

Removal of excess fluoride from water using waste residue from alum manufacturing process

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Abstract

The ability of waste residue, generated from alum manufacturing process, to remove fluoride ion from water has been investigated. Series of batch adsorption experiments were carried out to assess parameters that influence the adsorption process. The factors investigated include the effect of contact time, adsorbent dose, thermal pretreatment of the adsorbent, neutralization of the adsorbent, initial fluoride concentration, pH of the solution and effect of co-existing anions. Results showed that Adsorption of fluoride is fairly rapid in first 5 min and thereafter increases slowly to reach the equilibrium in about 1 h. The removal efficiency of fluoride was increased with adsorbent dosage. About 85% removal efficiency was obtained within 1 h at an optimum adsorbent dose of 16 g/L for initial fluoride concentration of 10 mg/L. Heat treatment and surface neutralization of the adsorbent did not improve the fluoride removal capacity and efficiency. The amount of fluoride adsorbed increased with increasing initial fluoride concentration. The percentage of fluoride removal remains nearly constant within the pH range of 3–8. The adsorption data at ambient pH were well fitted to the Dubinin–Radushkevick (D–R) isotherm model with a capacity of 332.5 mg/g of the adsorbent. The adsorption kinetic was found to follow a pseudo-second-order rate equation with an average rate constant of 2.25 g min⁻¹ mg⁻¹. The presence of bicarbonate at higher concentrations (100–500 mg/L) decreased the fluoride removal efficiency while other anions (chloride, sulfate, phosphate and nitrate) have no significant effect within the concentration range tested. The overall result shows that the waste residue is efficient defluoridating material.

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1. Introduction

Fluoride ion exists in natural waters and it is an essential micronutrient in humans in preventing dental caries and in facilitating the mineralization of hard tissues, if taken at a recommended range of concentration. Higher level of fluoride in groundwater is a world-wide problem, which includes various countries from Africa and Asia as well as USA [1]. Ethiopia is among the most affected nations in Africa by the fluoride problem. Fluoride concentration as high as 33 mg/L has been reported in drinking water sources in Ethiopia [1]. Excess fluoride in drinking water is prevalent in all of the Rift Valley Regions of the country [2,3]. According to the Ministry of Water

Resources of Ethiopia, rural drinking water supply in the Rift Valley Region is, to a large extent, dependent on groundwater [4,5]. Hence, it becomes necessary to bring down the fluoride concentration within permissible limit of 1.5 mg/L according to the guideline values of the Quality and Standard Authority of Ethiopia [4]. The Ministry of Water Resources on the bases of economical, practical and technical considerations proposed guideline for drinking water quality of fluoride at 3.0 mg/L [5]. The limit varies among countries and the age of people exposed. World Health Organization (WHO) has set a limit range between 0.5 and 1 mg/L [6]. After many years of use of drinking water from drilled wells in the Rift Valley, Ethiopia, dental and skeletal fluorosis has become a serious medical problem [2,3]. For communities in developing countries like the Rift Valley Regions of Ethiopia where the groundwater is fluoride rich and provision of alternative water supply is difficult, treatment of contaminated water is the only option to provide safe drinking water.

Available techniques for the removal of fluoride belong to the following major categories: chemical precipitation [7,8], mem-

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brane processes [9], adsorption by activated alumina [10,11] ion exchange [12,13], and Nalgonda technique [14]. Nalgonda technique is widely used in India because of its simplicity and cost effectiveness. However, the production of excess sludge is a concern. It is widely recognized that adsorption is an ideal and appropriate technique compared to other techniques, for small community water source defluoridation.

In recent years, the use of low cost adsorbents has been investigated to remove fluoride from water. Such materials include: hydroxy apatite, calcite, fluorspar, quartz [15], fly ash [16], silica gel [17], bone char [18], spent catalyst [19], zeolites [20], red mud [21], and bentonite [22]. Studies in Ethiopia as well as other developing countries indicated the possibility of using low cost adsorbents bone char, clay, diatomaceous earth, lateritic soils and other related materials [23–29]. However, the applicability of these low cost methods is limited either due to their low efficiency or lack of public acceptance. Therefore, it is of paramount importance to identify materials with high rate of removal, economically, socially and technically feasible for applications in rural communities.

In this study, the industrial waste residue, generated during the manufacture of aluminium sulfate (alum) from kaolin by the sulfuric acid process was used as defluoridating media. A large quantity of waste residue is generated from each batch of alum production at Awash Melkassa Aluminum Sulfate and Sulfuric Acid Factory, Ethiopia. Currently, an estimated amount of 4500–5000 tonnes of waste is accumulated in an open area, near to the factory. The waste discarded is highly acidic (pH of about 3) and hence it is considered as hazardous. At present, economically viable methods for its disposal or reuse are not known. Therefore, it is necessary to find a solution for the minimization of waste residue, which is economical and environmentally sound.

2. Materials and methods

2.1. Defluoridation material

The waste residue, generated during the manufacture of aluminium sulfate using kaolin and sulfuric acid, was collected from Awash Melkassa Aluminum Sulfate and Sulfuric Acid Factory, which is located at the central part of the Ethiopian Rift Valley Region. Samples were taken from more than 30 batches of aluminium sulfate production residues and then mixed to maintain homogeneity. The waste directly discarded contains about 52% of solid. The chemical compositions of this industrial byproduct are given in Table 1 [30]. The chemical composition of the waste material indicates the absence of any hazardous and carcinogenic substances in the material and hence it is suitable to use as a defluoridating agent.

The waste residue was sun-dried for 1 day and grinded to fine powder using mortar to a particle size range of 0.5–0.8 mm. This material is considered as untreated adsorbent. The material was further treated thermally at the preset temperature ranging from 100 to 700 °C in a furnace (Calbolite, ELF Model, Waglech International Ltd., UK) for 1 h. At the end of 1 h, the treated samples were kept in a desiccator and allowed to cool to room

Table 1

Percentage composition of the chemical constituents in waste residue [30]

Chemical composition	Percent (wt.%)
Quartz (SiO ₂)	39.991
Kaolin	8.883
Al ₂ (SO ₄) ₃	1.778
Al(OH) ₃	0.878
CaSO ₄	0.194
Fe ₂ (SO ₄) ₃	0.023
Fe ₂ O ₃	0.001
MgSO ₄	0.008
Na ₂ SO ₄	0.007
K ₂ SO ₄	0.005

temperature. This material is considered as thermally treated adsorbent. To prepare the neutralized media, a portion of the untreated media was suspended in distilled water and the resulting lower pH (about 3.2) was adjusted to pH of 7.30 using 0.1 M NaOH; then filtered after 2 days and dried at room temperature at an open air before use.

2.2. Reagent and standard solutions

Fluoride stock solution was prepared by dissolving 2.21 g of anhydrous sodium fluoride (99.0% NaF, BDH Chemicals Ltd Poole England) in 1000 mL distilled water in volumetric flask. Standards and F⁻ spiked samples at a required concentration range were prepared by appropriate dilution of the stock solution with distilled water. The total ionic strength adjustment buffer (TISAB) was prepared according to a recommended procedure, except that EDTA replaced CDTA [31].

2.3. Instrumentation

A pH/ISE meter (Orion Model, EA 940 Expandable Ion Analyzer) equipped with combination fluoride-selective electrode (Orion Model 96-09) was employed for the measurement of fluoride ion concentration. The method of direct potentiometry was used, where the concentration can be read directly. The fluoride ion selective electrode was calibrated prior to each experiment in order to determine the slope and intercept of the electrode. The pH was measured with pH/ion meter (WTW Inolab pH/ION Level 2, Germany) using unfilled pH glass electrode. The meter was calibrated whenever the measurements were made by using pH calibration buffers.

2.4. Batch adsorption studies

Adsorption experiments were conducted in 500 mL Erlenmeyer flask containing 500 mL of fluoride-spiked distilled water at room temperature (22 ± 2 °C). The adsorbent was placed in the flask and mixed with magnetic stirrer (Model 04803-02, Cole-Palmer-Instrument Company, U.S.A.) Continuously at 100 rpm (slow mixing) and 1000 rpm (fast mixing). The residual fluoride concentration was measured immediately after mixing 5 mL sample solution with the TISAB. All the experiments were performed in triplicate and the mean values were reported.

The effect of adsorbent dose and contact time was studied by varying adsorbent doses (4, 6, 10, 16 and 28 g/L) at constant initial fluoride concentration of 10 mg/L. The effect of mixing was investigated under static, slow and fast mixing conditions using magnetic stirrer. The influence of thermal treatment on fluoride removal efficiency was evaluated by using the adsorbent treated at different temperatures (100, 300, 400, 500, 600, and 700 °C). The effect of neutralization on fluoride removal efficiency was investigated by taking adsorbent dosages from 6 to 100 g/L which were mixed with 10 mg/L fluoride concentration for 1 h. To investigate the effect of initial fluoride concentration and contact time, experiments were conducted by varying fluoride concentrations from 5 to 40 mg/L at constant adsorbent dose of 16 g/L. The effect of raw water pH on the adsorption of fluoride on to the adsorbent was studied by varying the solution pH from 3 to 10, which was prepared by adjusting the pH to the desired level either with 0.1 M NaOH or 0.1 M HCl.

Isotherm experiments were conducted by varying the adsorbent dose from 1.0 to 20.0 g/L by maintaining the initial fluoride concentration and pH at 50 mg/L and 7.0, respectively. The equilibration time was 4 h under mixing condition. The samples were allowed to settle and residual fluoride ion concentrations were measured. The kinetic analysis of the adsorption data is based on reaction kinetics of pseudo-first-order and pseudo-second-order mechanisms. Adsorption kinetics was determined using constant surface loading of 16, 8 and 4 g/L corresponding to the initial fluoride concentration of 40, 20 and 10 mg/L, respectively, for the untreated adsorbent. The effect of co-existing anions (Cl^- , SO_4^{2-} , HCO_3^- , PO_4^{3-} , and NO_3^-) on fluoride adsorption efficiency of the adsorbent was also studied at constant fluoride concentration of 10 mg/L and adsorbent dose of 16 g/L by varying anion concentration from 5 to 500 mg/L. The selections of the anion concentrations are based on their availability in ground waters used for drinking purposes.

3. Results and discussions

3.1. Effect of adsorbent dose

The effect of untreated adsorbent dose on the fluoride removal was studied using different mass of adsorbent and initial fluoride concentration of 10.0 mg/L. As shown in Fig. 1, the residual fluoride decreases as the adsorbent dose increases. The reaction is fast during the initial 5 min and equilibrium was reached within 60 min (data not shown). This result is in agreement with the equilibrium time found for alum sludge and quartz which are reported in other studies [32,15]. It is evident that the adsorption process is very fast and most of the fluoride adsorbed in first 15 min and the equilibrium reached within 1 h. The time to reach equilibrium appears to be independent of initial fluoride concentration in the range of 5–20 mg/L. However, some variation in equilibrium time was observed with changes in adsorbent doses. The higher adsorbent doses (≥ 16 mg/L) requiring shorter equilibrium time (~ 45 min) and lower adsorbent doses (< 16 mg/L) requiring slightly longer equilibrium time (up to 60 min). Hence equilibration time of 1 h was considered as the optimum and chosen for further experiments.

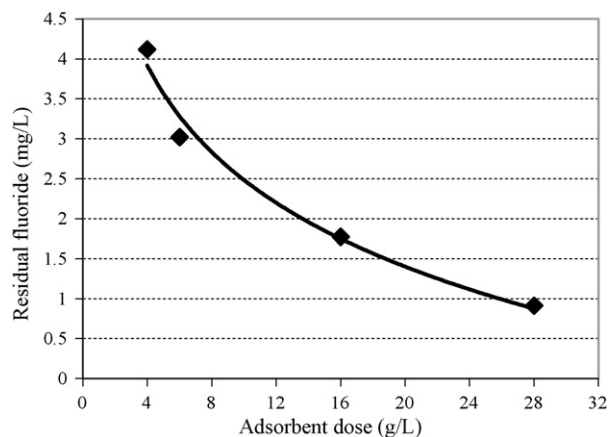


Fig. 1. Residual fluoride concentration as a function of adsorbent dose for the untreated adsorbent (initial concentration = 10 mg/L, reaction time = 60 min, and raw water pH 6.7–7.0).

The defluoridation efficiency was significantly increased with dose as shown in Fig. 2. The percent removal of fluoride increased significantly up to adsorbent dose of 16 g/L, but no significant change was observed beyond this dose. The increase in fluoride adsorption was possibly due to the increased in availability of F^- binding sites resulting from an increase in adsorbent dosage.

Higher dose of the adsorbent (greater than 16 g/L) will increase the amount of sludge, without causing a significant change on the amount of fluoride removed. This dose (16 g/L) could also be sufficient in reducing the amount of fluoride found in most of the drinking water of the Rift Valley Region of Ethiopia to a recommended concentration level, i.e., to the WHO proposed average, 1.5 mg F^- /L of water.

On the other hand, the adsorption capacity decreases with increasing dose (Fig. 2). To maintain maximum capacity and high removal efficiency, the surface loading (i.e., the mass ratio of fluoride to adsorbent dose) should be lower than the optimum value (i.e., the surface loading for optimum fluoride removal,

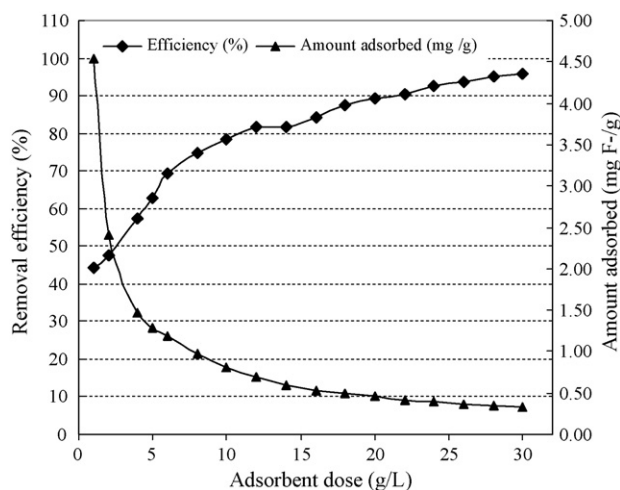


Fig. 2. Fluoride removal efficiency and capacity (mg/g) as a function of untreated adsorbent dose (initial fluoride concentration = 10 mg/L, contact time = 60 min, and pH 6.7–7.0).

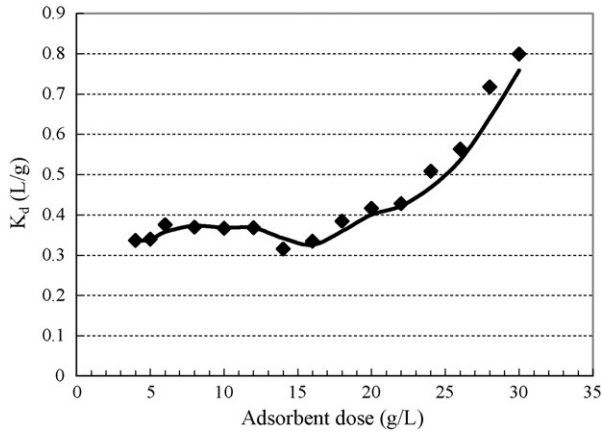


Fig. 3. The plot of K_d value as a function of adsorbent concentration (pH 7).

about 85%, obtained from Fig. 2 is 0.625 mg/g or less). A dose of 16 g/L corresponding to the capacity of about 0.53 mg F^- /g of adsorbent was considered for further adsorption experiments.

A distribution coefficient K_d which reflects the binding ability of the surface for fluoride mainly depends on pH and type of adsorbent surface. The distribution coefficient K_d value for fluoride of the adsorbent at pH 7 was calculated according to the following equation [32]:

$$K_d = \frac{C_s}{C_w} \text{ (L/g)} \quad (1)$$

where C_s is the concentration of fluoride in the solid particles (mg/g) and C_w is the concentration in water (mg/L). The concentration of fluoride in the solid phase was calculated based on measurement of fluoride in the water before and after the adsorption of fluoride on the solid phase. Fig. 3 shows the value of K_d as a function of adsorbent dose. It can be seen that the distribution coefficient K_d increases with an increase in adsorbent dose at constant pH, indicating the heterogeneous nature of the surface of the adsorbent. If the surface is homogeneous, the K_d values at a given pH should not change with adsorbent concentration.

3.2. Effect of thermal treatment

Fig. 4 shows change in the fluoride removal efficiency as a function of adsorbent thermal treatment temperatures. It can be seen that change in fluoride adsorption efficiency of the adsorbent was not significant when the material heated up to 300 °C. But further increase in temperature resulted in decreased removal efficiency. The efficiency decreases drastically after 500 °C. The maximum fluoride removal can be achieved at lower treatment temperature. The decrease in fluoride removal efficiency for the treatment temperature exceeding 500 °C may be caused by surface modification and/or changes in the composition of the adsorbent but it requires further study. Heat treatment may remove water and hydroxyl groups from the surface, and may reduce the number of reactive sites.

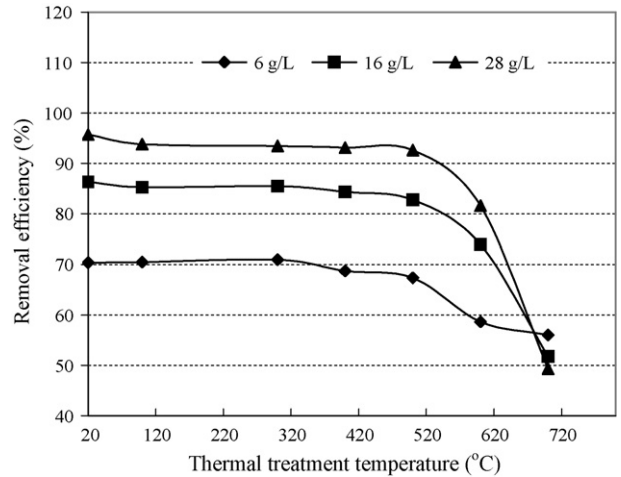


Fig. 4. Effect of thermal treatment on removal efficiency of the adsorbent (dose = 16 g/L, initial fluoride concentration = 10 mg/L, contact time = 60 min, and pH 6.7–7.0).

3.3. Effect of neutralization of the adsorbent

Fig. 5 shows the fluoride removal efficiency and capacity with doses of neutralized adsorbent. The results show both the capacity and efficiency decreased as compared to that of untreated (non-neutralized) adsorbent (Fig. 2) for a given adsorbent dose. This might be attributed to the deprotonation of the oxide surfaces. The hydroxylated surfaces of these oxides may develop positive charge on the surface at lower pH range. In addition, the pH of zero charge (pHpzc) for such oxide mixtures may vary from 5.5 to about 8.3 [33]. At pH values above the pHpzc the surface is negatively charged and fluoride will be adsorbed to a lesser extent at pH above 8 due to the repulsive forces between fluoride ion and negative charge of the surface.

3.4. Effect of initial fluoride concentration

Fig. 6 shows the residual fluoride concentration and capacity as a function initial fluoride concentration, at an adsorbent dose of 16 g/L at equilibrium (untreated adsorbent). The results indi-

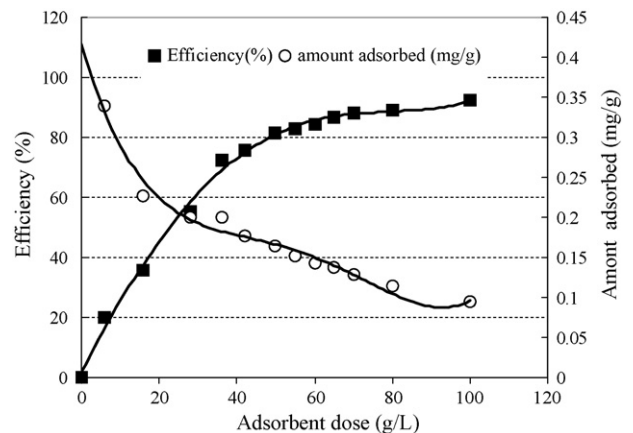


Fig. 5. Effect of neutralization on capacity and efficiency of the media (initial fluoride concentration = 10 mg/L, contact time = 60 min, and raw water pH 6.7–7.0).

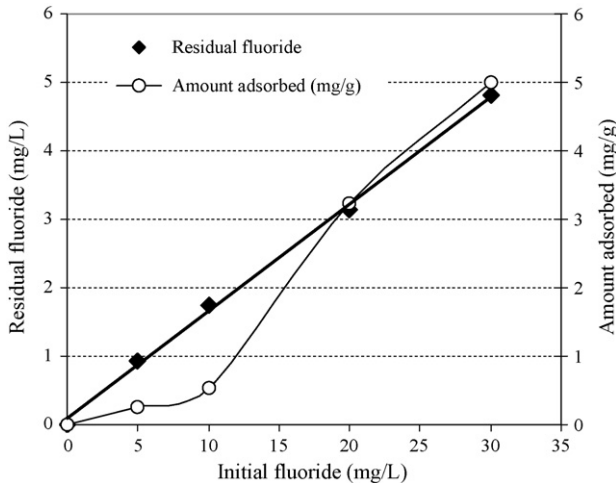


Fig. 6. Residual fluoride concentration and adsorption capacity of untreated adsorbent as a function of initial fluoride concentrations (adsorbent dose = 16 g/L and pH 6.7–7.0).

cate that the residual fluoride at equilibrium is a linear function of the initial fluoride content in water. This suggests the need of high adsorbent dose to reduce the residual fluoride to permissible level. The time to reach equilibrium is independent of initial fluoride concentrations (data not shown). The adsorption capacity increases with increasing initial concentration, which can be attributed to the utilization of less accessible or energetically less active sites because of increased diffusivity and activity of fluoride upon the increased concentration. The adsorption sites present on the interior surface of a pore may not be as easily accessible because of the resistance to the pore diffusion.

Besides the adsorption at the outer surface of the adsorbent, the adsorbate molecules may also diffuse in to the interior of the porous adsorbent [32]. Intraparticle diffusion model based on the theory proposed by Weber and Morris [34] was tested to identify the diffusion mechanism. According to this theory:

$$q_t = k_p t^{1/2} \quad (2)$$

where q_t is the amount adsorbed (mg/g) at a given time t (min); k_p (mg/g min^{1/2}) is the intraparticle diffusion rate constant.

Fig. 7 shows adsorption capacity of untreated adsorbent at different fluoride concentrations as a function of square root of time. As can be seen, a linear increase was not observed between the amount of fluoride adsorbed and square root of time, which indicates the control of surface adsorption [32]. If there is intraparticle diffusion, a linear relation will be observed. Hence, this result supports the fast equilibrium time. In addition, the plot of q_t against $t^{1/2}$ may present a multi-linearity, which indicates that two or more steps occur in the adsorption processes that limit the reaction. However, since there is no linear increase in Fig. 7, it is considered that film diffusion may not have influence on the reaction rate.

3.5. Effect of water pH

Fig. 8 shows the influence of initial solution pH on the fluoride removal efficiency and capacity of the adsorbent. It is apparent

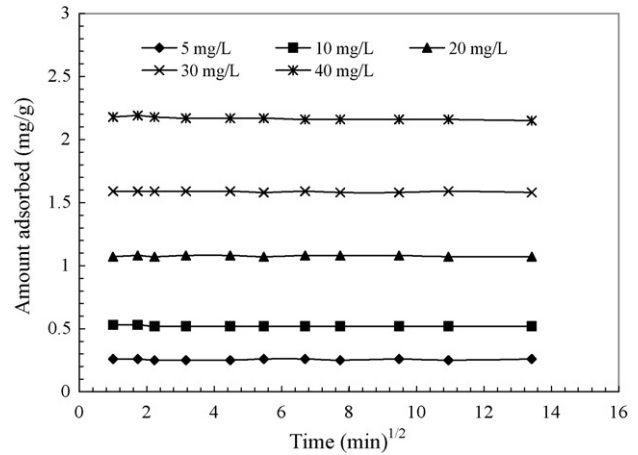


Fig. 7. Adsorption capacity (mg/g) of untreated adsorbent at different fluoride concentration function of time (adsorbent dose = 16 g/L and pH 6.7–7.0).

that the percentage of fluoride removal remains nearly constant within the pH range of 3–8. Further increase in the pH of the solution decreases the removal efficiency and the declining trend becomes significant at pH values >10. The fluoride uptake capacity of this media is not affected in the pH range less than or equal to 8, possibly due to the presence of positively charged and neutral sites at the surface of the adsorbent. The progressive decrease of fluoride uptake at pH > 8 is possibly due to the electrostatic repulsion of fluoride ion to the negatively charged surface and the competition for active sites by excessive amount of hydroxyl ions.

This result is in agreement with the work done by Shimeles et al. [25], who also found a broad pH range (4–9) for the adsorption of fluoride on aluminum hydroxide and with the work done by Shewangzaw [27], who found the local kaolin, the main constituent of this waste residue, as effective defluorinating media in acidic pH range (pH ≤ 6). The chemical composition of the solid component of the adsorbent (Table 1) showed that it was mainly composed of silica as SiO₂, hydroxides of aluminum and iron. The surface hydroxyl groups in this composite oxide

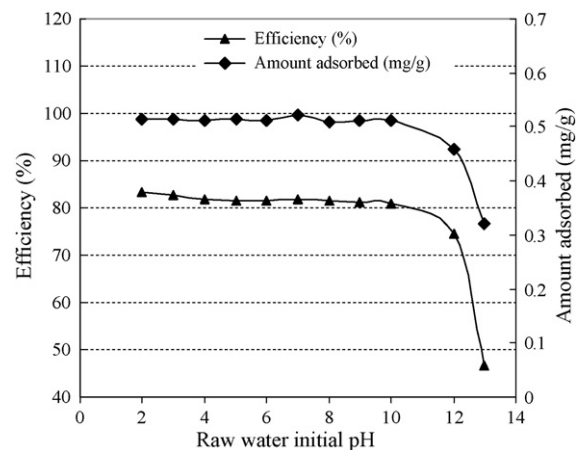
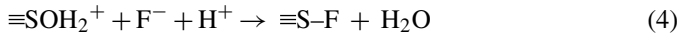


Fig. 8. Effect of raw water pH on fluoride removal efficiency and capacity of untreated adsorbent (initial F⁻ concentration = 10 mg/L, adsorbent dose = 16 g/L, and contact time = 60 min).

system are responsible for the retention of fluoride to various extents depending of pH and surface modification. Considering the experimental observation of pH variation, performance of thermally treated and neutralized media; the adsorption of fluoride may be best represented by the following two-step protonation/ligand exchange mechanism:



where $\equiv\text{S}$ represents silicon, aluminum, and iron solid surfaces.

This two-step mechanism is favourable at $\text{pH} < 6$. However, at $\text{pH} > 6$, fluoride ion is predominantly adsorbed by following mechanism:



3.6. Adsorption isotherm

The experimental data was fitted to Freundlich, Langmuir, Dubinin and Radushkevich (*R-D*), and Temkin isotherm models.

The linearized Freundlich adsorption isotherm is of the form

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (6)$$

where q_e is the adsorbed fluoride at equilibrium per unit mass of adsorbents (mg/g), K_f the minimum sorption capacity (mg/g) and $1/n$ is the adsorption intensity. C_e is the equilibrium concentration of fluoride (mg/L).

The Langmuir adsorption isotherm equation is represented in Eq. (7):

$$q_e = q_m \frac{BC_e}{1 + BC_e} \quad (7)$$

And the linearized form can be represented as:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{Bq_m} \left(\frac{1}{C_e} \right) \quad (8)$$

where, q_e is the amount of solute adsorbed per unit weight of material (mg/g), q_m the maximum adsorption capacity (mg/g), B the Langmuir constant, and C_e is the equilibrium solute concentration the essential characteristic of the Langmuir isotherm can be expressed by the dimensionless constant called equilibrium parameter, R_L , defined by:

$$R_L = \frac{1}{1 + BC_0} \quad (9)$$

where B is the Langmuir constant and C_0 is the initial adsorbate concentration (mg/L), R_L values indicate the type of isotherm to

be irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavourable ($R_L > 1$) [35–38]. The R_L value for the adsorption of is shown in Table 2.

Another equation used in the analysis of isotherms was the Dubinin and Radushkevich model [39–41]:

$$q_e = q_s \exp(-B\varepsilon^2) \quad (10)$$

where q_s is the D–R constant.

The sorption data was modeled by D–R isotherm to determine the adsorption type (physical or chemical). The linear form of this model [39–41] is expressed by:

$$\ln q_e = \ln q_s - \beta\varepsilon^2 \quad (11)$$

where q_e is the amount of fluoride adsorbed onto per unit dosage of the adsorbent (mol/g), q_m the monolayer capacity (mol/g), C_e the equilibrium fluoride concentration (mol/L), and β is the activity coefficient related to mean sorption energy (mol^2/kJ^2). ε is the Polanyi potential described as:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (12)$$

The mean sorption energy, E (kJ/mol), can be calculated by Eq. (13) [39–41]:

$$E = \frac{1}{\sqrt{-2\beta}} \quad (13)$$

the Temkin isotherm is given as:

$$q_e = \frac{RT}{b} \ln(K_T C_e) \quad (14)$$

which can be linearized as:

$$q_e = B_1 \ln K_T + B_1 \ln C_e \quad (15)$$

where

$$B_1 = \frac{RT}{b}$$

Temkin isotherm contains a factor that explicitly takes into the account adsorbing species and adsorbent interactions. The heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to adsorbate/adsorbate interactions [41]. This isotherm assumes that (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent and adsorbate interactions, and that (ii) the adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy [42]. A plot of q_e versus $\ln C_e$ enables the determination of the isotherm constants B_1 and K_T from the slope and the intercept, respectively. K_T is the equilibrium binding constant (L/mol) corresponding to the

Table 2

Isotherm parameters for the removal of fluoride by untreated adsorbent (initial fluoride concentration = 50 mg/L, equilibrium contact time = 4 h, pH 7.0, and temperature = 24 °C)

Freundlich constants	$K_F ((\text{mg/g})/(\text{mg/L})^{1/n}) = 0.33$	$1/n = 1.098$	$R^2 = 0.9299$
Langmuir constants	$q_m (\text{mg/g}) = 153.8$	$B (\text{L/mg}) = 0.0168; R_L = 0.862$	$R^2 = 0.9668$
Dubinin–Radushkevich constants	$q_s (\text{mg/g}) = 332.5$	$E (\text{kJ/mol}) = 7.812$	$R^2 = 0.9836$
Temkin constants	$K_T (\text{L/mg}) = 22026.46$	$B_1 = 0.0006$	$R^2 = 0.9689$

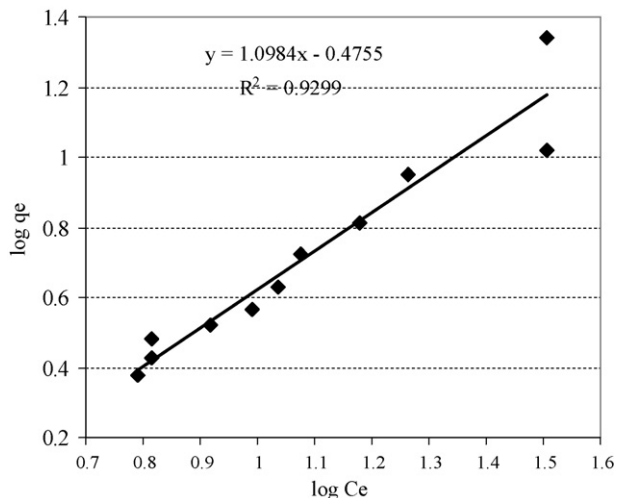


Fig. 9. Linearized Freundlich isotherm (initial fluoride concentration = 50 mg/L, equilibrium contact time = 4 h, pH 7.0, and temperature = 24 °C).

maximum binding energy and constant B_1 is related to the heat of adsorption.

Fig. 9 shows a plot of $\log q_e$ versus $\log C_e$. The constants $1/n$ as the slope and $\log k_f$ as the intercept. It is found that the related correlation coefficient R^2 value for the Freundlich model is 0.93. Freundlich isotherm with minimum adsorption capacity of 0.33 mg/g of the adsorbent. The experimental data did not fit well to the Freundlich isotherm model. The condition for the validity of a Freundlich type adsorption model is adsorption on heterogeneous surfaces [32].

In Fig. 10 plots of $1/q_e$ versus $1/C_e$ yield straight lines demonstrating that Langmuir sorption is followed by the sorption data very well. The value of q_m is 153.8 mg/g or 8.09×10^{-3} mol/g and the langmuir constant B is 0.0168. The results are summarized in Table 2. The values of R_L 0.862 in Table 2 also indicate favourable sorption of fluoride on to the adsorbent.

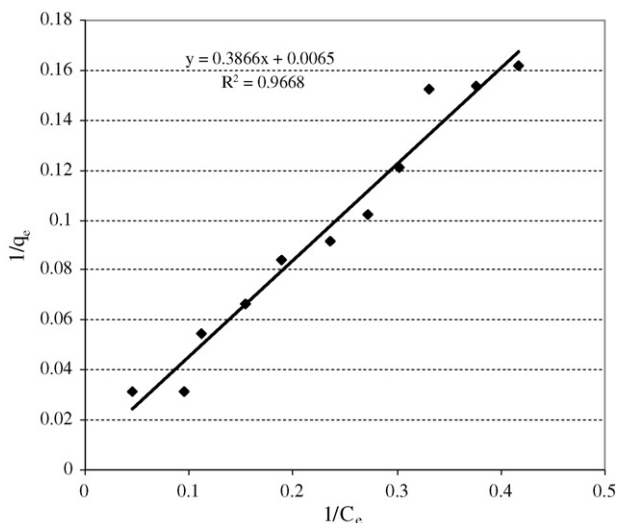


Fig. 10. Langmuir isotherm (initial fluoride concentration = 50 mg/L, equilibrium contact time = 4 h, pH 7.0, and temperature = 24 °C).

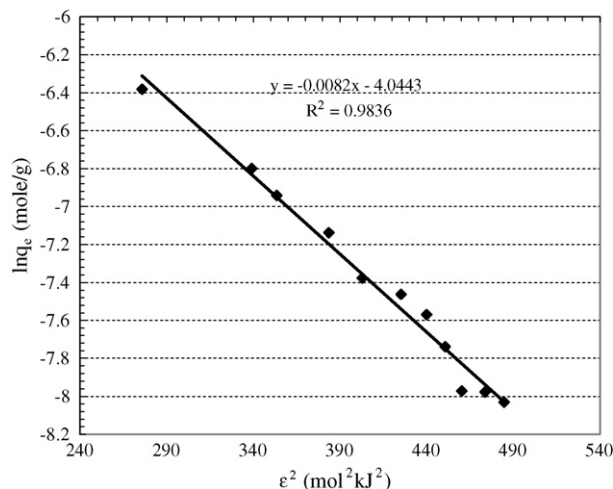


Fig. 11. $R-D$ isotherm (initial fluoride concentration = 50 mg/L, equilibrium contact time = 4 h, pH 7.0, and temperature = 24 °C).

Fig. 11 shows the $R-D$ plot for the adsorption of fluoride and the corresponding constants are presented in Table 2. The correlation coefficients for the $R-D$ isotherm are highest in comparison to the values obtained for the Freundlich, Langmuir and Temkin isotherms. Therefore, the $R-D$ isotherm is the best-fit isotherm for the adsorption of fluoride onto this adsorbent under the experimental conditions used in this study. The monolayer sorption capacity (q_s) was evaluated as 1.75×10^{-2} mol/g. The mean sorption energy (E) was found to be 7.812 kJ/mol for the adsorption of fluoride on the adsorbent. The E value ranges from 1.0 to 8.0 kJ/mol for physical adsorption and from 9.0 to 16.0 kJ/mol for chemical adsorption [39,40]. The value of E , which is nearly 8.0 kJ/mol, may suggest that, the mechanism for the adsorption of fluoride on the adsorbent is a combination of chemical and physical in nature.

Fig. 12 shows the Temkin isotherm plot for the adsorption of fluoride and the corresponding constants are presented in Table 2. A linear relationship between q_e and $\ln C_e$ indicates the applicability of this model to understand the adsorption mechanism. The corresponding constants are given in Table 2.

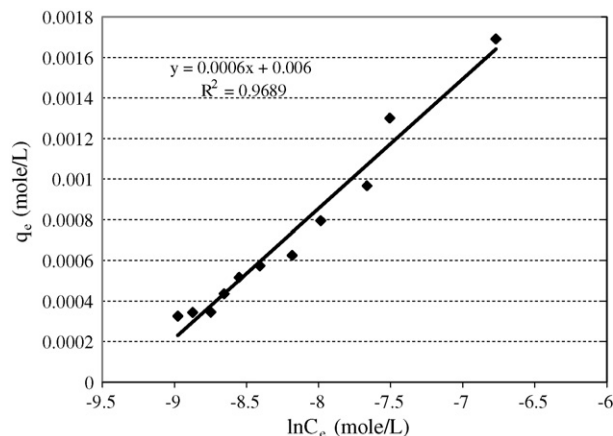


Fig. 12. Temkin isotherm (initial fluoride concentration = 50 mg/L, equilibrium contact time = 4 h, pH 7.0, and temperature = 24 °C).

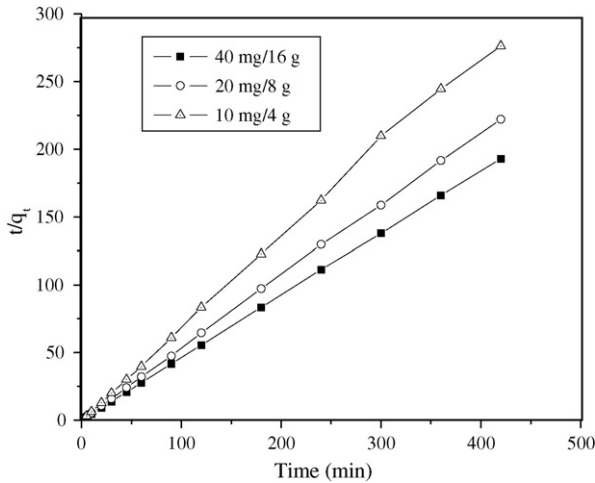


Fig. 13. Pseudo-second-order plot of fluoride adsorption kinetics on untreated adsorbent with initial fluoride concentrations to adsorbent dose of 40.0, 20.0, and 10.0 mg/L, and 16.0, 8.0, 4.0 g/L, respectively (pH 7.0).

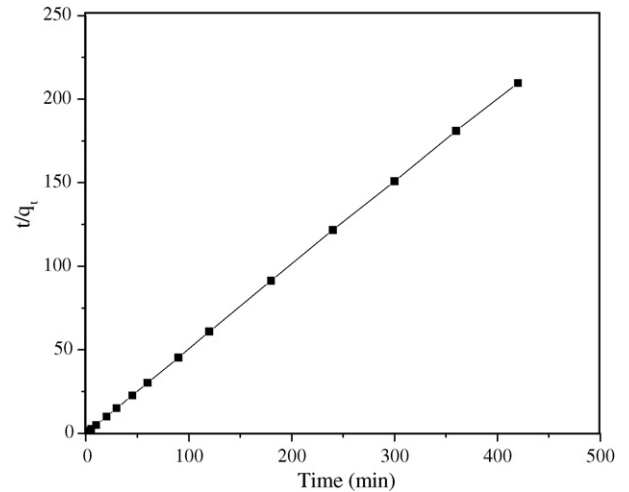


Fig. 14. Average pseudo-second-order plot of fluoride adsorption kinetics on untreated adsorbent with an initial load of 2.5 mg/g (pH 7.0).

3.7. Adsorption kinetics of fluoride

The adsorption kinetics was studied with initial fluoride concentrations of 40.0, 20.0, and 10 mg/L and corresponding adsorbent dose of 16.0, 8.0, 4.0 g/L, respectively, to maintain constant surface load of 2.5 mg fluoride/g of adsorbent. The kinetic analysis of the adsorption data is based on reaction kinetics of pseudo-first-order and pseudo-second-order mechanisms.

The uptake of fluoride on untreated adsorbent occurred rapidly, and reached equilibrium with in 60 min. The kinetics of adsorption were analyzed by using the Lagergren equation as shown below [32,43,44]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{16}$$

For the boundary conditions $t=0$ to $t=t$ and $q_t=0$ to $q_t=q_t$, the integrated form of Eq. (17) becomes:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \tag{17}$$

which is the integrated rate law for a pseudo-second-order reaction. Eq. (17) can be rearranged to obtain Eq. (18), which has a linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{18}$$

where k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the equilibrium rate constant of second-order sorption.

k_2 can be determined by plotting t/q_t against t of Eq. (18). The larger the k_2 value, the slower the adsorption rate. The untreated adsorbent can be described very well by the pseudo-second-order rate equation as shown in Fig. 13. The correlation coefficients were found as near to unity for the different initial fluoride concentrations. The three rate constants of the adsorbent were averaged to obtain a single rate constant of $2.25 \text{ g min}^{-1} \text{ mg}^{-1}$ as shown in Fig. 14.

3.8. Effect of co-existing anions

Ground water contains other anions such as sulfate, phosphate, nitrate, chloride and bicarbonate in addition to fluoride. Anion (Cl^- , SO_4^{2-} , HCO_3^- , PO_4^{3-} , and NO_3^-) concentrations of 5.0, 10.0, 20.0, 30.0, 40.0, 100, 200, 300, 400 and 500 mg/L were prepared by dissolving calculated amount of their sodium salt in 10 mg/L fluoride solution. The results of the removal efficiency of untreated adsorbent with concentration of each anion are shown in Fig. 15. Some studies showed that the presence of other co-existing ions in water have an effect on fluoride removal efficacy of oxide surfaces [32,45–47]. From the adsorption experiment results, it was observed that Cl^- , SO_4^{2-} , NO_3^- , HCO_3^- and CO_3^{2-} ions show negative effect on removal of fluoride. It was also found that both the anions HCO_3^- and CO_3^{2-} showed significant reduction of fluoride removal due

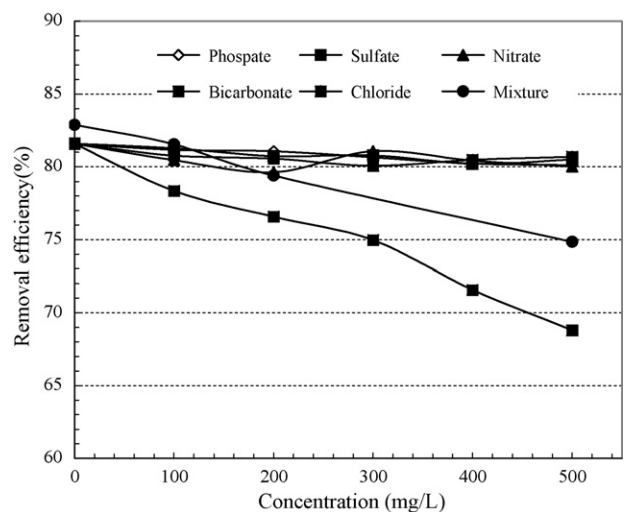


Fig. 15. Fluoride removal efficiency of untreated adsorbent at different anion concentrations (adsorbent dose = 16 mg/L, initial F^- conc. = 10 mg/L and contact time = 60 min).

to the change in pH as well as the competing effect of these co-anions [45].

The results show that the presence of bicarbonate at higher concentrations (100–500 mg/L) decreased the fluoride removal efficiency while other anions (chloride, sulfate, phosphate and nitrate) have no significant effect within the concentration range tested. The fluoride adsorption efficiency of the adsorbent decreased from about 82 to 68% in the presence of 500 mg/L bicarbonate ion. The effect of bicarbonate ion on fluoride removal efficiency of the adsorbent may be related to the increase in the pH of the raw water to above 8. From Fig. 15 it can be noted that, the affinity sequence for anion adsorption on this adsorbent is in the order bicarbonate \gg phosphate $>$ sulfate \approx nitrate \approx chloride. In the presence of all other anions in the same solution, the effect of bicarbonate ion on fluoride removal efficiency of the adsorbent becomes lesser possibly due to the buffering effects by other ions. Detailed mechanistic aspect of the competitive adsorption reactions requires further investigation.

The results are in good agreement with to the similar work done by other workers Karthikeyan et al. [45,48] for activated alumina. It was found that fluoride removal efficiency of activated alumina is not significantly affected by chloride, sulfate and nitrate but significantly affected by bicarbonate ion.

4. Conclusions

The results reveal that low cost locally available industrial waste material generated from aluminum sulfate manufacturing process is promising material to remove excess fluoride from water. Adsorption of fluoride is fairly rapid in first 5 min and thereafter increases slowly to reach the equilibrium in about 1 h. Based on the results obtained it can be concluded that about 85% of fluoride was removed within the first 5 min at an optimum adsorbent dose of 16 g/L in pH range of less than 8 for initial F^- concentration of 10 mg/L. The adsorption followed second-order rate kinetics, and data fit in to linear form of Dubinin–Radushkevick (D–R) isotherm model with a capacity of 332.5 mg/g of the adsorbent. The adsorbent fluoride removal efficiency is affected significantly with bicarbonate ion concentrations and little or no effect by other anions such as phosphates, chlorides, sulfates and nitrates.

Since most of the rural populations in the Rift Valley Region of Ethiopia can not easily afford treated water or bottled water for daily consumption, this efficient, easily and locally available material has to be considered to establish a sustainable solution to the fluoride problem in the Rift Valley Region of Ethiopia.

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