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. SEM, EDX, XRD, and FT-IR analysis are applied to describe the structure and nature of unmodified and modified bentonite clay. The physicochemical characteristics of the adsorbent were also investigated by its moisture content, pH, apparent density, specific surface area, cation exchange capacity and its point of -zero charge determination. SEM image reveals 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 are considered as impurity. Raw bentonite (RB) clays have shown very low fluoride removal efficiency (47.19%). Modification of the clay surface with HCl (ATB) and aluminum oxide (AOMB), 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 the result, aluminum oxide modified bentonite clay was chosen for further investigation and its result is 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 batch using clay-based minerals and leads to shorter reaction times thus far from equilibrium.
- Column -experimentation using clay minerals was difficult but this study apply 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; Jendoubi 2017; Kofa et al. 2017; Ullah et al. 2017). Fluorosis and its complications affect over two-hundred million people globally today (Fawcett et al. 2006). The World Health Organization (WHO) has set a fluoride limit of 1.5 mg/L in drinking water (Organization WH 1993). Many as Seventy 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 Eleven million population in Great Ethiopia’s Rift Valley depend on fluoride-contaminated ground water sources (Tekle-Haimanot et al. 2006).

As a result, in regions where the water supply is mostly from groundwater, fluoride removal from source of water must be prioritized. It can be reduced or eliminated from drinking water using a variety of technologies. To minimize the elevated level of fluoride from source of drinking water, a variety of potential drinking water methods were already identified and tested in various parts of the world. The following are the fluoride removal methods: Precipitation and coagulation, filtration and oxidation, and biological oxidation and ion-exchange, Adsorption and membrane technology (Cox & DiNunzio 1977; Vhahangwele et al. 2014; Singh et al. 2016; Bharti 2017; Maity et al. 2018; Mudziwana et al. 2018; Talat et al. 2018; Yami et al. 2018; Ye et al. 2018; Gan et al. 2019). Adsorption is one of these processes that 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; Gebrewold et al. 2018; Maity et al. 2018).

Clay minerals, a low-cost adsorbent, have recently piqued researchers’ 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; Mudziwana 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; Rosenqvist 2002; Steudel et al. 2009; Ismadji et al. 2015). As a result, it is highly recommended to make an adsorbent suitable for groundwater de-fluoridation if it has an economic viability and its practicality, particularly in developing countries like Ethiopia (Walther 2009). However, for long-term defluoridation of drinking water, especially for countries affected by fluoride, hunting for suitable fluoride adsorbents with the possibilities of local production continues to be of critical importance. Bentonite clay synthesized by aluminum oxide, HCl, and raw was investigated for removal fluoride efficiency in a fixed bed column in this research work. Material characterization techniques like EDX (electro diffraction x-ray), FT-IR (Fourier-transform infrared spectroscopy), XRD (X-ray diffraction), and SEM (scanning electron microscopy) were used to characterize the materials. The results of this study would be beneficial to water utilities that have elevated fluoride levels in their source of water for consumption.

MATERIALS AND METHODS

Reagents and preparation of adsorbents

Except for the raw bentonite, all of the reagents used in this analysis are analytical grade. The following is a list of reagents and chemicals used for this research work. All chemicals are provided by Merck S.P.L, Worli, Mumbai, India-40001. Sodium Fluoride (NaF), Aluminum Sulphate Al₂(SO₄)₃.16H₂O, SPANDS reagent, Zircony-chloride, Sodium-Arsenate, Methylene Blue (25 gm), Hydrochloric acid (HCl), Potassium chloride(KCl), Potassium bromide, Sodium Hydroxide (NaOH), (KBr), Acetic acid, Sodium carbonate (Na₂CO₃), Sodium Sulphate (Na₂SO₄),Potassium dihydrogen phosphate (KH₂PO₄), Sodium Carbonate (Na₂CO₃), Potassium Nitrate (KNO₃), and Sodium Chloride (NaCl). Moreover, the following laboratory equipment’s 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 in India. After that, the washed bentonite sample was dried in an oven for 24 hours at 105 °C. The sample was then minced with a hand crusher and made ready for use. According to Eren and Asin 2009, the raw bentonite clay was adjusted (Eren & Asin 2009), where 0.4 M HCl aliquots was mixed with 150 gm of base material (bentonite sample). Moreover, before modifying by a 0.4M HCl, the sample was frequently washed with ultra-pure water (RO) and sun-dried. Then, the mixture was stirred at 60 °C for 2 h using incubator shaker. Following that, the sample was filtered out of the solution and cleaned with ultra-pure water until it eliminates any residual trace acid till the filtrate pH is neutral. Filtrate was then oven desiccated for 24 hours at 105 °C, crushed, and sieved into particle sizes ranging from 0.212 to 2 mm, and labeled as Acid-Treated Bentonite (ATB). In order to make aluminum modified bentonite sample, 20 g of Al₂(SO₄)₃.14H₂O was dissolved into 100 ml of double distilled water in a beaker. Then, 60 gm 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 minutes. The sample was labelled Al³⁺.
modified bentonite clay after it was purified and washed with deionized water after it was equilibrated for 24 hours (AOMB). Muger et al. published a study in 2014 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 (pH_pzc). To evaluate the pH of every sample, 10 g of sample was positioned in a 100-ml beaker, 20 ml of ultra-pure water was added, and the mixture was agitated with rpm of 330 for 30 minutes. 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 per literature reported by soliva et al. 2010 (Huerta-Pujol et al. 2010) and also 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 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 has been used to figure out the phase of a crystalline substance. The XRD analysis was performed on unit cell dimensions with Cu radiations of Kα1 (Å): 1.54205, Kα2 (Å): 1.544426, Kα2/Kα1 intensity ratio: 0.50, Kα (Å): 1.541874, Kβ (Å): 1.392250. The X-ray tube was worked 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 36.195 sec, with form of scan: continuous, minimum step size Omega:0.001, minimum step size 2Theta:0.001 and anode material: copper, Anodized aluminum sample holder. Before being put in the specimen room, the samples were washed in an acetone solution. For the study, the specimen holder was placed in the X-ray diffractometer. Data were analyzed by X’pert high score plus program. SEM was used to obtain information about samples surface topology, composition and properties by exposing the samples with beams at magnifications of 1000x, 5000x and 10000x. These samples were also exposed for Electro-diffraction x-ray (EDX) analysis.

**The point zero charge of the adsorbents (pH_pzc):** The surface characterization of metal oxides/hydroxides relies heavily on pH_pzc. pH_pzc calculates in what way simply an adsorbent can adsorb ions in aqueous solution during the adsorption process. The salt supplement method was used to calculate the point of zero charge (pH PZC) of untreated, Acid Treated, and Al-bentonite clay (Farooq et al. 2012; Dayananda et al. 2014). A sequence of 100 mL flasks are filled with 40 mL of 0.1 M KCl, 0.01MKCL, and 0.001MKCL. For an added amount of a 0.1 M of (NaOH & HCl) solutions to the mixture, the initial pH (pHi) of the solutions was balanced between 2.8 and 12, and 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 on an orbital incubator shaker (Nicolab instruments, New Delhi, India) for 24 hours at 30 degrees Celsius, then kept for 48 hours. The solutions were filtered after equilibration, and the (pH) values as final pH of the filtrate were calculated once more. The disparity between (pHi) and (pHf) values was plotted against pHi (ΔPH = ΔpHi − pHf). Aluminum oxide modified bentonite and HCl-treated bentonite clay were treated in the same way. The validity of the procedure was well explained on the study by Kumar et.al in 2011 (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 normally described in milliequivalents per 100 g of dry clay (meq/100 g). 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 (Equation (2)) (Kahr & Madsen 1995) were used to examine, associate, and found the CEC value and investigate the outcome of particle size on the value of the CEC of the raw bentonite (RB), Acid-treated bentonite (ATB) and Al³⁺-Modified bentonite clay (AOMB).

Using the pH equilibrium method, Salim’s et al.2018 (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 applied to a beaker glass containing 5 gm of different particle size bentonite (0.212 mm,0.425 mm,06 mm and 1.25 mm). A magnetic stirrer was then used to stir the mixture for 1 hour. The pH of the supernatant was determined. All of the measurements were taken three times, and the average and standard deviations were calculated.

CEC (meq per 100 g of clay) = (pH observed − pH acetic acid) × 22  

(1)
The clay combined with ultra-pure water till a homogeneous slurry is collected in order to extract the CEC using the (MB) titration technique. The mixture is then slowly added to a known concentration of methylene blue (MB). A magnetic stirrer is then used to stir up the mixture for 1 minute. After that, a bright blue radiance around the dim blue of the droplet was continuously observed after taking a drop on a filter paper. The blue radiance on the filter paper fades when the replacement between bentonite and methylene blue ends, and the amount of the MB reported decreases.

\[
\text{CEC (meq per 100 g of clay)} = \frac{100}{F \times V \times NMB} \tag{2}
\]

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

Also, to determine the surface area of the adsorbents (Equation 3) was used following the procedure developed by Kahr and Madison in 1995 (Kahr & Madsen 1995).

\[
\text{SSA} = Mf \times 130 \times 6.02 \times 10^{-2} \frac{m^2}{g} \tag{3}
\]

where \(Mf\) is the methylene blue adsorbed per 100 gm of clay and \(SSA\) is specific surface area in \(m^2/g\).

**Experimentation of fluoride adsorption**

The raw and synthesized bentonite clay was checked for fluoride adsorption using fixed bed column of a borosilicate tube with ratio of internal diameter to height: 0.05. The diameter-to-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 ends. Using a peristatic pump, the column was then continuously fed fluoride-contaminated water at a desired volumetric flow rate of 15 mL/min.

A blank column operation was also employed to make sure that the filter used would not change the fluoride concentrations of the inlet solution. At a predefined time, intervals of 30 min samples were collected in a beaker (5 L) and measured the residual fluoride level in the effluent using 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 (WHO guideline for drinking water of fluoride content).

The effect initial influent concentration was performed for experimental runs on initial influent fluoride concentrations of (5, 10 and 12 mg/l by keeping flow rate of 15 mL/min and 10 cm bed depth constant.

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

\[
q_e = \frac{C_0 - C_e}{m} \times V \tag{4}
\]

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.

Maximum removal efficiency \((R\%)\) is calculated by using Equation (5):

\[
R(\%) = \left(\frac{C_0 - C_e}{C_0}\right) \times 100 \tag{5}
\]

where, \(R, C_0\) & \(C_e\) are the removal efficiency (\%), the initial fluoride concentration & 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 percent, 0.345 percent, and 0.104 percent, respectively. In contrast to raw bentonite, 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 of the RB, ATB, and AOMB, respectively, was found to be 2.62 g/cm³, 1.23 g/cm³, and 1.25 g/cm³. The raw bentonites were slightly denser than the improved ones, since apparent density is a measurement of the compactness of clay minerals. The small density difference between raw and modified bentonite may be due to the organic content of the clay. The starting materials for clay can also vanish 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 have pH values that are similar to 7.2.

Surface morphology

SEM results for Bentonite samples at 1000x, 5000x and 1000x magnification (Figures 3 and 4) 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 that could be predominantly Silica and alumina.

Mineralogy

The XRD analysis of the adsorbents is shown in Figure 3. The mineralogical and crystallographic characterization of these samples were performed as revealed in Table 1. From the peaks observed in the figure, the results obtained from x’pert software shows that the three samples have the following compositions in common. Alumina (Al₂O₃) = 17%, calcite (CaCO₃) = 22%, Silica(O₂Si) = 22%, bornite (Cu₃FeS₄) = 8%, Hematite (Fe₂O₃) = 16%, Quartz (SiO₂) = 22%, Green cinnabar (Cr₂O₃) = 16% and burnt ochre = (Fe₂O₃) 20% (Figure 3). The other crystallographic parameters are shown in Table 1. The crystallographic parameters (figure) as Calculated density (g/cm^3): 2.65, Volume of cell (10^6 pm^3): indicating the crystal system of Hexagonal structure, a (Å): 4.9134, b (Å): 4.9134, c (Å): 5.4053, Alpha (°):90.0000, Beta (°):90.0000, Gamma (°):120.0000. The maximum peak list that quartz, Silica and calcite (Table 1) exist is expressed in terms of d-spacing: 3.34200, 2Theta[deg]: 26.652 and intensity (%): 100.

Figure 1 | Schematic diagram that represent the fixed bed column.
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 by analyzer (EDX) as shown in the Figure 4.

From the results of SEM-EDX spectrum, it was observed that the untreated clay consists of Al, Si, Na, Mg, O, K, Ti and Fe in every spectrum. The spectrum reveals $(Ca,K, Mg, Fe)xAl2O3.ySiO2.nH2O$, and the value of composition is shown in Table 2.

The three samples EDX result shows that the major composition is Si, Al and Fe with 23.79%, 10.55% & 14.84% weight respectively for RB samples. The other elements like Cl, Na, Mg, Ti, Ca & K are exist at lower percentage weight and considered as impurities of the material caused by several factors: the purification of bentonite is less clean, less clean oven circumstances and other factors.

### FT-IR analysis

In Figure 5, it was shown 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. Samples spectra reveals 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,
respectively, were 400–4,250 cm\(^{-1}\) and 0.145 cm\(^{-1}\). The Al–Al–OH group deformation peaks at 444.51 cm\(^{-1}\), 464.01 cm\(^{-1}\), and 459.99 cm\(^{-1}\) are close to those recorded by Paralo in 2014 (Parolo et al. 2014). The bending and stretching vibrations of the hydroxyl groups at 3,625 cm\(^{-1}\) and 1,640 cm\(^{-1}\) are allocated to the hydroxyl groups in the silicate layers in the FTIR 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 inner hydroxyl group with higher Al–OH material, respectively. Nwosu in 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 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 AOMB adsorbent.
Cation exchange capacity (CEC)

Higher CEC values shown in Table 3 by applying methylene blue method, implies due to corresponding surface activity a greater layer charge has happened. Therefore, Raw bentonite can have a higher CEC, which shows the existence of the contact forces between the surrounding molecules and clay surface.

On the other hand, the results obtained by pH equilibration method (Figure 6) is also determined comparatively for different particle sizes of pH equilibrium method.

It is clearly observed from the two methods (refer Table-3- the methylene blue method vs Figure-7- the pH equilibrium method) that the CEC of the three adsorbents were found relatively the same values.

The smaller particle provides more surface area and leading to more sorption sites and to greater sorption. The increase in particle size from 0.212 mm to 1.25 mm didn’t show any change in CEC per SSA values for the case of AOMB and slight decrease for the case of raw bent as shown in Figure 7(a) and 7(b) respectively. 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, flowrate, and adsorbent bed depth on column adsorption was investigated. Different initial concentrations of fluoride (2 mg/l, 5 mg/l and 10 mg/l) were tested for constant flowrate of 15 ml/min, adsorbent packing depths of 2, 6 & 10 cm using 1.5 cm diameter borosilicate glass column (Figure 1) with 20 cm height subjected to continuous flow of the fluoride solution in downward direction. But, for this particular paper, the materials were tested for only 5 mg/L of fluoride concentration, 10 cm bed depth and 15 ml/min flowrate.

Figure 8 compares the RB, ATB, and AOMB adsorption capacity and fluoride removal performance. At time = 60 minutes, RB clays have a very poor fluoride removal efficiency (47.19 percent). Surface H+ and cation modification with AO, on the other hand, increased fluoride removal efficiency to 79.77 percent and 94.38 percent (using ATB and Al-bent, respectively) at time = 60 minutes. The increased fluoride removal capability of the AO amended clays is thought to be due to the presence of aluminum oxide (hydroxide) (AO). When compared to RB and ATB, the figure clearly shows that AOMB has a higher fluoride adsorption capability. The sum of Al in AOMB (13.08 percent wt or mol Al/kg in Table 1) is primarily responsible for this.

By plotting Ct/C0 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 break-through period due to fluoride’s strong affinity for higher density and stable electropositive species of Al$^3+$. 

Mechanism of adsorption

The effectiveness and efficiency of the adsorbent is dependent on the material reactivity of the adsorbent. pH value 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 found to be 7.1, 5.8 and 7.8, respectively. However, for Acid treated bentonite, ΔpH versus pHi plot shows 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 raw bentonite clay, according to this result. Mugera et al. in 2014 observed a rise in pH_{PZC} of bentonite clay after modification for Al^3+ -modified bentonite (Vhahangwele et al. 2014).

### Table 3 | Values of SSA area and CEC by the Methylene blue adsorption method

| Adsorbent | Volume of addition of methylene blue (ml/7.5gm) | Calculated (SSA) Specific Surface Area (m²/g) | Calculated cation-exchange capacity (meq/100 g) | Calculated cation-exchange capacity per SSA (meq/m²) |
|-----------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|--------------------------------------------------|
| RB        | 3 ml                                          | 52                                            | 28.78                                         | 6\times10^{-3}                                   |
| ATB       | 25 ml                                         | 429                                           | 19.04                                         | 0.4\times10^{-3}                                  |
| AOMB      | 30 ml                                         | 520                                           | 15.87                                         | 0.3\times10^{-3}                                  |

Figure 6 | Effect of particle size on CEC value by using pH equilibrium Method.

Figure 7 | Effect of particle size on CEC and CEC/SSA value by using methylene blue Method.
Figure 8 | Comparison of (a) fluoride removal percentage of three clay based media and (b) breakthrough curve of the three adsorbents (Column condition – 10 cm Bed depth, 15 ml/min flow rate, 5 mg/l initial fluoride concentration).

Figure 9 | Plot of $pH_{PZC}$ of RB, ATB and AOMB.
Generally, adsorption is caused by the electrostatic attraction between the fluoride ion and the main constituents of Bentonite clay.

CONCLUSIONS

The experimental outcomes exhibited that it is practicable to use HCl treated bentonite (ATB) and aluminum hydroxide modified bentonite clay for fluoride removal as an adsorbent in a fixed-bed adsorption process.

SEM micrographs confirmed that raw bentonite surface of was rough and which favors for uniform application of surface coating of aluminum upon it. The EDX spectra shows Al$^{3+}$ was successfully deposited on the clay material surface of which was confirmed by the detection of more Aluminum spectrum on modified bentonite clay than the raw bentonite. The uptake of fluoride has occurred at pH$_{PZC} > 7$ (RB), pH$_{PZC} > 5.9$ (ATB), pH$_{PZC} > 7.8$ (Al-Mbent) by established hydroxyl groups between the fluoride ions and sorbent surface from 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 image reveals particles are dispersed homogeneously and are irregular in shape. XRD and EDX analysis reveals that the bentonite is composed of seven peaks: CaCO$_3$, SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, Cu$_5$FeS$_4$ and Cr$_2$O$_3$ as content of bentonite chloride is considered as impurity.

The column studies with aluminum modified bentonite clay showed that the maximum adsorption of fluoride in all operating conditions than the raw and HCl-treated bentonite. Also, the maximum adsorption of fluoride in raw bentonite is more delayed. Fluoride concentration decreased with increasing adsorption doses; the permitted value of fluoride in drinking water (<5 mg L$^{-1}$) was obtained for an adsorbent bed depth packed with aluminum modified bentonite. The application of the advanced technologies for fluoride removal specially for small communities residing in rural areas is not feasible due to its complexity and affordability. In developing countries like Ethiopia, application of cost effective and simple de-fluoridation technologies like aluminum modified bentonite clay minerals as reported in this work may be preferable than advanced technologies. This study, therefore has advantages on reducing fluoride level from groundwater in which it has good adsorption capacity, ease of preparation, local availability and proven filter for drinking water application.

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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.
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