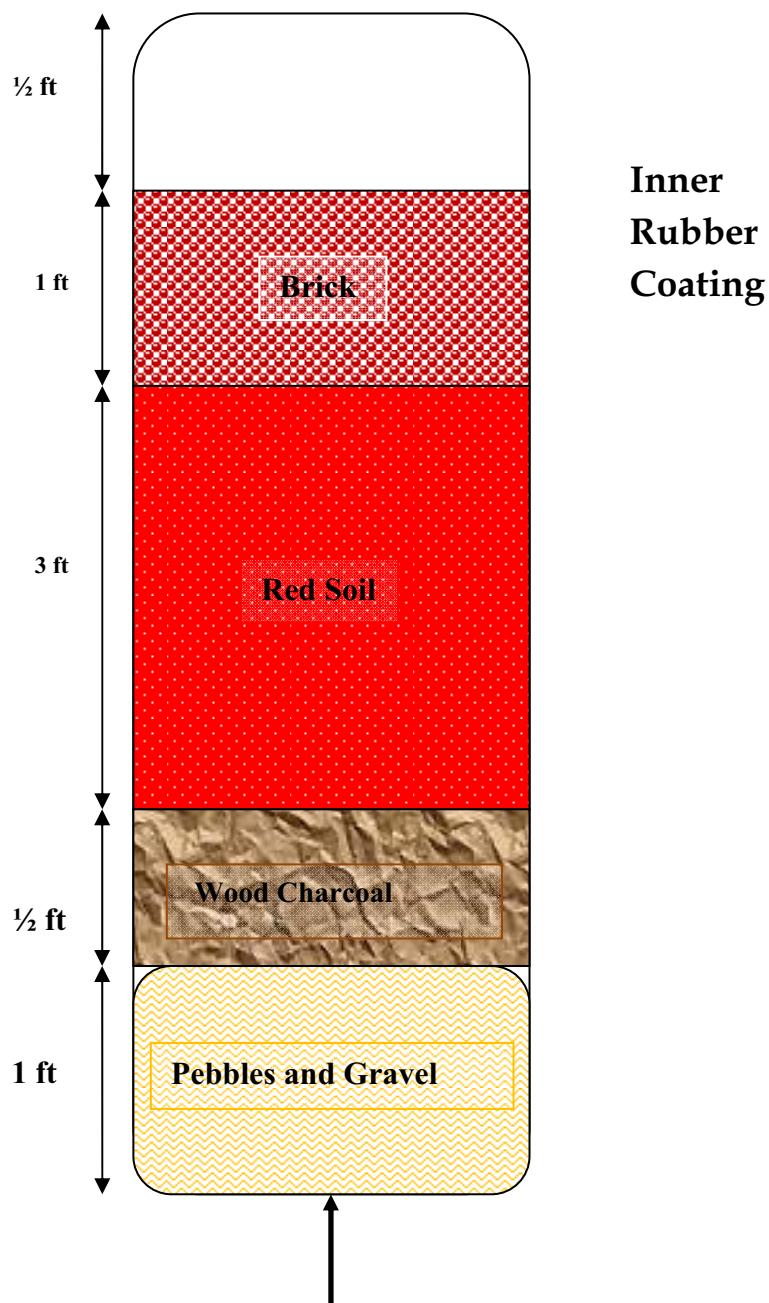
Fig.9 Model of FRT erected

Variation of fluoride removal with time was studied after the erection of the column /unit, the defluoridation setup was then connected to the public water supply from the overhead tank of 50,000L capacity and it was allowed to flow through the defluoridation column (Fig .9). The flow through the column was observed for 24hrs after the erection in 2hours time interval. The water was continuously pumped to the OHT (by normal process) and it is passed though the defluoridation column erected. The continuous observation shows that the initial concentration of 4.5 mg/l was reduced to 2.5 mg/l in the first sample collected

later there was a decrease in the fluoride concentration around 0.5mg/l after 14hrs of erection (Fig.10). Later it was almost stable around 0.68 mg/l.
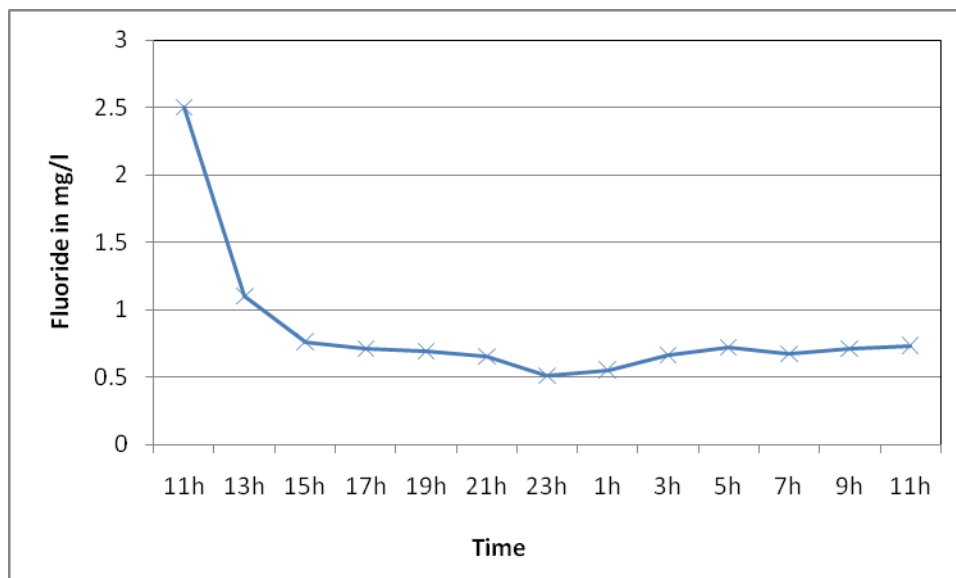

Fig.10 Rate of fluoride removal in 24 hours monitoring immediately after the erection of FRT

Water supply to the dependent local village community was provided for four hours approximately two hours in the morning and two in the evening. The material capacity was observed from 3rd day 7th day 10th and 15th day (Fig.11). Later new material was refilled and further similar observations were made, four similar refilling and similar time interval observations were made. An average of the time period observations are shows that during morning the water supply was from 6.00 am to 8.00 am.
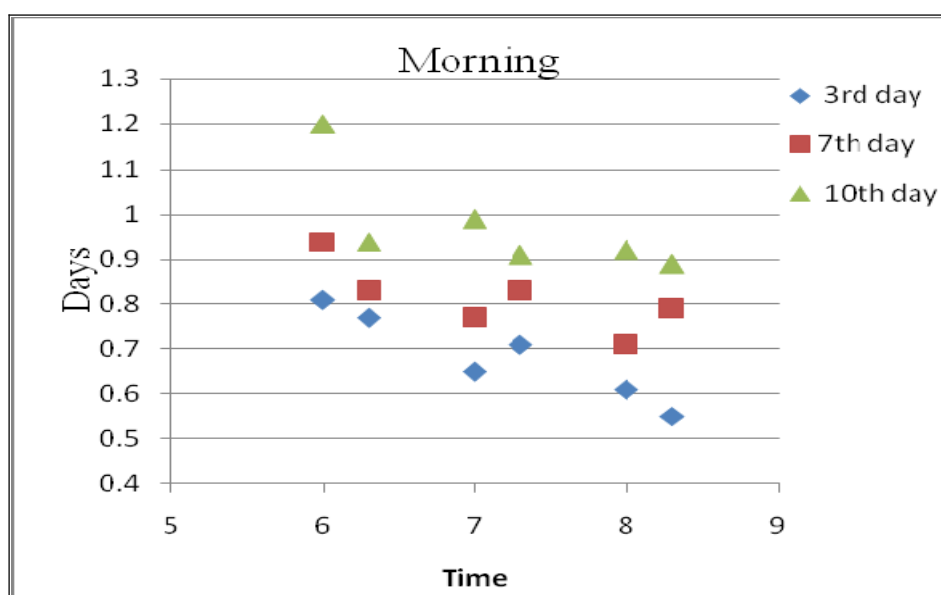

Fig.11 Four times average of fluoride removal from FRT (Morning)

Half an hour interval observation shows that there is a decrease in fluoride concentration with time. It is also due to the variation in water level in the OHT; at initial time period the water level in the tank is more and the rate of flow is more which results in lesser contact time and the removal is lesser. But as the time passes the water level in the tank reduces and contact time increases which results in further removal of the fluoride ions in water.
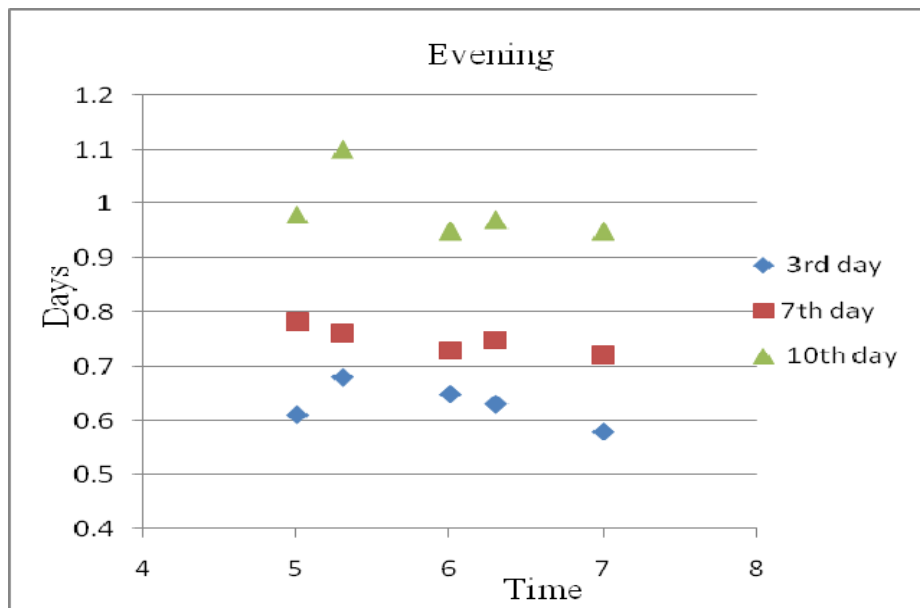

Fig.12 Four times average of fluoride removal from FRT (Evening)

It is also observed that the efficiency of the fluoride removal decrease with days and at the 10th day it's almost near the permissible limit, (Fig.12) so it is refilled again. It is interesting to note that the trend of the fluoride removal remains the same. Similar trend was also noted in the evening 2 hrs of delivery. It is also to be noted that the F removal capacity may also vary with the variation in the groundwater pH. Though the source of groundwater may remain the same it may vary with time.

Characterization of Red soil used in the FRT

The red soil was characterized by powder X-ray diffraction (PXRD) using Shimadzu 600 X-Ray Diffractometer. The PXRD patterns were collected in continuous scan mode with monochromatic CuKa (l=1.5418 Å) radiation that was selected using a curved germanium (111) monochromator. X-rays which were produced at the X-ray source (copper radiation)

were reflected at the germanium monochromator (111 planes) giving pure Cu Ka radiation which was diffracted by the sample. The data were collected in the range from 10.0 to 80.0^o (2θ) by a linear PSD which was set at a step size of 0.5^o (2θ) and counting time of 60s per step. Compound identification was made using a search-match computer program supported by the Joint Committee on Powder Diffraction Standards database JCPDS (1997) together with diffraction profiles obtained from standards of red soils and clay minerals as reported in literature (Mineral database, 2002).

The mineralogical characteristics of the lateritic soil used in this study are shown by the PXRD patterns in (Fig.13). The raw phase profiles qualitatively indicate presence of gibbsite (Al(OH)$_3$) as shown by intense reflection at 2θ angle of 17.93° (d= 4.94 Å), and double at 2θ angle of 20.51° probably combining the literature reflections at d= 4.34 Å and 4.30 Å of a crystalline gibbsite. Intense kaolinite (Al$_2$Si$_2$O$_5$(OH)$_4$) reflections are also shown at 2θ angles of 11.58° and 24.80°.
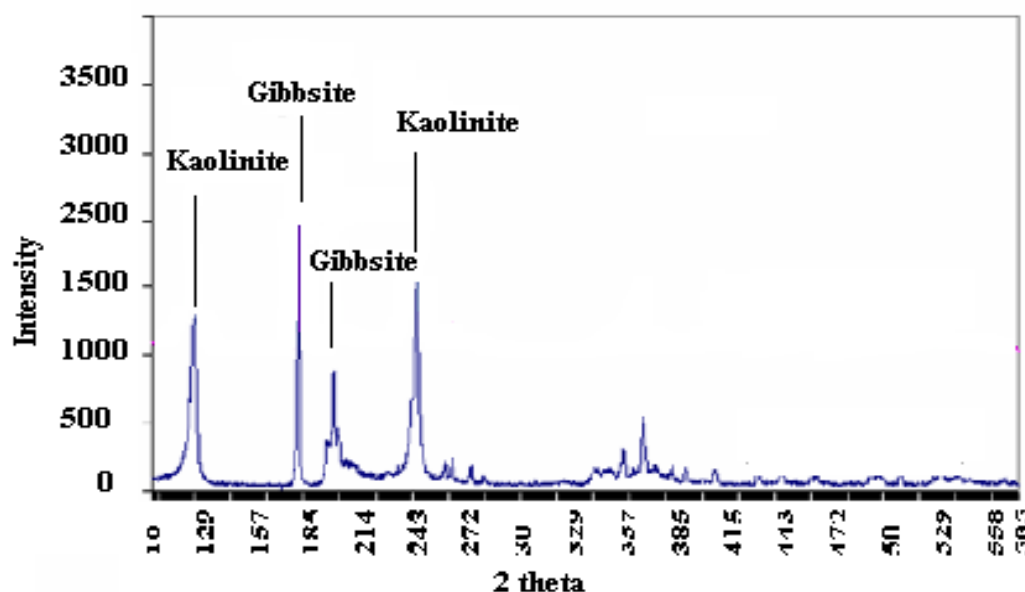

Fig.13 PXRD profile of the red soil used for Defluoridation in the study Gibbsite and Kaolinite reflection are indicated within the profile.

The removal of fluoride in this lateritic soil is not only due to gibbsite but also due to kaolinite. The kaolinite structure includes highly accessible hydroxyl groups positioned on the gibbsite layers which allow for anion exchange (Kau et al., 1997).

	Initial fluoride Conc.(Mg/L)	Equil.Fluoride Conc.(Mg/L)	Fluoride removed (Mg/L)	Defluoridation capacities (%)
Red soil	8.00	0.52	7.6	95

Table.2 Fluoride concentration and defluoridation capacities of red soil at 2.5g/200ml solution of 8 Mg/L F⁻

Ions	PO_4^{3-}	SO_4^{2-}	CO_3^{2-}	NO_3^-	Cl^-	Ca^{2+}	K^+	Na^+
Correlation	-0.29	-0.61	+0.91	-0.05	+0.75	-0.91	-0.15	-0.11

Table.3 Correlation coefficients between increase in concentration and decrease in fluoride concentration in defluoridation with bauxite.

Reaction was assumed to be a direct indication of the reaction progressing with the concentration change of Al^{3+} in both gibbsite and kaolinite, which was difficult to monitor (due to lack of quantitative characterization of this heterogeneous material).It was also assumed that the bauxite concentration was significantly larger than that of fluoride. The observed kinetics can thus be treated as pseudo-first order kinetics.

In order to determine the maximum dose of the lateritic soil in a 200 ml solution of 8 mg/L F⁻, different masses of this soil were mixed with the solution and the equilibrium residual fluoride concentration was determined. The equilibrium concentrations decreased quickly with increase in mass of the soil used in defluoridation upto about 10g dose. After this point the equilibrium concentrations were within 0.05 to 0.2 mg/L. (Table.2) This implied that increasing the mass of material per volume of water would only increase defluoridation efficiency up to a dose of 10g/200ml (1g/20ml).

Effects of various ions on defluoridation

Table.3 presents correlation coefficients between initial concentrations of various ions in solution and concentrations of fluoride that were attained in solution after defluoridation. Positive correlation shows that more fluorides remained in solution when the concentration of

the particular ion was increased. Negative correlation shows greater fluoride removal as concentration of the particular ion increases. Carbonates and chlorides showed high direct positive correlation indicating that higher initial concentrations of carbonates and chlorides resulted in more fluorides remaining in solution (high concentration of residual fluoride in water). Carbonates and chloride hindered defluoridation in the material. The negative effect of carbonates on fluoride sorption could be explained on the basis of comparative solubility of carbonates and fluorides. Carbonates being generally less soluble in water than fluorides interacted more strongly with Al^{3+}ions than the fluorides. Chloride hindrance to defluoridation was a result of similarity of chemistry between fluorides and chlorides both ions being halides. General selectivity trends Sulphate>Iodide >Nitrate >Bromide >Chloride >Fluoride for sorption also place chloride before fluoride ion (NAS, 1998).

Calcium ions showed a high negative correlation indicating a decrease in residual fluoride concentration with increase in calcium ion concentration. Calcium thus enhanced defluoridation and this could be attributable to the formation of CaF_2. Sulphate ions had a moderate enhancement on fluoride sorption a result that contradicts general selectivity trends as above. From such a trend sulphate would be expected to interfere with de-fluoridation yet sulphate enhances defluoridation with lateritic soil. This is in part explained by specific ion interaction implying that fluorides interact more with specified material compared to sulphate ion. There exists ion combinations that will noted here to general selectivity trends (Coulson and Richardson, 1997).

Effect of pH in treated water from FRT

It was observed that the pH of the solution increased after defluoridation indicating release of OH^- ions. This therefore suggests a precipitation mechanism where Al^{3+}ions from the material react with the F^- ion to form stable AlF_3 that precipitate out releasing OH^-in the process. At high pH, the lower efficiency could be due to both LeChatelier's principle and competition. The ions OH^- and $F^-$are isoelectronic with same charge and ionic radii. The higher the concentration of OH^-, the more difficult it is for OH^- already attached to Al^{3+} to be replaced by F^- and go into solution. Similar observation has been made by earlier researchers who noted optimum pH of defluoridation by clay minerals at pH 5.8 of the F^- solution (Moges, 1996).

Conclusion

The ability of soil to absorb fluorine from solution has been studied by earlier researchers (Bower and Hatcher, 1967). The rate of adsorption is found to be higher in the apatite prepared by hydrothermal+microwave followed by microwave method. The fluoride removal by the natural material apatite (hydrothermal+microwave method) has more effective. The natural material study reveals that the Redsoil is an effective DF agent and it varies with time . the filed experiments show that there are variations in DF capacity with time due to the variation in Flow rate, variation in height of the water column in the tank, pH and co-exiting ions in the groundwater. The process of ion exchange and adsorption are believed to be the chief governing factors in DF. Nevertheless, our study gives hopes for using low-cost locally available natural material for removing excess fluoride from drinking and domestic water especially for removing for the rural population.

References

1. Apambire, W.B., Boyle, D.R. and Michel, F.A. (1997) Geochemistry, genesis, and health implications of fluoriferous ground waters in the upper regions of Ghana.. Environ Geology 33: 13.

2. Asheesh Kumar Yadav., Kaushik, C.P., Anil Kumar Haritash., Ankur Kansal., Neetu Rani. (2006)   Defluoridation of groundwater using brick powder as an adsorbent. Journal of Hazardous Materials B128 289–293.

3. Babovich, R.D. (1957) Rendering water fluorine free at the source of supply, chemical abstract, Vol 51. pp.1840.

4. Banks, D., Rehnann, C and Skarphagen, H (1998) The comparative hydrochemistry of two granitic island aquifers: The isles of scilly, UK, and the Hvaler Islands, Norway., Science of the total environment, vol. 209, no2-3, pp. 169-183

5. Bower, C A. and Hatcher, J T. (1967). Adsorption of fluoride by soils and minerals. Soil Sci 103:209-218.

6. Boyle, D R. (1992) Effects of basic exchange softening on fluoride uptake in groundwater of the Moncton sub-basin Canada: In Kharaka Y K, Meast A S (ed) Water rock interaction pp 771-774.

7. Boyle, D.R. and Chagnon, M. 1995. An incidence of skeletal fluoroisis associated with ground waters of the maritime carboniferous basin, Gapse Region Quebec, Canada.Envior Geo chem. Health 17; 5-12

8. Bulusu ,KR and Nawlakhe, W.G (1992) Defluoridation , National environmental engineering Research Institute, Nagpur. Oct

9. Bulusu, K.R. and Nawlakhe, W.G.(1992) Defluoridation, National environmental Engineering Research Institute, Nagpur.oct.

10. Chidambaram S, Ramanathan AL, Srinivasamoorthy K (2003) Lithological influence on the groundwater chemistry-Periyar district a case study In: Conference on coastal and freshwater issues 173p

11. Coulson, JM., Richardson, JF. (1997). Chemical engineering 3rd Edn,Butterworth-Heineman: Oxford.

12. Elrashidi, MA., Lindsay, WL. (1986) Chemical equilibria of fluorine in soils: a theoretical development. Soil Sci; 141:274–80.

13. JCPDS (1997). In *Powder Diffraction File*. JCPDS International Centre for Diffraction Data. Swarthmore, Pennsylvania.

14. Kau, PMH., Smith, DW., Binning, P. (1997). Fluoride retention by Kaloin clay. J. of Contaminant Hydrol. 28:267-288. NAS (Nuffield Advanced Science) A (1998). Ion Exchange: Special Study. Penguin Books publication.

15. Killedar, D.J. and Bhargava, D.S. (1993) Effects of Stirring rate and temperature on Fluoride removal by Fishbone Charcoal.

16. Kulkarani DN and NawlakheWG (1974) Serpentine- its limitation as a defloridation medium. Indian J.Environ. Health 16(2) pp151-158

17. Kulkarani, DN and Nawlakhe W.G (1974) Serpentine –Its limitations as a defluoridation medium. Ind J Environ Hlth 16- 2: 151 – 158.

18. Kunin, R. and Mc Gaivey. (1948) Ind Eng Chem 1265, 41 Chemical abstract 42 4427. Swope, G.H., and Hess, R.H. 1937. Removal of fluoride from natural water by Defluoride-Industrial Engineering Chemistry vol 29, p 424.

19. M. Agarwal,M., Rai,K., Shrivastav,R., Dass,S. (2003) Deflouridation of water using amended clay Journal of Cleaner Production 11 ,439–444.

20. Marimuthu, M. and Sivasamy, A. (1994) Defluoridation by zeolites and apophylite fluoride vol 27 No 2 (81-88).

21. McKee, R.H. and Johnston, W.S. (1934) Ind.Engg. Chem 26 pp 849-850

22. Mineral database (2002). http://webmineral.com/data last update: 10/16/06

23. Moges, G., Zrwge, F., Socher, M. (1996). Preliminary investigations on the defluoridation of water using fired clay chips. J. of Afr. Earth Sci., 21.,(4):479-482.

24. Runaska, W.K., Awane, M. and Kaijima, T. (1951) Chem. abstract, 45, 7725.

25. Street JJ, Elwali AMO. Fluorite solubility in limed acid sandy soils. Soil Sci Soc Am J 1983;47:483–5.

26. Trivedi, A.R., Ghevarie, Z.G., Praikh, H.N. and Jain, N.M. (1990) Incidence of high fluoride in ground water in parts of Sabarkantha, district, Gujarat, Western India.vol 13.

27. Viswanathan, C. R., Purushottam, D., Rao, G. R., Vaityanathan, D. and Franchis, P. (1974) Proceedings of the Symposium on Fluorisis Hyderabad pp 217-255.