

ACTIVATED ALUMINA: DEFLUORIDATION OF WATER AND HOUSEHOLD APPLICATION – A STUDY

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ABSTRACT

In fluoride endemic areas, especially small communities with staggered habitat, defluoridation of potable water supply is still a problem. In this respect household defluoridation techniques with attendant regeneration would be more appropriate and the present study is directed towards development of point-of-use domestic candle-type filters for removal of fluoride from water employing activated alumina (AA) which is a proven material for defluoridation. Batch sorption kinetic studies employing activated alumina for sorptive removal of fluorides from water were conducted and observed to be dependent on various system parameters like contact time, pH, dose and ionic environment. Down-flow column studies further demonstrated the practical applicability and effectiveness of activated alumina in removing fluorides from an initial fluoride concentration of 5.0 mg FL^{-1} at a flow rate of 955 L/h/m^2 to the permissible limits of $< 1.0 \text{ mg FL}^{-1}$. Experimental studies were also conducted to investigate the household applicability of activated alumina for removal of fluorides by filling the candles of domestic (candle) water filters with AA and found to be effective. Further, regeneration studies (cyclic adsorption – desorption studies) indicated that the spent AA may be regenerated and this would offset the overall cost of fluoride removal.

1.0 INTRODUCTION

Fluorides in drinking water may be beneficial or detrimental depending on its concentration and total amount ingested. Fluoride is beneficial especially to young children below eight years of age when present within permissible limits of $1.0 - 1.5 \text{ mg F litre}^{-1}$ for calcification of dental enamel. Excess fluorides in drinking water cause dental fluorosis and/or skeletal fluorosis (Sorg, 1978). Indian standards for drinking water recommend an acceptable fluoride concentration of $1.0 \text{ mg F litre}^{-1}$ and an allowable fluoride concentration of $1.5 \text{ mg F litre}^{-1}$ in potable waters (BIS 10500, 1991).

Defluoridation is normally accomplished by precipitation (coagulation) and adsorptive processes. Fluoride removal by chemical precipitation using alum, iron, lime and

magnesium compounds, and calcium phosphate was investigated by several researchers (Boruff 1934, Culp and Stoltenberg 1958, Nawlakhe et al. 1974, and Parker and Fong 1975). Kempf et al. (1938) and Culp and Stoltenberg (1958) studied the use of filter alum for removal of fluoride and reported requirement of high doses of alum.

Sequential addition of lime, bleaching powder (for disinfection) and alum or aluminum chloride known as the Nalgonda Technique (Bulusu et al., 1979) is found effective, economic and is extensively used in India for defluoridation of community water supplies; but has some problems associated with operation and sludge disposal (Srimurali and Karthikeyan, 1998). In this respect, removal of fluoride by adsorption onto Activated carbon, Activated Alumina (AA) and other low-cost materials appears to be attractive and has received wide attention. Adsorption onto low-cost materials like lime stone (Xanxin wang, 2002), kaolinite, bentonite, charfines, lignits and nirmali (*strychnos potatorium*) seeds extract (Srimurali et al., 1998), bone char (Killedar and Bhargava, 1988), Serpentine (Bulusu et al., 1979), and Sulfonated saw-dust carbon (Bhakuni, 1970) are of limited scope.

Defluoridation of water by AA was first suggested by Boruff (1934) and further detailed studies by Swope and Hess (1937), Maier (1947 and 1953), Savinelli and Black (1958), Harmon and Halechman (1965), Zebbon and Jewett (1968), Wu and Nitya (1979) and Balusu and Nawlakhe (1988) demonstrated the effectiveness of AA for defluoridation of water – however sorption capacity of AA was found varying and the variation was attributed to varying water quality parameters like pH, alkalinity, TDS, etc., ionic environment i.e., presence of mono and/or divalent anions and cations, physico-chemical properties of AA and regeneration procedures.

Several of the small and medium community defluoridation plants are nonfunctional for most of the time perhaps due to operational and maintenance problems and therefore simple to operate point-of-use domestic filters would be of immense use in providing fluoride free water. Hence, the present study was undertaken to investigate in detail various aspects of removal of fluorides by AA by conducting batch studies and continuous down-flow column studies. Further, studies were also conducted to investigate the household applicability of defluoridation by AA employing domestic point-of-use candle type filters that are in wide use in India as well in several other developing countries. Domestic point-of-use candle type filters are two tier compartments with porcelain candles fitted in the upper chamber. Water to be filtered is poured in the upper chamber and filtered water is collected in the lower chamber and a tap is fitted for withdrawal of filtered water. Filters are available in sizes of 16 to 34 L, made of stainless steel, plastic, ceramic or even clay and costs INR 300-1200 (US\$ 7-30).

2. EXPERIMENTAL PROCEDURE

Activated alumina (Glaxo laboratories India Ltd., Mumbai, India) was used in the present investigation. A stock fluoride solution of 50.0 mg F litres⁻¹ was prepared by dissolving 110.5 mg of reagent grade sodium fluoride in 1.0 litre of glass-distilled water and a test fluoride solution of 5 mg F litre⁻¹ was prepared fresh from stock fluoride solution by appropriate dilution. The pH of the distilled water was in the range of 6.9 to 7.1 and all the experiments were conducted at room temperature of 32±2°C. Batch sorption tests were conducted to investigate the effect of controlling parameters like contact time, dose and pH. To a 50 mL of the test solution of 5.0 mg F litre⁻¹ taken in reagent bottles, 5 g litre⁻¹ of AA was added and stirred in a horizontal shaker (Yarco Instruments, Chennai, India) operated at 180 rpm for varying time. A number of such identical reagent bottles were employed as duplicates. To determine the equilibrium sorption time, samples were withdrawn at time intervals of 5, 10, 20, 30, 45, 60, 120 and 180 minutes, filtered through Whatman No. 42 filter paper and the filtrate was analyzed for residual fluoride concentration by SPANDS method, outlined in the Standard Methods for Examination of Water and Wastewater (APHA, 1995) using a spectrochem MK-II spectrophotometer (AIMIL Instruments, New Delhi, India).

The effect of pH on fluoride removal was found by adjusting the pH of the test solution of 5.0 mg F litre⁻¹ to initial pH value of 9.0±0.10, 8.0±0.10, 7.0±0.10, 6.0±0.10, 5.0±0.10, 4.0±0.10 and 3.0±0.10 using 0.1N HCl or 0.1N NaOH; a fixed quantity (10 g litre⁻¹) of AA was added and mixed for the equilibrium sorption time, and analyzed for residual fluoride content.

To study the effect of an increase in the dose of AA on removal of fluoride, experiments were conducted by adding varying doses of 2.5, 5.0, 10.0, 15.0 and 20.0 g litre⁻¹ to a test solution containing initial fluoride concentration of 5 mg F litre⁻¹. The samples were then agitated upto equilibrium time and residual concentration was found.

Preliminary study on the effect of monovalent and divalent anions and cations encountered in water supplies like chlorides, carbonates, sulphates, sodium, potassium, calcium and magnesium on removal of fluoride was found by spiking test fluoride solution with different concentrations of monovalent and divalent anions and cations and investigated for percent removal of fluorides.

To assess the usefulness and practical aspects of fluoride removal by AA, down flow column studies were conducted using 10 mm I.D. glass column. Ordinary tap water spiked with a fluoride concentration of 5.0 mg F litre⁻¹ was used as test solution. The column was first filled with glass wool and overlain with fine sand to a depth of 2.5 cm. A filter paper was placed over the sand layer and then filled with AA to a depth of 2.5 cm (weight of 2.7 g). Maintaining constant flow rate, samples were collected at different time intervals and analyzed for residual fluoride content.

To find the feasibility of domestic application of AA, studies were conducted employing ceramic candle type domestic water filters. Inside of the candles were filled with AA and plugged with cotton (Figure 1). Test fluoride solution of tap water containing varying fluoride concentrations (2-20 mg F/L) were passed through the water filter. Samples were collected at regular time intervals and analyzed for residual fluoride content.

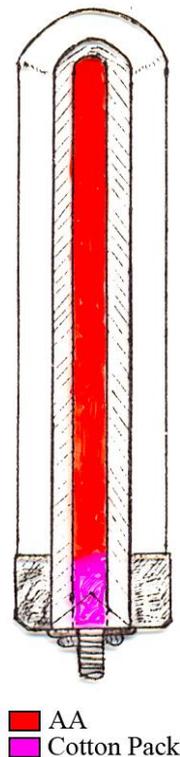


Fig.1 : Details of House hold filter's candle filled with AA.

3. RESULTS AND DISCUSSION

Details of studies conducted with AA are presented and discussed below.

3.1 Effect of Contact Time

Figure 2 shows the progression of sorption reaction, the percent removal of fluorides by AA after different contact times. As the contact time increases, % removal increases rather rapidly, but then gradually approaches a more or less constant value denoting attainment of equilibrium. The sorption reaction may be considered to be occurring in three distinct phases. First, the initial rapid phase in which rate of removal is very rapid and this occurs within initial twenty minutes. This may perhaps be due to instantaneous sorption reaction in which fluoride ions adsorb rapidly onto the surface of AA due to specific chemical interaction (or affinity) and due to diffusive and other

driving forces. In the second phase, rate of sorptive uptake decreases due to lesser sorption as a result of migration of fluoride ions from the film / boundary layer to interior pore / capillary surfaces. In the last phase, i.e., after 60 minutes, the rate of removal levels off significantly denoting attainment of equilibrium and this may perhaps be due to non-availability of sorption sites. As there was no significant increase in % fluoride removal after 60 minutes, an equilibrium time of 60 minutes was chosen and this was employed in all subsequent experiments.

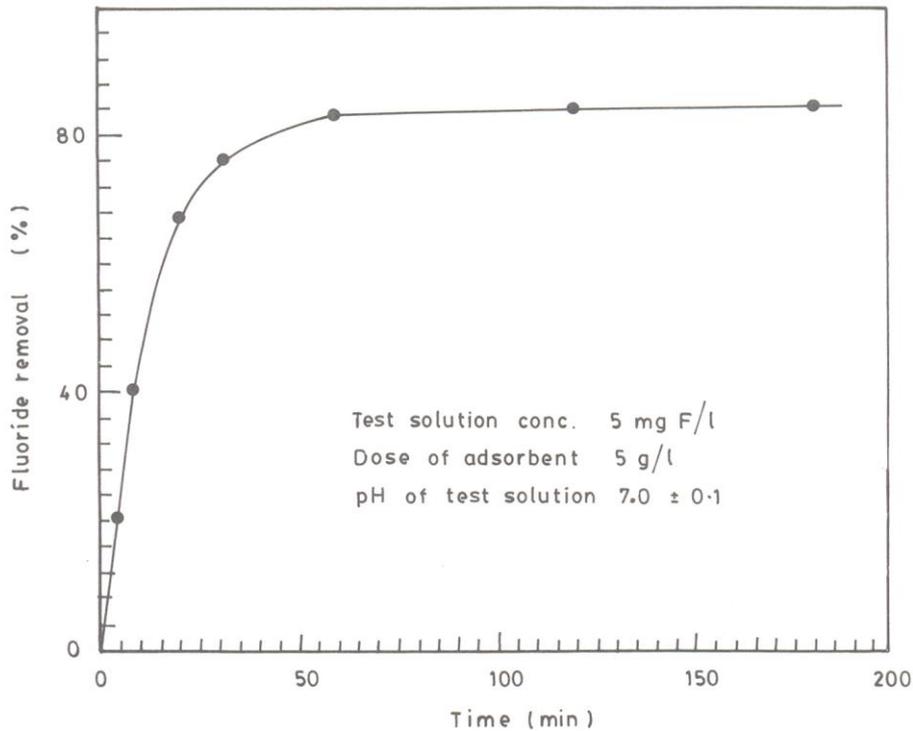


Fig.2 Effect of contact time on removal of fluoride by activated alumina

3.2 Effect of pH

The influence of pH on removal of fluoride studied employing test solutions adjusted to initial pH values of 9.00 ± 0.10 , 8.00 ± 0.10 , 7.00 ± 0.10 , 6.00 ± 0.10 , 5.00 ± 0.10 , 4.00 ± 0.10 and 3.00 ± 0.10 and Figure 3 shows the effect of pH on removal of fluoride by AA. As the pH of the test fluoride solution is increased from 3.00 to 9.00, removal of fluoride remains more or less constant at around 92 – 94% upto a pH of 7.00 but drastically reduces to 35% at a pH 9.00. This drastic reduction in removal with increasing pH is characteristic of anion sorption with a distinctive pH-sorption edge (Hohl and Stumm, 1976 and Benjamin and Leckie, 1981). The pH sorption edge is a narrow pH region often about 2 pH units wide in which sorption behaviour changes rather dramatically. In the present case, the decrease in sorption with

increasing pH, i.e. pH-sorption edge is characteristic of anionic sorption i.e. nearly complete removal at low pH to no removal at higher pH values (Davis and Leckie, 1980) and indicates formation of ligand-like complexes whose tendency to sorb decreases with increasing pH (Davis and Leckis, 1980).

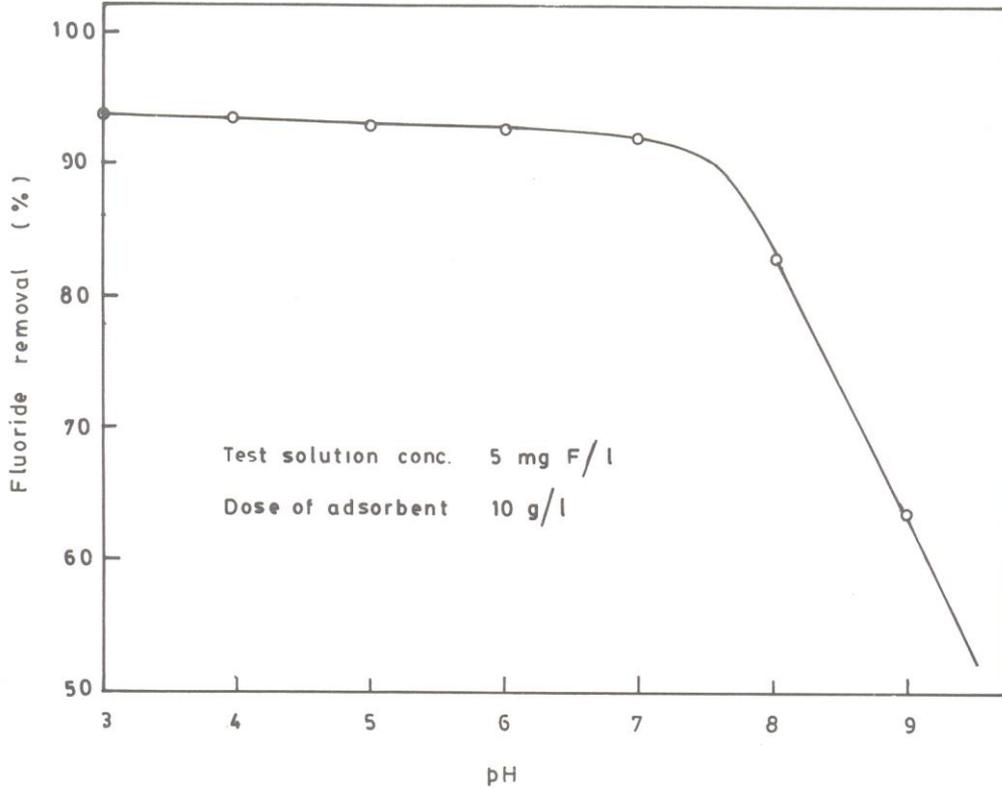


Fig.3 Effect of pH on removal of fluoride by activated alumina.

Higher removal at lower pH values may be due to surface reactions of the type ion-exchange, and/or hydrolysis occurring simultaneously (Hohl and Stumm, 1976 and Benjamin and Leckie, 1981) leading to change in the electrokinetic properties of the surface of AA resulting in a reduction of the negative charges at the surface of AA which enhances sorption of negatively charged fluoride ion (Bulusu and Nawlakhe, 1988).

3.3 Effect of dose of Activated Alumina on Removal of Fluoride

Removal of fluoride from water increased with an increase in the dose of AA and the experimental results are presented in Figure 4. It follows from the figure that fluoride uptake increased as the dose of AA is increased from 2.5 g litre⁻¹ (75%) to 10 g litre⁻¹

(95%) to 20 g litre⁻¹ (96%). At higher doses of the adsorbent, more sorbent surface will be available for the sorption reaction and this result in higher removal. It may also be observed that initially the removal of fluoride increases as the dose is increased, but beyond certain dose range, there is no significant increase in removal. This may be due to exhaustion i.e. non-availability of fluoride ions or even due to non sorbability of fluoride ions as a result of sorbent-sorbate interaction.

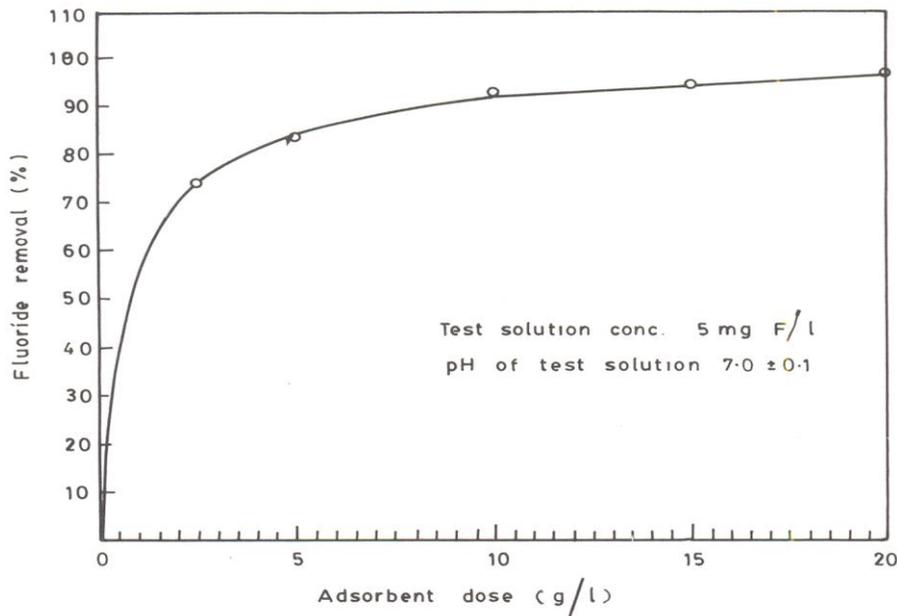


Fig.4 Effect of adsorbent (activated alumina) dose on removal of fluoride

3.4 Effect of Ionic Environment on Removal of Fluoride

Effect of monovalent and divalent anions and cations like Chlorides (Cl^-), Carbonates (CO_3^{2-}), Sulfates (SO_4^{2-}), Sodium (Na^+), Potassium (K^+), Calcium (Ca^{++}) and Magnesium (Mg^{++}) on the removal of fluoride from water by AA was investigated and the results are presented in Figures 5 and 6. It follows from the results that presence of Chlorides (Cl^-) has very little effect on removal of fluoride upto a concentration of 200 mg litre⁻¹. So also is the presence of Sulfate (SO_4^{2-}) ions. But the presence of carbonate ions exhibited a strong influence on the sorption capacity resulting in a decrease in sorption capacity an initial 83% removal at (no) zero carbonate ions to around 32% at a carbonate ion concentration of 200 mg/L.

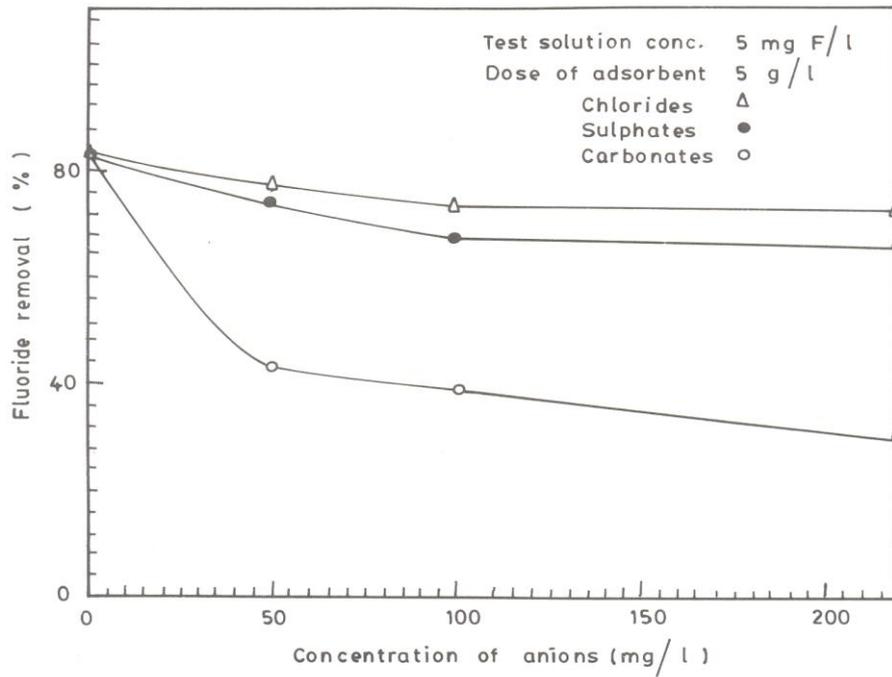


Fig.5 Effect of anions on removal of fluoride by activated alumina.

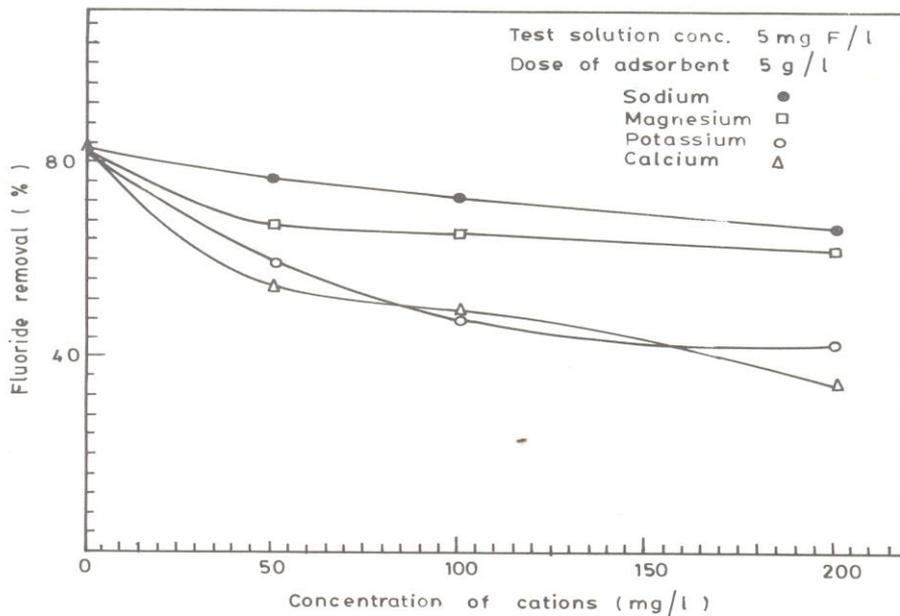


Fig. 6 Effect of cations on removal of fluoride by activated alumina

In the case of cations, presence of Sodium and Magnesium ions upto a concentration of 200 mg/L resulted in a marginal decrease in sorptive removal whereas presence of Potassium and Calcium cations registered a significant reduction in percent removal of fluorides especially at higher concentration of 100 to 200 mg/L. Presence of

monovalent carbonate anion and potassium cation and divalent calcium ion at higher concentrations resulted in a significant reduction in sorption capacity from 80% to around 40%. Increasing alkalinity results in decreased capacity of AA for removal of fluoride from water (Savinelli & Black, 1958) augurs well with the present observation of reduction in capacity with increasing concentration of carbonate ions and also pH. Savinelli and Black (1958) also reported that high concentration of Chloride and Sulfate ions (upto 1000 mg litre⁻¹) has very little effect on sorption capacity of AA and observed a concomitant release of sulfate ions into solution phase.

3.5 Column Studies with Activated Alumina

To investigate the practical aspects of application of AA for removal of fluoride from water, dynamic down-flow column studies were conducted at a flow rate of 955 L/h/m² facilitating a contact time of 7-8 minutes. Samples were collected at regular time intervals and analyzed for residual fluoride content. The column was operated till complete exhaustion and the break through profile is shown in Figure 7. Column studies clearly indicate the effectiveness of AA in removing fluoride from an initial fluoride concentration of 5.0 mg litre⁻¹ to permissible limits of < 1.0 mg F litre⁻¹.

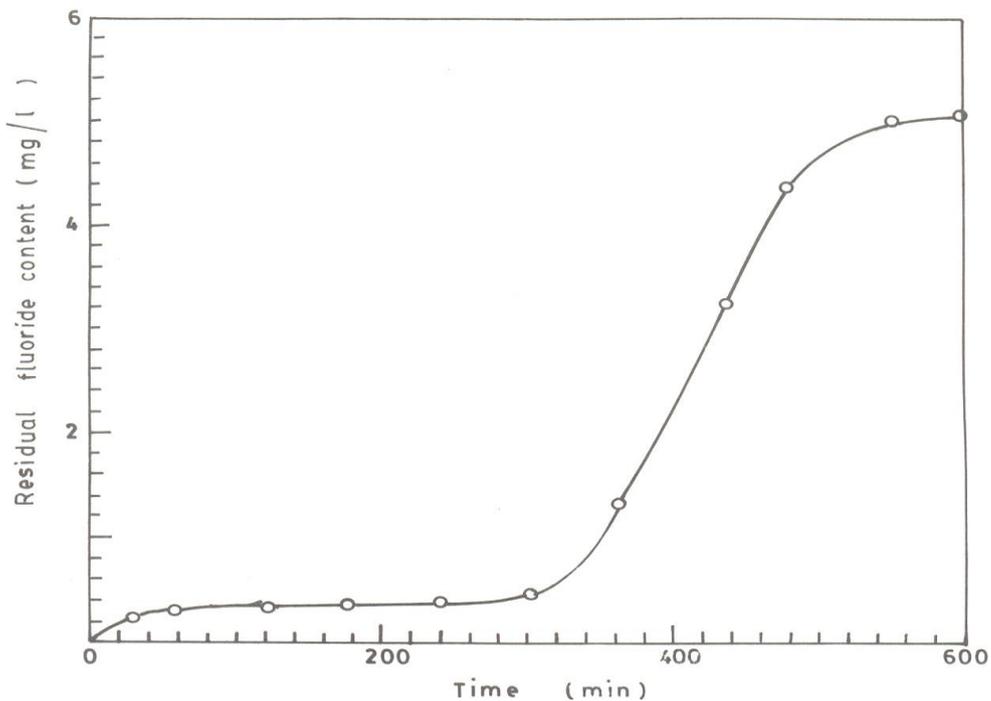


Fig.7 Break through profile for adsorption of fluoride by column filled with activated alumina .

3.6 Studies with Candles filled with Activated Alumina

Since the column studies demonstrated practical applicability of AA, further studies conducted to investigate household applicability of AA for removal of fluoride from water by employing point-of-use domestic candle type filters (Domestic water filters are generally available in three different capacities, viz. 16L with 1 candle, 24L with 2 candles and 34L with 3 candles). Hollow portion of the candles were filled with AA and the opening is closed with cotton. Fluoride concentrations ranging from 2.0 mg/L to 20 mg/L were employed. Test fluoride solution was taken in the upper chamber containing the candles(s) and the filtered water was collected at regular time intervals and analyzed for residual fluoride content and the quantity of water that can be effectively filtered to obtain filtered water having fluoride concentration < 1.0 mg F litre⁻¹ from varying initial fluoride concentrations are computed and are given in Table 1.

Table 1: Quantity of fluoride free water obtained by candle filters of different capacities from water containing varying concentration of fluorides

Initial Fluoride concentration (mg litre ⁻¹)	Quantity of filtered water (< 1.0 mg F litre ⁻¹) obtained with a filter of capacity, L		
	16 litres (1 candle)	24 litres (2 candles)	34 litres (3 candles)
2	48.0	96.0	144.0
3	24.0	48.0	72.0
4	16.0	32.0	48.0
5	12.0	24.0	36.0
6	9.6	19.2	28.8
7	8.0	16.0	24.0
8	6.9	13.7	20.6
9	6.0	12.0	18.0
10	5.3	10.7	16.0
11	4.8	9.6	14.4
12	4.4	8.7	13.1
13	4.0	8.0	12.0
14	3.7	7.4	11.0
15	3.4	6.9	10.3
16	3.2	6.4	9.6
17	3.0	6.0	9.0
18	2.8	5.6	8.5
19	2.7	5.3	8.0
20	2.5	5.0	7.6

It may be observed from the Table that the existing domestic candle type filters may be used for removal of fluoride by simply filling the hollow portion with AA and plugging with cotton. However, after exhaustion, the candles have to be refilled with fresh /regenerated AA.

3.7 Regeneration Studies

Regeneration studies of exhausted AA with distilled water, 0.1N NaOH and 0.1N HCl (Table 2) indicate that 0.1N NaOH is effective with 80% regeneration whereas distilled water and 0.1N HCl could regenerate 30% and 22% respectively. Cost analysis indicate that the approximate cost (recurring) of fluoride free ($< 1.0 \text{ mg litre}^{-1}$) water is Indian Rupees 40/ mg F/100L (US \$1.0/mg F/100L). Regeneration and repeated use of AA may further reduce the recurring cost.

Table 2: Regeneration Studies with different regenerants

Sl. No.	Regenerant	Initial fluoride concentration	Final fluoride concentration	% Regenerated
1	Distilled water	5.0	1.5	30
2	0.1 N HCl	5.0	1.1	22
3	0.1 N NaOH	5.0	4.0	80

4. IMPLICATIONS

Batch adsorption studies indicated the effectiveness of AA in removal of fluoride from water. The data further denotes that an increase in pH, alkalinity, carbonates and calcium resulted in a decrease in sorption capacity. Presence of chlorides, sulphates, potassium, sodium and magnesium has marginal influence on sorption capacity. Removal of fluoride from water by AA is possibly exchange sorption (Savinelli and Black, 1958). Draw flow column studies indicated practical utility of AA for removal of fluoride.

A notable feature of this study is domestic application of AA for removal of fluorides. Studies with domestic candle type water filter by filling the hollow portion of the candles with AA were found to be effective in removal of fluoride. Therefore, in endemic areas, ordinary domestic candle filters may be used for removal of fluorides as well from water especially when public supplies are non-functioning or inadequate. Further, regeneration studies revealed that spent AA may be regenerated and this would offset the overall cost of fluoride removal which may be useful especially for rural/semi-urban areas.

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