Reduction of Fluorine in Water Using Clay Mixed with Hydroxyapatite

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Abstract

There was a gradual increase in the adsorption capacity of the Clay-HAp (C-HAp) mixture for the fluoride ions as time increased. A maximum adsorption capacity of 0.995mg/g and fluoride removal of 99.5% of the initial fluoride concentration was observed at the time (30 min) of the maximum adsorption. C-HAp mixture showed that the equilibrium concentration of fluoride decreased with increasing adsorbent dose. The maximum adsorption capacity was found to be 18.409 mg/g for the adsorbent dose of 1.25 g/L. The fluoride removal efficiency remained the same from pH 2-4 and increased steadily to pH 6, hence maximum adsorption was observed at pH of 6. As the initial fluoride concentration increased, the adsorption capacity of the C-HAp also increased. . The equilibrium data for the adsorption fitted the Freundlich more than Langmuir isotherm models. The adsorption mechanism was analyzed for pseudo first and second order reactions. The values of correlation coefficient ($R^2 = 1.00$, 0.9999 and 1.00) of the second order model for the three concentrations (5.0, 10.0 and 15.0 mg L^{-1}) were equal or closer to unity than the first order model.

Keywords: fluoride, clay, hydroxyapatite, adsorption, isotherm, defluoridation

1. Introduction

Fluoride is one of the most important elements for both human and animal health. Within the permissible limit of $0.5 – 1.5$mg L^{-1}, fluoride serves to maintain healthy teeth and bones. On the other hand, elevated levels of fluoride (>1.5mg L^{-1}) can cause long-term diseases such as dental ($1.5 – 4.0$mg L^{-1}) and skeletal fluorosis ($4.0 – 10.0$mg L^{-1}). These diseases are usually associated with molting of teeth in mild cases, soft bones and neurological damage in severe cases (Fan *et al.,* 2003)

Water is the major contributor of the total fluoride intake in the human body. Thus, it is very crucial to determine the amount of fluoride present in drinking water especially for communities in developing countries. Most rural communities in developing countries depend on natural sources of water such as rivers, streams, boreholes and dams for their water supply (Dang-i and Soboyejo, 2013). Water in many parts of the world contains levels of fluoride that is greater than 0.5 mg L^{-1} and this is mainly due to the natural presence of fluoride in the earth's crust, agricultural and industrial activities (Srimurali *et al.,* 1998). The main sources of high levels of fluoride in natural water sources include; addition of fluoride by volcanic activities, high-water rock interactions and low calcium concentrations (Symonds *et al.,* 1988)

The prevention of the adverse effects associated with high fluoride concentration can be a herculean task, which requires suitable socio-economic conditions of knowledge, motivation, discipline and techniques (Fentahum, 2010). There are several methods that can be used in the defluoridation of water highly contaminated with fluoride. These methods can be generalized into the following; Precipitation, Adsorption and Membrane based methods (Fentahum, 2010). Usually when dealing with the process of precipitation, soluble chemicals are added to the water and they remove the fluoride either by precipitation, co-precipitation or adsorption onto the initial precipitate.

The use of precipitation as a means of defluoridation has being exploited by many researchers using materials such as calcium phosphate, iron, lime and magnesium compounds and alum (Boruff, 1934; Nawlakhe*et al.,* 1974; He and Cao, 1996; Eva et al., 2009). Materials such as lime and magnesium leaves the treated water with high pH making the water unsafe for consumption. Studies have also shown that in using alum, large amounts are required due to its low efficiency in fluoride removal. It also comes with the problem of large sludge disposal (Shrivastava and Vani, 2009)

Membrane methods for fluoride removal in water involves processes such as nanofiltration (Tahaikt et al., 2007), reverse osmosis (Min *et al.,* 1984), electrodialysis (Nalan*et al.,* 2008) and electrocoagulation (Sanjeev*et al.,* 2009). These processes require high technical know-how and also come with a high cost of maintenance. These limitations make this method unsuitable for developing countries. In the adsorption process for fluoride removal, various materials such as aluminum oxide hydroxide, various types of clays and red mud, bone char etc. are employed (Fawell*et al.,* 2006). The adsorption method presents a promising opportunity for fluoride removal especially in developing countries since it involves the use of low cost materials.

Since the people who rely on underground water as their source of drinking water are poor, it is only prudent to use methods for defluoridation that are not cost intensive and easy to maintain. It was based on these reasons that this work sought to investigate the fluoride removal capacity and adsorption characteristics of clay mixed with hydroxyapatite.

2. Materials and Methods

2.1. Sample Collection and Treatment

The clay sample was collected from Siriguclay deposits at Kasina-Nankana District of Upper East Region, Ghana. The sample was collected along a pit sank in the clay deposit and at a depth of 10cm. The sample was then placed in a polythene bag, transported and stored in the laboratory. The clay sample was then sundried till completely dried. Impurities such as leaves and debris of plants parts and stones were removed from the clay. The sample was then pulverized, sieved through a 3mm sieve and stored in small polythene bag in the laboratory for analysis.

2.2. Hydroxylapatite Synthesis

The hydroxyapatite (HAp) used in this work was synthesized in the laboratory using diluted 85% ortho-phosphoric acid, (H_3PO_4) and calcium hydroxide, $Ca(OH)_2$ in a water bath at a temperature of 90ºC.
All the reagents used were of analytical grade, and were obtained from the laboratory of the Department of Applied Chemistry and Biochemistry, University for Development Studies.

2.3 Fluoride Uptake by Doped Clay (C-Hap)

The adsorption experiment was carried out to determine the effect of contact time, adsorbent dose, initial fluoride concentration and pH and also to determine which adsorption isotherm best fit the adsorption of fluoride in water using clay doped with hydroxyapatite. The following equations were used in the experiment.

$$\text{Equilibrium concentration}, Ce = \frac{Abs + 0.0863}{-0.223} \qquad (1)$$

$$\text{Adsorption capacity}, Qe = \frac{(Co - Ce)V}{m} \qquad (2)$$

$$\% \text{ Removal} = \frac{Co - Ce}{Co} \times 100\% \qquad (3)$$

Where, Abs = Absorbance, Co = Initial fluoride concentration of fluoride in sample water, Ce = Equilibrium concentration of fluoride, V = Volume of sample water taken and m = Mass of adsorbent taken.

2.3.1. Effect of Contact Time

A mass of 0.3gHAp and 0.2 g of clay were weighed into a set of seven conical flasks and 0.5g of only clay into one conical flask as a control. 100.0mL of 5 mg L^{-1} fluoride solution was added to each conical flask. The flasks were shaken from 10 to 60minutes at a time interval of 10minutes. The mixtures were then filtrated and 5.0ml portion of each filtrate with 1.0mL of acid zirconyl-SPADNS were taken to determine the amount of fluoride remaining after the adsorption process using SM22PC UV/visible spectrophotometer at a wavelength of 570nm.

2.3.2effect of Adsorbentdose

HApmasses ranging from 0.0125g to 0.1625g were weighed into seven different conical flasks and 0.0125g of clay was added to each flask. 100.0mL of 5.0mg L^{-1} fluoride solution was added to each flask and shaken for 30minutes. The mixtures were filtrated and 5.0mL portion of each filtrate with 1.0mL of acid zirconyl-SPADNS were taken to determine the amount of fluoride remaining after the adsorption process using SM22PC UV/visible spectrophotometer at a wavelength of 570nm.

2.3.3 Effect of Ph on Fluoride Uptake

A mass of 0.10g HAp and 0.025g of clay were weighed into a set of six conical flasks. 100.0mL of 5mg L^{-1} fluoride solution, which were adjusted to pH 2 to pH 12 using 0.1M hydrochloric acid and 0.1M sodium hydroxide, were added to conical flasks and shaken for 30min. The mixtures were filtrated and 5.0mL portion of each filtrate with 1.0mL of acid zirconyl-SPADNS were taken to determine the amount of fluoride remaining after the adsorption process using SM22PC UV/visible spectrophotometer at a wavelength of 570nm.

2.3.4 Effect of Initial Concentration on Fluoride-C-Hap Interaction

A mass of 0.10g HAp and 0.025g of clay were weighed into a set of five conical flasks each containing 100.0mL of fluoride solution of different concentrations of 2.0, 4.0, 6.0, 8.0 and 10.0mg L^{-1}. The flasks were shaken for 30minutes and the mixtures were filtrated. 5.0mL portion of each filtrate with 1.0mL of acid zirconyl-SPADNS were taken to determine the amount of fluoride remaining after the adsorption process using SM22PC UV/visible spectrophotometer at a wavelength of 570nm.

2.3.5 Equilibrium Isotherm Studies

A mass of 0.10g HAp was put into a set of eight conical flasks containing 0.025g of clay each. 100.0mL portion of fluoride solution with concentration ranging from 5.0–40.0mg L^{-1} at 5.0mg L^{-1} interval was used in the determination. The flasks were shaken at an average room temperature of 32ºC for 30min. The mixtures were then filtrated and 5.0mL portion of each filtrate with 1.0mL of acid zirconyl-SPADNS were taken to determine the amount of fluoride remaining after the adsorption process using SM22PC UV/visible spectrophotometer at a wavelength of 570nm.

2.3.6 Adsorption Kinetics of Fluoride Uptake by Clay- Hap (C-Hap) Mixture

A volume of 100.0mL of 5.0mg L^{-1} fluoride solution was put into four sets conical flasks each containing 0.075g of the adsorbent. The flasks were shaken at an average room temperature of 32ºC for 30min. The mixtures were then filtrated and 5.0mL portion of each filtrate with 1.0mL of acid zirconyl-SPADNS were taken to determine the amount of fluoride remaining after the adsorption process using SM22PC UV/visible spectrophotometer at a wavelength of 570nm. The experiment was repeated for 10.0mg L^{-1} and 15.0mg L^{-1} using 0.100g and 0.125g of the adsorbent respectively.

3. Results and Discussion

3.1. Adsorption Experiment

3.1.1. The Effect of Contact Time on Fluoride Uptake by C-Hap

Careful analysis of the research results suggested that there was a gradual increase in the adsorption capacity of the Clay-HAp (C-HAp) mixture for the fluoride ions as time increased from 10 minutes to 30 minutes (Figure 1.0). Maximum adsorption occurred at 30 minutes and the equilibrium time was noted to be 40 minutes. It is therefore evident that the adsorption of fluoride ions by the C-HAp mixture was fast since the maximum adsorption was obtained at 30 minutes as compared to Iraqi palm-date used in the removal of Nickel and Lead in aqueous solution. The Maximum adsorption for their study was noted to occur at 60 minutes for both metals (Ameh and Odoh, 2012). It was noted in this study that C-Hap has a maximum adsorption capacity of 0.995mg/g and removed 99.5% of fluoride. It was observed that adsorption increases rapidly for 30 minutes, and slows down until equilibrium is attained. The rapid adsorption is considered to be due to the availability of large number of active sites on the adsorbent surface. These sites reduced as time progressed until equilibrium was established (Sanjay et al., 2009; Ameh and Odoh, 2012; Jimoh et al., 2013). Furthermore, the rapid rise in adsorption is seen as the instantaneous adsorption or external surface adsorption as noted for anion adsorption by Apea and Ephraim(2012). This seems to suggest that the C-Hap removes fluoride from water through surface adsorption mechanism, and the fluoride transfer is possibly controlled by pore and film diffusion processes.
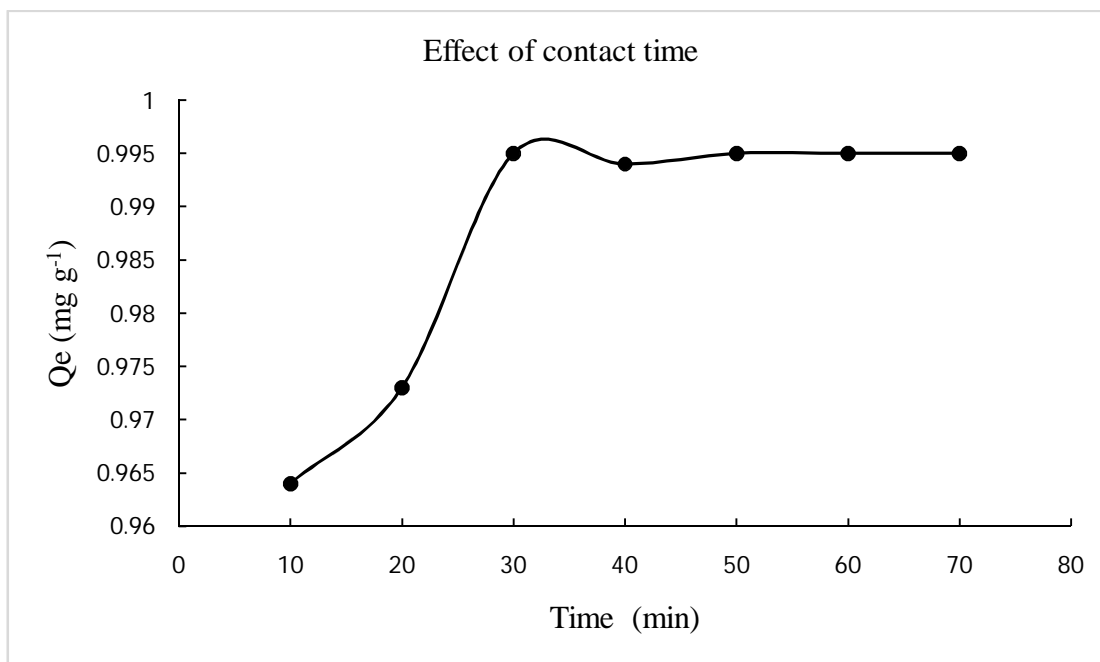
Figure 1: Effect of Contact Time on Fluoride Removal in Water by Clay-HAp

3.1.2 Effect of Adsorbent Dosage on Fluoride Uptake by C-HAp

Experiment on the relationship between the adsorbent dosage and extent of fluoride ion uptake by the C-HAp mixture revealed that the equilibrium concentration of fluoride decreases with increasing adsorbent dose (0.025-0.175 g/100mL). A closer look at Figure 2 revealed that the percentage removal of fluoride increased with increasing adsorbent dose while adsorption capacity decreased gradually with dosage. The maximum adsorption capacity for C-Hap was noted to be 18.409 mg/g for the adsorbent dose of 1.25 g/L and thereafter no significant increase in fluoride uptake was observed for additional increase in adsorbent dosage. This may be because active sites have less or on adsorbent atoms to interact with and hence are available to attract adsorbates. Also at higher dosage of absorbent, there is the tendency of overlap or aggregation of the active site, which may result in active site interaction with adsorbent atoms rather than adsorbates and hence decreases the total adsorption area (Annadurai et al., 2002; Ameh et al., 2012)
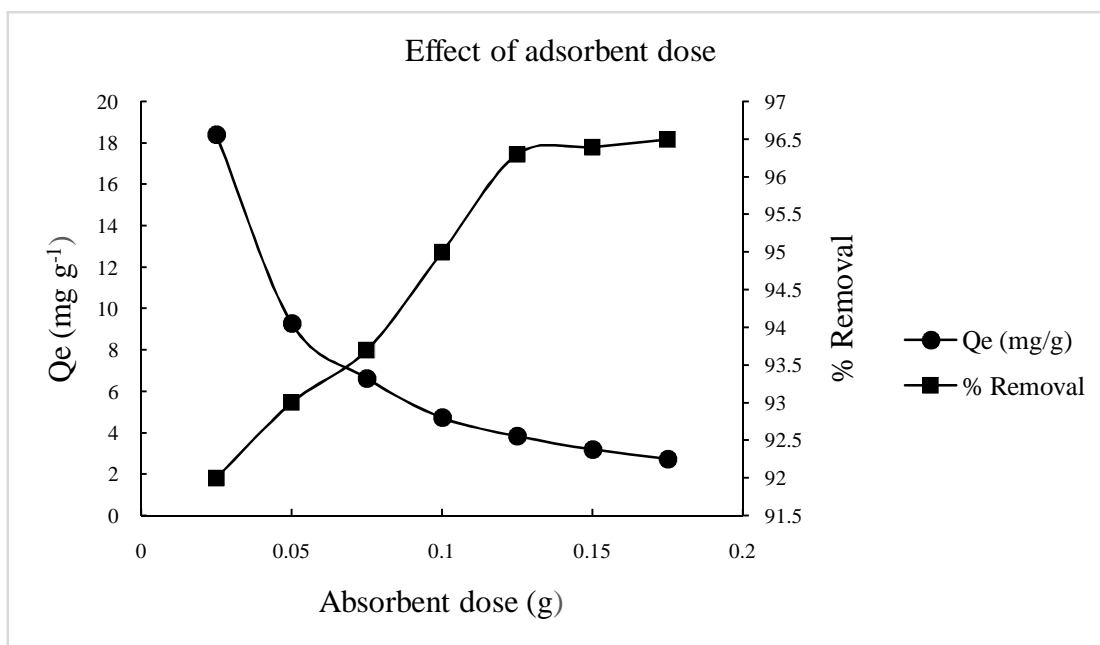

Figure 2: Effect of Adsorbent dose on Fluoride Removal in Water by C-HAp.

3.1.3 The Effect of Ph on Fluoride Uptake by C-Hap

The effect of pH on the adsorption ability of C-HAp mixture was studied (Figure 3) and it was observed that the fluoride removal efficiency remained the same from pH 2-4 and increased steadily to pH 6, hence maximum adsorption was observed at pH of 6. According to Turner et al., (2005), the pH of a solution affects the surface charge of the adsorbent material. At lower pH, more H^+ ions are present in the solution and as a result, they compete favorably with the adsorbent surface (which is also positively charged) for the fluoride ions. On the other hand, at pH above 6, fluoride ion adsorption decreases probably due to the development of a negative charge on the adsorbent surface, and/or stronger competition from hydroxide (OH^-) ions since both OH^- and F^- have the same charge and ionic radius. Therefore lower values of adsorption are observed at higher pH because of repulsion between the fluoride ion and the adsorbent surface (Fentahum, 2010)
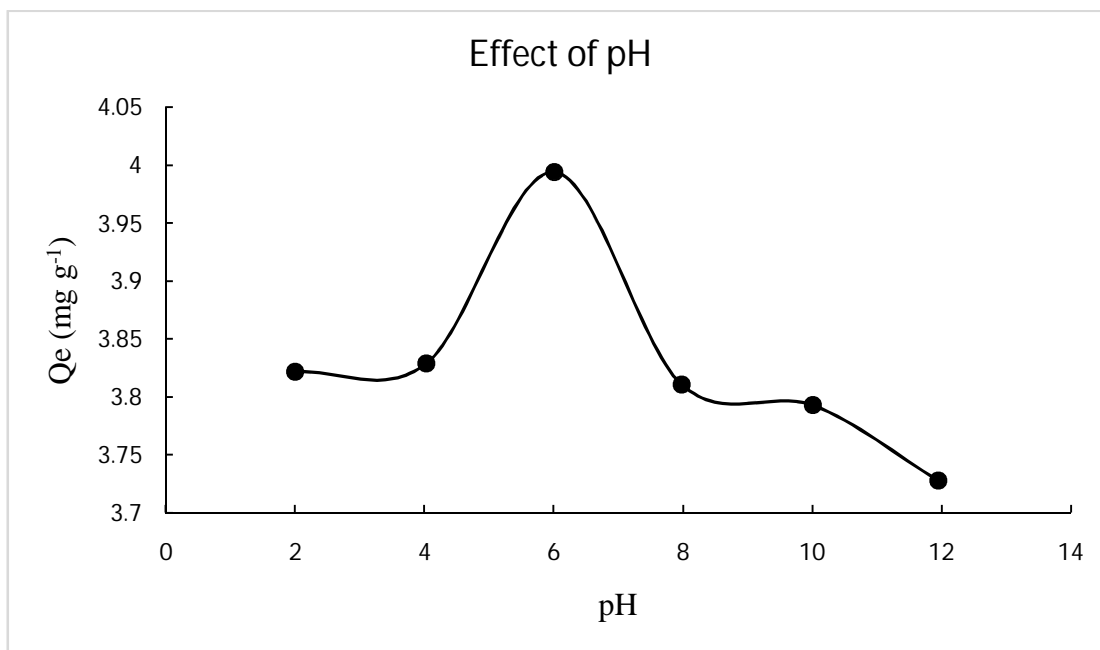

Figure 3: Effect of pH on Removal Fluoride in Water by C-HAp.

3.1.4 Relationship between Fluoride Concentration and Extent of Adsorption

The effect of initial concentration of fluoride on its uptake was studied at different initial fluoride concentrations ranging from 2.0-10.0 mg/l (Figure 4). The results indicated that as the initial fluoride concentration increased, the extent of adsorption of the fluoride also increased. The observation is apparent due to the availability of higher number of fluoride ions resulting in higher concentration gradient. With the increase in fluoride concentration in solution phase, the availability of fluoride ions also increases at the solid–solution interface, resulting in the increase in adsorption performance.
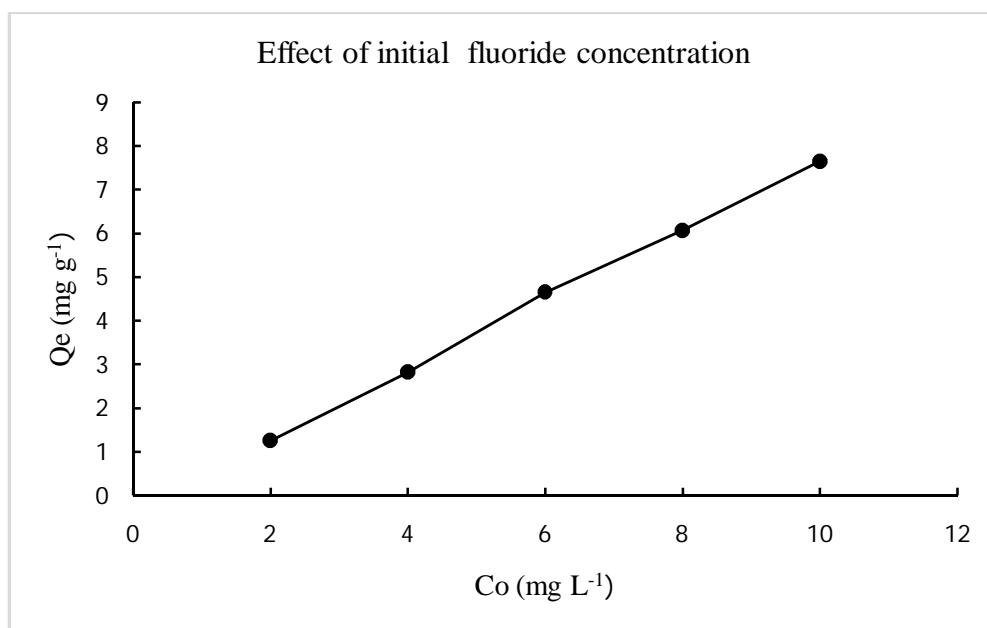
Figure 4: Effect of Initial Fluoride Concentration on Fluoride Removal in Water by C-HAp.

3.2. Equilibrium Isotherm Studies

Adsorption isotherms were employed to characterize the adsorption of adsorbate onto adsorbent from aqueous solution. Adsorption isotherms can provide information about the nature of the physico-chemical interaction involved in the adsorption process. (Fan,2003). In this work, the two most widely used isotherm models, Freundlich and Langmuir isotherm models were employed. The experiment was carried out at eight different initial fluoride concentrations for an adsorbent dose of 0.125g/100mL as shown in Table 1 and Figure 5.

Table 1: Data for Equilibrium Isotherm Studies

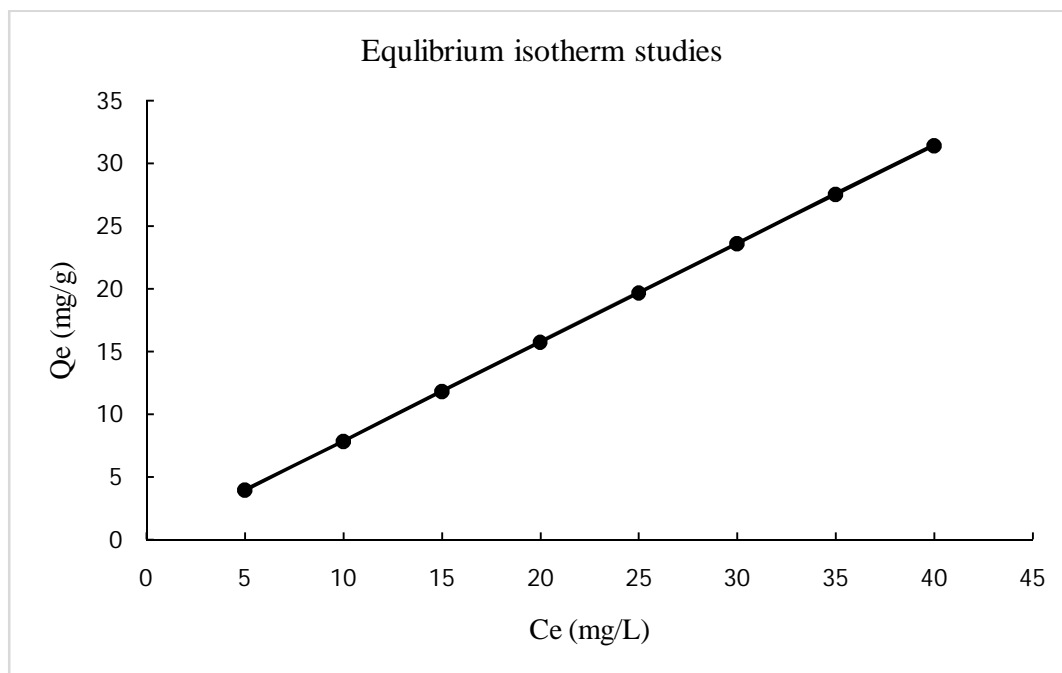| Co (mg/L)	ABS (nm)	Ce (mg L^{-1})	Co – Ce (mg L^{-1})	Qe (mg g^{-1})
5.0	-0.097	0.048	4.952	3.962
10.0	-0.124	0.169	9.831	7.865
15.0	-0.133	0.209	14.791	11.832
20.0	-0.150	0.286	19.714	15.771
25.0	-0.172	0.384	24.616	19.693
30.0	-0.190	0.465	29.535	23.628
35.0	-0.204	0.528	34.472	27.578
40.0	-0.240	0.690	39.311	31.449

Figure 5: Plot for Initial Concentration for Equilibrium Isotherm Studies

3.2.1 Langmuir Isotherm

The Langmuir model assumes a monolayer adsorption onto a surface containing a finite number of adsorption sites with uniform energy of adsorption and a single layer of adsorbed solute at a constant temperature (Fentahun, 2010). The Langmuir equation presented below in linearized form:

$$\frac{Ce}{Qe} = \frac{1}{KQ_{max}} + \left(\frac{1}{Q_{max}}\right)Ce \qquad (4)$$

Where Q_{max} is the adsorption capacity for a complete monolayer adsorption in mg/g and K is the Langmuir adsorption equilibrium constant in L mg^{-1}. The constants Q_{max} and K were determined by plotting Ce/Qe against Ce as shown in Figure 6.
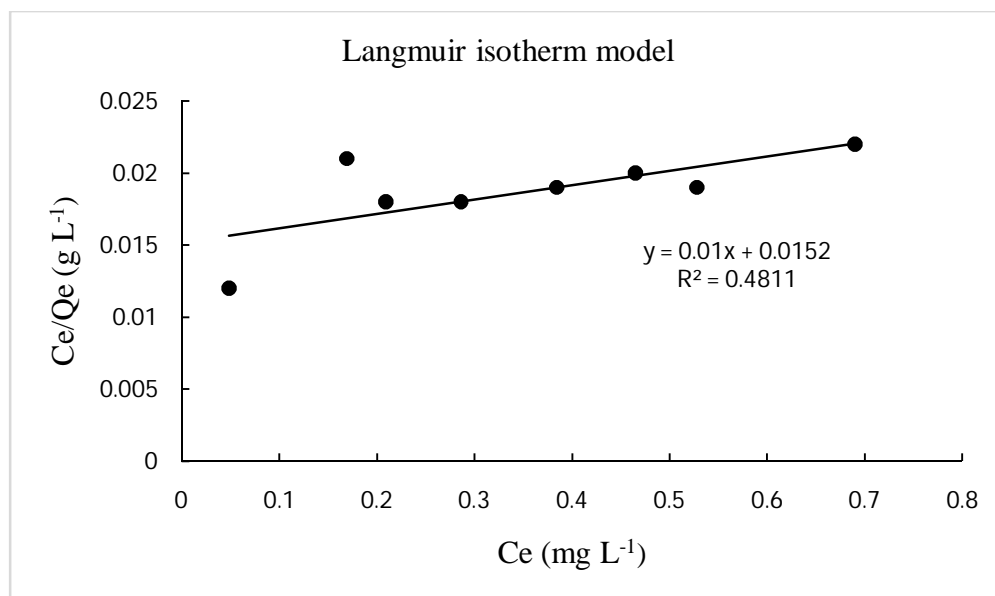

Figure 6: Langmuir Isotherm Plot

The sorption capacity, Q_{max}, which is a measure of the maximum adsorption capacity corresponding to complete monolayer coverage, was 100.00 mg g^{-1}. The adsorption coefficient, K that is related to the apparent energy of sorption for F$^-$by clay doped with HAp was 0.66 L mg^{-1}. Finally it was found that the related correlation coefficient R^2 value is nowhere near to unity (0.4811) as shown in Table 2 below. This indicated that the Langmuir model does not give a good fit to the adsorption process (Fentahun, 2010).

Table 2: Summary of Adsorption Isotherm Parameters

LANGMUIR			FREUNDLICH		
Q_{max}	K	R^2	K_f	1/n	R^2
100.0 mg/g	0.66 L/mg	0.4811	42.91 mg/g	0.819	0.9779

3.2.2. Freundlich Isotherm

Freundlich isotherm assumes unlimited adsorption sites, which correlated better with heterogeneous surface of the adsorbent media (Fentahun, 2010). The Freundlich equation in its linear form is given as:

$$logQe = logK_f + \frac{1}{n}logCe \qquad (5)$$

Where, K_f is the minimum sorption capacity (mg g^{-1}) and 1/n is the adsorption intensity. The constants K_f and 1/n were determined by plotting log Qe against log Ce as shown in Figure 7.
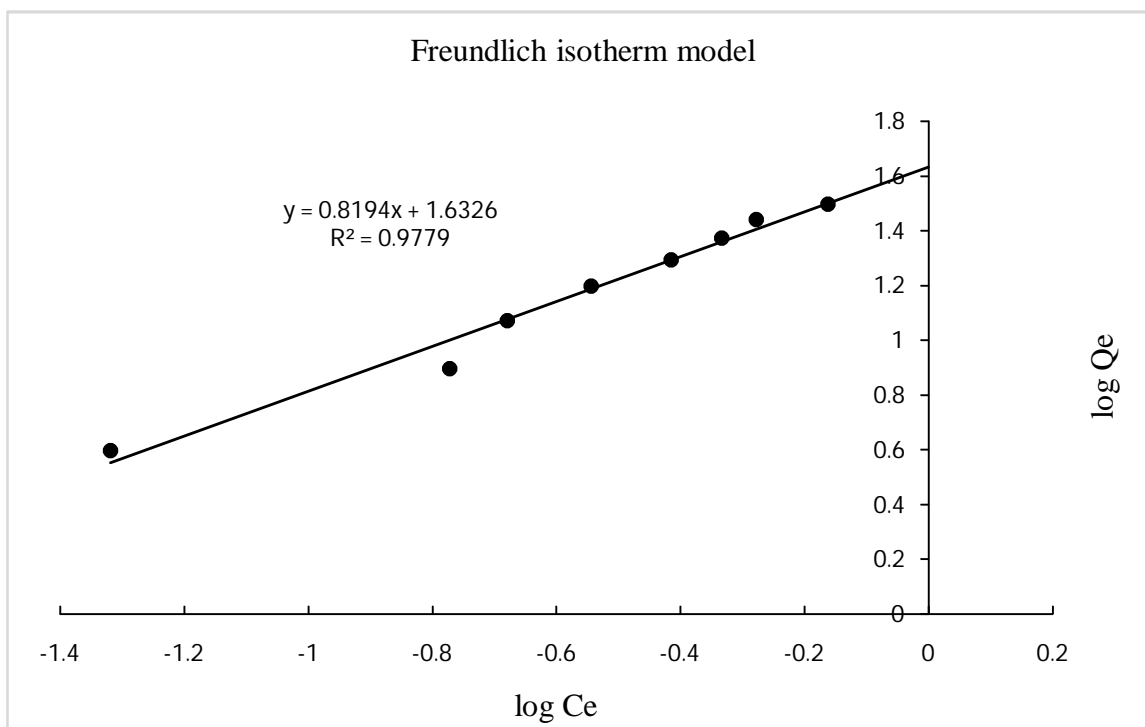

Figure 7: A Plot for Freundlich Isotherm Model

The minimum adsorption capacity and the intensity of the adsorption are usually estimated by Freundlich isotherm model. The Freundlich constants K_f and 1/n of the adsorption isotherm was 42.914 and 0.819 respectively (Table 2).Hence the minimum adsorption capacity for the adsorption process was 42.914 mg/g and it was found that the related correlation coefficient R^2 value for the Freundlich model was (0.9779). The low value of 1/n (less than 1) indicates the favorable condition of the adsorptions. Hence, Freundlich isotherm is a good model for defluoridation using clay doped with HAp (Nan, 2012).

3.3. Adsorption Kinetics

The dynamics of adsorption describes the rate of fluoride uptake, which in turn governs the duration time of the adsorption reaction (Nan, 2012). The data for the kinetic studies for5.0mg L^{-1}, 10.0mg L^{-1}, and 15.0mg L^{-1}of fluoride using 0.075g, 0.100g, and 0.125g of the adsorbent respectively, were analyzed to determine the kinetic characteristics of Fluoride-C-HAp system.

The kinetic data were fitted to pseudo first and second order reaction models, and the results of the analysis are as presented in figures 8-10. The linearized forms of pseudo first and second order reactions as expressed by Ibrahim et al., 2006, are given below respectively;

$$\log(Qe - Qt) = \log Qe - \frac{K_1}{2.303}t \qquad (6)$$

$$\frac{t}{Qt} = \frac{1}{K_2 Qe^2} + \frac{t}{Qe} \qquad (7)$$

Where Qe and Qt (mg/g) = amount of fluoride adsorbed at equilibrium and time t respectively, K_1 and K_2 (g min^{-1}. mg^{-1}) = equilibrium rate constant of first and second-order adsorption respectively and t = contact time (min).
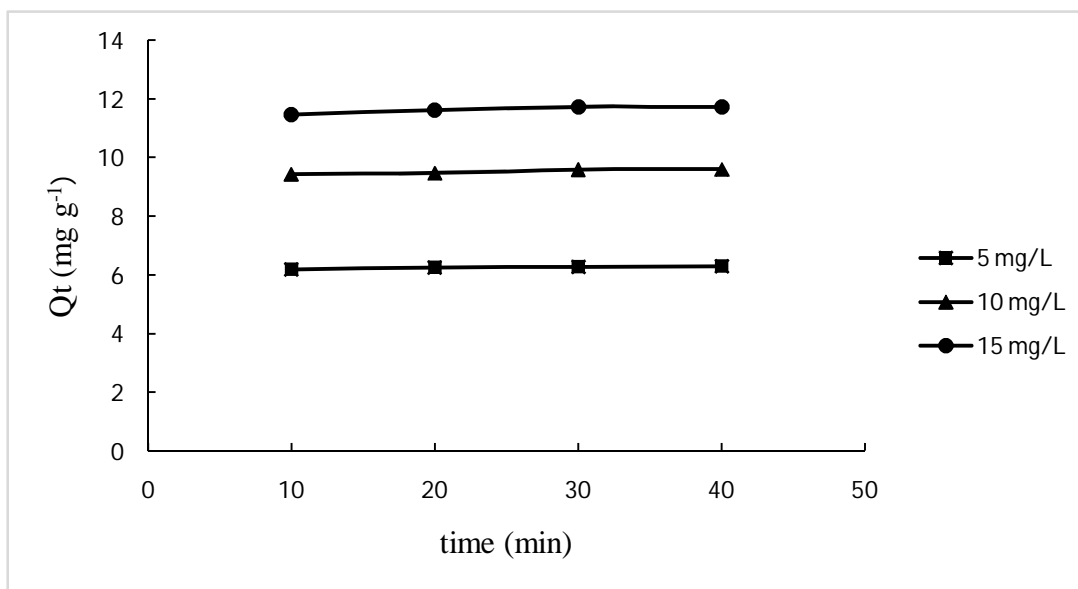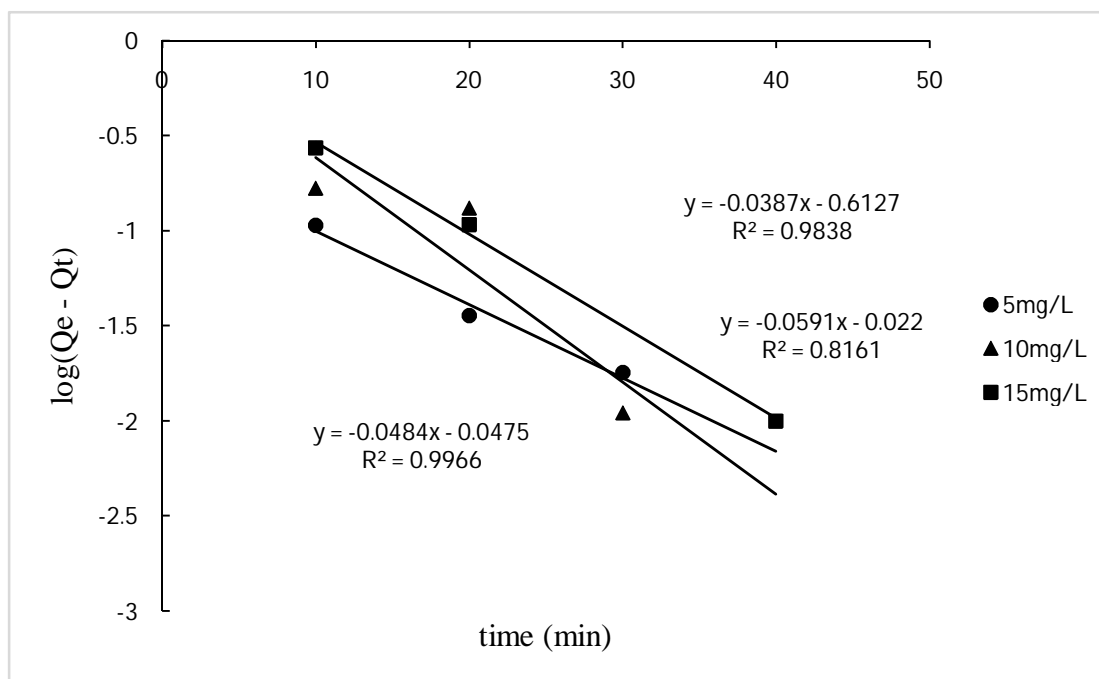

Figure 8: Adsorption Kinetics Analysis of Fluoride

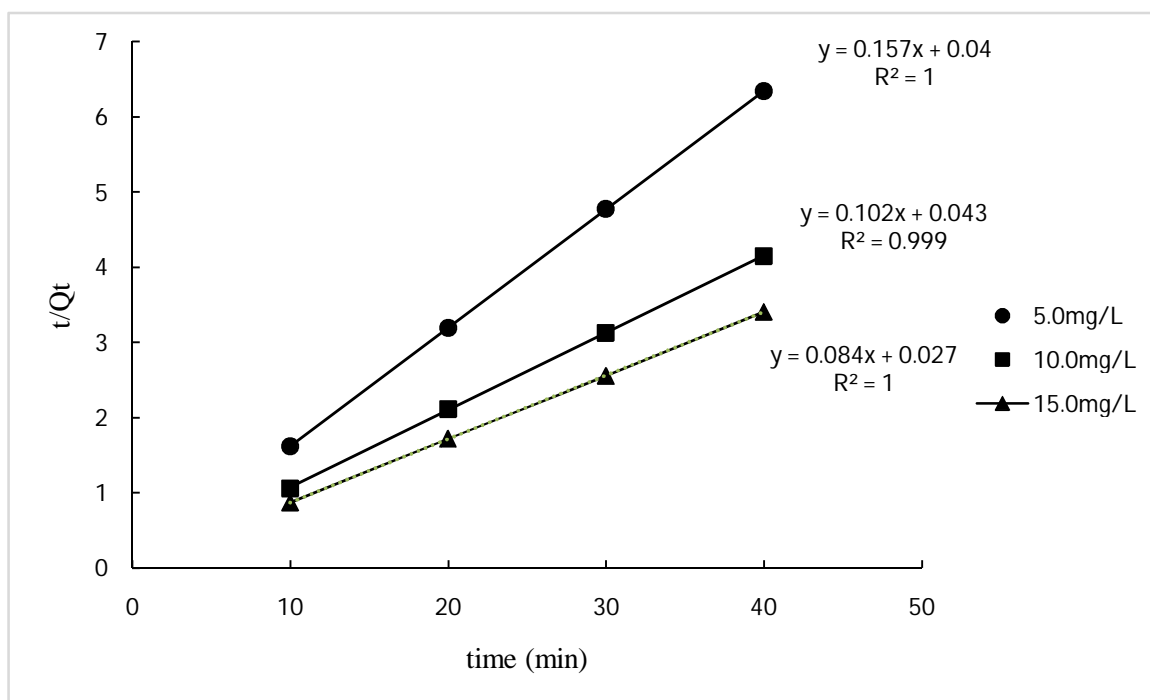**Figure 9: A Plot for Pseudo first order Mechanism of Fluoride**

Figure 10: A Plot for Pseudo Second Order Mechanism of Fluoride

The summery of the parameters and the correlation co-efficient for the pseudo first order and pseudo second order are presented in Table 3.

Table 3: Parameters and Correlation Co-Efficient of Adsorption Kinetic Models

Adsorbate/ adsorbent (mg/L)/(g/100mL)	Exp.Qe (mg/g)	Pseudo first order model			Pseudo second order model		
		Cal. Qe (mg/g)	K_1 (g/min.mg)	R^2	Cal. Qe (mg/g)	K_2 (g/min.mg)	R^2
5.00/0.075	6.300	0.868	0.098	0.9838	6.300	0.630	1.0000
10.00/0.100	9.600	0.951	0.136	0.8161	9.700	0.247	0.9999
15.00/0.125	11.740	0.896	0.111	0.9966	11.834	0.261	1.0000

The values of the R^2 statistic (R^2 = 1.00, 0.9999 and 1.00) of the second order model for the three fluoride concentrations (5.0, 10.0 and 15.0 mg L^{-1}) were higher than the R^2-values for pseudo first order kinetic model. Additionally, the calculated Qe (6.300, 9.700 and 11.843 mg g^{-1}) values of pseudo second order model for the three concentrations are in good accordance with the experimental values (Qe =6.300, 9.600 and 11.740 mg g^{-1}) than the pseudo first order kinetic model. The larger the Kvalue the slower the rate of the reaction. These gave an indication that, the adsorption of fluoride by clay doped with HAp follows the pseudo second order kinetic model and this according to Nan (2012), suggest the occurrence of a chemisorption process involving ion exchange.

4. Conclusion

Clay doped with HAp had considerable potential for the removal of excess fluoride from water. In addition, the C- HAp has proven to be an effective low cost adsorbent for the removal of fluoride from water. Adsorption of fluoride was very rapid in the first 30 min and equilibrium was reached at 40 min. For a given initial fluoride concentration, the removal efficiency of the adsorbent increased with increasing adsorbent dose. The maximum adsorbent dose was found to be 1.25 g L^{-1}.Solution pH is the most important parameter affecting adsorption capacity of the adsorbent. Maximum fluoride removal occurred at pH 6. The Freundlichisotherm model best describe the adsorption characteristics of C-HAp. The maximum and minimum adsorption capacities were noted to be 100.0mg g^{-1} and 42.91mg g^{-1} respectively for the Langmuir and Freundlich isotherms. Adsorption kinetics was effectively described by pseudo-second order kinetic model and provided the best correlation with the experimental results, suggesting the occurrence of a chemisorption process involving ion exchange

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