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INVESTIGATION ON DEXTEROUS REMOVAL OF FLUORIDE FROM WATER AND WASTEWATER USING CHINA CLAY AS CHEAPER, ABUNDANT AND EASILY AVAILABLE LOW COST ADSORBENT

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ABSTRACT

Exposure to fluoride beyond the recommended level for longer duration causes both dental and skeletal fluorosis. Thus, the development of cost- effective, locally available and environmentally low cost adsorbents for fluoride removal from contaminated water sources is absolutely required.In the present study, China clay, locally available in Patharghatt village ofBhagalpur district, Bihar (India), was used as an adsorbent for fluoride removal from aqueous solutions. Adsorption experiments were carried out by using batch adsorption technique. 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 g/L, 200 min, 10 mg/L, and 6.7 respectively. The performance of the adsorbent was also tested under optimum conditions using groundwater samples. Langmuir and Freundlich isotherm models were applied to describe the equilibrium data. Compared to Langmuir isotherm (R^2 = 0.90), the Freundlich isotherm (R^2= 0.99) model was better fitted to describe the adsorption characteristics of fluoride on China clay. The Langmuir maximum adsorption capacity was 1.75 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 = 0.60 for the intra particlediffusion model indicates that the intra particle diffusion model does not apply to the present studied. The maximum fluoride removal was observed to be 90% under the optimum conditions,

1. INTRODUCTION

Water is a source of life, a fundamental requirement for health and main need for industrialization. It is essential for all forms of growth and development: humans, animals and plants. However, the suitability of water for a specific purpose can be affected by other substances dissolved or suspended in it. Contamination of drinking water by fluoride is one such example. In addition to arsenic and nitrate, which cause large-scale health problems, fluoride is classified as one of the contaminants of water for human consumption by the World Health Organization (WHO).[1] 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.[2] There are many ores, minerals, and rocks present inside the earth's crust, which are the natural sources of fluoride. The major sources of fluoride in groundwater are weathering and geochemical dissolution of fluoride- bearing rocks such as sellaite (MgF), fluorspar (CaF_2), cryolite (Na_3AlF_6), and fluorapatite (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.[3] 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.[4] Fluoride is known to have both beneficial and detrimental effects on health, depending on the dose and duration of exposure. The optimum fluoride level in drinking water should be below 1.5 mg/L.[5] Low amount of fluoride is necessary in the prevention of tooth decay and the development of proper bone structure in humans and animals. It is considered to be a micronutrient for humans since it prevents dental caries by decreasing the rate of demineralization of the dental enamel or reverses the progression of existing decay by promoting the rate of

demineralization. High doses of fluoride lead to the development of dental and skeletal fluorosis, depending on the concentration of fluoride in drinking water.[2,6] Thus, 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 manifestationof 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.[7] Fluorosis not only affects the body of persons but also renders them socially and culturally crippled.[8] For instance, younger people showing symptoms of high dental fluorosis (severe pitting and coloration of teeth) find it difficult to smile comfortably in public. Fluoride contamination of groundwater and related health hazards are a worldwide problem. China and India are among the most affected, and other countries such as Ethiopia, Kenya, Ghana, and Tanzania have serious problems related to fluoridecontamination.[9] Hence, it is estimated that more than 260 million people worldwide are affected by fluorosis.[5] Most endemic fluorosis occurs in rural areas of developing countries, where the less-developed economy and technological challenges aggravate the problem of unsafe drinking water. Fluoride concentration above 1.5 mg/L has been reported from many parts of Ethiopia, but the highest levels are found in the Rift Valley, the lowland area with the highest volcanic activity in the country. In the Ethiopian Rift Valley, about 14 million people rely on water sources that contain high concentrations (above 5 mg/L) of fluoride. Therefore, an economical and effective method for fluoride removal in drinking water is of great importance.[10] 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 groundwater, and rain water), increasing the nutritional status of the population at risk (adequate intake of calcium reduces the risk of dental fluorosis during the childhood), and by removing excessive fluoride from drinking water. De-fluoridation of drinking water appears to be a simpler practical solution to prevent the adverse effects of fluoride. Hence, the development of de-fluoridation technologies, preferably low-cost and environmentally friendly, capable of reducing the fluoride concentration below the limit established by the WHO is of paramount importance.[7] 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. The fluoride concentration of the treated solution still remains about 8.0 mg/L due to the solubility of the formed precipitate. Chemical precipitation may also produce large amount of sludge.[7,9–11] Membrane separation process mainly contains reverse osmosis and nanofiltration. Even though it can produce water with extremely high purity, itsuffers from high energy consumption and membrane fouling. In electro-dialysis process, fluoride ions transfer through a semipermeable membrane due to an electric potential. It is costly and easily influenced by coexisting ions.[1] Most of the available de-fluoridation techniques are complex, require skilled labor, and have a high initial and maintenance cost and technically non feasible for rural areas. Hence, the need to find locally available de-fluoridation media for safe and easy use at both household and small community levels is desirable.[3–6] Adsorption is the preferred technique for de-fluoridation 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. It has the added advantage that it can be applied to a decentralized water supply system. The availability of different adsorbents in large amounts and low costs make them potential candidates for the defluoridation in remote areas.[2–5]

2. MATERIALS AND METHODS

2.1. Preparation of Stock and Standard Solutions

A 1000 mg/L stock solution of sodium fluoride (NaF) was prepared by dissolving 2.21 g of anhydrous sodium fluoride (99.0% NaF) in distilled water in a 1 L volumetric flask and diluting to the mark. Other standard fluoride solutions of the required concentrations were prepared by serial dilution of the stock solution with distilled water.

2.2. Preparation of Total Ionic Strength Adjustment Buffer

Calibration and determination were carried out by addition of total ionic strength adjustment buffer (TISAB). The TISAB was prepared following a recommended procedure by dissolving 57 mL glacial acetic acid, 58.0 g sodium chloride, 7.0 g of sodium citrate and 2.0 g of EDTA in 500mL distilled water and then the pH was adjusted to 5.3 with 5M sodium hydroxide solution and then made up to 1000 mL in a volumetric flask with distilled water.[6]

2.3. Adsorbent (China clay) Preparation

The physico-chemical nature of the adsorbate significantly affects the rateand extent of adsorption of pollutants from water and wastewaters by adsorption technique. The chemical constituents of various adsorbents vary from sample to sample depending upon the source of collection. Therefore, the characterization of adsorbents

is quite essential in order to have a better insight into the mechanism of the adsorption process. China clay is a mineral of kaolinite group. It does not swell with addition of water. The alumina content present in it does not form isomorphous series with any other metallic compounds. It is generally used in the manufacture of different types of ceramic goods. It has been used by several workers[12-16] as an adsorbent for water and wastewater treatment by adsorption process. It was collected from Patharghatt village of Bhagalpur district, Bihar (India). It was used as such without any pretreatment just after sieving through 53µm pore size sieve. The different chemical constituents of adsorbents were determined using gravimetric, EDTA and colorimetric methods.[17-18] The chemical analysis and characterization of China clay is given in Table1. The material was washed with distilled water to remove dirt and dried under sun. 30 g of powdered adsorbent was taken in a 1 L plastic bottle and 100 mL of 1 mol/L $AlCl_3 \cdot 6H_2O$ and a certain amount of 3 mol/L NaOH was immediately added into the mixture. The mixture was shaken at room temperature for 2 hours on a shaker at 200 rpm. The mixture was centrifuged after equilibration, and the recovered solid was scooped into a 1 L bottle containing some distilled water. After acidifying the mixture with 0.1M HCl to pH 2, it was shaken for 40 min and centrifuged. The solid was washed with distilled water with repeated centrifuging until the pH of the supernatant was 6.0. The solid residues were dried in the oven at 105°C for 12 hours, cooled in the desiccators. The dry adsorbent was stored in a corked plastic bottle until use.

Table1: Chemical analysis of China clay as Adsorbent.

Constituents	Percentage by weight
SiO_2	46.22
Al_2O_3	38.40
CaO	0.86
Fe_2O_3	0.68
MgO	0.37
Loss of ignition	13.47
Particle size	53µm
Mean Particle size diameter	$51x10^{-4}$ cm
Surface Area	13.52 m^2g^{-1}
Porosity	0.330
Density	2.692 gcm^{-3}

2.4 Batch adsorption studies

The metal solutions used in this study were prepared as the stock solutions. 100ml of adsorbate solution of known concentration was taken in the 250 ml conical flask and 1gm of each adsorbent was added separately at definite pH and temperature. For a wide range contact time 20-180 minutes, after that the solution was filtered by whatmann-42 filter paper and concentration of the filtered solution was determined by atomic absorption spectrophotometer. The percentage removal was determined by the following expression. The amount of adsorption efficiency was calculated by,

Percentage adsorption = [(C*o* – Ce)/C*o*] x100

Where, Co = initial concentration of metal ion in the solution and Ce = final concentration of metal ion in the solution. The amount of fluoride adsorbed (adsorption capacity), qe (mg/g), at equilibrium by the adsorbent was calculated from the following expression[19]:

$$qe=[(Co–Ce)/m]xV \quad (1)$$

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 *g*, and V is the volume of the fluoride solution in L. The fluoride removal efficiency (percent fluoride removal) was calculated using the following equation[20]:

$$\text{Percent fluoride removal} = [(Co – Ce) /Co] \times 100 \quad (2)$$

2.5 Adsorption Isotherms and Kinetics

Adsorption isotherms are useful for describing how the adsorbate will interact with the adsorbent (understanding the mechanism of the adsorption) and give an idea about the theoretical maximum adsorption capacity of the adsorbent.) eequilibrium data were tested for fitness into the Langmuir and Freundlich isotherm models. Langmuir isotherm[21] depends on the assumption that uptake happens on a homogenous surface by monolayer sorption without intercalation between adsorbed particles. The Freundlich adsorption isotherm is based on the equilibrium sorption on heterogeneous surfaces by multilayer sorption with interaction between adsorbed particles.[22] 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.[23] In this study, pseudo first-order and pseudo second-order kinetic models were employed for understanding the kinetics of adsorption process.

3. EFFECT OF DIFFERENT PARAMETERS

3.1. Effects of Adsorbent Dose

The amount of contact surface between an 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 mass of the adsorbent, viz., 2, 5, 10, 15, 20, and 25 g/L, keeping other parameters constant at their respective optimum conditions (initial fluoride concentration=10 mg/L, pH=6.7, contact time=200 min and Rotational Speed=200 rpm). The percentage fluoride removal was determined, and the results are shown in Figure 2. It was observed that there was an increase in fluoride removal efficiency with increasing dose of the adsorbent. This is due to the increase in surface area and availability of more active sites for adsorption of fluoride.[24] Removal of excess fluoride from water by aluminum hydroxide[25] and lateritic soil[26] also revealed similar results when the adsorbent dose increases. 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 this study, the optimum dose was found to be 25 g/L with the fluoride removal efficiency of 85% at an optimum pH of 6.7.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. In principle, the adsorbent can be reused, regenerating it with NaOH.

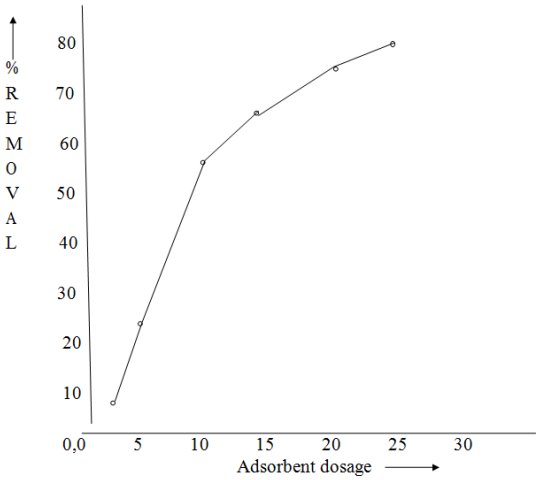

Figure 1: Effect of adsorbent dosage on the adsorption capacity of China clay (initial fluoride concentration=10 mg/L, pH=6.7, contact time=200 min, and Rotational Speed=200 rpm).

3.2. Effect of Initial adsorbate 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 time=200 min, and adsorbent dose=25 g/L).The results obtained were plotted as percentage removal of fluoride versus initial concentration of the fluoride ion in the solution as shown in Figure 2.

It was clear (Figure 2) that the percentage removal of the fluoride ion has decreased with an 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.[27] 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 93% to 56% when a fixed dose of the adsorbent used as the initial concentration of the fluoride increases from 5 to 70 mg/L. Similar studies[25-26,28] also pointed out that there was a decrease in fluoride removal efficiency of the adsorbents with increasing initial concentrations of fluoride.

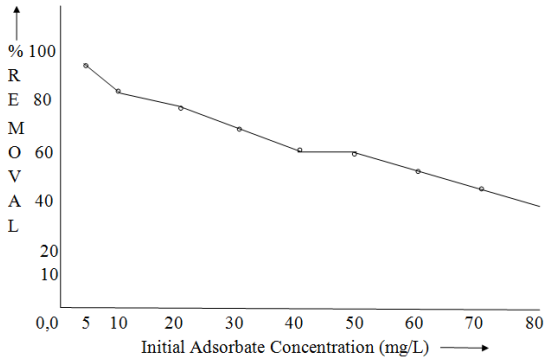

Figure 2: Effect of initial adsorbate concentration on China clay (adsorbent dose=25 g/L, contact time=200 min, pH=6.7, and Rotational Speed= 200 rpm).

3.3. Effect of pH

The pH of the solution is an important factor in the adsorption process since it affects the adsorbent surface properties and ionic forms of fluoride in the solution.[29] The effect of pH on the removal of the fluoride ion from an aqueous solution was studied by varying it from 3–10 while keeping other parameters constant. The pH adjustments were achieved by addition of small amounts of 0.1M NaOH or 0.1M HCl. Figure 3 shows the effect of pH on the fluoride removal efficiency of the adsorbent.

Most adsorbents used in fluoride removal have narrow working pH ranges and usually show optimum performance in acidic pH range. One study indicated that maximum fluoride removal efficiencies were obtained at pH=3 for fluoride adsorption by pumice from aqueous solutions.[30] However, the pH of natural groundwater with high fluoride content is in the range of 7.6 to 8.6 in most cases.[31] Within this pH range, unlike most other de-fluoridation adsorbents, the adsorbent used in this study (diatomite modified by treating it with aluminum hydroxide) showed high performance, about 90% removal efficiency at 25 g/L dose and an initial fluoride concentration of 10 mg/L (Figure 3). The higher adsorption at lower pH indicates that an increase in H^+ ion the adsorbent surface makes the surface of the adsorbent positively charged resulting in electrostatic attraction between positively charged adsorbent surface and fluoride ions. The decrease in removal efficiency at higher pH values can be attributed to the competition for the active sites by OH^- ions and the electrostatic repulsion of anionic fluoride by negatively charged

diatomite surface. Fluoride removal above point of zero charge pH value must have been byion-exchange as OH^- ions would predominate over $H3O^+$ ions.[31] pH zero point of charge is the pH value at which the sorbent exhibits zero net electrical charge on the surface when submerged into an electrolyte.

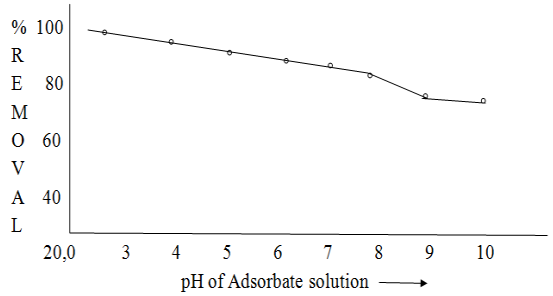

Figure 3.Effect of pH on the adsorption (initial fluoride concentration=10mg/L, adsorbent dosage=25 g/L, contact time=200 min, and Rotational Speed=200 rpm).

3.4. Effect of Contact Time

The study of the effect of contact time to the removal efficiency was carried out by varying it from 40 to 300 minutes, keeping other parameters constant at optimum values (pH=6.7, dosage of adsorbent= 25 g/L, and initial concentration=10 mg/L). Figure 4.shows the effect of contact time on the de-fluoridation capacity of the adsorbents.

It was clear that (Figure 5) as contact time increases percent removal also increases initially and gradually attains almost an equilibrium condition in nearly 200 minutes and remains more or less constant thereafter. The increase was not significant for longer contact times since the reaction (de-fluoridation) is fast during the initial minutes. The slower adsorptionat the later stage is due to a gradual diffusion of the adsorbed external fluoride to the inner adsorbent surface of the porous adsorbent for adherence, providing new fluoride binding sites on the external surface. A maximum of 90% removal could be accomplished by China clay. Similar patterns were also observed by other researchers.[32-36] Thus, China clay has better de-fluoridation efficiency compared to other adsorbents.

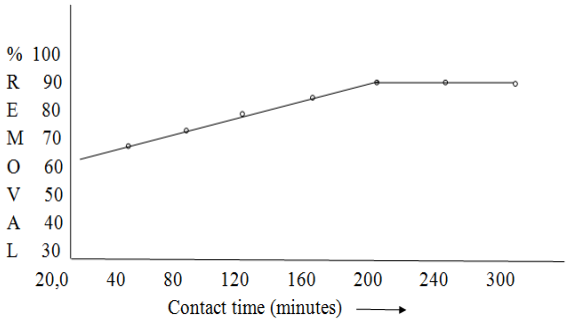

Figure 4: Effect of contact time (initial fluoride concentration=10 mg/L, adsorbent dosage=25 g/L, pH= 6.7, and Rotational Speed=200 rpm).

4. ADSORPTION ISOTHERMS

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.[37] Freundlich and Langmuir isotherms are the most commonly used models to investigate the adsorption processes. The 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.[21] The Langmuir equation is written as,

$$qe = \frac{qm\ KL\ Ce}{1+KL\ Ce} \quad (3)$$

Where qe (mg/g) is the amount of fluoride adsorbed per unit mass of the adsorbent at equilibrium, qm (mg/g) is the maximum amount of the fluoride per unit weight of the adsorbent to form a complete monolayer on the surface, KL (L/mg) is an adsorption equilibrium constant related to the affinity of the binding sites and energy of adsorption, and Ce (mg/L) is the equilibrium concentration of the fluoride in solution.

The linear form of Langmuir isotherm is most commonly used and is given as follows[38]

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

The values of Langmuir constants qm and KL are calculated from the slope and intercept of the linear plot Ce/qe versus Ce. A plot Ce/qe versus Ce should be a straight line with a slope 1/*q*m 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:

$$R_L = \frac{1}{1+KL.Co} \quad (5)$$

The values of RL indicate the type of bio-sorption isotherm and there arefour possibilities for the RL value,
(i) $0 < RL < 1$ for favorable sorption,
(ii) $RL > 1$ for unfavorable sorption,
(iii) RL=1 for linear sorption, and
(iv) RL=0 for irreversible sorption.

The linear Langmuir isothermal plot and corresponding constants are given in Figure 5 and Table 2 respectively. The plot of Ce/qe versus Ce under optimum conditions gave a straight line with a correlation coefficient (R^2=0.888) as shown in Figure 5. The correlation coefficients are, however, less than those of Freundlich isotherm as can be seen from Figure 5.Freundlich isotherm assumes that the adsorption of the adsorbate occurs on the heterogeneous surface by multilayer sorption. 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.[38] It is given by the linear form of the Freundlich isotherm model.

$$\ln(qe - qt) = \ln qe - k1.t \quad (6)$$

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)" versus "t" give a straight line with an intercept of "ln qe" and slope of "− k1".The pseudo-second-order model assumes that chemisorptions 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[39] as follows:

$$\frac{t}{qt} = \frac{1}{K_2.q^2e} + \frac{1}{qe}.t \quad (7)$$

The equilibrium adsorption capacity (qe) and the second-order constant k2 (g/mg·h) can be determined experimentally from the slope and intercept of plot t/*q*t versus *t*. A plot of t/qt against t gives a straight line with an intercept of 1/k2q²e and slope of 1/qe.Table 2 shows the values of pseudo-first-order and pseudo-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.[40] The value of k_2 is high which indicates the tested adsorbent is effective for fluoride adsorption.

Table 2: Calculated Langmuir and Freundlich isotherm parameters.

Calculated Freundlich isotherm constants	KF	0.291
	1/n	0.461
	R^2	0.985
	RL	0.440
Calculated Langmuir isotherm constants	b (L/mg)	0.200
	R^2	0.900
	*q*m (mg/L)	1,671

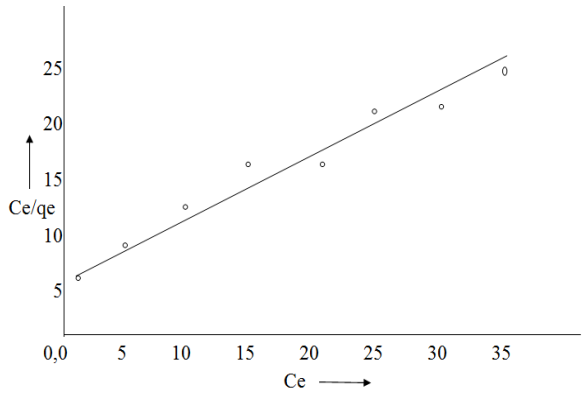

Figure 6: Langmuir adsorption isotherm for fluoride removal by China clay under optimum conditions.

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

Pseudo-first-order kinetic constants	k1	0.0023
	qe	0.1245
	R^2	0.8675
Pseudo-second-order kinetic constants	qe	0.3604
	K2	0.9200
	R^2	1.0000
Intra-particle diffusion model parameters	kid	0.0016
	R^2	0.5964

5. Adsorption Mechanisms

The probable mechanism controlling the sorption rate was evaluated using the intra-particle diffusion model. The McKay and Poots equation is expressed as[41],

$$qt = kid\ t^{1/2} + I, \quad (8)$$

Where qt is the amount of fluoride adsorbed (mg/g) at time t (min), kid is the intra-particle diffusion rate constant (mg/g·min½), and I (mg/g) is a constant that has to do with the thickness of the boundary layer. Accordingto the model, plot of uptake qt versus *t* ½ should give a linear line if intra- particle diffusion is involved in the sorption process. kid and I values are obtained from the slopes and intercept of the linear plot, respectively. Since plot of qt against *t*½ 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, which 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 sorption rate determinant because of the much smaller size of fluoride ions to the pores of the sorbent. The ionic radius of fluoride is 1.33 Aº.[42]

6. CONCLUSIONS

China clay was found to be an effective adsorbent for the de-fluoridation of aqueous solution and natural groundwater. The maximum percentage removal of fluoride and adsorption capacity were 90% and 1.75 mg/g, respectively, for 10 mg/L fluoride concentration under optimum adsorption conditions (contact time:200 min, adsorbent dosage: 25 g/L, pH 6.7, at room temperature and Rotational speed=200 rpm). 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 chemisorptions. 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 F− to the sorbent 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. This adsorbent is cheaper, abundant, and easily available in huge amount in India.

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