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RESEARCH PAPER

Aqueous Phase Removal of Fluoride as Fluorosis agent Using Montmorillonite Clay as a Natural Nanoadsorbent

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ABSTRACT

A natural nanomaterial, montmorillonite clay, was collected, purified, and then applied in the removal of fluoride. To obtain the activated montmorillonite clay, 150 g of the grounded montmorillonite clay was weighed and refluxed in 500 mL of 1M HCl at 120 °C for one hour thirty minutes. Fluoride was determined with the aid of SPADNS reagent (2-parasulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfanate) using UV/visible spectrophotometer (Model JENWAY 6300) at the wavelength of 570 nm. Adsorption parameters studied were adsorbent dose, contact time, and pH effect. Fluoride was removed with a maximum percentage of 83.5% at optimum pH of 2 with contact time of 50 minutes and adsorbent dose of 2.0 g as well as temperature of 25°C. Two most used kinetic models were employed in this research, pseudo-first order and pseudo-second order. The experimental data were found to follow pseudo-second kinetic than pseudo-first order. Thus, montmorillonite clay as a natural nanoadsorbent could be used to remove fluoride which could help in the prevention of dental fluorosis.

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INTRODUCTION

A nanomaterial is an object that has at least one dimension in the nanometre scale (approximately 1 to 100 nm). There are three categories of nanomaterials which include three (3D), two (2D) and one (1D) dimension. Minerals such as clay are nanostructured and clays are a type of layered silicate characterised by a fine 2D crystal structure. Clays are natural nanomaterials occurring in nature without human modification or processing [1]. Recently, industrial and biomedical applications of nanosized clay particles have been increasing rapidly [2]. Clay nanomaterials (montmorillonite, halloysite, kaolin, and bentonite) are arguably among the most industrially popular nanosized materials available in thousands of tons which are extensively used in a number of applications. Consequently, the evaluation of toxicity of clay nanoparticles towards freshwater organisms is crucially important, however, it was discovered that they exhibit little or no toxicity [4]. Excess fluoride in drinking water causes harmful health effects such as dental and skeletal fluorosis[5].The maximum allowable level of fluoride in drinking water has been set at a concentration of 1.5 mg/L by the World Health Organisation [6]. The most preventive measures are the provision of drinking water containing fluoride within the tolerance limit. To do this, different methods are employed including ion exchange, precipitation and adsorption. However, adsorption using low cost agricultural waste and natural material would be more effective. Different materials or adsorbents used in defluoridation include natural clay [7-9], fired clay [10], bentonite/chitosan bead [11], Pumice [12], montmorillonite clay [13], Al^{3+}-modified bentonite clay [14], coconut Hush [15], and kaolinite clay [16] and rice husk ash [17]. The role of fluoride level of drinking

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water in the etiology of dental fluorosis and the prevalence of dental fluorosis in both dentitions and teeth have been also assessed. Although no change was noted in clinical grades, some changes were noted in biochemical parameters such as serum fluoride and urine fluoride levels. Based on the results, a significant decrease was noted in serum fluoride level of the patients in group A and group B after three months of treatment. This decrease was more significant in group A treated with calcium and vitamin D3 supplements than that in group B treated with ascorbic acid and vitamin D3 supplements [18]. Some researchers [19-23] reported that fluorosis is irreversible and as such its prevention is appropriate, using various intervention measures. Fluoride poisoning can be prevented or minimized using alternative water sources, by removing excessive fluoride from drinking water, and by improving the nutritional status of populations at risk. The simple interventions include provision of surface water, rain water and consumption of Low fluoride ground water. Other interventions are defluoridation of water through flocculation and adsorption. Most of spectrophotometric methods proposed for the determination of fluoride are based upon the bleaching action of fluoride ion on colour systems; for example, aluminium-catechol violet, thorium-alizarin, zirconium-eriochrone cyanide R, zirconium-quinalizarin and zirconium -SPADNS. These reactions lead to an inverse relationship; a decrease in colour intensity with increasing fluoride concentration. One of the important dyes used is trisodium 2-(parasulfophenylazo)-1,8-dihydroxy-3,6- napthalene disulfonate, commonly known as SPADNS. The dye reacts with metal ions to give a coloured complex. In the SPADNS method, zirconium reacts with SPADNS to form a red coloured complex. Fluoride bleaches the red colour of the complex, and hence, the change in absorbance can be measured using a spectrophotometer [24].

The objective of this study is to use natural nanomaterial; montmorillonite clay in order to remove high level of fluoride, as it is the best way of controlling fluorosis. The study is accomplished by evaluating the effects of nanoadsorbent dose, contact time, and pH.

MATERIALS AND METHOD

Materials

List of Reagents/Apparatus

The reagents used were as follows: SPADNS reagent (2-parasulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfanate), TISAB (Total Ionic Strength Adjustment Buffer), sodium hydroxide(NaOH), sulphuric acid (H_2SO_4), sodium fluoride (NaF), zirconyl chloride octahydrate, sodium chloride (NaCl), sodium citrate, concentrated acetic acid, hydrochloric acid (HCl), acetic acid (CH_3COOH), weighing balance, filter paper(what man No-1), pipette(10ml), pH meter, motar and pestle, muffle furnance, hot plate(electric tung), measuring cylinder, oven, micrometer sieves, beakers, standard volumetric flasks, tap water, deionized water, and test tubes.

Sample Collection

The montmorillonite clay was collected from Tallase town in Balanga Local Government Area of Gombe State, Nigeria.

Preparation of Solution

Fluoride Standard

1000mg/L stock solution was prepared by dissolving 2.21 g of NaF in 1 L deionized water. By serial dilution, various concentrations of 0, 1, 2, 3, 4 and 5mg/L were prepared for standard calibration.

Preparation of SPADNS Reagent

0.192 g of SPADNS was dissolved in 100 ml of deionized water. 0.0266 g of zirconyl chloride octahydrate was also dissolved in 25 ml of deionized water, and 20 ml of HCl was added to the solution and the deionized water was added up to 100 ml marked. The SPADNS reagent was obtained by mixing SPADNS and zirconyl chloride in equal volumes. The SPADNS reagent is stable for more than two years, if stored away from light.

Preparation of TISAB

5.8 g of NaCl chloride and 1.2 g of sodium citrate were mixed, and 50 ml deionized water was added and shaken, 5.7 ml of concentrated acetic acid was also added. The pH of the solution was then adjusted using pH meter by adding a solution of 5.0 mol/L NaOH (4.0g in 10ml) to give pH of 5.0-5.5 which is the ideal range for a working electrode sensitive to fluoride.

Preparation f 1 m Hydrochloric Acid (HCl)

1M HCl was prepared by using 30.9 ml of concentrated HCl into 1000 ml volumetric flask and filled to the marked with distilled water.

Preparation and Activation of Montmorillonite (Clay)

The montmorillonite clay was washed several times with tap water and then distilled water. It was also dried in an oven at 120 ^{0}C for seven hours until a constant weight was obtained and then air dried for another two hours. The montmorillonite clay was ground and 150 g was weighed and refluxed in 500 mL of 1M HCl at 120 ^{0}C for one hour thirty minutes. The activated montmorillonite clay was then washed for several times with distilled water to remove the residual acid until it became neutral. It was then air dried for two days, ground and sieved using 105 mesh size and kept for analysis [25].

Adsorption Studies

All the experiments in these studies were carried out in a 500 ml conical flask containing a suitable volume of fluoride. Various fluoride concentrations of 0, 1, 2, 3, 4, 5 and 6 mg/L were prepared for standard curve. To each of the prepared concentration, 1 ml of SPADNS reagent was added, and the absorbance of each concentration was then recorded at the wavelength of 570 nm using UV/visible spectrophotometer. For the adsorption studies, after adding the amount of adsorbent, the flasks were agitated using magnetic stirrer while studying the parameters such as the effect of adsorbent dose, pH, and contact time.

After the adsorption process, the flash content was filtered using Whatman filter paper. To the filtrate obtained, 1ml of SPADNS reagent was added before analysis using UV/visible spectrophotometer (Model JENWAY 6300) at the wavelength of 570 nm. The adsorption percentage of the adsorbate and the amount adsorbed, q_e (mg/g), were calculated according to the following equation,

$$Removal\ \% = \frac{(C_i - C_e)x\ 100}{C_o} \quad (1)$$

$$Amount\ adsorbed, q_e = \frac{(C_i - C_e)xV}{m} \quad (2)$$

Where C_i is the initial concentration of Congo red solution in mg/L, C_e is the equilibrium concentration of Congo red solution in mg/L, m is the mass of the adsorbent in grams, V is the volume of Fluoride test solution in litters (L), and q_e is the amount adsorbed in mg/g.

Kinetic Studies

Pseudo first-order and pseudo second-order kinetic models were used to determine the kinetics of adsorption of fluoride on the activated montmorillonite clay surface. Correlation co-efficient (R^2) was used to determine which of the model best describes the kinetics of the adsorption of fluoride on activated montmorillonite clay. Values of R^2 close or equal to 1 indicates that there is high degree of accuracy of the values to the model used. Adsorption kinetic studies describe the amount of solute taken up by the activated montmorillonite clay with respect to time of exposure [26].

The pseudo-first order equation is represented as follows:

$$\log(q_e - q_e) = log q_e - \frac{K_1 t}{2.303} \quad (3)$$

where K_1 is the Lagergren rate constant of adsorption (1/min). The plot of log (q_e-q_t) against $t_,$ gives a linear relationship from which q_e and K_1 are determined from the intercept and slope of the plot, respectively.

The pseudo-second order equation can be represented by the following linear form in Equation 4,

$$\frac{t}{q_e} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

where K_2 is the second order rate constant of adsorption (g/mg min). The values of K_2 and q_e are determined from the intercept and slope of the plot of t/q_t againt t.

RESULTS AND DISCUSSION

Calibration Curve

The absorbance of each prepared concentration of fluoride is presented in Table 1 from which the calibration curve, Fig. 1, was obtained. From Fig. 1, the correlation coefficient (R^2) value of 0.9745 indicates the fitness of experimental data and all fluoride concentrations in this studies were obtained from equation of the graph, Fig. 1.

Effect of adsorbent dose

The optimum adsorbent dose for fluoride adsorption after the required contact time of 50 minutes was experimentally verified. The concentration of fluoride was fixed at 5 mg/L while

Table 1. Standard calibration curve results

Concentration (mg/L)	Absorbance
0	0.000
1	0.025
2	0.048
3	0.065
4	0.081
5	0.125

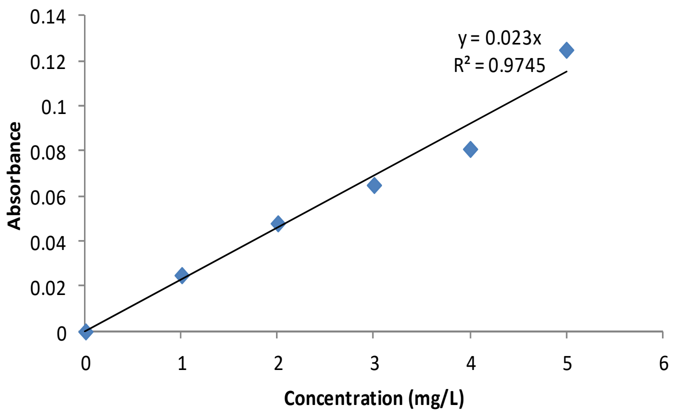

Fig. 1. Standard calibration curve

Table 2. Effect of adsorbent dose

Adsorbent Dose (g)	C_i (mg/L)	C_e (mg/L)	$C_i - C_e$ (mg/L)	% Removal
0.5	5	2.478	2.522	50.4
1.0	5	2.217	2.783	55.7
1.5	5	1.826	3.174	63.5
2.0	5	1.347	3.653	73.1
2.5	5	1.347	3.653	73.1

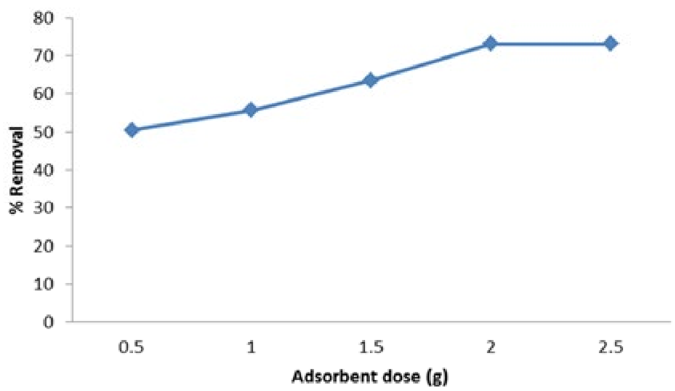

Fig. 2. Effect of adsorbent dose graph for fluoride at adsorbate concentration of 5 mg/L, contact time of 50 (minute), temperature of 25 °C, and various adsorbent dosages of 0.5, 1.0, 1.5, 2.0 and 2.5 g

the adsorbent dose was varied from 0.5 to 2.5 g. The percentage of fluoride removed by different adsorbent doses is given in Fig. 2 and Table 2. The fluoride adsorption increases with the increase in amount of the adsorbent. Thus, higher doses of the adsorbent provide more active sites. The dose of the adsorbent having the optimum fluoride removal efficiency was found to be 2.0 g, and further addition of higher doses of the adsorbent did not result in considerable increase in defluoridation. This is due to overlapping of the active sites at higher concentrations of the adsorbent, thus reducing the net surface area. Similar results were reported by [8, 11, and 17]. Hence, 2.0 g of activated montmorillonite clay was taken as the dose possessing the optimum fluoride removal efficiency and this was fixed as the dose for further experiments.

Effect of contact time

The percentage defluoridation by montmorillonite as a function of time is shown in Fig. 3 and Table 3. The contact time was varied from 10 to 60 minutes at constant adsorbent concentration of 2.0 g, initial concentration of fluoride, 5 mg/L and temperature of 25 °C. The percentage of the fluoride removed increased linearly in the early stages up to 50 minutes and there after remained static. This means that the adsorbent requires a minimum amount of fluoride. Similar results were reported by [8, 11, and 17]. The optimum contact time was found to be 50 minutes with a percentage of fluoride removal of 78.3%, Fig. 3.

Effect of pH

Defluoridation studies were carried out in the pH range of 2 to 12. The plot of the percentage of fluoride removed by montmorillonite clay at pH 2 to 12 is given in Fig. 4 and Table 4. Montmorillonite possesses appreciable defluoridation efficiency

Table 3. Effect of contact time

Time (minute)	Absorbent (g)	C_i (mg/L)	C_e (mg/L)	$C_i - C_e$ (mg/L)	% Removal
10	2	5	2.391	2.391	52.2
20	2	5	2.174	2.174	56.5
30	2	5	1.826	1.826	63.5
40	2	5	1.522	1.522	69.6
50	2	5	1.086	1.086	78.3
60	2	5	1.086	1.086	78.3

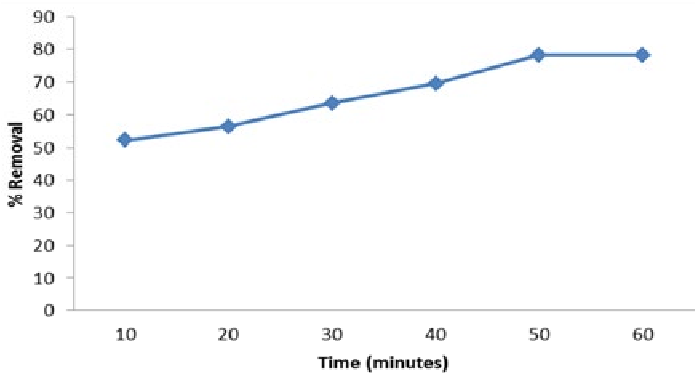

Fig. 3. Effect of contact time graph for fluoride at adsorbent dose 2.0 g, initial fluoride concentration of 5 mg/L, temperature of 25°C, various contact times of 10, 20, 30, 40, and 50 minutes,

Table 4. Effect of pH

pH	Absorbent (g)	Time (min)	C_i (mg/L)	C_e (mg/L)	$C_i - C_e$ (mg/L)	% Removal
2	1.5	50	5	0.826	4.177	83.5
4	1.5	50	5	1.043	3.957	79.1
7	1.5	50	5	1.347	3.653	73.1
10	1.5	50	5	1.522	3.478	69.6
12	1.5	50	5	2.217	2.783	55.7

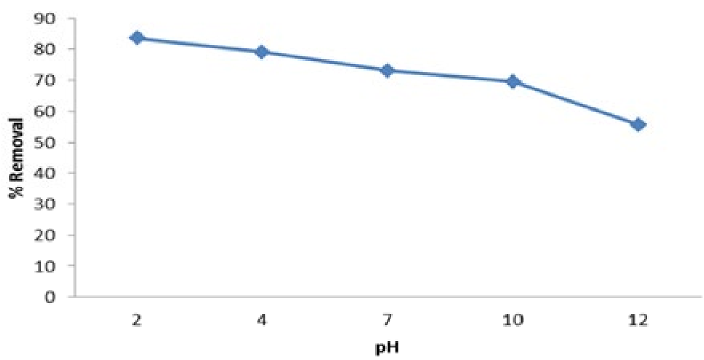

Fig. 4. Effect of contact time graph for fluoride at adsorbent dose 2.0 g, initial fluoride concentration of 5 mg/L, temperature of 25°C, contact time of 50 minutes, and various pHs of 2, 4, 7, 10 and 12

Table 5. Kinetic parameters of the fluoride adsorption on activated montmorillonite clay

Adsorbent	Pseudo-first order			Pseudo-Second order		
	K_1(i/min)	q_e(g/mg)	R^2	K_2 (g/mg min)	q_e(g/mg)	R^2
Activated Montmorillonite Clay	0.1419	548.15	0.9716	0.0018	56.18	0.9744

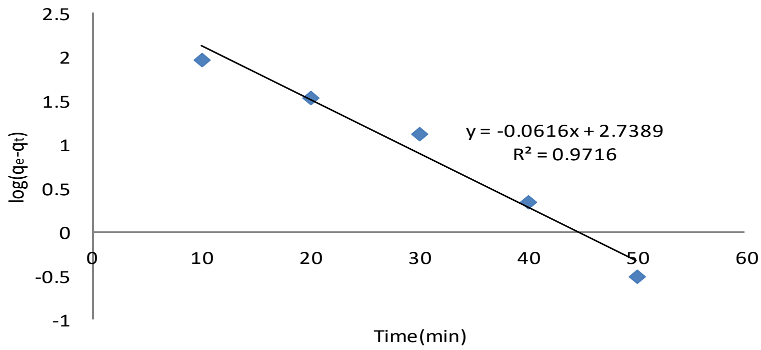

Fig. 5. Pseudo-first order kinetic plot

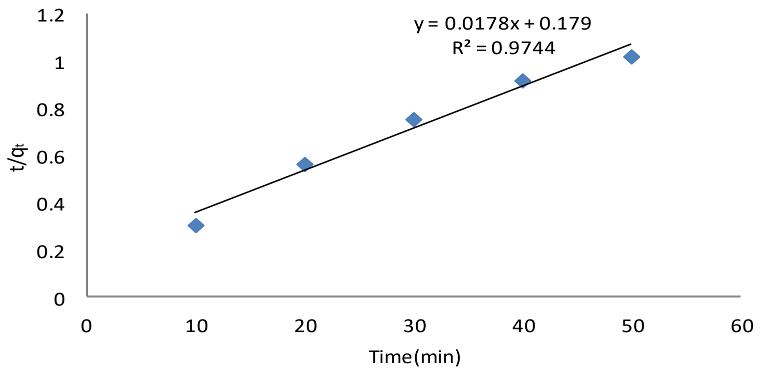

Fig. 6. Pseudo-second order kinetic plot

throughout the pH range studied. The percentage of fluoride removed at pH 2 is 83.5% which decreases as the pH increases. For example, at pH 7, the percentage of fluoride removed is 73.1%, while at pH 10, it is 69.6% and at pH 12 the fluoride removed is 55.7%. The influence of pH on the pronounce adsorption of fluoride on the surface of the material at low ranges leads to the assumption that chemisorption dominates in this range and physisorption occurs at higher pH ranges. The decrease in the adsorption of fluoride on its surface reflects a reduction in the quantity of the positive charges. The percentage of fluoride removal is 83.5% at low pH; pH= 2. It was due to the availability of more H^+ ions in the surface of the adsorbent and thereby greater adsorption of fluoride. Hence, fluoride adsorption increases at low pH levels as more of the surface sites are positively charged. In solution, the ionization of sodium fluoride leads to the formation of negatively charged fluoride ions. The adsorption of fluoride onto the surface of the material is due to the development of positively charged surface sites. The reduction in the percentage of adsorption of fluoride at higher pH level is due to the increasing electrostatic repulsion between the negatively charged surface sites of the adsorbent and fluoride ions [17].

Kinetic Studies

Pseudo first-order and pseudo second-order kinetic models were used to determine the kinetics of adsorption of fluoride on the activated montmorillonite clay surface. Correlation co-efficient (R^2) was used to determine which of the model best describes the kinetics of the adsorption of fluoride on activated montmorillonite clay. The results of the kinetic models were summarized in Table 5, whereas Figs. 5 and 6 indicate pseudo-first and pseudo-second graphs, respectively. Thus, pseudo-second order was found to fit the experimental data with correlation co-efficient value of 0.9744.

CONCLUSION

A natural nanomaterial, montmorillonite clay, was collected, purified, and then applied in the removal of fluoride. Adsorption parameters studied were adsorbent dose, contact time, and pH. Fluoride was removed with a maximum percentage of 83.5% at optimum pH of 2, contact time of 50 minutes, and adsorbent dose of 2.0 g as well as temperature of 25°C. Two most used kinetic models were employed in this research, pseudo-first and pseudo-second order. The experimental data was found to follow pseudo-second kinetic than pseudo-first order. Thus, montmorillonite clay as a natural nanoadsorbent could be used to remove fluoride which could help in the prevention of dental fluorosis.

CONFLICT OF INTEREST

The author declare that there is no conflict of interests regarding the publication of this manuscript.

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