Evaluation of bentonite clay in modified and unmodified forms to remove fluoride from water

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ABSTRACT

The feasibility of fluoride adsorption from aqueous solutions using naturally available bentonite clay in both modified and unmodified forms is investigated in this report. Scanning electron microscopy (SEM), energy dispersive X-ray (EDX), X-ray diffraction (XRD), Fourier-transform infrared spectroscopy analysis was applied to describe the structure and nature of modified and unmodified bentonite clay. The physicochemical characteristics of the adsorbent were also investigated for moisture content, pH, apparent density, specific surface area, cation exchange capacity and its point-of-zero charge. SEM images reveal particles are dispersed homogeneously and are irregular in shape. XRD and EDX analyses reveal that the bentonite is composed of seven materials: calcite, silica, alumina, hematite, bornite and green cinnabar, and chloride which are considered as impurities. Raw bentonite clays have shown very low fluoride removal efficiency (47.19%). Modification of the clay surface with HCl and aluminum oxide, on the other hand, increased fluoride removal efficiency to 79.77% and 94.38%, respectively. At 5 mg/L initial fluoride concentration, 10 cm bed depth packed dose of adsorbent, and 180 min breakthrough time, a 2.88 mg/g of fluoride removal capacity was observed. As a result, aluminum oxide modified bentonite clay was chosen for further investigation and the results are not presented here.

Key words: adsorbent characterization, drinking water, fluoride adsorption, low-cost material

HIGHLIGHTS

- Clay minerals adsorption experimentation for low fluoride concentrations (5, 10, and 12 mg/L) was successful.
- Most of the experimentation done so far are in batches using clay-based minerals and leads to shorter reaction times and thus are not at equilibrium.
- Column experimentation using clay minerals was difficult, but this study used the clay as a filter media through surface modification of the adsorbent.

INTRODUCTION

Fluoride has a lot of negative effects on humans, including skeletal and dental fluorosis, but it does have some benefits for enamel strengthening at low concentrations. Long-term exposure increases the risk of developing severe bone deformation, as well as negative health consequences on endocrine systems such as the renal, intestinal, and immune systems (Ghosh et al. 2012; Peckham & Awofeso 2014; Vithanage & Bhattacharya 2015; Jandoubi et al. 2018; Kofa et al. 2017; Ullah et al. 2017). Fluorosis and its complications affect over 200 million people globally (Fewtrell et al. 2006). The World Health Organization (WHO) has set a fluoride limit of 1.5 mg/L in drinking water (World Health Organization 1993). Many nations, the majority of which are in Southeast Asia and South Asia, have naturally contaminated drinking water supplies with fluoride (Rasool et al. 2015). Countries like China, Chile, India, Bangladesh, Hungary, and Mexico have recorded fluoride concentrations greater than 1.5 mg/L (Smedley et al. 2002). Ethiopia, like other developing countries, is dealing with a water shortage as well as fluoride pollution, especially in the Central Rift Valley. It is estimated that over 11 million people in

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Ethiopia’s Great Rift Valley depend on ground water from sources that are contaminated with fluoride (Tekle-Haimanot et al. 2006).

As a result, in regions where the water supply is mostly from groundwater, fluoride removal from the source must be prioritized. It can be reduced or eliminated from drinking water using a variety of technologies. To minimize elevated levels of fluoride in the drinking water source, a variety of methods have already been identified and tested in various parts of the world: precipitation and coagulation, filtration and oxidation, and biological oxidation and ion-exchange, and adsorption and membrane technology (Cox & DiNunzio 1977; Vhahangwele et al. 2014; Singh et al. 2016; Bharti 2017; Maity et al. 2018; Mudzielwana et al. 2018; Talat et al. 2018; Yami et al. 2018; Ye et al. 2018; Gan et al. 2019). Adsorption is commonly used due to the broad variety of natural and synthetic adsorbents available, ease of operation, low cost, and high performance depending on the nature of the adsorbents (Bharat et al. 1996; Srimurali et al. 1998; Biswas et al. 2009; Chen et al. 2011; Paudyal et al. 2013; Zhang et al. 2013; García-Sánchez et al. 2017; Gebbawold et al. 2018; Maity et al. 2018).

Clay minerals, a low-cost adsorbent, have recently generated interest as an adsorbent and have been identified as a key adsorbent for removing anions from ground water (Karthikeyan et al. 2005; Thakre et al. 2010; Gitari et al. 2013; Vhahangwele et al. 2014; Kofa et al. 2017; Assaoui et al. 2018; Mudzielwana et al. 2018). Clay materials including bentonite, gibbsite, kaolinite, and lignite were used to remove anions from aqueous solution (Hang & Brindley 1970; Madsen 1977; Goldberg 1989; Apambire et al. 1997; Ronseqvist 2002; Steudel et al. 2009; Ismadji et al. 2015). It is recommended to make an adsorbent suitable for groundwater defluoridation for economic and practical reasons, particularly in developing countries like Ethiopia (Walther 2009). However, for long-term defluoridation of drinking water, especially in countries affected by fluoride, the search for suitable fluoride adsorbents that can be produced locally continues to be of critical importance. Aluminum oxide (AOMB), hydrochloric acid (HCl)-treated (ATB), and raw bentonite (RB) was investigated for removal fluoride efficiency in a fixed-bed column. Material characterization techniques like energy dispersive X-ray (EDX), Fourier-transform infrared spectroscopy (FT–IR), X-ray diffraction (XRD), and scanning electron microscopy (SEM) were used to characterize the materials. The results of this study are beneficial to water utilities that have elevated fluoride levels in their water sources.

**MATERIALS AND METHODS**

**Reagents and preparation of adsorbents**

Except for the raw bentonite, all the reagents used in this analysis were analytical grade. The following is a list of reagents and chemicals used for this research work. All chemicals were provided by Merck S.P.L, Worli, Mumbai, India-40001. Sodium fluoride (NaF), aluminum sulfate Al₂(SO₄)₃.16H₂O, SPANDS reagent, zircony-chloride, sodium–arsenate, Methylene Blue (25 gm), HCl, potassium chloride (KCl), potassium bromide (KBr), sodium hydroxide (NaOH), acetic acid, sodium carbonate (Na₂CO₃), sodium sulfate (Na₂SO₄), potassium dihydrogen phosphate (KH₂PO₄), potassium nitrate (KNO₃), and sodium chloride (NaCl). The following laboratory equipments were used: magnetic stirrer, analytical balance meter, oven, vacuum filter, crucible, volumetric flasks, beakers, and plastic wash bottles.

The ultra-pure water was used to wash the raw bentonite clay samples obtained from India. After that, the washed bentonite sample was dried in an oven for 24 h at 105 °C. The sample was then minced with a hand crusher and made ready for use. The raw bentonite clay was adjusted according to Eren & Afsin (2009), where 0.4 M HCl aliquots were mixed with 150 g of base material (bentonite sample). The sample was frequently washed with ultra-pure water (reverse-osmosis water) and sun-dried before the addition of 0.4 M HCl. Then, the mixture was stirred at 60 °C for 2 h using an incubator shaker. The sample was then filtered and the sample cleaned with ultra-pure water until all residual trace acid was removed and the filtrate pH was neutral. The filtrate was then oven-desiccated for 24 h at 105 °C, crushed, and sieved into particle sizes ranging from 0.212 to 2 mm, and labeled as acid-treated bentonite (ATB). To make the aluminum modified bentonite sample, 20 g of Al₂(SO₄)₃.14H₂O was dissolved in 100 mL of double-distilled water in a beaker. Then, 60 g of clay mineral was mixed with 900 mL of double ultra-pure water. Using an incubator shaker, the clay solution was slowly applied to the alum solution while constantly stirring for 60 min. The sample was labeled Al³⁺-modified bentonite (AOMB) clay once it had been purified and washed with deionized water and equilibrated for 24 h. Vhahangwele et al. published a study that inspired this practice (Vhahangwele et al. 2014).
Adsorbent characterization techniques

The physical properties of the adsorbent materials were characterized for moisture content (%), apparent density (g/cm³), pH, particle density, and pH at point-of-zero-charge (pHpZC). To evaluate the pH of every sample, 10 g of sample was placed in a 100-mL beaker, 20 mL of ultra-pure water was added, and the mixture was agitated at 330 rpm for 30 min. The pH of each sorbent sample was determined in triplicate using the pH meter WTW INOLAB pH 720 (Allen 1999). Apparent density of the adsorbent was determined as reported by Huerta-Pujol et al. (2010) and the moisture content of each adsorbent sample was estimated using the American Standard Testing Method as a guideline (Allen 1999).

The functional groups of the samples were determined using Nicolet iS50 FT-IR spectrophotometer (USA) to characterize functional groups in the bentonite sample and to fingerprint specific minerals. For all spectra, the percentage of absorbance with respect to wavelength (cm⁻¹) was plotted at room temperature in the range 400–4,250 cm⁻¹. The PAN analytical XRD instrument was used to conduct the XRD analysis, which determined the phase of a crystalline substance. The XRD analysis was performed on unit cell dimensions with Cu radiations of Kα1: 1.54205 Å, Kα2: 1.544426 Å, Kα2/Kα1 intensity ratio: 0.50, Kr: 1.541874 Å, Kβ: 1.392250 Å. The X-ray tube operated at 45 kV and 40 mA, and the diffractometer’s 2θ angle was moved from 5° to 80.002° scan rate with a phase size of 0.02° and time per step of 36.195 s, with a continuous form of scan; minimum step size Ω = 0.001; minimum step size 2θ = 0.001; copper anode material; and an anodized aluminum sample holder. Before being put in the specimen room, the samples were washed in an acetone solution. The sample holder was placed in the X-ray diffractometer. Data were analyzed using X’pert high score plus program. SEM was used to obtain information about the sample’s surface topology, composition, and properties by exposing the samples to beams at magnifications of ×1,000, ×5,000, and ×10,000. These samples were also analyzed using EDX.

The pHpZC of the adsorbents: The surface characterization of metal oxides/hydroxides relies heavily on pHpZC. pHpZC calculates how an adsorbent adsorbs ions in an aqueous solution during the adsorption process. The salt supplement method was used to calculate the pHpZC of untreated, ATB, and AOMB clay (Farooq et al. 2012; Dayananda et al. 2014). A sequence of 100 mL flasks were filled with 40 mL of 0.1 M KCl, 0.01 M KCl, and 0.001 M KCl. The initial pH (pHi) of the solutions was balanced between 2.8 and 12 using 0.1 M of NaOH and HCl. The pH of the mixture was determined with a pH meter (WTW INOLAB instruments pH 720). By adding 0.1 KCl, the solution added to each tube volume was precisely balanced to 50 mL. In addition, 0.5 g of untreated adsorbent (i.e. bentonite clay) was applied, and the mixtures and tubes were kept in an orbital incubator shaker (Nicolab instruments, New Delhi, India) for 24 h at 30°C and, then kept for 48 h. The solutions were filtered after equilibration, and the final pH of the filtrate (pHf) was calculated. The disparity between pHi and pHf values was plotted against pHi (ΔpHi = ΔpHf – pHf). AOMB and ATB clay were treated in the same way. The validity of the procedure was explained by Kumar et al. (2011) for nano-alumina.

Surface area (SSA) and cation-exchange capacity (CEC): CEC is a measurement of exchangeable mineral charge that is described in milliequivalents (meq) per 100 g of dry clay. A larger CEC value means more layer charge and, as a result, more surface activity. As a result, CEC is a proxy for the forces of contact between the molecules and clay surfaces that surround it. Methods like pH equilibrium (Equation (1)) (Rihayat et al. 2018) and methylene blue (MB; Equation (2)) (Kahr & Madsen 1995) were used to examine, associate, and determine the CEC value, and also to investigate the effect of particle size on the CEC value of the raw bentonite (RB), ATB and A13+-modified bentonite clay (AOMB).

Using the pH equilibrium method, Rihayat et al. (2018) methods were followed when measuring and calculating CEC values. A 1 M acetic acid solution was prepared, and 25 mL of the solution was added to a beaker glass containing 5 g of different particle size bentonite (0.212 mm, 0.425 mm, 6 mm, and 1.25 mm). A magnetic stirrer was used to stir the mixture for 1 h. The pH of the supernatant was determined. All the measurements were taken three times, and the average and standard deviations were calculated.

\[
\text{CEC (meq/100 g of clay)} = (\text{pH observed} - \text{pH acetic acid})\times 22
\]  
(1)

The clay was combined with ultra-pure water to form a homogeneous slurry was collected to extract the CEC using the methylene blue (MB) titration technique. The mixture was slowly added to a known concentration of MB and mixed using a magnetic stirrer for 1 min. A drop from the mixture was removed and placed onto filter paper and a bright blue radiance around the dim blue of the droplet was observed. The blue radiance on the filter
paper faded once the reaction between the bentonite and MB ended, and the amount of MB reported decreased.

\[
\text{CEC (meq/100 g of clay)} = \frac{100}{F \times V \times NMB}
\]

(2)

where \( F \) is weight of the sample, \( N \) is the MB solution normality (i.e. 0.028 N), and \( V \) is the necessary volume of MB at the time of titration.

To determine the surface area of the adsorbents, Equation (3) was used, following the procedure developed by Kahr & Madison (1995).

\[
\text{SSA} = Mf \times 130 \times 6.02 \times \frac{10^{-2} \text{m}^2}{g}
\]

(3)

where \( Mf \) is the MB adsorbed per 100 g of clay and SSA is specific surface area in \( \text{m}^2/g \).

**Experimentation of fluoride adsorption**

The raw and synthesized bentonite clay was checked for fluoride adsorption using a fixed-bed column of a borosilicate tube with an internal diameter: height ratio of 0.05. The diameter: height ratio of columns was varied between 0.0375 and 1, which was believed to be effective for reactions to occur (Sulaiman et al. 2009; Ma et al. 2011; Abu Bakar et al. 2019). To prevent the adsorbent from floating, the column was filled with the necessary amount of adsorbent material between two layers of glass wool at the top and bottom. Using a peristatic pump, the column was continuously fed fluoride-contaminated water at a desired volumetric flow rate of 15 mL/min as shown in Figure 1.

A blank column operation was also used to make sure the filter would not change the fluoride concentrations of the inlet solution. At a predefined time, samples were collected in a beaker (5 L) at 30-min intervals and the residual fluoride level in the effluent was measured using a spectrometer at known wave length (570 nm). The breakthrough time (\( t_B \)) was recorded when the point of concentration reduced to 1.5 mg/L, which is WHO guideline for drinking water of fluoride content.

The fluoride removal efficiency of the three adsorbents were evaluated for experimental runs on initial influent fluoride concentrations of 5 mg/L, flow rate of 15 mL/min and 10 cm bed adsorbent depth.

The mean values were recorded after all experiments were carried out in triplicate. Equations (4) and (5) were used to calculate the percentage removal and adsorption potential, respectively.

\[
q_e = \frac{C_0 - C_e}{m} \times V
\]

(4)

where \( q_e \), \( C_0 \), \( C_e \), \( m \) and \( V \) are the adsorption capacity in mg/g, the initial fluoride content, the effluent concentrations (mg/L), adsorbent mass (g), and the volume of solution (L), respectively.

**Figure 1 | Schematic diagram of the fixed-bed column.**
Maximum removal efficiency (R%) is calculated by using Equation (5):

\[ R(\%) = \left( \frac{C_0 - C_e}{C_0} \right) \times 100 \]  

(5)

where \( R \), \( C_0 \) and \( C_e \) are the removal efficiency (%), the initial fluoride concentration and effluent concentration (mg/L), respectively.

RESULTS AND DISCUSSIONS

Characterization of the adsorbent

Physical properties

RB, ATB, and AOMB had moisture content values of 1.67%, 0.345%, and 0.104%, respectively. In contrast to RB, the acid and alum alteration of the adsorbent did not appear to induce a noticeable difference in the moisture content of the adsorbents.

The apparent density, which is a measure of the compactness of the clay minerals, of the RB, ATB, and AOMB was 2.62 g/cm\(^3\), 1.23 g/cm\(^3\), and 1.25 g/cm\(^3\), respectively. The RBs were slightly denser than the improved ones. The small density difference between the raw and modified bentonite may be due to the organic content of the clay. The starting materials for clay can disappear during modification due to its volatilizing nature, according to the literature (Pendyal et al. 1999).

The pH value of the clay content was used to assess whether it was acidic or alkaline. RB, ATB, and AOMB had pH values of 7.16, 5.8, and 7.6, respectively, suggesting that the substance is more neutral. As per the literature (Nwosu et al. 2018), the pretreated clay samples had pH values of 7.2.

Surface morphology

SEM results for bentonite samples at ×1,000, ×5,000, and ×10,000 magnification (Figure 2(a), 2(b), 2(c), respectively) were used to clearly identify all the morphological clay properties and larger interactions of the samples in SEM at higher resolutions. SEM images indicate irregularity in shape and show the dispersion of clay minerals, which could be predominantly silica and alumina.

Figure 2 | Micrographs of SEM analysis of the RB (a, b, and c are magnified by ×1,000, ×5,000, and ×30,000 respectively).
Mineralogy

The XRD analysis of the adsorbents is shown in Figure 3. The mineralogical and crystallographic characterization of these samples are shown in Table 1. The peaks in Figure 3 show that the three samples have the following compositions in common: alumina ($\text{Al}_2\text{O}_3$) = 17%, calcite ($\text{CaCO}_3$) = 22%, silica ($\text{O}_2\text{Si}$) = 22%, bornite ($\text{Cu}_5\text{FeS}_4$) = 8%, hematite ($\text{Fe}_2\text{O}_3$) = 16%, quartz ($\text{SiO}_2$) = 22%, green cinnabar ($\text{Cr}_2\text{O}_3$) = 16%, and burnt ochre ($\text{Fe}_2\text{O}_3$) = 20% (Figure 3). The other crystallographic parameters are shown in Table 1. The crystallographic parameters are calculated density 2.65 g/cm$^3$, volume of cell (10$^6$ pm$^3$): indicating that the crystal system of hexagonal structure, $a$: 4.9134 Å, $b$: 4.9134 Å, $c$: 5.4053 Å, Alpha 90.0000°, Beta 90.0000°, Gamma 120.0000°. The maximum peak list for quartz, silica and calcite (Table 1) is expressed in terms of d-spacing: 3.34200, 2θ 26.652°, intensity 100%.

Figure 3 illustrates variations in the crystallinity of the adsorbent. The well-defined peaks display the crystalline nature of the bentonite clay, while the hollow peak shows the non-crystalline unstructured nature of the bentonite clay.

Chemical composition

The chemical composition of three samples were analyzed using EDX, as shown in Figure 4. From the results of SEM–EDX spectrum, the untreated clay consisted of Al, Si, Na, Mg, O, K, Ti, and Fe in every spectrum. The spectrum reveals (Ca,K,Mg,Fe)x$\text{Al}_2\text{O}_3\cdot y\text{SiO}_2\cdot z\text{H}_2\text{O}$, and the value of composition is shown in Table 2. The EDX results for the three samples shows that the major composition is Si, Al, and Fe with 23.79%wt, 10.55%wt, and 14.84%wt respectively for the RB samples. The other elements like Cl, Na, Mg, Ti, Ca, and K exist at lower percentage weights. They are considered as impurities of the material and can be caused if the purification of bentonite is not clean and if the oven conditions are not correct.

FT-IR analysis

Figure 5 shows the spectra of FT-IR for RB, ATB, and AOMB clay before and after fluoride adsorption: (a, b) RB before and after fluoride adsorption, (c, d) ATB before and after fluoride adsorption, and (e, f) AOMB before and after fluoride adsorption.
after fluoride adsorption. Samples spectra reveal the existence of various functional groups in the sample layer. There is a shift in absorbance spectra in the same wavelength. This shows that the modification has improved the surface activity of the adsorption onto clay minerals. The deterioration or loss of such bands, in combination with the above-mentioned change in chemical composition and acidity, suggests limited reduction of Fe, Al, and Mg from the clay matrix. The range of wavenumber and resolution of the spectra were 400–4,250 cm\(^{-1}\) and 0.145 cm\(^{-1}\), respectively. The Al–Al–OH group deformation peaks at 444.51 cm\(^{-1}\), 464.01 cm\(^{-1}\), and

**Figure 4** | SEM-EDX micrographs of (a) RB with (b) elemental counts per second/eV for RB, and (c) ATB with (d) Elemental counts per second/eV for ATB, and (e) AOMB with (f) Elemental counts per second/eV for AOMB.

**Table 2** | EDX characterizations of the elemental composition (percent by weight) of RB, ATB, and AOMB

<table>
<thead>
<tr>
<th>Elements</th>
<th>O</th>
<th>Si</th>
<th>Fe</th>
<th>Al</th>
<th>Cl</th>
<th>Na</th>
<th>Mg</th>
<th>Ti</th>
<th>K</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDX (%wt)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Before treatment</td>
<td>37.91</td>
<td>23.79</td>
<td>14.84</td>
<td>10.55</td>
<td>0</td>
<td>2.82</td>
<td>1.80</td>
<td>2.24</td>
<td>1.35</td>
<td>0.66</td>
</tr>
<tr>
<td>After acid treatment</td>
<td>24.04</td>
<td>10.95</td>
<td>9.36</td>
<td>6.59</td>
<td>3.8</td>
<td>3.4</td>
<td>0.84</td>
<td>0.75</td>
<td>0.24</td>
<td>0.11</td>
</tr>
<tr>
<td>After Al-modification</td>
<td>45.67</td>
<td>16.83</td>
<td>15.81</td>
<td>13</td>
<td>0</td>
<td>2.57</td>
<td>1.16</td>
<td>2.46</td>
<td>2.03</td>
<td>1.74</td>
</tr>
</tbody>
</table>
459.99.55 cm$^{-1}$ are close to those recorded by Paralo et al. (2014). The bending and stretching vibrations of the hydroxyl groups at 3,625 cm$^{-1}$ and 1,640 cm$^{-1}$ are due to the hydroxyl groups in the silicate layers in the FT-IR range of raw montmorillonite. The calcite impurity that has not been extracted during the purification of raw montmorillonite is responsible for the band at 1,430 cm$^{-1}$.

Peaks at 3,623.22 cm$^{-1}$ and 3,702.31 cm$^{-1}$ in the octahedral layer were due to inner surface N–H stretching and an inner hydroxyl group with more Al–OH, respectively. Nwosu et al. (2018), also reported the same results at bands at 3,697 and 3,620 cm$^{-1}$, respectively. More precisely, the spectra for AOMB Figure 5(e) and 5(f) show

**Figure 5** | FT-IR spectra of unmodified and modified bentonite clay before and after fluoride adsorption for the three adsorbents.
that there is almost no alteration in the spectral pattern before and after adsorption. This means that physical forces are more likely than chemisorption to adsorb fluoride onto the AOMB adsorbent.

**CEC**

The higher CEC values shown in Table 3 by applying the MB method implies that a greater layer charge has occurred due to surface activity. RB therefore can have a higher CEC, which shows the existence of the contact forces between the surrounding molecules and clay surface.

The results obtained with the pH equilibration method (Figure 6) were compared for different particle sizes. It is observed that both methods (refer to Table 3 versus Figure 6) resulted in similar CEC value for all adsorbents.

By comparing the MB method (Table 3) with the pH equilibrium method (Figure 7), the CEC of the three adsorbents were found to be relatively similar.

The smaller particle provides more surface area and leads to more sorption sites and to greater sorption. The increase in particle size from 0.212 mm to 1.25 mm does not show any change in CEC per SSA values for AOMB (Figure 7(a)) and there is a slight decrease for RB as shown in Figure 7(b). As a result, increasing particle size decreases the material’s sorption rate.

**Fixed-bed adsorption study on fluoride removal**

The effect of various parameters such as initial fluoride concentration, flow rate, and adsorbent bed depth on column adsorption was investigated. Different initial concentrations of fluoride (2, 5, and 10 mg/L) were tested for constant flow rate of 15 mL/min. Adsorbent packing depths of 2, 6 and 10 cm using 1.5 cm diameter borosilicate glass column (Figure 1) with 20 cm height were subjected to continuous flow of the fluoride solution in a downward direction. However, in this study, the materials were tested for only 5 mg/L of fluoride concentration, 10 cm bed depth, and 15 mL/min flow rate.
Figure 8 compares the RB, ATB, and AOMB adsorption capacity and fluoride removal performance. At 60 min, RB clays have a very poor fluoride removal efficiency (47.19%). Surface H⁺ and cation modification with aluminum oxide, on the other hand, increased fluoride removal efficiency to 79.77% and 94.38% (using ATB and AOMB, respectively) at 60 min. The increased fluoride removal capability of the aluminum oxide-amended clays is thought to be due to the presence of aluminum oxide (hydroxide). When compared to RB and ATB, the figure clearly shows that AOMB has a higher fluoride adsorption capability. The total Al in AOMB (13.08 wt% or mol Al/kg in Table 1) is primarily responsible for this.

By plotting \( C_t/C_0 \) against time, \( t \) (min), as shown in Figure 8, breakthrough profiles were plotted for each parameter to analyze the best condition for efficiently removing fluoride. The field under the breakthrough curve is equal to the maximum column capacity, \( q \) (mg/g), for a given parameter. Higher fluoride removal capacity of 2.88 mg/g was observed at 5 mg/L initial fluoride concentration, 10 cm bed depth packed dose of adsorbent, and 180 min breakthrough period due to fluoride’s strong affinity for higher density and stable electropositive species of Al³⁺.

**Mechanism of adsorption**

The effectiveness and efficiency of the adsorbent is dependent on the material reactivity of the adsorbent. The pH is a useful variable for the indication of the adsorption property. In this study, the behavior of the adsorbents was briefly elaborated on the basis of the pH\(_{PZC}\) (isoelectric point) and mean of pH value. The salt supplement method was used to determine the pH\(_{PZC}\) of the adsorbents. The pH\(_{PZC}\) of (a) RB (b) ATB, and (c) AOMB is shown in Figure 9. The pH\(_{PZC}\) values for RB, ATB, and AOMB were 7.1, 5.8, and 7.8, respectively. However, for ATB, ΔpH versus pH\(_i\) plot shows that the pH\(_{PZC}\) touches the x-axis at 5.9. The clay surface is negatively
charged when the pH is above pH_{PZC}, and positively charged when the pH is below pH_{PZC}. The high pH_{PZC} in both raw and AOMB indicates that the clay is dominated by alumino-silicate materials and other cations or oxides. The addition of acid and aluminum oxide to raw bentonite clay raises the pH_{PZC}, extending the pH spectrum for anions adsorption. The AOMB clay is supposed to have a higher adsorption potential for fluoride ions than the RB clay, according to this result. Vhahangwele et al. observed a rise in pH_{PZC} of bentonite clay after modification for AOMB (Vhahangwele et al. 2014).

Generally, adsorption is caused by the electrostatic attraction between the fluoride ion and the main constituents of bentonite clay.

**CONCLUSIONS**

The experimental results show that ATB and AOMB clay can be used for fluoride removal as an adsorbent in a fixed-bed adsorption process.

SEM micrographs confirmed that the RB surface was rough, which favors the uniform application of aluminum surface coating. The EDX spectra shows Al^{3+} was successfully deposited on the clay material surface, which was confirmed by the presence of more aluminum spectra on the modified bentonite clay than on the RB. The uptake of fluoride occurred at pH_{PZC} >7 for RB, pH_{PZC} >5.9 for ATB, pH_{PZC} > 7.8 for AOMB by established hydroxyl groups between the fluoride ions and sorbent surface in the fluoride-contaminated drinking water. Because of their surface structure, bentonites have a lot of potential as adsorbents. Modification of the surface of bentonite enhances the adsorptive capacity by increasing surface binding sites. The presence of exchangeable cations on its surface makes alteration easier. The acidic and neutral surfaces of the samples examined indicate a positive capacity to remove different contaminants such as anions like fluoride in this case. SEM images reveal that particles are dispersed homogeneously and are irregular in shape. XRD and EDX analysis reveals that the bentonite is composed of major minerals such as SiO_{2}, Al_{2}O_{3}, Fe_{2}O_{3}, and CaCO_{3} and other impurities.

![Figure 9](http://iwaponline.com/wst/article-pdf/doi/10.2166/wst.2021.220/905439/wst2021220.pdf)

**Figure 9** | Plot of pH_{PZC} of RB, ATB, and AOMB.
In the column studies, AOMB clay showed maximum adsorption of fluoride in all operating conditions compared to the raw and ATB. Also, the maximum adsorption of fluoride in raw bentonite is more delayed. Fluoride concentration decreased with increasing adsorption doses; the permitted fluoride level in drinking water (<5 mg/L) was obtained for an adsorbent bed depth packed with AOMB. The application of advanced technologies for fluoride removal for small communities residing in rural areas is not feasible due to its complexity and affordability. In developing countries like Ethiopia, cost-effective and simple defluoridation technologies, like the AOMB clay minerals as reported in this work, may be preferable to advanced technologies. AOMB has an advantage of reducing fluoride levels in groundwater due to its good adsorption capacity, ease of preparation, local availability, and it is a proven filter for drinking water.

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CONFLICTS OF INTEREST

The authors declare no competing interests.

ETHICAL APPROVAL

This research work complies with the research project’s ethical standard.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES


Rosenqvist, J. 2002 Surface Chemistry of Al and Si (Hydr)Oxides, with Emphasis on Nano-Sized Gibbsite (α-Al(OH)3). [Doctoral thesis, comprehensive summary], Umeå University, Sweden.


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