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ADSORPTION ISOTHERM AND KINETICS OF REMOVAL OF FLUORIDES FROM WATER AND WASTEWATER BY ADSORPTION TECHNIQUE USING LOW COST ADSORBENT LIKE RED MUD.

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ABSTRACT

Fluoride contamination in drinking water due to natural and anthropogenic activities has been recognized as one of the major problems worldwide imposing a serious threat to human health. In the present study, Red Mud was used as an adsorbent for fluoride removal from aqueous solutions. Adsorption experiments were carried out by using batch adsorption contact method. The effects of different parameters affecting efficiency of fluoride removal such as adsorbent dose, contact time, initial fluoride concentration, and pH were investigated and optimized. The optimum adsorbent dose, contact time, initial fluoride concentration and pH values were 25 gm/L, 180 min, 10 mg/L, and 6.7, respectively. Langmuir and Freundlich isotherm models were applied to describe the equilibrium data. Compared to Langmuir isotherm ($R^2 = 0.890$), the Freundlich isotherm ($R^2 = 0.990$) model was better fitted to describe the adsorption characteristics of fluoride on adsorbent. The Langmuir maximum adsorption capacity was 1.67 mg/g. The pseudo second order model was found to be more suitable than the pseudo first order to describe the adsorption kinetics. The low correlation coefficient value of $R^2 = 0.596$ for the intra-particle diffusion model indicates that the intra-particle diffusion model does not apply to the present studied. The maximum fluoride removal was observed to be 89% under the optimum conditions which indicated that Red Mud can be used as efficient, cheap, and ecofriendly adsorbent for the removal of fluoride from wastewater.

KEYWORDS: Adsorption, Red Mud, Isotherm, Kinetics, pH.

1 INTRODUCTION

The population explosion and rapid industrial growth demands huge quantity of fresh water to meet various requirements. Most of the rural population depends on the ground water sources for drinking purposes which generally contain underground deposits such as salts and minerals. One such is the fluoride which causes an adverse impact on human as well as animal health if fluoride concentration is higher. Consumption of water having excess fluoride over a prolonged period leads to a chronic ailment known as fluorosis. Fluoride contamination of groundwater by natural as well as anthropogenic sources is a major problem worldwide, imposing a serious threat to human health. Water contamination by fluoride from industrial activities includes effluent discharge, fertilizers and pesticides, fluorosilicate and fluorocarbon polymer synthesis, coke manufacturing, glass and ceramic manufacturing, electronics manufacturing, electroplating operations, steel and aluminum manufacturing, metal etching (with hydrofluoric acid), and wood preservatives.[1] The major sources of fluoride in groundwater are weathering and geochemical dissolution of fluoride- bearing rocks such as selenite (MgF_2), fluorspar (CaF_2), cryolite (Na_3AlF6), and Fluor apatite (calcium fluorophosphates, ($Ca_5(PO_4)_3F$). Because of the long contact time of fluoride-bearing ores, minerals, and rocks with groundwater, there is a constant leaching of fluoride ions that is responsible for the high fluoride concentration in groundwater as well as oceanic water.[2] Fluoride enters into the human body through a variety of sources like water, food, air, medicine, and cosmetics. Among these, drinking water is the most common source which makes fluoride available to human beings.[3] The optimum fluoride level in drinking water should be below 1.5 mg/L.[4] Low amount of fluoride is necessary in the prevention of tooth decay and the development of proper bone structure in humans and animals. High doses of fluoride lead to the development of dental and skeletal fluorosis, depending on the concentration of fluoride in drinking water.[2,5] Fluoridation units should be established at drinking water treatment plants if the fluoride concentration is less than the desired quantity, and extra amount of fluoride must be removed from the water using appropriate methods if the fluoride concentration exceeds the permissible value. Dental fluorosis is the most common manifestation of chronic use of high- fluoride water and is characterized by discolored, blackened, mottled, or chalky-white teeth. Skeletal fluorosis occurs over long-time consumption of drinking water with >4 mg/L fluoride during adolescence which may disrupt the mineralization of bones leading to severe and permanent bone and joint deformations.[6] Fluorosis not only affects the body of persons but also renders them socially and culturally crippled.[7] Fluoride contamination of groundwater and related health hazards are a worldwide problem. Fluorosis is a disease for which no medical treatment exists and considered as crippling disease, and prevention is the only solution for this menacing problem. Fluoride poisoning (fluorosis) can be prevented or minimized by using alternative water sources (like surface water, low fluoride ground water, and rain water), increasing the nutritional status of the population at risk. Defluoridation of drinking water appears to be a simpler practical solution to prevent the adverse effects of fluoride. Hence, the development of defluoridation technologies, preferably low-cost and environmentally friendly, capable of reducing the fluoride concentration below the limit established by the WHO is of paramount importance.[6] Different technologies have been used for the removal of fluoride from drinking water including precipitation, coagulation, membrane-based processes, ion-exchange methods, and adsorption methods. Lime and alum are used to form insoluble precipitates with fluoride in precipitation and flocculation process. Adsorption is the preferred technique for defluoridation at community and household levels in rural areas because of its low cost and ease of operation, high efficiency, easy accessibility, environmental benignity, and needless of operational skill and electric power to run, and since adsorbents can in principle be reused and recycled making it ideal for use in less-developed rural areas. The availability of different adsorbents in large amounts and low costs make them potential candidates for the defluoridation in remote areas.[2–4] Red Mud is of particular interest as an adsorbent due to its unique properties such as high porosity, high permeability, small particle size, high surface area, low thermal conductivity, and chemical inertness.[8] The effectiveness of adsorption techniques is greatly dependent on the physicochemical properties of the adsorbent. Therefore, the main aim of this study is to investigate the effectiveness, capacity and efficiency of fluoride ion-adsorptive removal by Red Mud as an adsorbent from aqueous solutions.

2. MATERIALS AND METHODS

2.1 Preparation of Standard and Stock Solutions

A 1000 mg/L stock solution of sodium fluoride (NaF) was prepared by dissolving 2.21 gm of anhydrous sodium fluoride in distilled water in a 1 L volumetric flask and diluting to the mark. Other standard fluoride solutions of the required concentrations for calibrating the fluoride ion- selective electrode were prepared by serial dilution of the stock solution with distilled water.

2.2 Adsorbent Preparation

Red Mud is a waste product obtained from aluminium industries. It has been used in the manufacture of different types of ceramic products since long time. Production of bricks[9-11] thermal insulators[12], acoustic tiles[13], corrosion inhibition primer[14], heavy clay products[15] and additive for concrete and mortar[11] are prepared from it. Red Mud has been used as desulphurising agent for the removal of hydrogen sulphide and industrial gases.[16-17] It has also been found useful for wastewater treatment.[18-21] Recently, it has been used as a cheap adsorbent for the removal of organic substances like 1- butanethiol from kerosene oil.[22] Red Mud was obtained from Hindustan Aluminium Corporation, Mirzapur, UP (INDIA). The sample was subjected to repeated washing to remove free alkalis, heated in oven, cooled at room temperature and passed through 53μm pore size sieve. The Chemical analysis of Red Mud was given below:

Table 1: Chemical analysis of Red Mud as.

Constituents	Percentage by weight
Fe_2O_3	39.45
Al_2O_3	22.65
TiO_2	13.80
SiO_2	8.55
CaO	5.20
Loss of ignition	10.25
Particle size	53 μm
Mean Particle size diameter	$48x10^{-4}$ cm
Surface area	10.27 $m^2 g^{-1}$
Porosity	0.197
Density	2.632 gcm^{-3}

The Infra-redspectrum of adsorbent was recorded in KBr and nujol null using Perkin Elmer Spectrophotometer, Model 783 and 621 in the range of 4000-200 cm^{-1}.

2.3 Apparatus and Instruments

An electronic balance was used for weighing adsorbents and chemicals for solution preparation. An oven was used for drying the adsorbent and glass wares during analysis. A pH glass electrode was used to measure the pH values of sample solutions. A pH/ISE meter (Orion model, EA 940 Expandable Ion Analyzer, USA) equipped with a combination fluoride ion-selective electrode (Orion Model 96-09, USA) was used for the determination of fluoride in the samples and standards solutions.

2.4 Fluoride Adsorption Studies

The batch adsorption studies were conducted in order to optimize various experimental parameters like contact time, initial fluoride concentration, adsorbent dose, and pH which can affect the adsorption efficiency of fluoride onto Red Mud. Batch mode adsorption studies were carried out by agitating 25 g/L of the adsorbent in 50mL of 10 mg/L fluoride solutions at pH 6.7 for 180 min taken into 250mL plastic bottles. The fluoride solutions were agitated by a magnetic stirrer with a hot plate at room temperature. The pH was adjusted to the desired level either with 0.1M NaOH or 0.1M HCl. All experiments were carried out at temperature of 25°C. The amount of fluoride adsorbed qe (mg/g) at equilibrium by the adsorbent was calculated from the following expression.[23]:

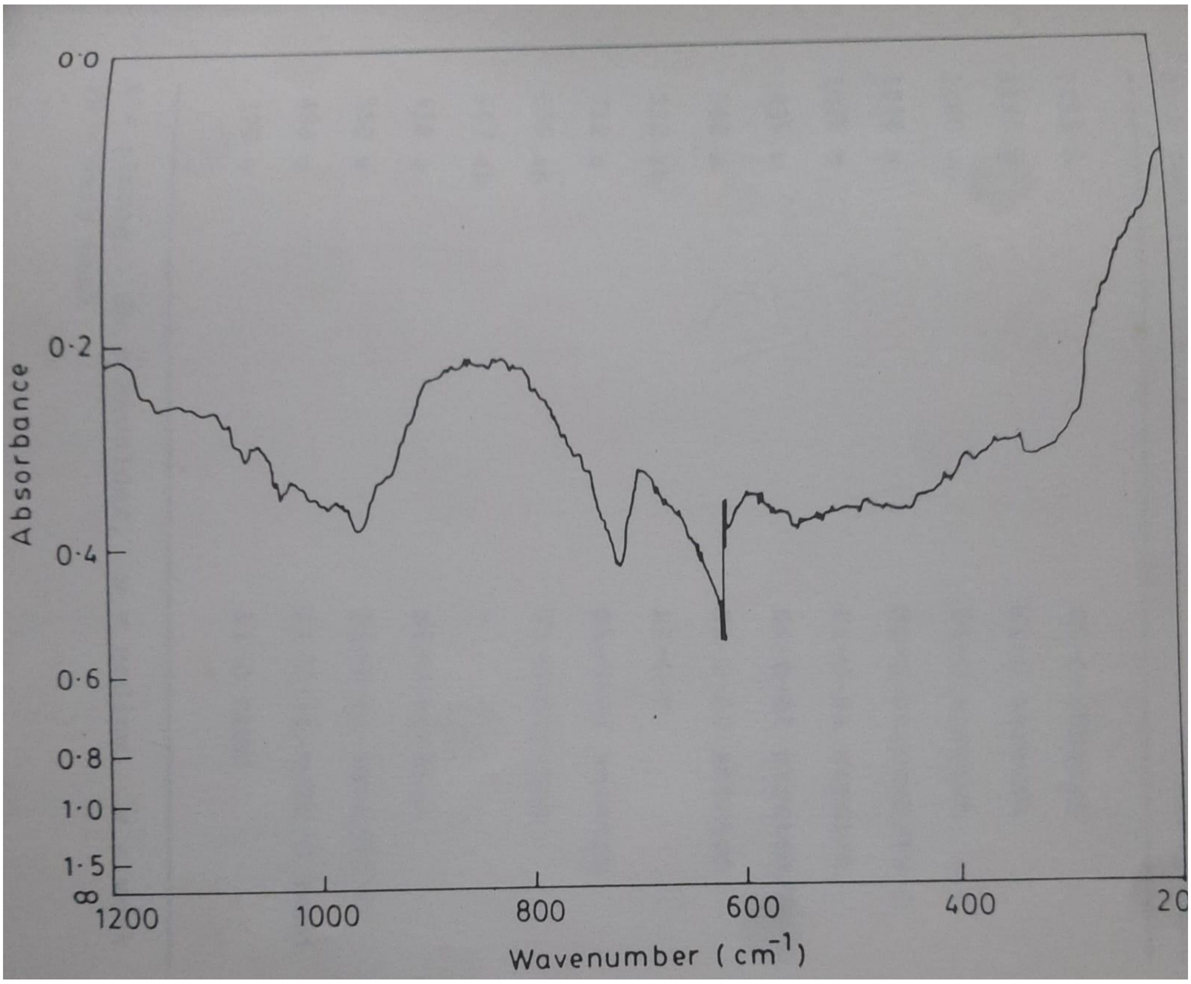

Figure 1: Infra-red spectrum of Red Mud.

$$qe = \left[\frac{Co - Ce}{m} \right] V \qquad \text{……..(1)}$$

Where, Co and Ce are the initial and equilibrium concentrations of the fluoride solution, respectively (in mg/L). m is the mass of the adsorbent in gm and V is the volume of the fluoride solution in L. The fluoride removal efficiency (percent fluoride removal) was calculated using the following equation.[24]:

$$\text{Percent fluoride removal (\% removal)} = \left[\frac{Co - Ce}{Co} \right] 100 \qquad \text{……..(2)}$$

2.5 Adsorption Isotherms and Kinetics

Adsorption isotherms are useful for describing how the adsorbate will interact with the adsorbent and give an idea about the theoretical maximum adsorption capacity of the adsorbent. The equilibrium data were tested for the Langmuir and Freundlich adsorption isotherm models. Langmuir isotherm[25] depends on the assumption that uptake happens on a homogenous surface by monolayer adsorption without interaction between adsorbed particles. The Freundlich adsorption isotherm is based on the equilibrium adsorption on heterogeneous surfaces by multilayer adsorption with interaction between adsorbed particles.[26] The linear forms of both Langmuir and

Freundlich isotherm models were used to describe the adsorption capacity for a particular range of adsorbate and concentration. These linear forms were plotted for the fluoride adsorption data, and their respective isotherm constants were calculated. Adsorption kinetics is the most significant characteristic representing adsorption efficiency of the adsorbent.[27] In this study, pseudo first order and pseudo second order kinetic models were employed for understanding the kinetics of adsorption process.

3. RESULTS AND DISCUSSION

3.1 Effect of Initial Fluoride Concentration

The effect of initial concentration on the extent of removal of the fluoride was studied by varying the concentrations from 5 to 70 mg/L, while keeping other parameters constant at their respective optimum values (pH = 6.7, contact times = 180 min and adsorbent dose = 25 g/L). The results obtained were plotted as percentage removal of fluoride vs initial concentration of the fluoride ion in the solution (Figure 2). The percentage removal of the fluoride ion has decreased with increase in initial concentration of the fluoride ion. This is due to saturation of the active sites of the adsorbent at higher concentrations due to the presence of more fluoride ions than the adsorption capacity of the adsorbent and the higher ratio of fluoride ions over available active surface sites with increasing initial fluoride concentration at constant mass of the adsorbent.[28] At low concentrations of the fluoride ions, sufficient numbers of active sites are available on the adsorbent and hence, most of the fluoride ions interact with the active sites on the adsorbent. Thus, percentage removal of fluoride increases until equilibrium is reached. The percentage removal of the fluoride ion has decreased from 92.80% to 55.60% when a fixed dose of the adsorbent used as the initial concentration of the fluoride increases from 5 to 70 mg/L.

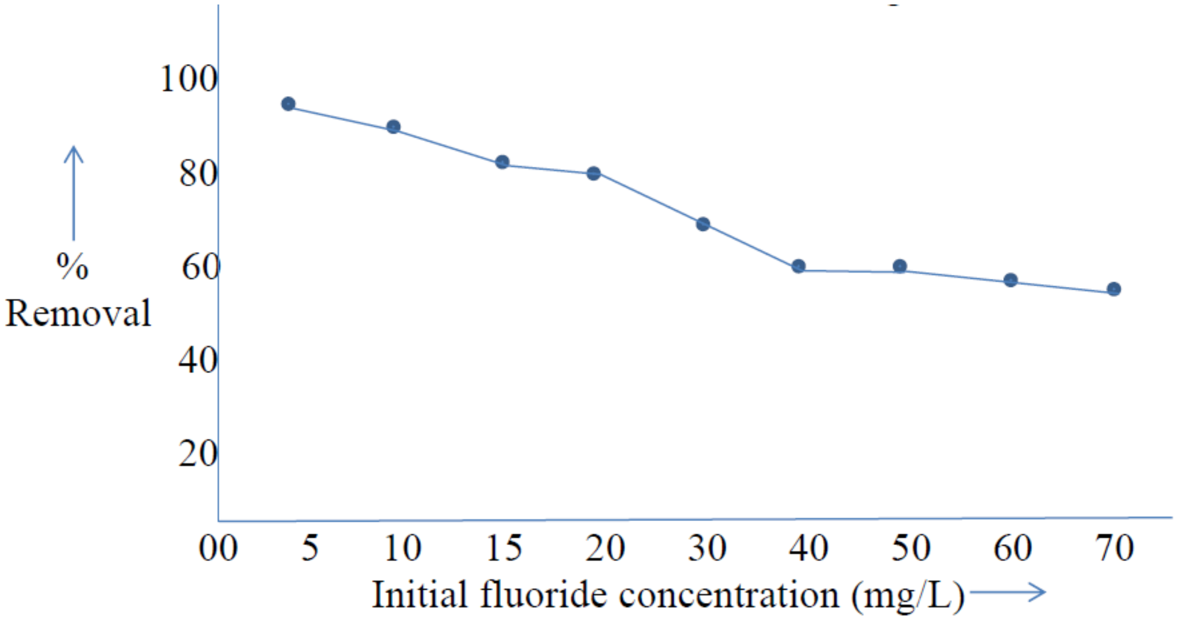

Figure 2: Effect of initial fluoride concentration on Red Mud (adsorbent dose=25 g/L, contact time=180 min, pH=6.7 and speed=140 rpm).

3.2 Effects of Adsorbent Dose

The amount of adsorbent and adsorbate solution plays an important role in adsorption process. The effect of adsorbent mass on fluoride removal efficiency was studied by varying the amount of the adsorbent, viz., 2, 5, 10, 15, 20, and 25 g/L, while keeping other parameters constant at their respective optimum conditions. There was an increase in fluoride removal efficiency with increasing dose of the adsorbent (Figure 3). This is due to the increase in surface area and availability of more active sites for adsorption of fluoride.[29] But after a specified adsorbent dose, the percentage removal did not increase considerably and that dose was considered as optimum dose of the adsorbent. At higher dosage beyond the equilibrium, there was no appreciable increase in the percent fluoride removal due to the availability of excess adsorption sites than that of adsorbents, assuming that the number of adsorption per unit mass of adsorbents remains constant. In such case, the optimum dose was found to be 25 g/L with the fluoride removal efficiency of 83%. The percentage removal of fluoride increased with increasing adsorbent dose, while adsorption capacity decreased gradually with dosage. The decrease in the adsorption capacity is due to the fixed initial fluoride concentration and the increased solid dose for the fixed solute load resulting in a lower availability of fluoride ions per unit mass of adsorbents.

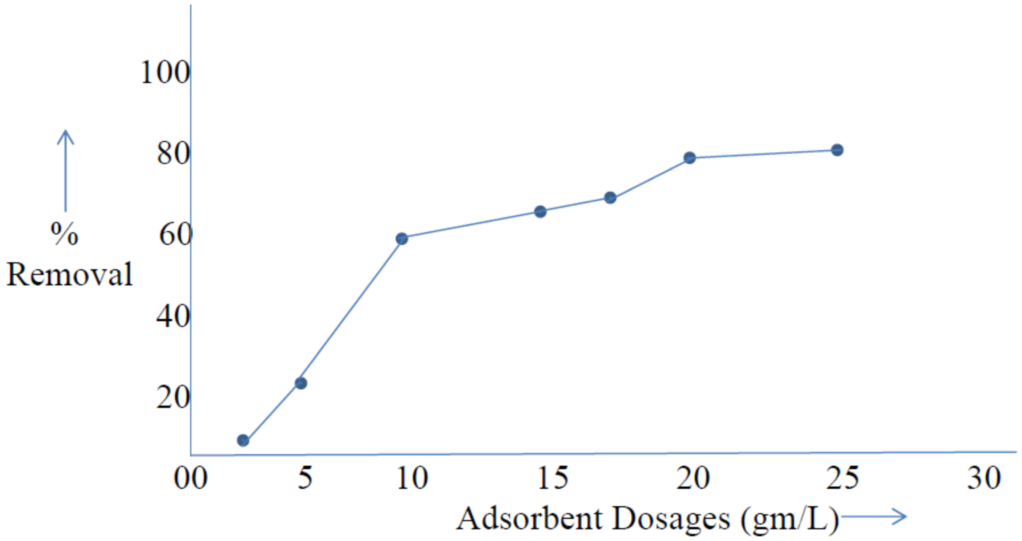

Figure 3: Effect adsorbent dose (Concentration=10mg/L, contact time=180 min, pH=6.7 and speed=140 rpm).

Adsorption Isotherms

An adsorption isotherm is the graphical representation of the amount of fluoride adsorbed per unit weight of the adsorbent as a function of its equilibrium concentration in the bulk solution at constant temperature. It gives general idea about the maximum amount of fluoride ions that could be removed and the effectiveness of the adsorbent in removing fluoride ions from water.[30] Freundlich and Langmuir isotherms are the most commonly used models to investigate the adsorption processes. Langmuir model assumes that adsorption is monolayer and is dependent on the assumption that the adsorbent surface consists of active sites having a uniform energy.[31] The Langmuir equation is written as,

$$qe = \frac{qm.KL.Ce}{1+KL.Ce} \qquad \text{........(3)}$$

Where, qe (mg g^{-1}) is the amount of fluoride adsorbed per unit mass of the adsorbent at equilibrium, qm (mg g^{-1}) is the maximum amount of the fluoride per unit weight of the adsorbent to form a complete monolayer on the surface, *K*L (L mg^{-1}) is an adsorption equilibrium constant related to the affinity of the binding sites and energy of adsorption, and *C*e (mg L^{-1}) is the equilibrium concentration of the fluoride in solution. The linear form of Langmuir isotherm is most commonly used and is given as follows[32]:

$$\frac{1}{qe} = \frac{1}{KL\,qm}\,\frac{1}{Ce} + \frac{1}{qm} \qquad \text{........ (4)}$$

$$\frac{Ce}{qe} = \frac{1}{KL\,qm} + \frac{Ce}{qm} \qquad \text{........(5)}$$

The values of Langmuir constants qm and KL are calculated from the slope and intercept of the linear plot Ce/qe vs Ce. A plot Ce/qe vs Ce should be a straight line with a slope 1/qm and intercept as 1/KLqm. The essential feature of the Langmuir isotherm model can be expressed by means of a separation factor or equilibrium parameter (RL), which is calculated according to the following equation:

$$R_L = \frac{1}{1+KLCo} \qquad \text{........ (6)}$$

The values of *R*L indicate the type of bio-adsorption isotherm, and there are four possibilities for the *R*L value.

(i) 0 < RL < 1 for favorable adsorption,
(ii) RL > 1 for unfavorable adsorption,
(iii) RL = 1 for linear adsorption, and
(iv) RL = 0 for irreversible adsorption.

The linear Langmuir isothermal plot and corresponding constants are given in Figure 7 and Table 1, respectively. The plot of Ce/qe versus Ce under optimum conditions gave a straight line with a correlation coefficient (R^2 = 0.890) as shown in Figure 7. The correlation coefficients are, however, less than those of Freundlich isotherm as can be seen from Figure 8. Freundlich isotherm assumes that the uptake of the fluorides occur on the heterogeneous surface by multilayer adsorption. It is also assumed that the stronger binding sites are occupied first, and that the binding strength decreases with the increasing degree of site occupation.[33] It is given by,

$$qe = K_F.Ce^{1/n} \qquad \text{........(7)}$$

The linear form of the Freundlich isotherm model is,

$$\log qe = \log K_F + \left(\frac{1}{n}\right) \log Ce \qquad \text{........(8)}$$

where qe (mg g^{-1}) is the equilibrium amount of fluoride adsorbed per unit mass of the adsorbent, Ce (mg L^{-1}) is the equilibrium concentration of fluoride in the bulk solution, KF (mg g^{-1})(mg L^{-1})^n is a constant known as Freundlich coefficient indicating the adsorption capacity of the adsorbent and the dimensionless constant 1/*n* indicates the intensity of the adsorption or surface heterogeneity and its value ranges between 0 to 1. In general, as the KF value increases the adsorption capacity of adsorbent for a given adsorbate increases. The plot of log qe vs log Ce gives a straight line with a slope of 1/*n* and the intercept yields the value of log KF, indicating multilayer adsorption capacity. The linear Freundlich isothermal curve and the corresponding constants are given in Figure 7 and Table 1, respectively. The plot of log qe vs log Ce for the adsorption of fluoride on adsorbent gave a straight line with a high correlation coefficient ($R^2 = 0.990$) which indicates good fit of data to the Freundlich isotherm than the Langmuir isotherm. The better fitness of the data to Freundlich adsorption isotherm suggests that the adsorption of fluoride involving multilayer adsorption on the surface of the adsorbent was heterogeneous. Similar results were reported on equilibrium and kinetic studies for the adsorption of fluoride onto commercial activated carbons.[34] Table 2 presents the calculated parameters for Langmuir and Freundlich isotherms. Compared with the Langmuir isotherm ($R^2 = 0.888$), the Freundlich isotherm ($R^2 = 0.990$) model was better fitted to describe the adsorption characteristics of fluoride on adsorbent. The value of 1/*n*(0.461) lying between 0.1 to 1.0 and that of *n* (2.17) lying in the range 1 to10 both confirmed the high bond strength between the adsorbate and adsorbent, and it also confirmed the adsorbent surface was heterogeneous. Furthermore, the heterogeneity of the adsorbent surface is established by the low values of the parameter 1/*n*. The small value for the magnitude of the Langmuir constant b (0.2 L mg^{-1}) indicates a low heat of adsorption.[35] The RL value (0.44) lying between 0 to 1 indicated favorable conditions for adsorption. The values of qm obtained from the Langmuir model is 1.67 mg g^{-1}.

Table 2: Calculated Langmuir and Freundlich isotherm parameters.

Isotherms	Parameters	Values
Langmuir isotherm	b	0.200
	R²	0.890
	qm	1.670
Freundlich isotherm	KF	0.290
	1/n	0.461
	R²	0.990
	RL	0.440

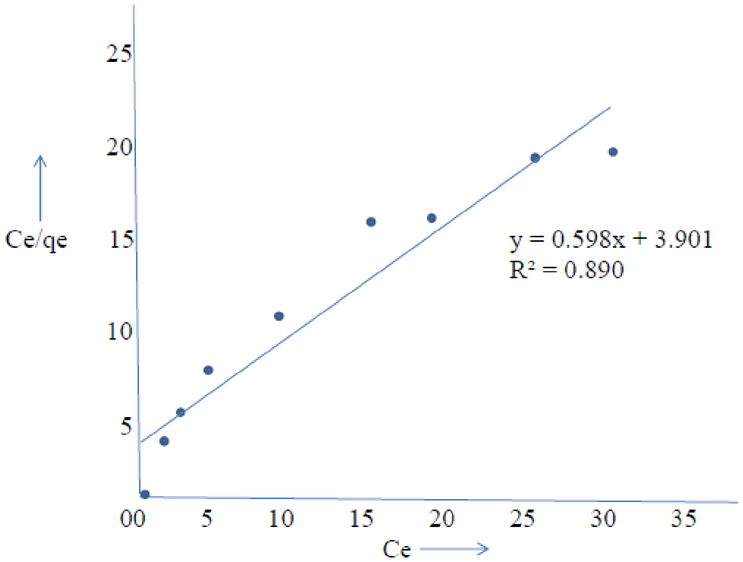

Figure 4: Langmuir adsorption isotherm plot.

Adsorption Kinetics

Kinetic modeling gives information about adsorption mechanisms and possible rate controlling steps such as mass transport or chemical reaction processes. The adsorption rate is an important factor for a better choice of material to be used as an adsorbent, where the adsorbent should have a large adsorption capacity and a fast adsorption rate. Pseudo first order and pseudo second order models were used to study the adsorption kinetics. For the pseudo first order model, the adsorption rate is expected to be proportional to the first power of concentration, where, the adsorption was characterized by diffusion through a boundary.[36] For the pseudo first order model under initial and end boundary conditions t = 0 to t = t and qt = 0 to qt = qt a linear equation is obtained as follows:

$$\ln (qe - qt) = \ln qe - k_1 t \qquad \text{……..(9)}$$

where qe and qt are the amounts of solute adsorbed at equilibrium and at a given time t, respectively and k_1 is the first order rate constant. A plot of "ln (qe − qt) vs t gives a straight line with an intercept of ln qe and slope of ($-k_1$). The plot for pseudo first order is given in Figure 8. The pseudo second order model assumes that chemisorption may be the rate- controlling step in the adsorption processes. For the pseudo second order model under the initial and end boundary conditions t = 0 to t = t and qt = 0 to qt = qt, a linear equation is obtained [40] as follows:

$$\frac{t}{qt} = \frac{1}{k_2q^2e} + \frac{1}{qe}\,t \qquad \text{……..} (10)$$

The equilibrium adsorption capacity (qe) and the second order constant k_2 (g $mg^{-1}h^{-1}$) can be determined experimentally from the slope and intercept of plot t/qt vs t. A plot of t/qt against t gives a straight line with an intercept of $1/k_2q^2e$ and slope of 1/qe. The plot for pseudo second order is given in Figure 9. Table 2 shows the values of pseudo first order and pseudo second order kinetic constants and intra-particle diffusion model. The value of correlation coefficient (R^2 =1) is high for the pseudo second order kinetic model compared to that of pseudo first order (R^2 = 0.867), and this indicates that the experimental data of the present study best fits to the pseudo second order model.[37] The value of k_2 is high which indicates the tested adsorbent is effective in fluoride adsorption.[38]

Adsorption Mechanism

The probable mechanism controlling the adsorption rate was evaluated using the intra-particle diffusion model. The McKay and Poots equation is expressed as.[39]

$$qt = k_{id} \,.\, t^{1/2} + I \qquad \text{……..}(11)$$

where qt is the amount of fluoride adsorbed (mg g^{-1}) at time t (min), kid is the intra-particle diffusion rate constant (mg $g^{-1}min^{1/2}$), and I (mg g^{-1}) is a constant that has to do with the thickness of the boundary layer.

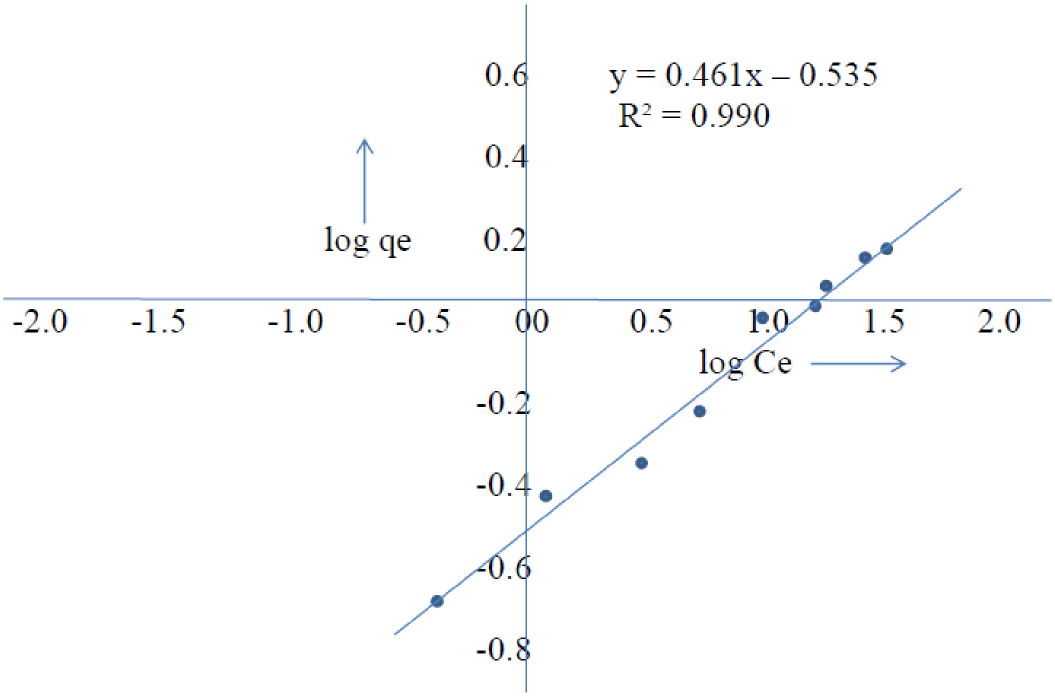

Figure 5: Freundlich adsorption isotherm plot.

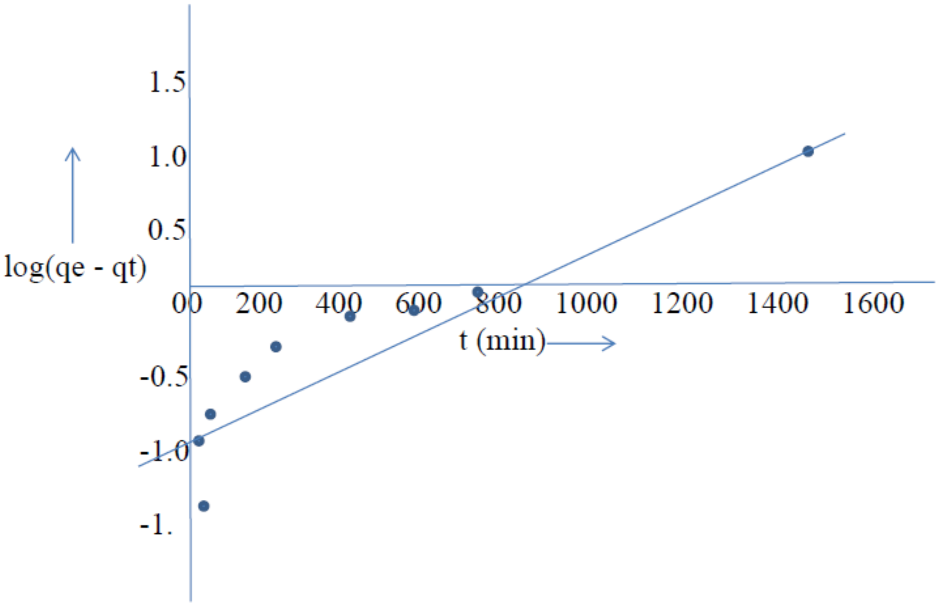

Figure 6: Pseudo first order plot for kinetic data.

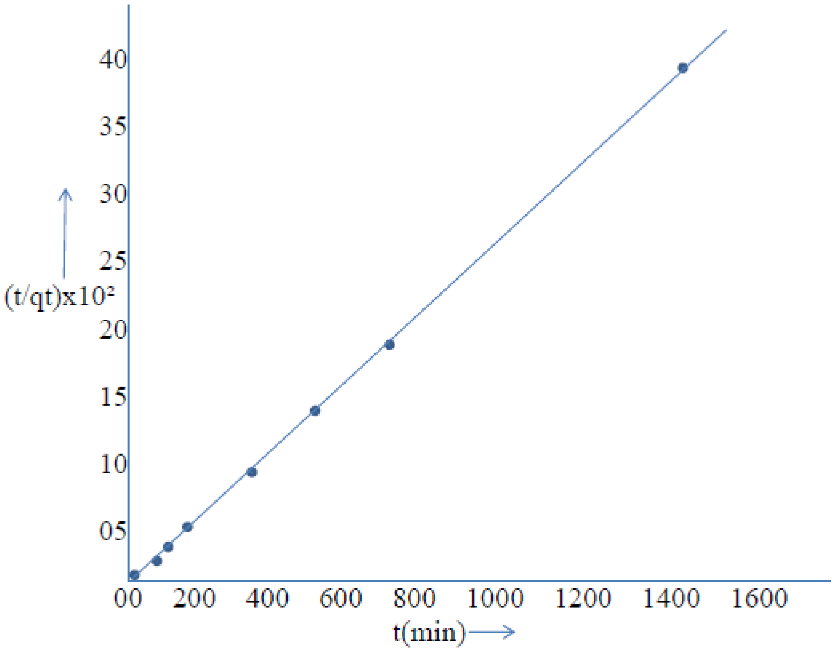

Figure 7: Pseudo second order plot for kinetic data.

Table 3: Pseudo first order and pseudo second order kinetic constants and intra-particle diffusion model parameters.

Kinetics	Parameters	Values
Pseudo-first order	k_1	0.0023
	qe	0.124
	R^2	0.867
Pseudo-second order	k_2	0.920
	qe	0.360
	R^2	1.000
Intra-particle diffusion	kid	0.001
	R^2	0.596

According to the model, Plot of qt vs ($t^{1/2}$) should give a linear line if intra-particle diffusion is involved in the adsorption process. kid and I values are obtained from the slopes and intercept of the linear plot, respectively. If the plot of qt vs $t^{1/2}$ is linear, intra-particle diffusion would be the rate-determining step. The low correlation coefficient value of $R^2=0.596$ for the intra-particle diffusion model (Table :2) and the fact that linear portions of the curves do not pass through the origin (Figure :10) indicate that the intra-particle diffusion model is not the rate-determining step of the adsorption process. Intra-particle diffusion could possibly not be the adsorption rate determinant because of the much smaller size of fluoride ions to the pores of the adsorbent. The ionic radius of fluoride is 1.33 A^0.[35] Thus, the probable mechanism controlling the rate of fluoride sorption onto the adsorbent is either the electrostatic attraction of fluoride ions to the positively charged adsorbent surface or the ion-exchange at the surface.[40-41] If the data exhibit multi linear plots, then two or more steps influence the adsorption process. In general, a mass transfer process is diffusion controlled and its rate is dependent upon the rate at which components diffuse towards one another.[42]

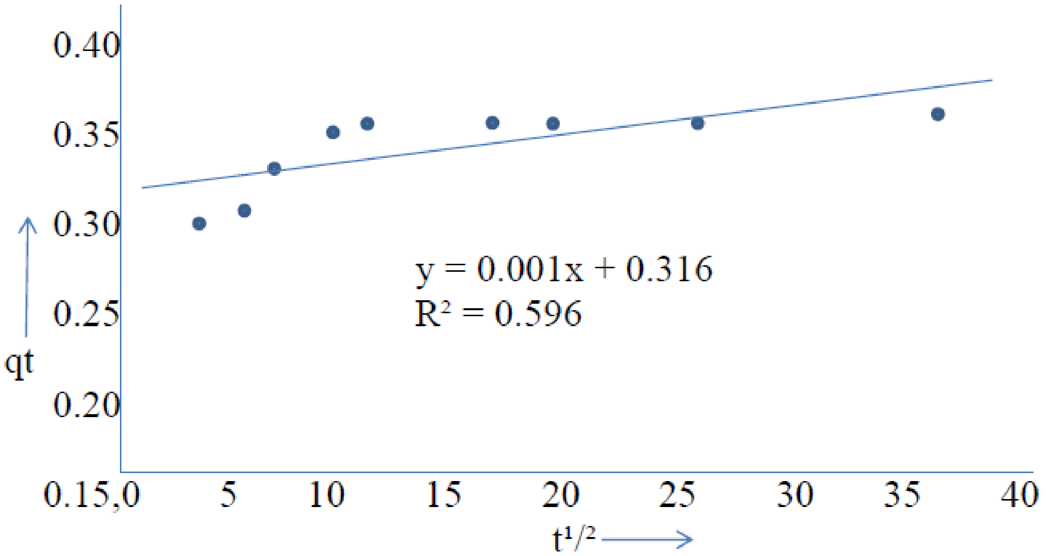

Figure 8: Intra-particle diffusion kinetic plot.

CONCLUSIONS

China clay was found to be an effective adsorbent for the removal of fluoride from aqueous solution and natural groundwater. The maximum percent fluoride removal and adsorption capacity were 89% and 1.67 mg/g, respectively, for 10 mg/L fluoride-spiked water under optimum adsorption conditions. The adsorption data fitted well with Freundlich adsorption isotherm with a good correlation coefficient value which indicates multilayer adsorption on the heterogeneous adsorbent surface. Adsorption kinetics was studied by using pseudo first order and pseudo second order kinetic models. The data fitted better to pseudo second order kinetics which showed that the adsorption was by chemisorption. Since intra-particle diffusion was not the rate-limiting mechanism, the adsorption rate limiting step was most probably the process involving ion exchange or attraction of adsorbate to the adsorbent surface. The results of the study showed that this low-cost adsorbent material can be employed for fluoride removal from groundwater and other water samples which contain excessive amount of fluoride which could be detrimental to human health.

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