

# Chapter 13

## Design of a Domestic Defluoridizing Unit



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**Abstract** While trace amounts of fluorine are essential for life, its excessive intake leads to a disease known as fluorosis. It is a predominant ailment in majority of the countries inclusive of India. It is caused also by drinking fluoride containing water. Retention of fluorine in bones and teeth occurs through  $F^--(OH^-)$  exchange on their inorganic component known as hydroxylapatite. Endeavour of the present study is to design a column using activated alumina as an adsorbent for continuous defluoridation of water for domestic purpose. As a part of it, operational defluoridation capacity of alumina was determined by variation of different factors (amount of alumina, time, temperature, added salts). A family of four members was taken as a model. The initial and final fluoride concentrations were taken as 2.0 and 0.7 ppm, respectively. Dimension of the unit (adsorbent bed diameter and height) was determined.

**Keywords** Design · Domestic defluoridizing unit · Fluorosis

### 13.1 Introduction

Human beings and animals suffer from fluorosis due to extended acquaintance with fluoride containing water, air or food. India stands in the top listed countries which are challenged with fluorosis problem in view of obligatory consumption of water having high quantities of fluoride (1–48 ppm) [1]. In India, Andhra Pradesh State is one among the many affected belts by endemic fluoride [2]. As per Indian standards,

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acceptable limit of fluoride concentration in drinking water is  $1.0 \text{ mg L}^{-1}$ , whereas its permissible limit is  $1.5 \text{ mg L}^{-1}$  [3]. Though higher concentrations of fluoride cause fluorosis, its lower concentration is proved to be useful. Fluoride plays a vital role in mineralization of some of the hard tissues [4]. Fluoride is added to community water in some of the countries including USA as a part of health measure in order to inhibit dental decay [5]. Fluoride concentration in  $\text{mg L}^{-1}$  and associated potential health effects can be given as:  $<0.5$  (dental carries are prevented minimally),  $0.5\text{--}1.5$  (favourable to prevent the dental carries),  $1.5\text{--}4$  (causes dental fluorosis),  $4\text{--}10$  (dental and skeletal fluorosis) and  $>10$  (crippling fluorosis) [6]. Dental fluorosis can be easily recognized by symptom—mottling of teeth [7].

About 300 mg of fluorine per kg is its abundance in earth crust [8]. Fluorspar, cryolite and fluorapatite are some of the fluorine-containing minerals which undergo weathering process leading to its accumulation in soil and hence in water [9]. In some of the areas like Ethiopian Rift Valley, high fluoride concentration in drinking water can be related to volcanic deposits being the natural fluoride sources [10]. High concentrations of fluoride were noticed in thermal waters having basic pH [11]. Different anthropogenic and industrial activities release fluoride into the environment. Some of them are manufacturing units of fertilizers, pesticides, glass, electronics and aluminium [12].

Water supply in rural areas of a maximum number of countries is suffering from poor quality and quantities. Ion exchange, reverse osmosis (RO) and electro-dialysis are the popular methods in developed countries, but they require high capital cost, maintenance and technical backing [13]. Problems in disposal of large volumes of sludge and high operational cost are opposing the adopting the well-known Nalgonda technique. The other defluoridation methods (adsorption, nanofiltration, ion exchange, solar distillation and reverse osmosis) have their own advantages and disadvantages. Hence, adoption of the method must be based on local needs. Compared to other defluoridation methods, adsorption method is more preferable in view of easy operation, lack of sludge formation, low capital cost and easy replacement of exhausted bed [14]. However, the well-known adsorbent—animal charcoal—is facing resistance due to the prevailing social customs. Though a large number of cost-effective biosorbents are reported for defluoridization in the literature, their technical usage in rural areas is not possible in immediate course of time. In spite of availability of a wide variety of adsorbents, AA is the best choice in developing countries. Hence, activated alumina is selected as an adsorbent in the present study.

The rural community in Chebrolu mandal has been distressed by fluorosis (both dental and skeletal) due to consumption of water having more fluoride concentration than the permissible limits. Chebrolu mandal of Guntur District, Andhra Pradesh, was taken as one unit for fluoride estimation in groundwaters. Apart from fluoride estimation, chloride and total hardness were also estimated. Based on this compilation, it is found that in some villages like Gudavarru and Veera Nayakuni Palem, the fluoride concentration is more than the limit 1.5 ppm given by WHO. An effort has been made to design an economically practicable defluoridation unit with continuous flow, which can be used in rural areas.

## 13.2 Experimental

### 13.2.1 Selection of Activated Alumina

The literature survey shows that cost of the treated water by activated alumina is less compared to other defluoridizing agents [15]. Compared to adsorption of  $\text{CaCO}_3$  (0.03 mg  $\text{F}^-$  per g), activated alumina is proved to be better adsorbent (0.57 mg  $\text{F}^-$  per g) [15, 16]. A number of researchers are worked on defluoridation of water using AA since the suggestion of Boruff [17]. Bulusu and Nawlakhe [18] established that its sorption capacity is variable and depends on water quality parameters, ionic environment and regeneration procedures. Simultaneous occurrence of different reactions at AA surface (like ion exchange and hydrolysis) causes a variation in surface electrokinetic properties [19]. It helps to increase the sorption of fluoride ions due to a decline of negative charges at its surface [18]. Hence, activated alumina was selected as an adsorbent for defluoridation of water. Commercially available technical grade activated alumina granules supplied by Sethiya Solvents & Chemicals, Tamil Nadu, were used.

### 13.2.2 Batch Adsorption Studies

In each system, 300 mL of water (containing 2 ppm of fluoride, 113 ppm of chloride, 420 ppm of total hardness) is taken in a 500-mL polyethylene container and maintained at 31 °C. The solution is stirred at 240 rpm mechanically for definite period after the addition of desired amounts of adsorbent. The suspension is filtered through a sintered crucible (G4). The filtrate is tested for fluoride by SPADNS method, chloride by silver nitrate method and hardness by EDTA method [20]. The final fluoride concentrations were measured by Zr-SPADNS method [21]. The fluoride concentration in the sample after defluoridation is calculated from absorbance value of its coloured solution and standard curve. The same procedure is adopted for all the experiments carried out by varying amount of adsorbent, contact time, temperature and added salts. The percentage removal of fluoride/chloride/total hardness of water is calculated from  $C_0$  (initial concentration in solution) and  $C_e$  (final concentration in solution after adsorption).

### 13.3 Results and Discussion

#### 13.3.1 Batch Mode Defluoridation of Water by Activated Alumina

It is very well-known fact that activated alumina acts as an efficient defluoridizing agent. Therefore, it is thought worthwhile to know the effect of various factors affecting the defluoridation capacity of activated alumina, before designing the column for continuous defluoridation of water using activated alumina as an adsorbent.

It is observed that with an increase in the amount of activated alumina, an increase in the % removal of fluoride is observed (Fig. 13.1a). It can be explained based on the increased active sites availability causing an improvement of active surface area, especially at higher adsorbent doses [22]. Afterwards, equilibrium is attained beyond certain dose. The effect of the agitation time on the removal of fluoride ion is shown in Fig. 13.1b, which clearly indicates that the removal of fluoride is fast during early time but turns out to be slow and almost decays with a further rise in the interaction period beyond 10 min. It hints that the fluoride removal rate is greater in the early phase because of availability of sufficient adsorbent surface area. A decrease in adsorption takes place with further increase in contact interaction period because of a decline in the accessibility to the active sites. Percentage of fluoride ion adsorption increased with an increase in contact time and the observed can be endorsed to the point that higher duration makes acquainted the fluoride ion to make adsorb on adsorbent [23]. The maximum adsorption percentage was recorded at 10 min with all adsorbents, and then onwards, sluggishness was observed. Per cent of defluoridation increased up to 31°C and then decreased (Fig. 13.2b). It shows that chemisorption is activated with an increase in temperature. Further confirmation of governing of chemisorption in the fluoride adsorption on activated alumina is evident as it obeys Langmuir's adsorption isotherm [24].

To study the effect of the existence of anions (like chloride) and cations (like calcium) on the defluoridation capacity of water, sodium chloride and calcium chloride were added. There is no effect of added anions like chloride on the defluoridation of

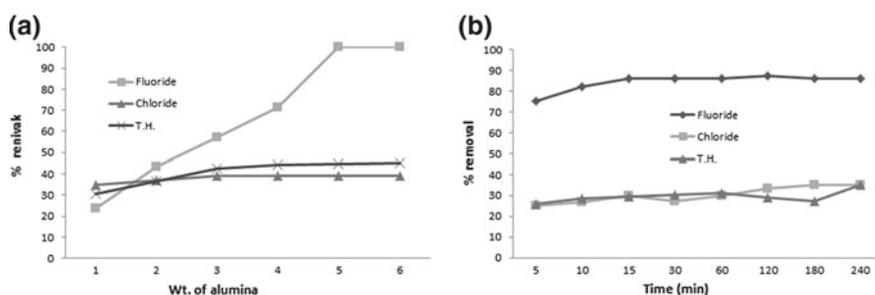
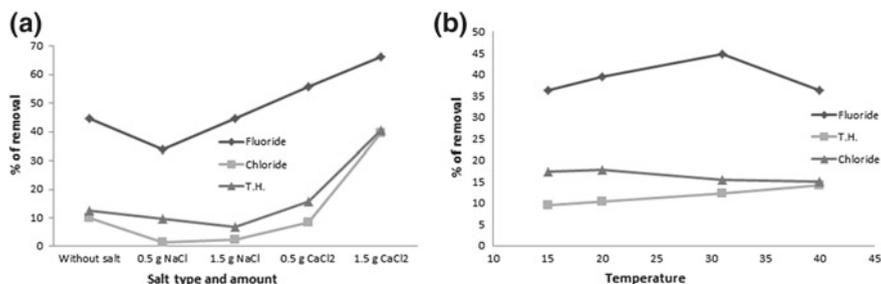


Fig. 13.1 Effect of **a** adsorbent dose and **b** time on % removal of fluoride



**Fig. 13.2** Effect of **a** salt type and amount, and **b** temperature on % removal of fluoride

water as there is no change in the defluoridization capacity with a rise in [chloride ion]. But, the concentration of fluoride decreased progressively with an increase in the concentration of the added calcium chloride (Fig. 13.2a). The observed decrease in fluoride concentration can be attributed to the added calcium ion because there is no effect of chloride ion on defluoridation. Moreover, it is an established fact that the fluoride can be removed as calcium fluoride by the calcium ions. In spite of high affinity towards fluoride by adsorbents containing Al, Zr, Mg and Ca, the presence of some anions (nitrate, sulphate, bicarbonate and phosphate) decreases their affinity [25–27]. Adsorption of chloride and nitrate ions on activated alumina is negligible, whereas sulphate and bicarbonate ions adsorb fairly well. Further, an increase in bicarbonate ions decreases the adsorption of fluoride on activated alumina due to its competitive adsorption [15]. As many other anions are present in the groundwater taken in the present case, the efficiency of fluoride ion adsorption decreases further.

In view of practical conditions, throughout the present study, defluoridation studies were carried out at neutral pH. However, defluoridation capacity of AA was reported as 3, 5.6 and 20 mg g<sup>-1</sup> for alkaline, neutral and acidic water, respectively [24]. Davis and Leckie [28] reported that fluoride sorption capacity decreases with an increase in pH due to a decline in the establishment of ligand-like complexes. It is a known fact that defluoridation by adsorption is interfered by hydroxide ions. Defluoridation by activated alumina can be explained by Stern model of double layer. Charge potential on alumina is zero when pH is 9. As hydrogen ion is the potential-determining ion for the surface charge of AA, it is positively charged when [H<sup>+</sup>] is greater (pH < 9). Hence, negatively charged fluoride ion adsorbs on oppositely charged AA. In addition, adsorption process is also governed by “specificity factor” and adsorption order: F<sup>-</sup> ≫ OH<sup>-</sup> ≫ HCO<sub>3</sub><sup>-</sup> ≫ Cl<sup>-</sup> = SO<sub>4</sub><sup>2-</sup> [24]. Therefore, defluoridation capacity of AA decreases with an increase in [HCO<sub>3</sub><sup>-</sup>].

### ***13.3.2 Determination of Operational Defluoridation Capacity of Alumina***

50 g of activated alumina is added to 1 l of water containing 2 ppm fluoride, 113 ppm chloride and 420 ppm of total hardness and allowed to be at equilibrium for 24 h and then filtered. The amount of removed fluoride is estimated colorimetrically based on the concentration of fluoride in the water before and after adsorption. The process is repeated with the same alumina with the addition of fresh samples of water added at the same amounts fluoride, chloride and total hardness. This process is repeated till there is no defluoridation by the alumina. The total defluoridation capacity is found to be 57 mg fluoride/50 g of alumina. Therefore, operational defluoridation capacity of the alumina is 1.14 mg fluoride/g of alumina. The literature survey shows that adsorption capacities ( $\text{mg g}^{-1}$ ) of AA (OA-25 grade), AA (AD101-F grade), acidic alumina, modified AA and third aluminium hydrate (TAH) are compiled as 1.78, 0.42, 8.4, 0.76 and 25.8, respectively [29]. Probably, there exists a high variance in “degree of activation” in variety of alumina products. Another justification may be a difference in pH in addition to the brand of the product. Most of the previous research works involve the usage of distilled water for fluoride ion solution preparation and high grade alumina with high adsorption capacity. But in the present study, it is based on water having different salts and technical grade alumina. Therefore, the operational capacity—1.14 mg/g—is considered while designing the column for defluoridation.

### ***13.3.3 Design of Continuous Defluoridizing Unit***

Compared to other defluoridation methods, packed bed adsorption method is more preferred. Some of its advantages are easier operation, reasonable capital and operational costs, no sludge formation and easy replacement of bed [30]. Batch method faces three main problems, i.e. (1) drying of filter bed and hence shortening of lifetime of filter for intermittent usage, (2) incomplete utilization of adsorbent and (3) limited release of defluoridate water at once. Hence, a continuous defluoridizing unit is designed in the present study. Combined filter contains two filter processes in the same structure to remove fluoride and microbes by using adsorbent and silver nitrate, respectively. However, in view of disadvantages like higher cost, maintenance requirement, low susceptibility to higher turbidity, etc., the concept of combined filters was not considered.

An attempt has been made to design the column using activated alumina as an adsorbent for defluoridation of water continuously for domestic purpose. A family of four members was taken as a model. The initial and final fluoride concentrations are taken as 2.0 and 0.7 ppm, respectively.

Daily personal water demand =  $D = 3$  l/consumer/day

Number of users =  $N = 4$

Operation period =  $OP = 2\frac{1}{2}$  months = 75 days  
 Operational sorption capacity =  $C = 1.14$  g/kg  
 Bulk density of alumina =  $\rho = 1.12$  kg/l  
 Raw water fluoride concentration =  $F_i = 2.0$  mg/l  
 Mean fluoride concentration in treated water =  $0.7$  mg/l  
 Volume ratio supernatant water/medium =  $VR_{SW/M} = 0.2$   
 Daily water treatment =  $Q = D \times N = 12$  l/day  
 Overall quantity of treated water in a filter period =  $V_T = Q \times OP = 900$  l  
 Overall quantity of removed fluoride in a filter period =  $F_T = \frac{V_T \times (F_i - F_o)}{1000} = 1.17$  g  
 Amount of  $Al_2O_3$  required for renewal =  $M = F_T/C = 1.03$  kg  
 Volume of  $Al_2O_3$  in filter =  $V_M = M/\rho = 0.916$  l  $\cong 0.95$  l  
 Treated no. of bed volumes during filter period =  $BV = \frac{V_T}{V_M} = 982$   
 Supernatant water volume capacity =  $V_{SW} = VR_{SW/M} \times V_M = 0.183$  l  $\cong 0.2$  l  
 Total volume of filter =  $V_F = V_m + V_{SW} = 0.95 + 0.2 = 1.15$  l.

### 13.3.4 Corresponding Dimensions

Karthikeyan et al. [24] studied the rate of water flow in a column filled with activated alumina. According to them, variation in column height and particle size causes a substantial alteration in water flow rate. Particle size increase caused a rise in pore volume leading to an enhancement of flow rate. Bed height increase results in an enhancement of offered resistance which leads to a decline in flow rate. In view of these two reasons, selection of bed height and particle size is the important parameter to be considered while designing a defluoridation unit. Important issue to be noted is that minimum contact period is required between adsorbent and fluoride ion to be removed. At the same time, very lower flow rate design will not be accepted by end-users. Taking into consideration the equal weightage of flow rate and defluoridation capacity, it is decided to choose the intermediate size of the particle in the range 140–180  $\mu$ m because both factors are optimal in the chosen range. Based on it, fixation of column height was done. Moreover, it is always advisable to select the ratio of column diameter to particle diameter as more than 20 to decrease the channelling chances [31, 32]. Several trails were made with different dimensions, and it is found that the optimum diameter as 7 cm for the decided quantity of alumina.

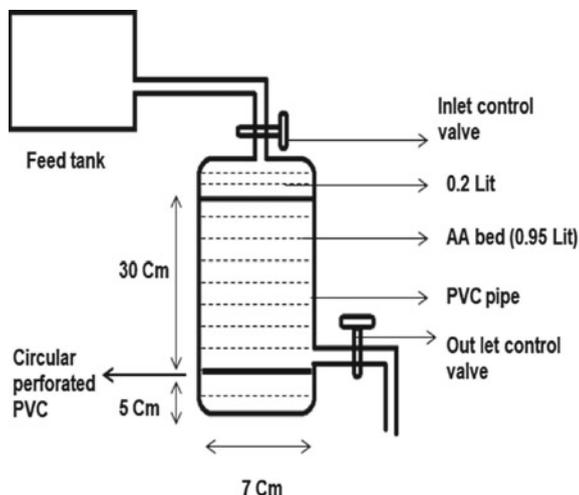
Filter diameter (selected) =  $\Phi = 7$  cm

Total height of the filter =  $H_F = V_F/[\pi \times (\Phi/2)^2] = 29.897$  cm  $\cong 30$  cm.

### 13.3.5 Defluoridation Studies on the Designed Unit

PVC pipe having an internal diameter of 7 cm was used for this study. The column was connected to a feed tank with inlet control valve. Activated alumina bed was fixed, and proper distribution in it was ensured by packing it between two circular

**Fig. 13.3** Design of the proposed house hold defluoridation unit



perforated PVC sheets. Plug pairs encompass these sheets which function as filtering medium to remove any dust/dirt from inlet and support to the bed, respectively (Fig. 13.3). Random packing of adsorbent is ensured by initial filling of the column with deionized water followed by activated alumina, whereas the reverse filling order may result in a decline of adsorbent efficiency due to the development of air gaps which leads to further channelling phenomenon. A closely packed adsorbent bed was ensured by soaking with distilled water and leaving for overnight. It is a known fact that activated alumina on hydration changes from the mineral form boehmite ( $\text{AlOOH}$ ) to gibbsite ( $\gamma\text{-Al(OH)}_3$ ) [33]. Further, it was also established that fluoride better uptake by it happens due to a change in surface morphology, which is done by soaking it for one day [34]. Hence, the above overnight soaking of bed with distilled water also helps to improve defluoridation. Process was carried out at room temperature. Column kept filled with feed water even during resting period. Practical aspects in the usage of AA for defluoridation of water were studied by regulating the flow rate in order to maintain minimum 5 min contact time. Input and output were collected at regular intervals of time in order to analyse the fluoride concentration. The residual amount of fluorine in outlet water was found to be within permissible limits. However, the three key issues involved in realization of any household defluoridation units are (1) motivation, (2) appropriate and cheap technique and (3) technical support including training on efficient regeneration to one of the villagers to continue without any support from external agencies [35]. Similar to defluoridation studies, decontamination units may be designed for the removal of heavy metals using agricultural waste as adsorbents [35–39].

### 13.3.6 Regeneration of Bed

A fourfold higher regeneration was observed with 0.1 N sodium hydroxide solution compared to 0.1 N hydrochloric acid solution. High negative charges are created on the surface of AA during elution of fluoride using sodium hydroxide. Hence, the already adsorbed  $F^-$  experience repulsion from the surface leading to their diffusion into solution [24]. For regeneration, the exhausted AA was shifted into a bag made up of nylon mesh and immersed in alkali solution for overnight with intermittent stirring. A marginal decrease in adsorption capacity was observed even after 25 regeneration cycles.

## 13.4 Conclusions

Lower values of operational defluoridation capacity of alumina can be explained based on the presence of competitive ions in the water to be treated. A continuous defluoridation unit was designed for domestic purpose using activated alumina as an adsorbent. The residual amount of fluorine in outlet water from the unit was found to be within permissible limits. Sodium hydroxide solution (0.1 N) was found to be the best regenerating agent for the exhausted bed.

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