

Investigations on activated alumina based domestic defluoridation units

Vivek Singh Chauhan, Pradeep Kumar Dwivedi, Leela Iyengar*

Department of Chemistry, Indian Institute of Technology, Kanpur 208016, India

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Abstract

Investigations were carried out on the defluoridation of fluoride-spiked ground water in domestic defluoridation units (DDU) with activated alumina (AA). Specific safe water yield (SSY) was determined as a function of AA amount and adsorbent depth. Reuse potential of exhausted AA was assessed by regenerating and reusing AA in multiple defluoridation cycles. High fluoride uptake capacity (FUC) from ground water matrix as well as retaining $\approx 95\%$ FUC up to five cycles showed the suitability of AA for defluoridation in DDU. SSY, liters of safe water/kg AA, was dependent on the AA amount and its depth. There was a significant decrease in SSY with the decrease in AA depth in different DDUs, even though the amount was maintained constant. The derived data from four DDUs, with 3–5 kg AA and depth ranging from 5 to 13 cm, showed that DDU design is one of the most important parameter to be considered for optimizing SSY.

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1. Introduction

Fluorosis is a chronic disease resulting from the consumption of excess fluoride, mainly through drinking water. India is among 23 nations in the world, where fluorosis is prevalent. It is estimated that around 62 million people in 19 states of India are affected with various forms of fluorosis, which include dental, skeletal and non-skeletal manifestations [1]. Excess fluoride is generally encountered in ground water and more than 80% of rural population in India depends on ground water as their drinking water source. Taking health effects into consideration, the World Health Organization has set a guideline value of 1.5 mg/L as the maximum permissible level of fluoride for drinking water [2]. BIS standards, for fluoride in drinking water, are 1.0 mg/L as permissible and 1.5 mg/L as maximum permissible level, respectively [3].

Remedial measures have to be considered for the prevention of fluorosis, if fluoride concentration in a water source exceeds the permissible level. A wide range of treatment procedures has been reported for the removal of excess fluoride from water. These can be broadly divided into three categories: precipitation, adsorption and membrane based. Precipitation methods involve

the addition of soluble chemicals to water. Fluoride is removed either by precipitation, co-precipitation or adsorption onto the formed precipitate [4–6]. Adsorption processes involve the passage of raw water through an adsorbent bed, where fluoride is removed by physical, ion exchange or surface chemical reactions with the solid matrix. A wide range of adsorbents, such as activated alumina, bone char, clay, zeolites, flyash, brick and specific ion exchange resins, have been reported for fluoride removal [7–14]. Other defluoridation methods include membrane based reverse osmosis and nanofiltration as well as electro dialysis and electrocoagulation [15–19].

Among these methods, activated alumina (AA) seems to be better suited for large-scale defluoridation due to its specificity and affinity towards fluoride, chemical/physical properties and bulk availability. There have been many reports on the use of AA for fluoride removal [20–26]. Among different modes of application of AA technology in the field, “point of use” domestic defluoridation units (DDU) may be more appropriate in the rural areas of developing countries, where the settlements are scattered.

The objective of the present study was to investigate the performance of domestic defluoridation units, with varying amounts of adsorbent and the bed depth, with an aim to arrive at design specifications. Reuse potential of AA was assessed by regenerating exhausted AA and reusing in subsequent defluoridation cycles.

* Corresponding author.

E-mail address: leela@iitk.ac.in (L. Iyengar).

Table 1
Properties of activated alumina

Serial no.	Characteristics	Value
1	Particle form	Spheres
2	Particle size (mm)	0.4–1.2
3	Surface area (minimum) (m ² /g)	310
4	Pore volume (cm ³ /g)	0.41
5	Bulk density (g/cm ³)	0.86
6	Loss on attrition (maximum) (wt.%)	0.1
7	Loss on ignition (250–1000 °C)	7

2. Materials and methods

2.1. Sorbent

An indigenous manufactured AA grade was used in this study. It was supplied in the particle size range of 0.4–1.2 mm. Properties of AA as provided by the manufacturers, are given in Table 1.

2.2. Test water

Test water for this study was prepared by spiking sodium fluoride to IIT tap water (borewell water) so as to maintain fluoride concentration of 10.5 ± 0.5 mg/L. Characteristics of IIT tap water, used for preparing test water, was periodically monitored and average values are presented as follows: pH 7.9–8.0; alkalinity, hardness, fluoride and sulphate of raw water were 325 mg/L as CaCO₃, 360 mg/L as CaCO₃, 0.8 and 55 mg/L, respectively.

2.3. Domestic defluoridation units (DDU)

Four domestic defluoridation units were used in this study. Amount of AA was varied from 3 to 5 kg and AA depth ranged from 5.0 to 13.0 cm (Table 2). Plastic microfilter assembly (slot opening <0.2 mm), with a 1.5 mm diameter hole in the threaded plug, was used to control raw water flow rate. With this device, around 9–10 L water could flow through the AA bed in an hour. These units were operated intermittently (so as to simulate field conditions) and around 40 L of raw water was passed through the units per day. Treated water samples were periodically collected for fluoride analysis.

Table 2
Specifications of domestic defluoridation units

Filters	S ₁	S ₂	S ₃	S ₄ ^a
Diameter (cm) (top/bottom)	22/22	24/24	25.5/25.5	36/30
Height (cm)	23	26	24	36
AA bed depth				
3 kg	9.0 cm (0.023)	6.5 cm (0.014)	6.0 cm (0.011)	5.0 cm (0.005)
4 kg	11.5 cm (0.030)	9.0 cm (0.019)	7.5 cm (0.014)	6.5 cm (0.007)
5 kg	13.0 cm (0.034)	11.0 cm (0.024)	9.5 cm (0.018)	8.5 cm (0.009)

Values in the bracket represent AA depth/DDU cross-sectional area.

^a Bucket type unit.

2.4. Regeneration of exhausted AA

Exhausted AA was transferred from DDU to a fine mesh nylon bag. The bag was placed in a plastic bucket with flow control device (4 mm aperture). Ten liters of 1% NaOH was passed through AA bed. After washing once with raw water to remove excess alkali, 1% H₂SO₄ was passed through the alkali treated AA. After washing with water, AA was dried in the oven at 120 °C overnight and was reused for subsequent defluoridation cycle.

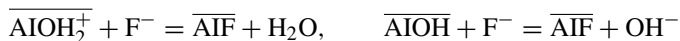
2.5. Fluoride analysis

Fluoride was analysed using combination fluoride electrode (Orion 96-09), which was connected to Orion meter (290A). The meter was calibrated with multiple standards in the range of 0.5–10 mg/L. Two milliliters TISAB III (Orion cat. no. 940911), recommended for samples having aluminium, was added to 20 mL sample. Concentration of fluoride was measured after 10 min.

3. Results and discussion

3.1. Performance of DDU

DDU S₁, with 3 kg AA, was used for this study. Fluoride concentration was determined in treated water periodically. Fig. 1 presents the plot of treated water volume versus F⁻ concentration. Fluoride level in treated water was more or less constant at around 0.4 mg/L up to 350 L. This was equivalent to ≈96.2% fluoride removal. Thereafter, fluoride concentration increased rapidly and around 550 L of test water (F⁻, ≤1.5 mg/L) could be treated with 3 kg AA. This was equivalent to around 167 bed volumes and fluoride uptake capacity (FUC) of 1788 mg F⁻ removed/kg AA. AA surface is amphoteric in nature and can exist as AlOH⁺, AlOH, and AlO⁻. Fluoride binding to AA is proposed to be due to exchange of surface hydroxyl groups, which can be represented by the following reactions.



Observations of a recent study by Valdivieso et al. [27], on temperature and pH effects on zeta potential and fluoride adsorption at the α-Al₂O₃/aqueous solution interface, are also in agreement with the above proposed mechanism. Further it was shown that

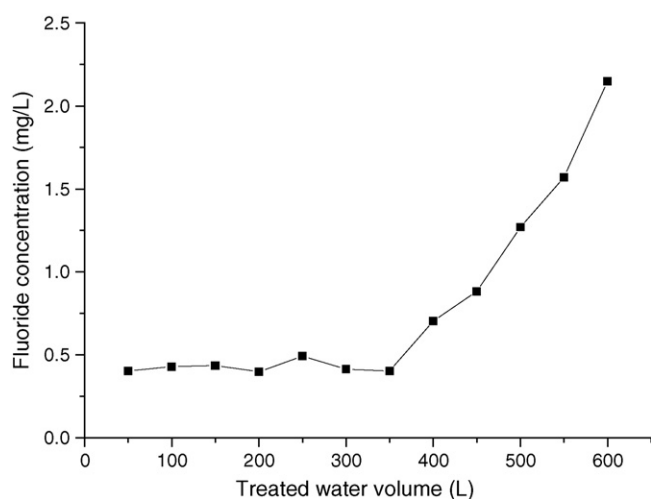


Fig. 1. Fluoride concentration in treated water during a typical defluoridation cycle in DDU S_1 having AA: 3 kg; raw water pH: 7.9–8.0; initial fluoride concentration: 10.5 ± 0.5 mg/L; flow rate: ≈ 9.5 L/h.

at a concentration of $10 \text{ mg F}^-/\text{L}$, F^- chemisorbs onto $\alpha\text{-Al}_2\text{O}_3$ as adsorption takes place even though the surface is electrically negative [27]. This indicates some amount of fluoride uptake can take place even when the surface is in the form of AlO^- .

Reported FUC of AA has ranged from 1000 to 9000 mg/kg AA depending on adsorption conditions [20,25]. Higher FUC are generally reported either from distilled water or when raw water pH is 5–6. Under these conditions, aluminium surface will be in the form, which is conducive for fluoride exchange. Further competitive ions such as HCO_3^- , which can bind to AA surface, are either absent or their effects are minimized [20,28].

Observed FUC in the present study, even at pH 7.8–8.0 and alkalinity of 325 mg/L, is higher than previously reported values under such conditions [20]. This could be due to high influent fluoride concentration or intermittent mode of operation. Fluoride removal by AA has been shown to be highly concentration-dependent and uptake capacity increased with the increase in initial fluoride concentration [20,23]. However, percent removal under batch conditions decreased with the increase in initial fluoride concentration [24]. Our observations are also similar in DDU with respect to FUC. Safe water volume, however, decreased with the increase in initial fluoride concentration (data not shown).

Higher FUC can also be due to the intermittent mode of operation of DDU. Under these conditions, the solid-phase fluoride concentration gradient has a chance to relax completely (approaching equilibrium) during the off periods. This leads to a high concentration gradient between the liquid and the surface of the solid, thus resulting in improved fluoride removal when the unit is used again [23].

3.2. Reuse potential of AA for multiple defluoridation cycles

Defluoridation of drinking water with AA in developing countries can only be cost effective when AA is reused for multiple cycles. The objective of regeneration is to remove all fluoride ions from AA surface, so that it can be effectively reused. Flu-

oride ions lose their attraction and become repelled by alumina, when the pH is >10.5 . Alkali treatment results in stripping the fluoride from AA surface. pH of the media after this treatment will be around 12. Acid treatment restores the fluoride binding potential of AA.

Regeneration procedure should be simple so that it can be easily performed in rural environment. With this in view, procedure described in 2.4 was developed. Exhausted AA was regenerated using 1% NaOH followed by acid treatment. Regenerated AA was reused in subsequent defluoridation cycles. Results showed that the volume of the safe water per cycle in DDU S_1 (with 3 kg AA) was 550 L in the first cycle and remained more or less constant up to five cycles. This showed that the regeneration procedure used is very effective in stripping fluoride ions from AA surface.

Earlier reports with Alcoa F-1, an extensively used AA grade in many laboratory studies as well as in full-scale defluoridation plants, have shown that regeneration is essentially complete by alkali and acid treatment [23,27]. Present study has shown that indigenously manufactured AA grade used in this study can also be effectively regenerated using a simple procedure.

3.3. AA amount in DDU and safe water yield

Four DDUs, S_1 to S_4 (Table 2), were evaluated with 3, 4, and 5 kg AA in the units. This resulted in AA depth increase from 9.0 to 13 cm for 3 and 5 kg AA in S_1 (Table 1). Similar increase was also observed in S_2 to S_4 . As expected, treated water volume (<1.5 mg/L) increased with the AA amount in the unit. For example, volume of safe water increased from 550 to 1050 L for 3–5 kg AA in S_1 (Table 3). Flow rate was mainly controlled by the orifice of flow control device, 9–10 L raw water could be passed through these units. Thus, calculated empty bed contact time (EBCT) with AA varied from 20 to 33 min for 3–5 kg AA. It has been reported that 5 min EBCT is sufficient for fluoride uptake if pH of raw water is around 6 [23]. At this pH, effect of bicarbonate, which is one of the major competing anion for fluoride binding to AA surface, is eliminated due to protonation. Ground water pH is generally in the range of 7.5–8.5. In a “point of use” unit such as DDU, pH decrease prior to defluoridation is not possible. Thus a longer EBCT may be beneficial under these conditions.

3.4. Effect of bed depth on safe water yield

Bed depth for the same amount of AA can be varied by changing DDU specifications. In the present study, bed depth for 3 kg

Table 3
Value of safe water ($\text{F}^- \leq 1.5$ mg/L) in domestic defluoridation units

	S_1 (L)	S_2 (L)	S_3 (L)	S_4 (L)
3 kg	550	450	400	282
4 kg	825	600	500	376
5 kg	1050	875	700	665

Specifications of domestic defluoridation units and raw water characteristics are given in Table 2 and Section 2.2, respectively.

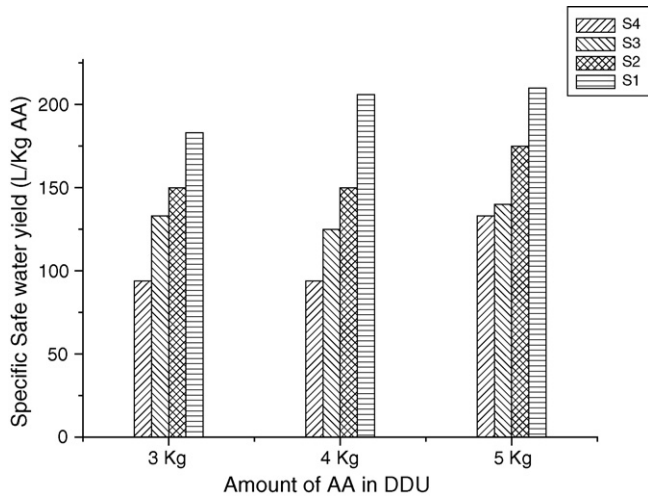


Fig. 2. Specific safe water yield with varying amount of AA in different DDUs having amount of activated alumina was varied from 3 to 5 kg; raw water pH: 7.9–8.0; initial fluoride concentration: 10.5 ± 0.5 mg/L; flow rate: ≈ 9.5 L/h.

AA was in the range of 5–9 cm in different DDU (S_1 to S_4). When AA amount was increased to 4 kg, depth ranged from 6.5 to 11.5 cm (Table 2). Performance of these units would reflect the specific effect of AA depth on safe water yield, as all other conditions are constant.

Specific safe water yield (SSY), expressed as litres of treated water with F^- concentration ≤ 1.5 mg/L per kg AA, ranged from 117 to 183 L in different DDUs with 3 kg AA (Fig. 2). Observed SSY, with 4 kg AA, increased from 94 to 206 L (Fig. 2) as the AA depth was increased from 6.5 cm (DDU S_4) to 11.5 cm (DDU S_1). Similar enhancement in SSY with depth was observed with 5 kg AA.

Adsorption of fluoride onto AA depends on various factors such as raw water characteristics as well as AA grade, particle size, flow rate and adsorbent depth. If the bed depth is decreased, even though the other conditions are maintained constant, concentration of the solute in treated water will rise sharply from the time the effluent is first discharged from the adsorber [29]. Thus there exists a critical minimum depth, which is to be maintained. Cylindrical column unit is considered as the best shape for adsorption. Hence a column unit (diameter 6.5 cm) was operated with 1 kg AA (depth 36 cm). Observed SSY 240 L was considered as the maximum possible for the raw water used in the present study. Efficiencies of domestic defluoridation units were calculated as the percent of that observed in the column unit.

Results showed that efficiency decreased as AA depth decreased. Seventy six percent efficiency could be achieved in DDU S_1 (Table 2; 3 kg AA), where AA depth was 9 cm and it was reduced to 49% in DDU S_4 (Table 2; 3 kg AA), where AA depth was only 5 cm. Maximum efficiency of 87.5% was observed with 5 kg AA in DDU S_1 with a depth of 13 cm.

Variation in SSY with 3–5 kg AA, where average depth was 9.0 cm, is shown in Fig. 3. Total volume of safe water increased with the increase in AA amount. However, SSY (L/kg AA) decreased even though the depth was same. This could be due to following reasons: (a) 9 cm is still not the minimum depth

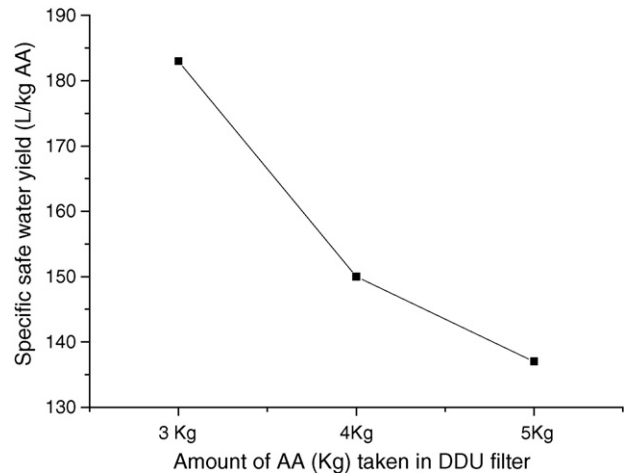


Fig. 3. Specific safe water yield with varying amounts of AA at adsorbent depth of 9.0 cm having AA: 3–5 kg; raw water pH: 7.9–8.0; initial fluoride concentration: 10.5 ± 0.5 mg/L; flow rate: ≈ 9.5 L/h.

required; (b) depth is not the only factor, which determines the breakthrough when the efficiency of two different units having different diameters is compared. As can be seen from Fig. 2, when AA depth was in the range of 11.5–13 cm in S_1 (Table 2) SSY was more or less similar. However, SSY in DDU S_2 with larger cross-sectional area was lower even though AA depth was 11.0 cm. These observations indicate that SSY may depend on depth as well as DDU cross-sectional area.

3.5. A simple model for prediction of SSY

FUC of AA depends on the raw water characteristics as well as AA grade, its particle size, depth and EBCT. There are many reports on the effect of these parameters in batch or fixed bed adsorption system in continuously fed column units [21,23,26].

Models have been proposed for fluoride uptake and for the prediction of length of the adsorption cycle. Such studies with DDU are scarce. Although it is known that cylindrical column units are the most suitable for adsorption system, preferred design for DDU is either bucket or conventional water filter type. Adsorbent depths in these units are determined by their dimensions, which in turn determine SSY. It has been generally observed that AA amount is increased in DDU with an aim to lengthen the defluoridation cycle, without giving due consider-

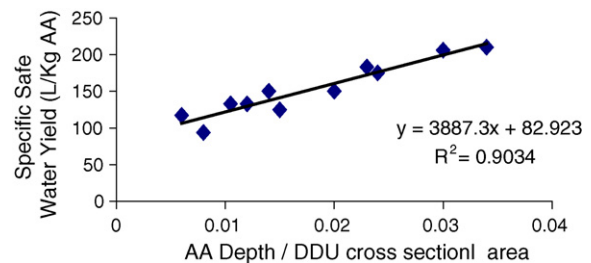


Fig. 4. Relationship between depth/surface area vs. specific safe water yield with varying amount of AA; raw water pH: 7.9–8.0; initial fluoride concentration: 10.5 ± 0.5 mg/L; flow rate: ≈ 9.5 L/h.

ation to its specifications. Hence there is a need for an empirical relationship between SSY and DDU dimensions.

The data derived in this study was fitted to the following relationship.

$$Y = mX + C$$

where Y is SSY and X is (depth/DDU cross-sectional area).

Fig. 4 shows that the experimentally observed SSY can be well represented by the above relationship. Performance of two prototype DDUs distributed by NGO's, in rural areas, were evaluated in the laboratory with the same raw water used in this study. These units had 5 kg AA and AA depth/cross-sectional area was 0.013 and 0.019. Observed SSY were 110 and 145 L, respectively, as against the predicted values of 130 and 155 L. AA grades in these units were different from that used in our laboratory studies. Although SSY depends on various parameters, these results have shown that adsorbent depth/cross-sectional area of DDU is one of the critical factors to be considered in its design.

4. Conclusions

Activated alumina exhibited a maximum fluoride uptake capacity of 2045 mg/L from ground water matrix under the experimental conditions used in this study. Exhausted AA could be regenerated and reused for five defluoridation cycles without much loss in efficiency. Safe water yield in DDU increased with the amount of AA. However, significant decrease in specific safe water yield was observed, when the adsorbent depth was decreased, for the same amount of AA, by changing the diameter of DDU. The variation of SSY with AA depth/DDU cross-sectional area was well represented by a linear relationship.

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