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A high-capacity aluminum hydroxide-based adsorbent for water defluoridation

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ABSTRACT

In this study, the properties and fluoride-uptake capacity of aluminum hydroxide-based (AO) adsorbent has been investigated. AO was synthesized, characterized, and tested in batch and column experiments. The surface area of the AO was found to be $37.7\,m^2\,g^{-1}$. The composition was determined to be 90% $Al(OH)_{2.8}(SO_4)_{0.1}$ (or 78.3% $Al(OH)_3$ plus 10.7% $Al_2(SO_4)_3$) with 10% Na_2SO_4 (as an impurity). The material is X-ray amorphous and scanning electron microscopic (SEM) studies show AO to be a network of fibers with a size range of 200–300 nm. Fluoride uptake was found to be unaffected by sodium salts of chloride and sulfate in concentrations up to 500 mg/L. A reduction of fluoride uptake with increasing concentrations of hydroxide and bicarbonate was ascribed to the pH dependence of fluoride sorption, while phosphate appeared to compete with fluoride for sorption sites. The surface site concentration determined by acid–base titrations is 0.5 meq/g (equivalent to a surface site concentration of 8 sites/nm^2) and an acidic component of 1.4 meq/g. Continuous packed column experiments showed that at a flow rate of 100 empty bed volumes (eBV) per day using deionized water, the fluoride uptake capacity was 26.2 mg F/g. The pH of treated water ranged between 4.4 and 7.0. In solutions representing buffering conditions of Ethiopian groundwaters (pH 8 ± 0.2, 10 mM $NaHCO_3$, 3,000 ppm CO_2) uptake capacities at 100 and 10 eBV/day were 4.65 and 9.0 mg F/g, respectively. Aluminum was initially released in concentrations ranging from 0.6 to 2.0 mg/L in solutions when the pH is less than 5. Initial salt concentrations were in the g/L range. With the introduction of calcite postcolumn treatment, the pH was maintained in the range of 7.5–8.5, which significantly reduced salt concentrations due to gypsum precipitation and prevention of early aluminum release were achieved. Due to its high uptake capacity compared with all commercially available adsorbents for fluoride removal, AO is a highly promising material for water defluoridation both at household and community levels.

Keywords: Fluoride; Adsorption; Aluminum hydroxide; Defluoridation; Ethiopia

1. Introduction

Elevated fluoride groundwater concentrations are associated with volcanic rocks and ashes, but also with arid climates, hydrological properties (e.g. residence time) and soil conditions (e.g. pH and soil type) [1–6]. The release of fluoride to groundwater is dependent on chemical and physical processes that take place between the groundwater and its geological

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environment. Fluorite (CaF_2) is the predominant mineral that controls the dissolved fluoride concentration in the groundwater [2,3,7]. Thus fluoride-rich ground waters are often associated with rocks with low calcium content, or high-pH conditions where sodium bicarbonate dominates the groundwater composition.

The effects of fluoride upon human health have been studied since the early twentieth century. Both the benefits of minimal exposure and the risks of high fluoride doses have been established [8]. While a low daily dose of fluoride is considered to be responsible for preventing dental caries; a higher daily dose has been linked to permanent dental and skeletal fluorosis [9]. Fluorosis has been reported in several parts of the world including Ethiopia, where fluoride concentrations in drinking water exceed the WHO guideline value of 1.5 mg/L [10–15,16]. Many water sources in Ethiopia contain fluoride in elevated concentrations up to 26 mg/L [17]. According to estimates of the Ethiopian Ministry of Water Resources, more than 11 million people in the Ethiopian Rift Valley rely on drinking water contaminated by fluoride [18]. Over 40% of deep and shallow wells are contaminated and over 80% of children suffer from different degrees of dental fluorosis and skeletal fluorosis is increasing, mainly among older people [15].

In areas where alternative drinking water sources are not available, as in the case of most tropical regions of developing countries, treatment of groundwater might be the most prioritized option. Common treatment methods that can be used to reduce fluoride levels in drinking water can be categorized into chemical precipitation by alum, lime, lime and alum and calcium chloride [19], adsorption on to activated alumina and aluminum-based adsorbents, clay and fly ash [9,20–24], ion exchange by synthetic resins and bone char [25–31] and membrane technologies, such as reverse osmosis and electrodialysis [32,33].

Defluoridation technologies implemented in rural Ethiopia seem not efficient enough to remove the unusually high fluoride contents in the ground water of Central Ethiopian Rift Valley. Low-cost methods such as adsorption on clays [22,34] and other locally available materials like diatomaceous earth and bone char [34] have been considered in few studies, but still not applicable due to low-fluoride removal efficiency. Recently, the possibility of using a locally produced aluminum sulfate and lime combination to precipitate fluoride (the Nalgonda technique) has been tested [34]. However, based on operational experiences at community scale, the Nalgonda technique is not simple for daily operation and is not efficient and applicable when fluoride concentrations exceeds 10 mg/L [34]. Activated alumina has been used to remove fluoride in the Wonji-Shoa and Methara Sugar Estates since 1962, but none of the plants are functional at present [22,34], which is attributed to the high running costs associated with import of activated alumina. Hence, there is a need to find a locally available high fluoride uptake capacity defluoridation media for household and small community applications. Preliminary results on the fluoride uptake performance of aluminum hydroxide (AO) have been published recently [35]. The result showed that the AO thermally treated at 300˚C has high fluoride removal efficiency (>90%) and that the granules are hard enough to be packed in a column for continuous operations. It was also shown that the batch adsorption data at ambient pH were fitted to Freundlich isotherm model with a minimum capacity of 23.7 mg F/g.

The objectives of this work are as follows: (a) to undertake chemical and physical characterization of the AO adsorbent, (b) to study the influence of co-existing anions in groundwater on fluoride uptake capacity, (c) to investigate the uptake capacity using surface titration methods and (d) to carry out column experiments to demonstrate its performance under various operation conditions.

2. Experimental

2.1. Adsorbent

The adsorbent (49.89 g), AO, was prepared by mixing locally available aluminum sulfate (100 g) ($Al_2(SO_4)_3.14H_2O$), which is produced by Awash Melkasa Aluminum Sulfate and Sulfuric Acid Factory in Ethiopia, in 500 mL of deionized water under continuous mixing conditions with magnetic stirrer until complete dissolution. The resulting lower pH (2.7) was adjusted to about pH of 7.0 using 2.0 M NaOH [35]. The AO was treated at a temperature of 300°C in a furnace (Carbolite, ELF Model, UK) for 1 h. It was then thoroughly washed with deionized water (repeated rinsing with up to 40 mL/g) to remove Na_2SO_4.

2.2. Analysis of fluoride

A fluoride stock solution (1,000 mg/L) was prepared from 99.0% NaF (Merck, Germany) in deionized water. Standards and samples were prepared by appropriate dilution of the stock solution. The fluoride concentration was measured with a pH meter (713 Metrohm, Switzerland) equipped with ion-selective fluoride electrode (Metrohm 6.0502.150, Switzerland) and Ag/AgCl reference electrode (6.0726.100 Metrohm, Switzerland). Analyses were performed on equal-volume mixtures of sample and total ionic strength adjustment buffer (TISAB), the latter being required to suppress interferences.

2.3. Characterization of adsorbents

The samples (0.1 g) were digested in a microwave digester in a 3:1 mixture (4 mL) of 30% HCl and 65% HNO_3 for 80 min and then diluted to 100 mL using deionized water [36]. The elemental composition (Li, B, Na, Mg, Al, Si, P, Cl, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Cd, Sn, Sb, Ba, La, W, Au, Hg, Ti, Pb, Th, U, Br, Bi, Cs, Nb) was determined by ICP-OES (SPECTRO CIROS^{CCD}, Germany), ICP-MS (Agilent 7500CX, USA), and sulfate was determined by ion chromatography (Metrohm 761, Switzerland). The absolute density was determined using the Pycnometer (MicroMeritics AccuPyc 1,330, USA). The surface area of the sample was determined by N_2 adsorption method (Thermofinnigan Sorptomatic 1,900, Germany). The samples were first outgassed at 110°C and then allowed to cool to room temperature. The X-ray diffraction (XRD) pattern of the AO was recorded by an X-ray diffractometer (X′pert PRO, PANalytica, the Netherlands) using Cu Kα radiation ($\lambda = 0.1542$ nm) with a 0.05°/min step scanned from 5 to 80° in 2θ angle. Scanning electron microscopy (SEM) analysis was carried out using a NOVA NANOSEM (FEI Company, USA) equipped with GAD detector, with an accelerating voltage of 5 kV. The point of zero charge (PZC) was measured by the zeta potential method (Malvern Instruments, [37]). The zeta potential (ζ) of AO was determined as a function of pH. Initially, 0.1 M HCl was added to the AO dispersion, which was then titrated by adding 0.1 M NaOH with a digital buret (BRAND, Germany). After each titrant addition, the pH was measured. The temperature of the scattering cell was fixed at 23 °C.

2.4. Batch experiments to determine the effect of coexisting anions

The effect of anions (HCO_3^-, SO_4^{2-}, Cl^-, and HPO_4^{2-}) on fluoride adsorption was studied in batch mode in the presence of anions that commonly exist in groundwater [38]. The solutions of the required concentration of anions (0–9 mmol/L) were prepared by dissolving the sodium salts of the respective anions in deionized water containing 20 mg/L fluoride. The pH of the solution was determined. Then, 1.6 g/L of AO was added and allowed to equilibrate for 60 min under continuous mixing conditions at room temperature (22 ± 2 °C). The residual fluoride concentration and pH of the solution were determined in the supernatant after overnight settling. Experiments were performed in triplicate. The standard error of the mean (SEM) was calculated as $\mathrm{SEM} = \mathrm{SD}/\sqrt{n}$, where SD is the standard deviation and n is sample size ($n = 3$).

2.5. Surface titration

The acid/base titrations were carried out at pH values between 5 and 10 with 0.5 g AO in electrolyte solution (0.1 M NaCl, 50 mL) under CO_2-free conditions, at a constant temperature of 25°C. The titrants used were 0.1 N NaOH and 0.1 N HCl. Before titration, the AO samples were equilibrated with the electrolyte solution for an hour, gently stirring under a continuous stream of purified, nitrogen with 100% humidity [39,40]. The AO was then rapidly titrated (60 s per titration step) to pH 10. The suspension was then equilibrated for 10 min prior to centrifugation to separate the solid from the solution. Both were then back titrated separately to pH of around 5. After 10 min, the procedure was repeated. The titration was performed by 665 Dosimat (Metrohm, Switzerland), with a combined pH glass electrode (WTW Inolab pH/ION Level 2, Germany) calibrated using Gran titration method [41]. This experiment was performed in duplicate and the statistical analysis was carried out for the two sets of data by calculating the 95% confidence interval for the true mean.

2.6. Column experiments

To evaluate the fluoride removal performance and possible release of contaminants from the filter material during continuous operation, columns of length 11 cm and internal diameter 3.4 cm were packed with AO filter material (1–2 mm particle size) and operated at constant fluoride concentrations (0 and 20 mg/L) and controlled flow rates (10 and 100 empty bed volumes (eBV) per day) using peristaltic pump (ISMATEC, REGIO-CPF Analog, Switzerland). These experiments were conducted in deionized water (DIW) and in buffered solutions (10 mM $NaHCO_3$ and P_{CO2} of 3,000 ppm) to represent the pH and buffer conditions for Ethiopian groundwater in the Rift Valley [42]. The effluent of one of the columns was passed through a container containing calcite ($CaCO_3$, 125 g). This amount of $CaCO_3$ ensured a retention time of around 2.4 h (10 eBV/day) to guarantee sufficient time for the neutralization processes to occur. The effluent of all columns was collected at defined time intervals and examined for pH, aluminum, sodium, sulfate, and fluoride concentration.

3. Results and discussion

3.1. Composition and characteristics of AO

The elemental composition of the AO is summarized in Table 1. The major components that make up more than 96% of the solid phase are aluminum, sulfate, and sodium, and the minor components are iron, silicon, potassium, calcium, manganese, and magnesium. From the analysis, the chemical formula of AO could be formulated as $Al(OH)_{2.8}(SO_4)_{0.1}$ (though the presence of unreacted alum and $Al(OH)_3$ cannot be excluded even though the later was expected as a major product). Therefore, the presence of sulfate and small amount of iron in AO would contribute to the higher fluoride uptake capacity. The sulfate that is associated with Al (0.94 mmol/g) is responsible for the acidity of the adsorbent and hence high fluoride uptake by AO, whereas sulfate content associated with Na (0.68 mmol/g) might be further reduced if the washing efficiency improved. The AO material appears brownish in color since it consists of Fe (0.44 mmol/g) as iron oxide. XRD analysis (data not shown) could not identify any crystalline structures and showed AO to be an amorphous compound. Representative low-magnification SEM image (16,000×) of the sample indicated the presence of a few Na_2SO_4 aggregates and an amorphous Al-hydroxide network of fibers with a size range of 200–300 nm (Fig. 1). It was not possible to differentiate between the presence of $Al(OH)_3$ and traces of alum or solid solutions of $Al(OH)_3$ with sulfate containing hydroxide phases. The results of density measurement showed that the density of AO was 2.39 g/cm^3, that is lower than the density of γ-Al_2O_3 (3.67 g/cm^3) [43]. The surface of AO was positively charged when solution pH was below its PZC (9.57), facilitating fluoride adsorption through the electrostatic attraction between fluoride and adsorbent.

3.2. Effect of coexisting ions on fluoride uptake

The effect of coexisting anions on the removal efficiency by AO is shown in Fig. 2. In the absence of other anions, over 90% of fluoride was adsorbed and the residual pH was 4.76 when no competing ions were present. The results also show that Cl^- and SO_4^{2-} have no significant effect on fluoride adsorption. A decrease in fluoride uptake is noted for HCO_3^-, but this is most likely to be related to an increase in pH with increasing HCO_3^- content, as the uptake is similar, for a given pH value, to solutions where OH^- has been added. Phosphate, however, appears to compete with fluoride. With the addition of 500 mg/L HPO_4^{2-}, fluoride uptake is reduced from around 95 to 75%.

These observations are in agreement with the literature. Maliyekkal et al. [44], have also reported a similar observation for the removal of fluoride using a new adsorbent material, magnesia amended activated alumina. As can be seen from Fig. 2, the error is within the acceptable range.

3.3. Surface properties of AO

The acid/base titrations are shown in Fig. 3. The first forward titration to pH 10.0 require 22.0 mL of 0.1 M NaOH to neutralize the remaining alum and/or $Al(OH)_3$/hydrobasaluminite solid solutions to deprotonate surface sites and dissolve Al ions as $Al(OH)_4^-$. The back titration of the solution (Tit 2) with 10.0 mL of 0.1 M HCl protonates the $Al(OH)_4^-$ species to $Al(OH)_2^+$ and is equivalent to 10 meq/g. The back titration of the solid (Tit 3) with 3.0 mL of 0.1 M HCl neutralizes surface sites. The difference between the forward and the two back titrations (Tit 1 – Tit 2 – Tit 3) is equivalent to the initial sample acidity and has a value of 1.8 meq/g. The repeat procedure (Tit 4, Tit 5, and Tit 6) shows that the volume of titrants required for Tit 4 (6.01 mL) is almost equivalent to the sum of Tit 5 (5.02 mL) and Tit 6 (2.21 mL) and results in a difference of −0.24 meq/g [(Tit 4 – Tit 5 – Tit 6) × (0.1 M/0.5 g)], which is more an illustration of the limits to the accuracy of this method.

The back titrations Tit 3 and Tit 6 have a similar value and result in an average value of 0.52 meq/g. It should be noted that the back titration start at pH 9.1

Table 1
Elemental composition, surface area (SA) and density of AO. Assuming Al to be present as $Al(OH)_3$, the measured composition represents 96.9% of the total weight. The remainder is primarily composed of Fe (24.7 mg/g). All other elements were present in concentrations below 3.0 mg/g

	Al	Na	SO_4	SA (m^2/g)	Density (g/cm^3)	PZC
mg/g	288	31.0	155	37.7	2.39	9.57
mmol/g	10.7	1.35	1.61			
mmol/g Na_2SO_4			0.68			
mmol/g Al–SO_4[a]			0.94			

[a] Al–SO_4 denotes SO_4 associated with Al salts.

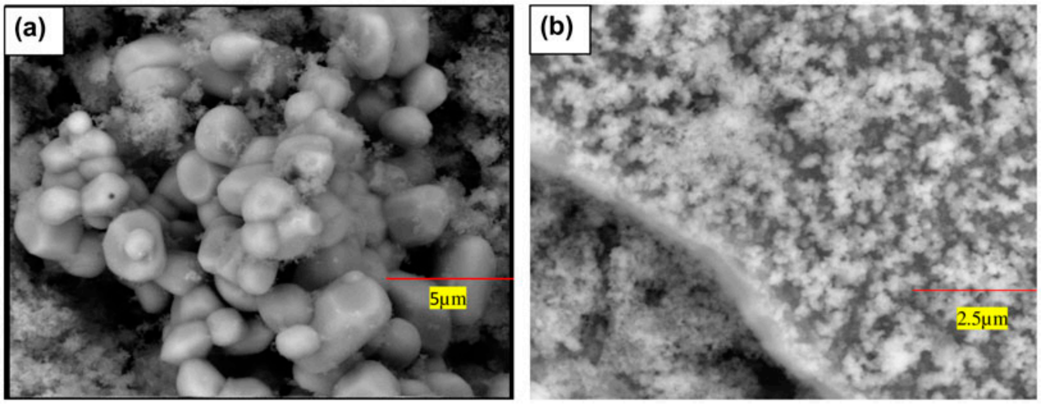

Fig. 1. SEM photographs of AO (magnification; (a) 16,000× and (b) 30,000×).

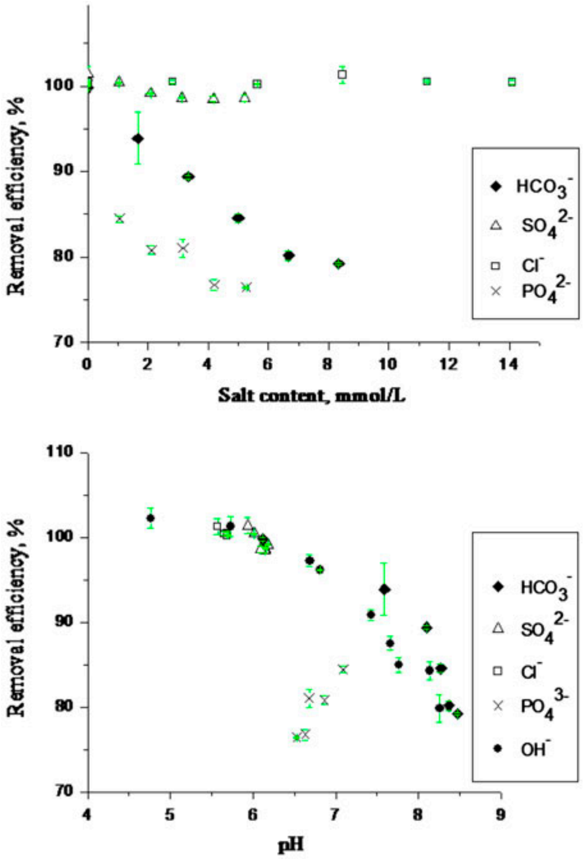

Fig. 2. Effect of coexisting anions on fluoride removal efficiency of AO.

and 8.7, respectively, which is below the PZC of 9.57 (Table 1). The titration thus protonates neutral surface sites, and thus the surface site concentration is 0.52 meq/g. This is equivalent to 8.5 sites/nm^2, which is in excellent agreement with the average site concentration of 8 sites/nm^2 for gibbsite compiled by Karamalidis and Dzombak [45].

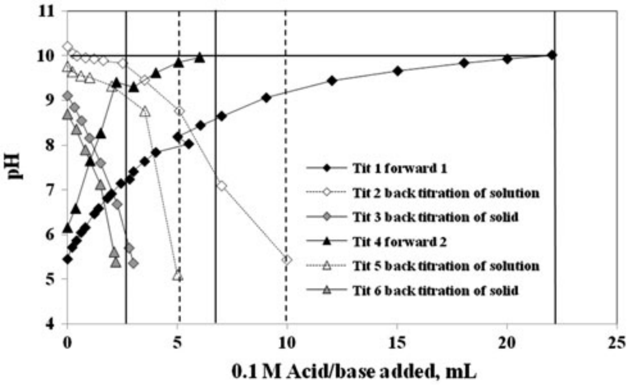

Fig. 3. Acid/base titration of the filter material between pH 5 and 10.

These results indicate that the sample acidity is greater than the surface site concentration. The surface area (37.7 m^2/g) is much lower than that of commercial Al-based products, such as activated alumina, 200–350 m^2/g [46] and a lower fluoride uptake through adsorption on surface sites could be expected. However, we postulate that the acidity increases the fluoride uptake capacity, primarily due to the reduction in pH. This is because the concentration of both protonated surface sites and acid sites, which served as fluoride binding sites, increased significantly with decreasing pH. The statistical analysis for the two sets of data indicates that it is 95% confidence that the true mean of solid acidity and surface site concentration in meq/g lies within the range of (1.23, 2.09) and (0.49, 0.53), respectively.

3.4. Packed bed column performance

The first set of experiments were run at a flow rate of 100 eBV/day using deionized water to follow the pH during column experiments with and without fluoride (0 and 20 mg/L) and to observe the release of potential contaminants. Fig. 4 shows that in the absence of fluoride the pH of the column effluent was consistently around 4. Aluminum was released to the treated water at a level above the U.S. EPA guideline value of 0.2 mg/L [47] within the first 50 eBV, but then declined presumably because readily soluble aluminum salts were flushed out of the column. The sodium and sulfate content of the effluent was high (1,500 and 6,000 mg/L, respectively) during the first flush (<10 eBV for Na and 20 eBV for SO_4^{2-}) and then dropped to below the WHO taste threshold limits (200 mg/L and 250–1,000 mg/L for Na and SO_4, respectively) [16].

In the presence of fluoride, the pH values of the treated water were higher, with an initial minimum of 4.4 but with constantly increasing values thereafter. The higher pH values may be explained by the exchange of fluoride for hydroxide groups at the AO surface. The fluoride uptake capacity to 1.5 mg/L (the WHO guideline value) was about 26.2 mg F/g AO, which is six times greater than the values reported for activated alumina, 3.8−4.5 mg F/g AA [16,48].

The second set of experiments was performed with waters buffered at around pH 8 with 10 mM $NaHCO_3$ and 3,000 ppm CO_2 to represent Ethiopian ground waters from the Rift Valley. At a flow rate of 100 eBV, the pH remained consistently above six, but the fluoride uptake capacity to 1.5 mg/L was reduced to 4.65 mg F/g (Fig. 5(a)), demonstrating the pH dependence of the sorption process. At a flow rate of 10 eBV/day (Fig. 5(b)), the fluoride uptake to 1.5 mg/L increased significantly to around 9 mg F/g. However, the pH was initially quite low (pH 4.7) and coincided with dissolved aluminum concentrations of 0.61 mg/L in the treated water. Aluminum concentrations of up to 2 mg/L were observed in the presence of fluoride after break-through even at the pH of around 8. Given the relative insolubility of $Al(OH)_3$ in the neutral pH range, this observation can possibly be ascribed to the solubilization of aluminum through complex formation with fluoride. As previously observed residual sodium sulfate was washed out

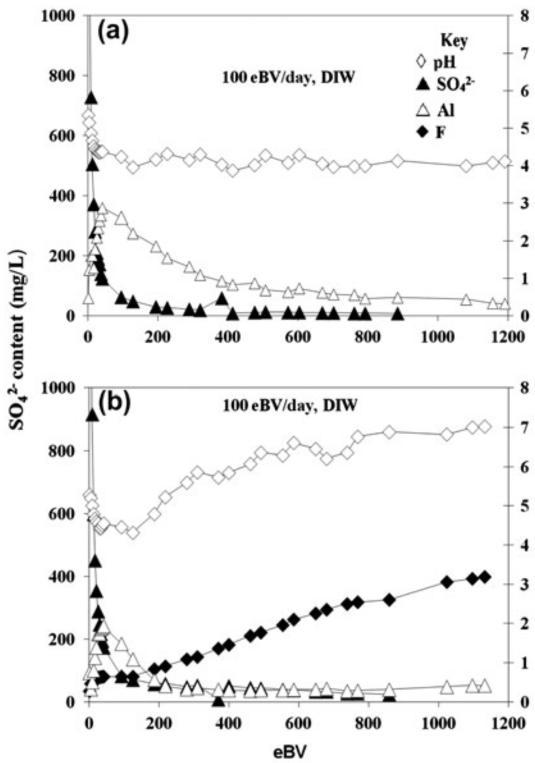

Fig. 4. Fluoride removal from deionized water with influent fluoride concentration of (a) 0, and (b) 20 mg/L at flow rate of 100 empty bed volume/day.

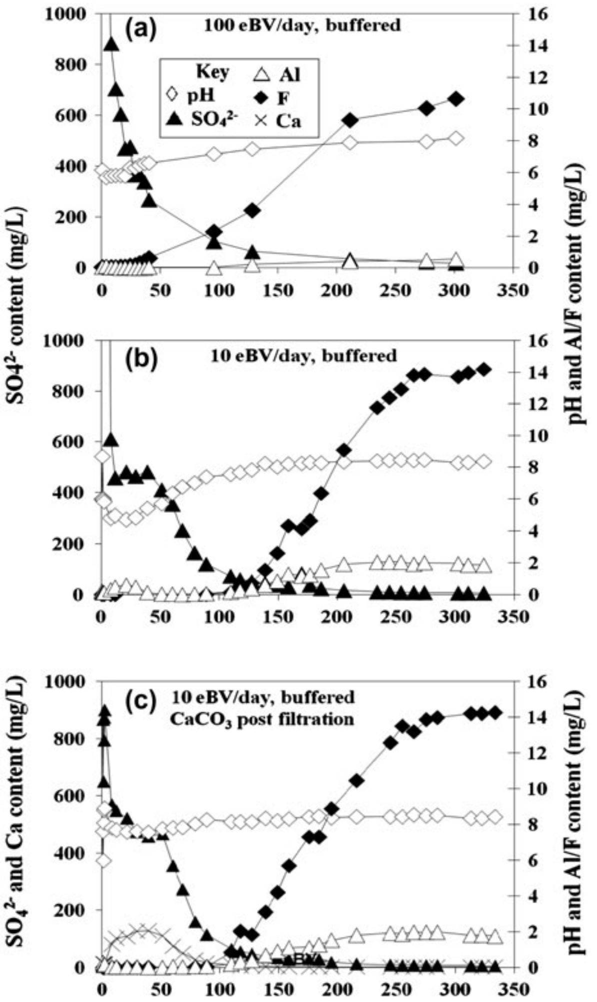

Fig. 5. Fluoride removal from raw water with influent fluoride concentration of 20 mg/L at flow rate: (a) 100, (b) 10, and (c) 10 empty bed volume/day.

within the first 20 eBVs. The sulfate concentrations remained above 400 mg/L for the first 50 eBVs and was probably released as the AO was neutralized by the release of OH^- ions during fluoride sorption.

With calcite postcolumn treatment (Fig. 5(c)) the pH value of the treated water was stabilized at between 7.5 and 8.5 and no early release of dissolved aluminum was observed. The fluoride uptake capacity was about 7.7 and 15.5 mg F/g until breakthrough concentration (1.5 mg/L) and complete exhaustion, respectively. Dissolved calcium in the treated water indicated that the calcite neutralizes the treated water and precipitates dissolved aluminum. However the calcite column did not remove aluminum–fluoride complexes. There was an additional benefit that SO_4^{2-} was also removed to acceptable limits (<500 mg/L) in the first flush (<8 eBV), most likely through the precipitation of gypsum ($CaSO_4{\cdot}2H_2O$).

4. Conclusions

AO material has the potential to be more effective at fluoride removal from groundwater than the widely used activated alumina. The study indicates that it is necessary to control flow rate at about 10 eBVs/day because of kinetic limitations. Moreover, the use of a post-treatment column containing calcite ($CaCO_3$) neutralizes pH and controls both aluminum and sulfate concentrations in the treated water. This approach enabled us to use directly an acid adsorbent while maintaining the high fluoride uptake capacity. The results have encouraged us to test the technology in small communities in the Ethiopian Rift Valley. The technology can be more economical for relatively low fluoride containing groundwater as the life time of the adsorption bed become longer. In addition, the local availability of raw material might be an advantage to sustain the technology. The possibility to produce AO at a large scale also appears to be simple in terms of equipment, procedure and locally availability of materials. The presence of bicarbonate ion in the untreated water and the pH dependence of the process might be considered as limitation of this technology. The results of long-term performance, regeneration potentials, and complete evaluation of overall cost will be reported in due course.

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