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Fluoride removal from water using magnetic Iron Oxide/Aluminium hydroxide composite

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ABSTRACT: Magnetic iron oxide/aluminum hydroxide composite material was synthesized in three successive steps by chemical co-precipitation methods and characterized for its surface properties and mineralogy using potentiometric mass titration and X-ray diffraction spectroscopic method, respectively. The result of XRD peak indicated that the structure of iron oxide was crystalline regardless of the different mass ratio of iron oxide and aluminum hydroxide. The point of zero charge was 9.5 indicating that the surface of $Fe_3O_4/Al(OH)_3$ is positively charged which is favorable condition for the adsorption of fluoride ion. The adsorption of fluoride on iron oxide/aluminum hydroxide was investigated using batch adsorption techniques. Results showed that at optimal mass ratio 5:2 of $Fe_3O_4/Al(OH)_3$ and adsorbent dosage at 4 g/L, the fluoride removal efficiency was found to be 89% from the initial concentration 10 mg/L. The residual aluminum after adsorption of fluoride was found to be 0.01 mg/L. Adsorption isotherm models followed the order: Freundlich > Langumir > D-R. The maximum adsorption capacity of $Fe_3O_4/Al(OH)_3$ was found to be 6.67 mg/g in the concentration range used in this study. Kinetics studies showed that the adsorption of fluoride onto $Fe_3O_4/Al(OH)_3$ proceeds according to a pseudo-second-order reaction model with an average rate constant of1.93×10^{-2}min (mg/g). The magnetic $Fe_3O_4/Al(OH)_3$was found to be an effective adsorbent for fluoride removal from drinking water.

Keywords/phrases: Defluoridation, Fluoride, Iron oxide/aluminium hydroxide composite, Water

INTRODUCTION

Fluoride (F^-) exists in natural waters with higher concentrations expected in ground waters (Fawell *et al.*, 2006). It is the most significant inorganic pollutant in groundwater affecting human health at the global scale (Thole, 2013). According to the World Health Organization guidelines (WHO, 2011),the permissible limit of fluoride is 1.5 mg/L. At higher concentration fluoride causes dental or sketetal fluorosis in human body. It also causes other harmful effect and diseases (Kloos and Redda Tekle-Haimanot, 1999; Meenakshi and Maheshwari, 2006; Fawell *et al.*, 2006). Fluoride is a major environmental problem resulting in harmful effect in human and animal health in many regions of the world. Ethiopia is one of those countries whose large population (8 million people) is affected by fluoride above 5 mg/L in Rift valley areas (SCHER, 2011; Rango *et al.*, 2018).

Fluoride can be found in the different environmental media like air, water, soil and food(Bisratewongel Tegegne *et al.*, 2013; Asamene Embiale *et al.*, 2014; Seid Mustofa *et al.*, 2014; Gebreegziabher Asayehegn *et al.*, 2014; Kassie Nigus and Chandravanshi, 2016; Yohannes Belete *et al.*, 2017; Lijalem Abeble Dagnaw *et al.*, 2017; Ayfokru Kassahun and Chandravanshi, 2019). Natural sources of fluoride are due to weathering and dissolution of minerals in water bodies, emission from volcanoes and aerosols marine, and manmade sources are fluoride used in industries and waste from various industrial processes (Liteplo *et al.*, 2002; Johansen, 2013).High levels of fluoride are found in the water bodies of the Rift Valley Region of Ethiopia, which is characterized by relatively high volcanic activity in the country (Redda Tekle-Haimanot *et al.*, 1995; Kloos and Redda Tekle-Haimanot, 1999). Volcanic deposits are the main natural source of fluoride in the Ethiopian Rift Valley and contributions from anthropogenic activities are negligible in this area. Consequently, problems related to the intake of high fluoride water are prevalent in this region of the country (Redda Tekle-Haimanot *et al.*, 2006).

Fluoride has many impacts on health therefore it needs various remedial measures for the removal of fluoride up to WHO permissible level. There are many way to remove fluoride such as to use alternative sources of safe water, prevention of industrial fluorosis by rigorous enforcement of procedures for minimizing industrial fluoride pollution and blending high fluoride with low fluoride water (Kloos and Redda Tekle-Haimanot, 1999; Renuka and Pushpanjali, 2013; Roy and Dass, 2013; Khairna *et al.*, 2015).If these alternative methods are not available, defluoridation is another option to remove fluoride. Defluoridation is a process to reduce or removal of high concentration of fluoride to optimal level. The available methods can be broadly classified into five categories, namely adsorption, coagulation/precipitation, ion-exchange, membrane based method (nano-filtration, ultra-filtration, reverse osmosis, electro dialysis and Donnan dialysis) and electrolytic, techniques (Tomar *et al.*, 2013).

Adsorption techniques have been quite popular due to their simplicity, cost effectiveness, and availability of wide range of adsorbent materials. When water is passed through the bed (containing defluoridating agent) this material retain the fluoride. The adsorbent gets saturated after a period of operation and requires regeneration. Most of developing countries use adsorption since it involves the use of low cost materials (Suneetha *et al.*, 2015; Waghmare *et al.*, 2015).Various materials such as activated alumina, aluminum hydroxide, aluminum oxide hydroxide, activated carbon, maghemite, activated bone char, industrial wastes, bauxite, kaolinite and various types of clays are some of the naturally occurring materials that have been used as adsorbent for fluoride removal (Kloos and Redda Tekle-Haimanot, 1999; Beneberu Shimelis *et al.*, 2006; Worku Nigussie *et al.*, 2007; Srimurali and Karthikeyan, 2008; Deshmukh *et al.*, 2009; Jayarathna *et al.*, 2015).

Most widely investigated magnetic materials are iron, cobalt and nickel compounds and alloys (Khan, 2015). Among the other materials, iron oxide particles is an economic solution for the most challenging environmental cleanup problems. Iron oxides are regarded as well-known adsorbent due to their high affinities toward inorganic pollutant, high selectivity in sorption processes, low-cost and environmental friendliness (Zelina, 2013). Most importantly iron oxide particles have often magnetic properties in nature and can be manipulated by external magnetic field gradients (Zelina, 2013). The crystal structure of magnetite give unique properties due to the presence of iron cations in two valence states, $Fe^{+2}$and Fe^{+3} in the crystal structure. Magnetite has the general formula Fe_3O_4(Lakay, 2009).

Aluminum based minerals have high binding affinity with fluoride. These adsorbents have widely been investigated by many researchers in the literature (Beneberu Shimelis *et al.*, 2006; Zhao *et al.*, 2010). However, aluminum based adsorbents are not easy for preparing the composite, have less magnetic properties and results in high aluminum concentration in water after treatment. Therefore, in order to get high magnetic properties, it is necessary to increase iron oxide and to obtain high fluoride adsorption capacity with a little amount of aluminum hydroxide to form iron oxide/aluminum hydroxide composite. Magnetic adsorbents are effective for fluoride treatment due to its simplicity, environmental friendliness, magnetic property, inexpensiveness of the method and speed of defluoridation as compared to the convectional separation. Furthermore, to reduce the health impact from aluminum concentration, the composite adsorbents comprising magnetic $Fe_3O_4/Al(OH)_3$ have therefore been synthesized.

Present study was carried out to investigate the effectiveness of magnetic $Fe_3O_4/Al(OH)_3$ composite for removal of fluoride ion from water. The effect of process parameters such as adsorbent dose, contact time, initial fluoride ion concentration and pH of the solution on the adsorption of fluoride ions using optimal ratio of magnetic $Fe_3O_4/Al(OH)_3$ composite were studied. The adsorption isotherms of adsorbent using different isotherm models were tested for this applicability. The adsorbents were also characterized to know the surface properties. The final goal of this research was to evaluate the removal efficiency of fluoride using magnetic $Fe_3O_4/Al(OH)_3$ composite.

Zhao *et al.* (2010) have prepared magnetic nanosized adsorbent using hydrous aluminum oxide embedded with Fe_3O_4 nanoparticle ($Fe_3O_4@Al(OH)_3$) and applied to remove excessive fluoride from aqueous solution. After water samples have been treated by $Fe_3O_4@Al(OH)_3$, the residual concentration of aluminum was about 0.07 mg/Lat pH 6.5. In the present study, magnetic composite $Fe_3O_4/Al(OH)_3$ was prepared by a simple method. The residual aluminum concentration in the treated water after adsorption of fluoride was 0.01 mg/L. Furthermore, the adsorption capacity of the magnetic composite was found to be higher than most the adsorbent reported in the literature.

MATERIALS AND METHODS

Preparation of adsorbent

Magnetic $Fe_3O_4/Al(OH)_3$ composite were prepared in three successive steps:

(1) Fe_3O_4 was prepared by chemical co-precipitation methods (Zhao *et al.*, 2010; Unsoy *et al.*, 2012; Jokar *et al.*, 2014). 7.99 g of $Fe_2(SO_4)_3$ and 5.56 g of $FeSO_4 \cdot 7H_2O$ were dissolved in 150 mL of deionized water. The mixture was stirred under nitrogen atmosphere for 45 min at 30°C. Then 1.5 M NH_4OH solution was added under vigorous stirring using magnetic stirrer at 80 °C until pH of the solution reached to 9 and the reaction was allowed to run for 2 h. Finally, the system was cooled at the room temperature and resulting black sediment separated by an external magnet and then washed several times by deionized water and ethanol two times and resuspended in 100 mL deionized water. The chemical reaction of Fe_3O_4 formation may be written as Eq. 1 (Lakay, 2009).

$$Fe^{+2} + 2Fe^{+3} + 8OH^{-} \rightarrow Fe_3O_4 + 4H_2O \quad (1)$$

(2) A 0.25 M aluminum nitrate solution and 0.5 M NH_4HCO_3 solution were prepared by dissolving 19.75 g and 46.75 g in 500 mL of deionized water, respectively. Then NH_4HCO_3 and $Al(NO_3)_3$ solutions were added (from two separate burettes) to 400 mL deionized water taken in a reaction vessel drop by drop to precipitate. The mixture was stirred vigorously for less than 3 h and maintained at 70 °C and the pH of the precipitate was controlled in the range of 7.5 to 8.5 using HNO_3 and/or NaOH. After the end of ageing a change of pH occur around 7. The precipitate were finally filtered, washed thoroughly with deionized water and subsequently with ethanol followed by acetone to avoid contamination of Na^+ ions. The precipitate was dried at room temperature and ground to fine powder using mortar (Fentahun Adeno *et al.*, 2014).The following chemical reaction occurs during the preparation:

$$NH_4HCO_3 + H_2O \rightarrow NH_4OH + H_2O + CO_2\uparrow \quad (1)$$

$$Al(NO_3)_3 + 3NH_4OH \rightarrow Al(OH)_3 + 3NH_4NO_3 \quad (2)$$

(3) Magnetic $Fe_3O_4/Al(OH)_3$composite of different mass ratio (0:1, 1:0, 2:2, 3:2, 4:2, 5:2 and 6:2) of Fe_3O_4 to $Al(OH)_3$ were obtained from two successive steps using dry mixing of the two adsorbents.

Preparation of fluoride standard and reagent

Standard stock solutions of fluoride (1000 mg/L F^-) was prepared by dissolving 2.21 g sodium fluoride into 1000 mL deionized water and stored under dark conditions. Standards and samples solutions of fluoride at a required concentration range were prepared by diluting an aliquot of the stock solution using deionized water. Standard fluoride solutions of 0.5, 1.0, 5.0, 10, and 20 mg/L were used for calibration of the instrument. The total ionic strength adjustment buffer (TISAB) was prepared by the reported method (Beneberu Shimelis *et al.*, 2006).

Instrumentation

A pH/ISE meter (Orion Model, EA940 Expandable Ion Analyzer) equipped with combination fluoride selective electrode was used to measure fluoride ion. The method of direct potentiometry was used, where the concentration can be read directly by ratio 1:1 of sample or standard with TISAB in a 50-mL plastic beaker, which regulates the ionic strength of samples and standard solutions, adjust the pH and avoid interferences (Tokalioĝlu *et al.*, 2004).The pH was measured with pH/ion meter (WTW Inolab pH/ION Level 2, Germany) using pH glass electrode. Residual aluminum after fluoride adsorption on to $Al(OH)_3$ and $Fe_3O_4/Al(OH)_3$ was measured by direct photometer. The aluminium content of the treated water was determined by flame atomic absorption spectrometry (Analytik Jena ZEE nit 700P, Jena, Germany).

The X-ray diffraction (XRD) pattern of the adsorbent Fe_3O_4, $Al(OH)_3$, 2:2$Fe_3O_4/Al(OH)_3$ and 5:2 $Fe_3O_4/Al(OH)_3$ were recorded on an X-ray diffractometer (miniFlex 600, Japan) using CuK*a* radiation to evaluate the phase composition. XRD spectra were performed between 10° and 80° (2θ). The point of zero charge (pH_{PZC}) of magnetic$Fe_3O_4/Al(OH)_3$composite was measured by potentiometric mass titrations technique (Eyobel Mulugeta *et al.*, 2015).

Batch adsorption studies

Batch adsorption experiments were performed by placing known amounts of the synthesized $Fe_3O_4/Al(OH)_3$ magnetic composite into 250 mL of aqueous solutions of fluoride in a conical flask and stirred using a magnetic stirrer at room temperature (22 ± 2 °C). A sample was periodically taken out from each flask and filtered the aqueous phase from suspension by applying a strong magnetic field (magnetic settlement), and isolate the supernatant before fluoride determination. The effect of adsorbent dosage (1-6 g/L), initial fluoride concentration (5-70 mg/L), contact time (30-480 min), raw water pH (4-11) and common ions (SO_4^{-2},PO_4^{-3},Cl^-, NO_3^- and HCO_3^-) were investigated by varying any one of the parameters and keeping the other parameters constant. All the adsorption studies were performed in triplicate and (mean ± standard deviation) was used to calculate adsorption capacity (mg F^- adsorbed/g of adsorbent) and fluoride removal efficiency (%) at a given contact time for the selected adsorbents

Adsorption isotherms

Adsorption isotherms were conducted using an adsorbent dose of 4 g/L and varying initial fluoride concentrations within the range between 5 and 70 mg/L. The experimental data obtained in the present work was tested with the Langmuir, Freundlich and Dubinin–Radushkevich, isotherm models. Linear regression was used to determine the best-fitting isotherm, and the applicability of isotherm equations was compared by the correlation coefficients.

Adsorption kinetics

The fluoride adsorption kinetics of linear form (pseudo-first-order, pseudo-second-order and intra-particle diffusion) of adsorbent was studied for each initial fluoride concentrations of 20.0, 10.0 and 5.0 mg/L with the corresponding adsorbent dose of 4, 2 and 1 g/L, respectively, at constant surface loading.

Effect of co-exiting ions

To investigate the effect of co-exiting ion on fluoride removal in the presence of anions most commonly found in water, including PO_4^{3-}, SO_4^{2-}, Cl^-, HCO_3^- and NO_3^-, the amounts of fluoride adsorbed by 4 g/L of the adsorbent, while keeping initial F^- concentration as 10 mg/L containing anions at a concentration ranging from 100-500 mg/L of each anion was determined from Na_2HPO_4, Na_2SO_4, NaCl, $NaHCO_3$, and $NaNO_3$. Samples were withdrawn after 3 h and analyzed for residual fluoride concentrations.

Statistical analysis of data

All the experiments were done in triplicate. The data were analyzed by Microsoft Excel. The results are reported as mean of the triplicate measurements.

RESULTS AND DISCUSSION

Calibration of electrode

The electrode was calibrated using a series of known concentrations of fluoride solution 0.5,1, 5, 10 and 20 mg/L. The potential of each solution was measured and plotted as a function of fluoride concentration. The slope of the curve was −57.2 mV/decade which was found in the optimum range (−57 to −60 mV/decade) and the standard deviation (SD) was 2.6 mV, which shows good precision. The correlation coefficient was 0.998 which indicated very good correlation between electrode potential and concentration of fluoride.

Optimization of magnetic Fe_3O_4 to $Al(OH)_3$ ratio

The optimal mass ratio of $Fe_3O_4/Al(OH)_3$ was obtained by varying the amount of Fe_3O_4 to $Al(OH)_3$ in different ratio (1:0, 0:1, 2:2, 3:2, 4:2, 5:2). The results demonstrated that unmodified iron oxide and aluminum hydroxide reached a removal efficiency of 7.3% and 99.3%, respectively. The removal efficiency of fluoride decreased significantly when the magnetic particles of Fe_3O_4 increased. The results are shown in Figure 1. However, increasing amount of magnetic Fe_3O_4 in the composite resulted in strong magnetization properties. Thus, separation of the treated water from adsorbents was accomplished easily by removing the adsorbent using an external magnet. When the mass ratio of Fe_3O_4 to $Al(OH)_3$ reached 5:2, there was no significant change in the percentage of fluoride removed but, further increasing of the Fe_3O_4 to constant $Al(OH)_3$ resulted in decreasing of fluoride removal efficiency. The fluoride removal efficiency of aluminum hydroxide without Fe_3O_4 was 99.3%. As the amount was Fe_3O_4increases the fluoride removal efficiency gradually decreases up to 88% due to decrease in $Al(OH)_3$ (which is mainly responsible for the removal of fluoride) but the magnetic property of the composite increases up to the ratio of 5:2 due to increase in the magnetic component (Fe_3O_4)of the composite (Zhao *et al.*, 2010). However, when the ratio of Fe_3O_4 to $Al(OH)_3$ was further increased the fluoride removal efficiency of the composite was substantially decreased due to decrease in $Al(OH)_3$. Similar results were also reported in the literature (Chai *et al.*, 2013; García-Sánchez *et al.*, 2016).Therefore, ratio of 5:2 was selected for further work due to higher magnetic component (Fe_3O_4) of the composite and comparable fluoride adsorption capacity of the composite.

It should be noted that magnetic property of the adsorbent does not result in fluoride removal. The strong/higher magnetic property of the adsorbent does not increase the fluoride removal efficiency. The strong/higher magnetic property of the adsorbent results in easiness of separation of the adsorbent after the removal of fluoride.

It should also be noted that the selection of 5:2 Fe_3O_4 to $Al(OH)_3$ magnetic composite was based on the easiness of separation of the adsorbent after the removal of fluoride while keeping the fluoride removal efficiency to a acceptable value. Even though lower ratios Fe_3O_4 to $Al(OH)_3$ magnetic composites have higher fluoride removal efficiencies, the separation of adsorbent after the removal of fluoride was not easy as compared to that of 5:2 Fe_3O_4 to $Al(OH)_3$ magnetic composite.

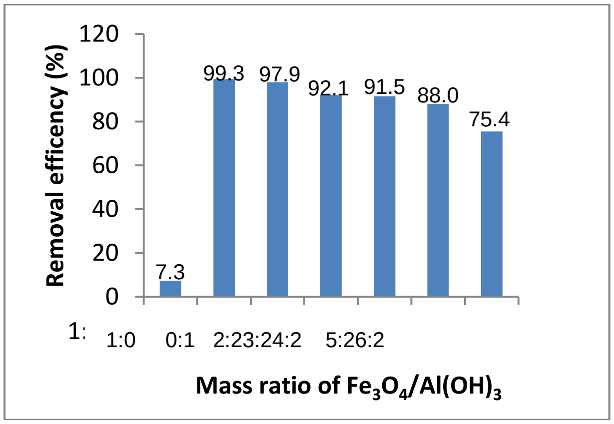

Figure 1. Effect of magnetic Fe_3O_4 to $Al(OH)_3$ on removal efficiency of fluoride (initial concentration = 10 mg/L, adsorbent dosage = 4 g/L, contact time = 180 min, pH = 7.0).

X-ray diffraction (XRD)

The XRD pattern of the adsorbents Fe_3O_4, $Al(OH)_3$, 2:2 $Fe_3O_4/Al(OH)_3$ and 5:2 $Fe_3O_4/Al(OH)_3$are shown in Figure2.The XRD pattern shown in (black) was amorphous aluminum hydroxide as it was also suggested by (Eyobel Mulugeta *et al.*, 2015; Meseret Dessalegne *et al.*, 2017). The XRD pattern shown in (red) has sharp peaks in the reflection angle range of 10-80° which indicated that the material (Fe_3O_4) has crystalline structure. In addition the sharp peaks at 30.3°, 32.12°, 35.76°, 43.5°, 57.3°, 62.96° and 71.48° are consistent with the expected composition of magnetite or maghemite (Zhao *et al.*, 2010; Zhang *et al.*, 2014).The XRD peaks of $Fe_3O_4/Al(OH)_3$ with different mass of Fe_3O_4 and $Al(OH)_3$ ratio were similar to the XRD peaks of Fe_3O_4. It can be seen that the intensities of the peaks decreased in 2:2 $Fe_3O_4/Al(OH)_3$ (blue). There is some difference in the XRD peaks observed for $Al(OH)_3$ of present study to that reported by Zhao *et al.* (2010). The reason for the difference in XRD peaks observed in the present work and that presented by Zhao *et al.* (2010) may be due differences in the method of preparation.

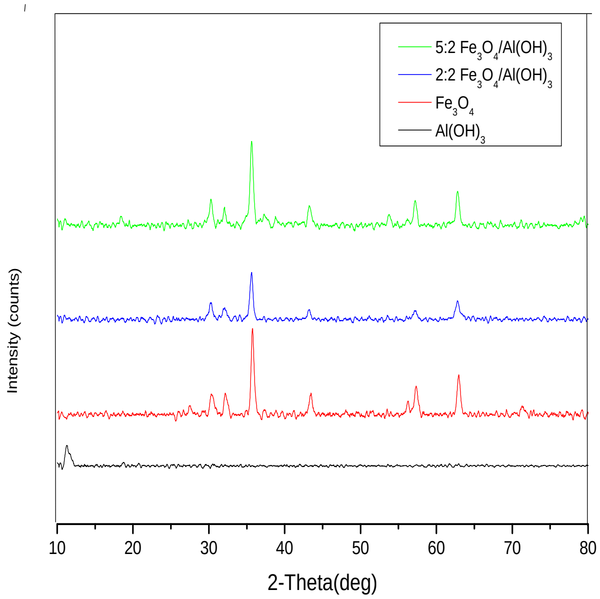

Figure 2. XRD pattern of $Al(OH)_3$ (black), Fe_3O_4 (red), 2:2 $Fe_3O_4/Al(OH)_3$ (blue) and 5:2 $Fe_3O_4/ Al(OH)_3$ (green).

Point of zero charge (PZC)

The point of zero charge (pH_{PZC}) of 5:2 Fe_3O_4/Al(OH)$_3$ was 9.5 (Figure3). This indicated the surface is positively charged when solution pH is below its pH_{PZC} (9.5) which is suitable for the adsorption of negatively charged anions, due to an electrostatic attraction or ion exchange between the fluoride and magnetic Fe_3O_4/Al(OH)$_3$ composite.

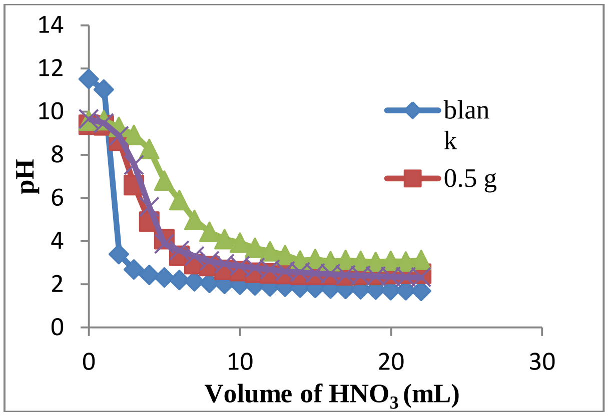

Figure3.Point zero charge (PZC) of magnetic Fe_3O_4/Al(OH)$_3$ composite.

Batch adsorption experiment

In preliminary batch experiment Fe_3O_4 was tested to evaluate its removal efficiency at initial concentration of fluoride 10 mg/L, adsorbent dosage of 4 g/L and contact time of 180 min. The fluoride adsorption capacity of Fe_3O_4 was low (0.18 mg/g). Therefore, the rest of the experiments were conducted using the optimized 5:2 Fe_3O_4/Al(OH)$_3$ adsorbent. On other hand, residual aluminum after adsorption of fluoride was tested for Al(OH)$_3$ and Fe_3O_4/Al(OH)$_3$ and the results were found to be 0.04 mg/L and 0.01 mg/L, respectively.

Effect of contact time and dosage was studied by the measuring residual fluoride concentration by varying a dosage of 1, 2, 3, 4 and 6 g at constant initial concentration of 10 mg/L (Figure4).The residual fluoride concentration vs time indicated that residual fluoride concentration decreased as adsorbent dosage as well as contact time increased. The rate of fluoride removal increased as function of time for several minutes. Rapid rate of fluoride removal was observed during first 60 min. But after 60 min the rate of removal became slower and reaches equilibrium with in the 180 min. This means the adsorption was completed in the first three hours indicating that longer time has a negligible effect on the adsorption. The rate of fluoride removal was fast in the beginning due to available of larger surface areaof the adsorbent and sufficient vacant adsorbing sites in presence of higher fluoride concentration gradient (Sheta Alemu *et al.*, 2014). Slower rate of removal was observed after 60 min due to limited vacant adsorption sites available (Gizachew Wendimu *et al.*, 2016). Therefore, 180 min was found to be enough for the removal of fluoride to less than the WHO maximum allowable concentration with 89.4% removal efficiency at an adsorbent dose of 4 g/L.

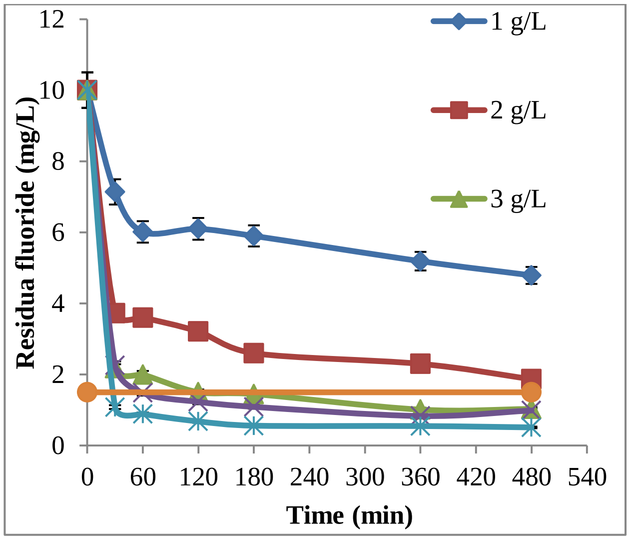

Figure4. Residual fluoride concentration as a function of time for different doses of magnetic Fe_3O_4/Al(OH)$_3$ (initial concentration = 10 mg/L).

The percentage removal of fluoride ion increased from 41 to 94% as adsorbent dosage increased from 1 to 6 g/L due to large availability of fluoride binding site as shown in Figure5. On the other hand, the amount adsorbed per unit mass of the adsorbent (adsorption capacity) decreased considerably. Due to adsorption sites remaining unsaturated and initial concentration of fluoride was constant (fewer fluoride ions per unit mass of adsorbent) during the adsorption process. To maintain reasonable capacity and high removal efficiency, the surface loading for optimum fluoride removal (about 89%), was a dosage of 4 g/L. Therefore, for the rest of study a dose of 4 g/L corresponding to adsorption capacity of 2.2 mg F^-/g and removal efficiency of 89.4% within 180 min were selected for further experiment and further increase in the dose result in too much wastage of material without further removing the fluoride.

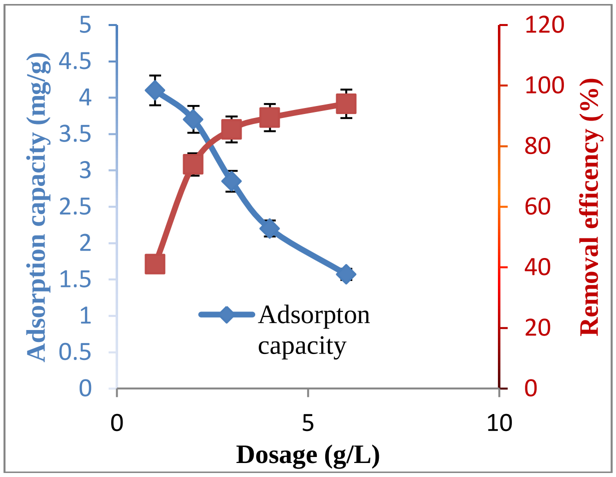

Figure5.Capacity and efficiency (%) as a function of adsorbent dose (C_o = 10 mg/L, contact time = 180 min).

Increase in the initial fluoride concentration results in a decrease of removal efficiency. However, the residual fluoride concentration at equilibrium increases with an increase in initial fluoride concentration and also the adsorption capacity increase with increase initial fluoride concentration. It was observed that rapid removal in low initial fluoride concentration at the initial stage than the high concentration of fluoride, due to the surface area and the availability of adsorption sites were relatively high and the F^- ions were easily adsorbed. At higher initial solution concentration, the total available adsorption sites are limited (utilization of less accessible or less active sites of the adsorbent due to increase diffusivity), thus resulting in a decrease in percentage removal of F^- ions. For the initial concentration of fluoride less than or equal to 10 mg/L and adsorbent dosage 4 g/L, more than 85% removal was observed within 3 hours contact time (Raul *et al*., 2012; Sheta Alemu *et al*., 2014).

Effect of initial pH

The effect of pH on the adsorption of F^- by magnetic $Al(OH)_3$is shown in Figure6. It can be seen that percentage of fluoride removal efficiency increased while the pH of the solution increased up to pH 6, practically remained constant within pH range 6-10 and reached maximum of 86.6% at pH = 7. Although decrease in the removal efficiency in the solution pH > 10 and pH <6. The point of zero charge (pH_{pzc}) of magnetic $Fe_3O_4/Al(OH)_3$ composite is 9.5, which means the surface of the adsorbent presents a net positive charge when pH ≤ 9.5. Therefore, the increase removal efficiency of fluoride in pH less than 9 can be attributed to the gradual increase in attractive forces or ion exchange. At pH ≥ 9.5, the surface of the magnetic $Al(OH)_3$ composite was negatively charged, which tended to repel the fluoride ions via electrostatic repulsion and decrease the fluoride adsorption (Zhao *et al.*, 2010). Likewise, the H^+ ions present in the solution reacts with the fluoride ions leads to weak ionized HF formation at the pH <5. Therefore, it is frequently noticed that at low pH, the adsorption of fluoride ion decreases and at high pH = 11, the competition between the fluoride ions and OH^- ions in aqueous solution for the adsorption sites was also likely to contribute to the reduction of fluoride removal in the alkaline (Tripathy *et al.*, 2006; Waghmare and Arfin, 2015).

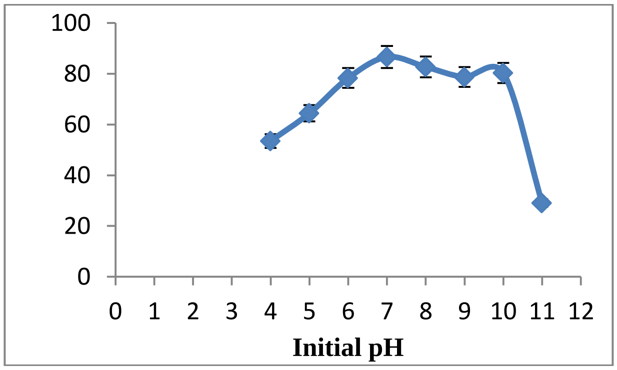

Figure6. Effect of initial pH on fluoride removal efficiency by magnetic $Fe_3O_4/Al(OH)_3$ composite (dose = 4 g/L, contact time = 180 min).

Adsorption isotherm study

Figure7 shows the experimental adsorption isotherm of fluoride on magnetic $Fe_3O_4/Al(OH)_3$ composite adsorbent. As can be seen from Figure7 the equilibrium adsorption capacities increases with increasing the concentration from 5 to 70 mg/L.

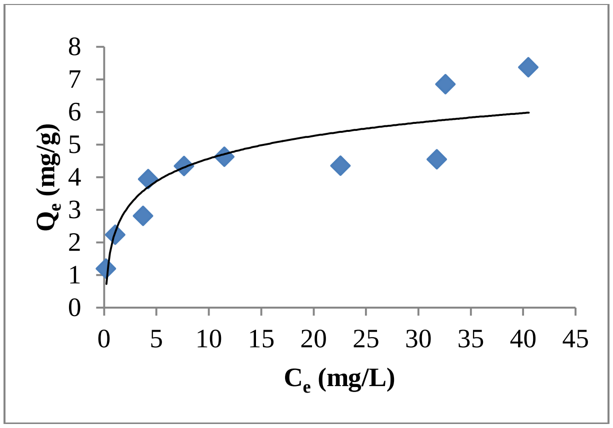

Figure7. Equilibrium adsorption data for the adsorption of fluoride on to magnetic $Fe_3O_4/Al(OH)_3$ composite (initial fluoride concentration = 5-70 mg/L, adsorbent dosage = 4 g/L, contact time = 180 min, initial pH = 7).

Langmuir isotherm model

The value of q_m and b constants and the correlation coefficient were determined from slope and intercept in the linear plot of C_e/q_evs. C_e and are presented in Table 1. The sorption capacity, q_m which is a measure of the maximum adsorption capacity corresponding to complete monolayer coverage, is 6.67 mg/g. The adsorption coefficient, b that is related to the apparent energy of sorption for F^- onto $Fe_3O_4/Al(OH)_3$ is 0.243 L/mg and the related correlation coefficient R^2 value is (0.879).

Table 1.Values of constants and coefficient of determination for adsorption isotherm data of Freundlich, Langmuir and Dubinin-Radushkevich isotherms.

Freundlich			Langmuir			Dubinin-Radushkevich		
K_F (mg/g)	n	R^2	q_m (mg/g)	b (L/mg)	R^2	q_s (mg/g)	E (kJ/mol)	R^2
2.08	3.28	0.911	6.67	0.243	0.879	2.4×10^{-4}	2.5	0.66

Freundlich isotherm model

From the experimental data Freundlich parameters along with correlation coefficients were obtained by plotting log (q_e) vs. log (C_e) and generated the intercept value of K_F and the slope of 1/nas shown in Table 1. The Freundlich constants K_F and 1/n of the adsorption isotherm was 2.08 and 0.305, respectively, and the related correlation coefficient R^2 value is 0.911. The low value of 1/n (less than 1) indicates favorable condition of adsorption (Zhao *et al.*, 2010). This indicated that the Freundlich model give a good fit to the sorption process.

Dubinin–Radushkevich (D-R) isotherm

The D-R isotherm was applied and the E value was 2.5kJ/mol. If E < 8 kJ/mol, the adsorption can be explained by simple physical interaction, which means that fluoride ions were attracted to magnetic $Fe_3O_4/Al(OH)_3$ via physical adsorption (Kilislioglu and Biligin, 2003).

Isotherm parameters and the correlation coefficients (R^2) obtained from the linear curves of each isotherm model are summarized in Table 1.Freundlich isotherm R^2 = 0.911 is higher than Langmuir isotherm R^2 = 0.879 and D-R isotherms R^2 = 0.66.It can be concluded that Freundlich isotherm is the best suited for adsorption of fluoride ion than Langmuir isotherm and D-R isotherms. Thusit can be predicted that the adsorption takes place on a heterogeneous in nature of adsorbent surface. The maximum adsorption capacity obtained from Langmuir model was found 6.67 mg/g.

Adsorption kinetics

The residual fluoride concentrations as a function of time are shown in Figure8. The fluoride adsorption on the magnetic$Fe_3O_4/Al(OH)_3$ exhibited an initial rapid uptake followed by a slower removal rate that gradually reached equilibrium. The initial rapid adsorption was presumably due to ion exchange with surface hydroxyl ions of the adsorbent. The phenomena are due to the availability of numerous active sites on the adsorbent. The slow adsorption in the later stage represents a gradual uptake of fluoride at the inner surface (Gizachew Wendimu *et al.*, 2016). For all initial concentration of fluoride, almost all adsorption processes were occurred within 60 min. More than 50% of the adsorption took place during the rapid rate period, the adsorption process increased gradually. Finally, it becomes almost constant at the equilibrium which was possibly caused by the decreasing of the driving force as it approaches to equilibrium.

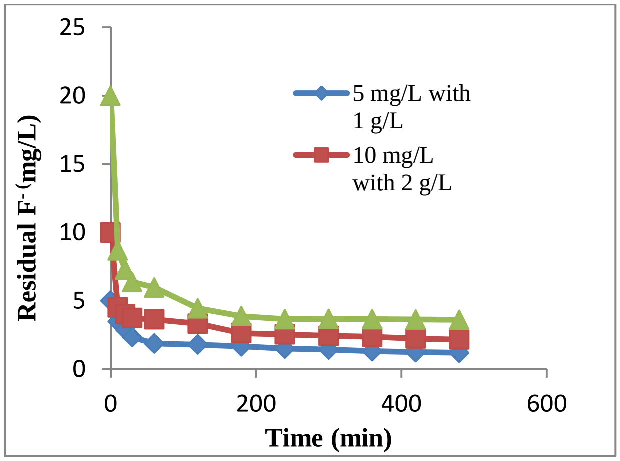

Figure8. Adsorption kinetics of fluoride on magnetic $Fe_3O_4/Al(OH)_3$ adsorbents at constant surface loading 5 mg/g (average pH = 7 and initial concentration = 10 mg/L).

The pseudo-first-orderrate constants for the three initial fluoride concentration of each adsorbent are close to each other. Thus the three rate constants of the adsorbent averaged to get single rate constants. From the data given in Table 2pseudo-first order kinetic predicts a lower value of the equilibrium adsorption capacity than the experimental value. Hence, pseudo-first-order equation cannot provide an accurate fit of the experimental data.

The pseudo-second-order rate constants for the three initial fluoride concentration of each adsorbent are close to each other. Thus the three rate constants of an adsorbent averaged to get single rate constants. Kinetic parameters, obtained by calculation from the slopes and intercepts of the Pseudo-second-order kinetic plots are shown in Table 3. The pseudo-first-order kinetic equation describes the kinetic data with (R^2 = 0.982). The pseudo second-order kinetic equation describes the present data best (R^2 = 0.999) in the concentration range of fluoride used for the adsorption study. The correlation coefficient values was much closer to 1 and the equilibrium adsorption capacities obtained with pseudo-second order model was closer to those of the results with experimental data. Thus, it is evident that the pseudo-second-order kinetics is the best representative for the adsorption kinetic of fluoride onto magnetic Fe_3O_4/Al$(OH)_3$ composite.

Table 2. Summary of the pseudo-first-order rate constants and correlation coefficients.

Initial F^- and adsorbent dose	Rate equation	R^2	k_1 (1/min)	$q_{e, cal}$ (mg/g)	$q_{e, exp}$ (mg/g)
5 mg/L with 1 g/L	$\log (q_e-q_t) = -0.002t + 0.238$	0.947	4.61×10^{-3}	1.73	3.81
10 mg/L with 2 g/L	$\log (q_e-q_t) = -0.003t + 0.056$	0.976	6.91×10^{-3}	1.14	3.92
20 mg/L with 4 g/L	$\log (q_e-q_t) = -0.006t + 0.026$	0.943	1.38×10^{-2}	1.06	4.10
Average	$\log (q_e-q_t) = -0.004t +0.107$	0.982	9.21×10^{-3}	1.28	3.95

Table 3.Summary of the pseudo-second-order rate constants and correlation coefficients.

Initial F^- and adsorbent dose	k_2 (mg/g min$^{(1/2)}$	Rate equation	R^2	$q_{e, cal}$ (mg/g)	$q_{e, exp}$ (mg/g)
5 mg/L with 1 g/L	1.28×10^{-2}	$t/q_t = 0.256t + 5.078$	0.998	3.91	3.81
10 mg/L with 2 g/L	2.18×10^{-2}	$t/q_t = 0.252t +2.918$	0.999	3.97	3.92
20 mg/L with 4 g/L	3.49×10^{-2}	$t/q_t = 0.240t + 1.647$	0.999	4.17	4.10
Average	1.93×10^{-2}	$t/q_t = 0.249t + 3.214$	0.999	4.02	3.95

Effect of co-existing anions

The presence of phosphate and bicarbonate (100-500 mg/L) decreased the fluoride removal efficiency approximately to 35% and 39%, respectively, while in case of sulfate, chloride and nitrate (100-500 mg/L) slightly decreased the removal efficiency to 82.3%, 88% and 87.8% (Figure 9). Overall, impact of major anion on the removal efficiency of fluoride on to magnetic Fe_3O_4/Al$(OH)_3$ followed the order: $PO_4^{3-} > HCO_3^- >> SO_4^{2-} > NO_3^- \sim Cl^-$(Figure 9) and these results are consistent with the work of Mulugeta *et al.*(2015)

and Gizachew *et al.* (2016). The fluoride removal decreased in the presence of phosphate due to the sorption competition occurred for the limited amount of sorption sites on $Fe_3O_4/Al(OH)_3$ and also divalent and trivalent anions have more effect than monovalent anions on adsorption capacity(Eyobel Mulugeta *et al.*, 2015). Also in the presence of bicarbonate decreased the removal efficiency at all concentration due to significance increase in pH of solution as increasing the concentration of HCO_3^- and competitive nature of HCO_3^- on to adsorption site (Srimurali and Karthikeyan, 2008).

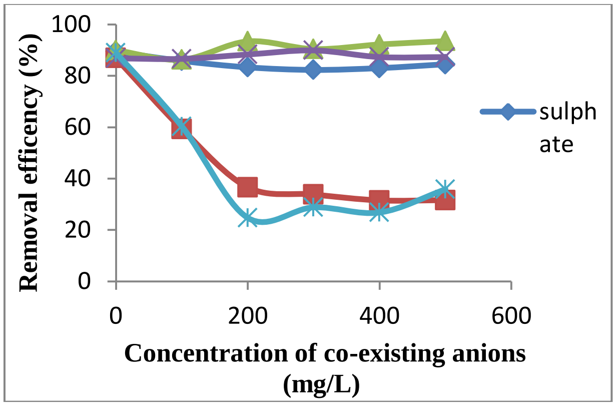

Figure 9.Fluoride removal efficiency of magnetic $Fe_3O_4/Al(OH)_3$at different anion concentrations (adsorbent dose = 4.0 g/L, initial concentration = 10 mg/L, contact time = 180 min).

Adsorption mechanism of the magnetic $Fe_3O_4/Al(OH)_3$

Based on pH_{PZC} and change in pH after adsorption studies a possible mechanism of removal of fluoride on to magnetic adsorbent can be represented as (i) while solution pH < pH_{PZC}, fluoride removed by ion exchange can be suggested as possible mechanism for fluoride removal process. To ensure this idea, the pH change studies were conducted at different initial pH and measuring the final pH after adsorption. As shown in Figure10, ΔpH was calculated by subtracting the pH at equilibrium time after addition of F^- from the initial pH. When the initial pH is lower than 8, an increase in ΔpH was observed after 180 min. However, when the initial pH is above pH of 8, ΔpH was observed to decrease. The increase in pH could be due to liberation of OH^- from magnetic adsorbent and then replaced by fluoride as shown in Eq. 4 (Fentahun Adeno *et al.*, 2014). This equation explains inner surface complexation of magnetic adsorbent which is chemical adsorption. Eq. 4 shows the ion exchange reaction (Wang *et al.*, 2009; Fentahun Adeno *et al.*, 2014; Meseret Dessalegne *et al.*, 2017):

$$Fe_3O_4\text{-}AlOH + F^- \rightarrow Fe_3O_4\text{-}AlF + OH^- \quad (3)$$

(ii) When initial pH > pH_{PZC}, the surface of adsorbent was negative charge therefore, fluoride adsorption capacity decreased due repulsion of the negatively charged surface and fluoride ions. When pH > pH_{ZPC}, the adsorbent act as a cation exchanger and adsorb Na^+ ion present in solution thereby releasing protons responsible for overall decreasing in final pH of the medium as shown in Eq. 5. Therefore, the adsorption could be due to the weak attractive force (van der Waal force). The result is also in agreement with the proposed adsorption mechanism, in discussion under the D-R isotherm test for adsorption energy value. If the magnitude of free energy of adsorption is <8 kJ/mol, the adsorption process corresponds to physical adsorption; adsorption might take place by van der Waal forces, which is evident from the decrease in final pH (Wang *et al.*, 2009).

$$Fe_3O_4\text{-}Al(OH)_3(s) + Na^+(aq) + F^-(aq) \rightarrow Fe_3O_4\text{-}AlO^-Na^+F^-(solid) + H^+ \quad (4)$$

Over all, mechanism of fluoride adsorption on to the magnetic aluminum hydroxide is a complex process which may be combination of chemical adsorption and inter particle diffusion according to the above experiments.

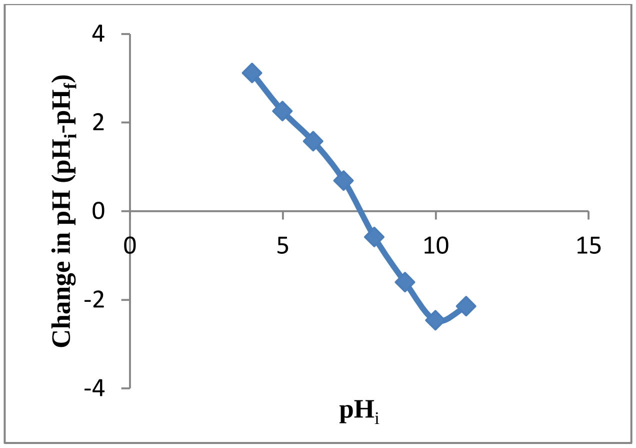

Figure10. Change in pH after adsorption process. (C_o = 10 mg/L, contact time = 180 min, dose = 4 g/L).

Comparison of different adsorbents on fluoride removal techniques

A comparison of the proposed magnetic $Fe_3O_4/Al(OH)_3$ adsorbent with the other adsorbent reported in the literature was made in terms of fluoride removal efficiency and the adsorption capacity (Table 4). The proposed magnetic $Fe_3O_4/Al(OH)_3$ adsorbent showed fluoride removal efficiency of 89% within 3 hours of equilibrium contact time with an adsorption capacity of 6.67 mg F^- per g of the adsorbent. Chai *et al* .(2013) reported a novel adsorbent of sulfate-doped Fe_3O_4/Al_2O_3 nanoparticles with magnetic separability for fluoride removal from drinking water. Its adsorption capacity is 70.4 mg/g with an equilibrium time of 8 hand the fluoride removal efficiency reached up to 90%. While the adsorption capacity of this adsorbent is much higher than the proposed adsorbent, its equilibrium time is longer and fluoride removal efficiency is comparable to the present adsorbent. García-Sánchez *et al.* (2016) modified natural magnetite ore (Fe_3O_4) with aluminum and lanthanum ions to increase the fluoride removal efficiency from aqueous solutions. Batch tests showed the adsorption efficiency of 90% and 96% for the aluminum and lanthanum modified materials, respectively. But its adsorption capacity (1.5 mg/g) is lower than the proposed adsorbent and its contact time is also long, 24 hours. Wang *et al.* (2009) investigated the fluoride removal potential of nano-scale aluminum oxide hydroxide (nano-AlOOH).Its fluoride removal efficiency is higher than 90% with an adsorption capacity of 3.26 mg/gand 6 hours equilibrium time. Its fluoride removal efficiency is comparable but its adsorption capacity is lower and equilibrium time is longer than the proposed adsorbent. Fentahun Adeno *et al.* (2014) studied the fluoride removal potential of nanoscale aluminum oxide hydroxide (nano-AlOOH). Its adsorption capacity is 20.75 mg/g with an equilibrium time of 1 hour. It has higher adsorption capacity and shorter equilibrium time than the proposed adsorbent. Jayarathna *et al.* (2015) investigated fluoride adsorption on γ-Fe_2O_3nanoparticles. A rapid adsorption occurred within 15 min by removing 95±3% and reached equilibrium thereafter. The removal of fluoride capacity is 3.65mg/g. Its fluoride removal efficiency is higher and faster than the present adsorbent. However, its adsorption capacity is lower than the proposed adsorbent. Maliyekkal *et al.* (2006) have investigated the adsorption potential of manganese-oxide-coated alumina (MOCA) and activated alumina (AA) for defluoridation of drinking water. The maximum fluoride uptake capacity for MOCA and AA are 2.85 and 1.08mg/g with equilibrium times 3 hours and 10 hours, respectively. The adsorption capacities are lower than the present adsorbent. The equilibrium time of MOCA is comparable with the present adsorbent but the equilibrium time of AA is longer than the proposed adsorbent. It can be stated that $Fe_3O_4/Al(OH)_3$ is effective and highly magnetic adsorbent for the removal of fluoride from aqueous solutions.

Table 4.Comparison of different adsorbent for the removal of fluoride from aqueous solutions.

Adsorbents	Adsorption capacity (mg/g)	Equilibrium time (h)	pH	Reference
Sulfate-doped Fe_3O_4/Al_2O_3 nanoparticles	70.4	-	7	(Chai *et al.*, 2013)
Modified natural magnetite with Aland La ions	1.5	24	7.8	(García-Sánchez *et al.*, 2016)
Nano-AlOOH	3.26	6	5.2 ± 0.2	(Wang *et al.*, 2009)
Nano-AlOOH	20.75	1	7	(Fentahun Adeno *et al.*, 2014)
$\gamma - Fe_2O_3$ nanoparticles	3.65	-	6.5	(Jayarathna *et al.* (2015)
Activated alumina (grade: AD101-F)	1.08	10	7	(Maliyekkal *et al.* 2006)
Manganese-oxide-coated alumina	2.85	3	7	(Maliyekkal *et al.*2006)
Synthetic nano-hyroxy- apatite (n-HAp)	4.575	1.6	5.0-6.0	(Gao *et al.* 2009)
Magnetic $Fe_3O_4/Al(OH)_3$	6.67	3	7	This study

CONCLUSION

This study investigated the removal of fluoride using magnetic $Fe_3O_4/Al(OH)_3$ composite. For a given optimal condition removal efficiency >85% was obtained from initial concentration of 10 mg/L fluoride at 180 min in neutral pH and dosage 4 g/L. Higher fluoride uptake capacity was in pH range6–10. The equilibrium adsorption data fitted well with Freundlich isotherm model than Langmuir isotherm and D-R isotherm models. The maximum adsorption capacity of the magnetic $Fe_3O_4/Al(OH)_3$ was 6.67 mg/g. The kinetic studies showed that adsorption reaction of fluoride removal by magnetic $Fe_3O_4/Al(OH)_3$ composite can be well described by pseudo-second-order kinetic. Among the ions present in experiment PO_4^{3-} and HCO_3^- showed a significant effect on fluoride adsorption capacity. The adsorption mechanism to remove the fluoride was due to ion exchange. Additionally, it is preferable to carryout defluoridation on $Fe_3O_4/Al(OH)_3$ at neutral water pH while preventing aluminum dissolution and moreover no acid/alkali treatment is required after treatment. The adsorbent has a magnetic property which makes its removal of fluoride from treatment media by applying magnetic field possible. These properties made the composite an efficient adsorbent for removal of fluoride ions from water.

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