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Alkali-treated fly ash for the removal of fluoride from aqueous solutions

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ABSTRACT

In the batch study, the adsorption performance of calcium hydroxide-treated fly ash (CFA) in the fluoride removal from aqueous solution was investigated. The effects of various adsorption controlling parameters such as contact time, dosage, solution pH, temperature, and agitation speed on fluoride removal was analyzed. Eighty-nine percent of fluoride was removed by CFA at solution temperature of 50˚C. The kinetic studies and isotherm studies were also performed to understand the sorption ability of CFA. The monolayer adsorption capacity from the Langmuir adsorption equation was found as 10.86 mg/g. Kinetic measurements suggested the involvement of pseudo-second-order kinetics in adsorption. It also suggested that particle diffusion process is not only a rate controlling step process. Overall, the present study showed that the adsorbent is environmental friendly, efficient, and a low-cost adsorbent which is useful for the removal of fluoride from aqueous solution.

Keywords: Adsorption; Alkali-treated fly ash; Batch study; Isotherms; Kinetic study

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1. Introduction

With the increase in the industrial activities, including pharmacy, fluorspar mining, semiconductor process, aluminum electrolysis, electroplating, generating electricity, and rubber and fertilizer production, the excessive fluoride has been drained into water bodies [1]. Water resource substitution is impossible; therefore, the removal of fluoride from aquatic environment is necessary. Moderate fluoride (0.5–1.5 mg/L) in drinking water is an essential micronutrient for the calcification of the dental enamel and bone formation [2]. Deposited fluoride contaminations are found in water mostly due to natural processes (geochemical reactions and volcanic emissions) and industrial activities (semiconductor, electroplating, steel, and fertilizer industries) [3]. Fluoride in water may be a double-edged sword depending on its concentration and the amount of that has been consumed [4]. The presence of fluoride in drinking water is beneficial to the production and maintenance of healthy bones and teeth, while excessive intake of fluoride provokes skeletal fluorosis, which is associated with serious bone abnormalities [5]. Due to dust, industrial production of phosphate fertilizers, and coal ash from the burning of coal and volcanic activity, fluorides are widely distributed in the atmosphere [6]. It must be noted that the problem of excess fluoride in drinking water is of recent origin in most of the countries. Fluoride is known to cause dental fluorosis, a defect of the tooth enamel caused by fluoride's interference with developing teeth [6,7].

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Fluoride is associated with Alzheimer's disease and other forms of dementia [7]. It has also been associated with low IQ and mental retardation in children, and can cause a crippling bone disease called skeletal fluorosis [6,7]. In more mild forms, symptoms of this disease include chronic joint pain, similar to the symptoms of arthritis [7]. Fluoride depresses the activity of the human thyroid gland and has been commonly used as an effective treatment for patients with overactive thyroids and also disrupts the activity of normally functioning hormones [7]. The WHO recommended the tolerance limit for fluoride in drinking water is 1.5 mg/L [6].

The selection of a particular treatment procedure depends on the nature of the effluent, waste type and concentration, presence of other constituents, level of removal required, and economics [8]. Conventional physico-chemical methods for removing fluoride ion concentration from water include chemical reduction, electrochemical treatment, ion exchange, precipitation, and evaporative recovery [9]. These processes have significant disadvantages, such as incomplete removal, high reagent or energy requirements, and generation of toxic sludge or other waste products, and are generally very expensive when the contaminant concentrations are in the range of 10–100 mg/L [10]. Among these methods, adsorption seems to be the most attractive method because of its high efficiency and easy handling nature. Activated carbon, the most widely used adsorbent in the treatment of wastewater, is expensive and may also require complexing agents to improve its ability to remove inorganic matter [11]. So, different low-cost adsorbents have been successfully exploited for the removal of fluoride, including synthetic ion exchangers, magnesia-amended silicon dioxide [12], $KMnO_4$-modified activated carbon [13], granular-activated carbons coated with manganese oxides, alum-impregnated activated alumina [14], magnesia/chitosan composite [15], magnesia-amended activated alumina granules [16], hydrous manganese oxide-coated alumina [17], and other materials.

The primary objective of this study is to determine the fluoride sorption ability of calcium hydroxide-treated fly ash (CFA) from aqueous solution. The study includes an evaluation of the effects of various operational parameters, such as initial fluoride ion concentration, contact time, dose, temperature, agitation speed, and pH on the fluoride adsorption process. The adsorption kinetic models and equilibrium isotherm models related with the process were also reported.

2. Materials and methods

2.1. Adsorbent

The thermal power plant waste material "fly ash" was used as adsorbent in the present study with some modifications. The adsorbent was collected from Neyveli Lignite Corporation, Neyveli in Tamil Nadu. The fly ash 100–150 μm was sieved, washed in deionized water to remove impurities, and dried at 70˚C for 24 h in an oven drier, and 30 g of it was treated with 100 mL of 10% of calcium hydroxide solution [18]. The mixture was then settled in an incubator for 3 h. After incubation, the excess solution was removed by filtration and dried at 70˚C for 24 h. The sample was then cooled to room temperature and transferred to airtight bottles for storage. All chemical reagents were of analytical grade. Deionized water was used in all experiments.

2.2. Characterization of the adsorbent

Conventional chemical as well as analytical techniques were employed to ascertain different characteristics of adsorbent. The moisture content and the loss on ignition were determined by heating a preweighed dry sample (left at 105˚C in an oven and then cooled in desiccators) to 600˚C over a period of 2 h [7]. Specific gravity was found using pycnometer method.

The point of zero charge (PZC) was determined using the solid addition method [19]. viz: a series of 100 mL conical flasks, 45 mL of 0.1 M KNO_3 solution was transferred. The pH_0 values of the solution were roughly adjusted from 2 to 10 by adding either 0.1 N HNO_3 or NaOH. The total volume of the solution in each flask was made exactly to 50 mL by adding KNO_3 solution. The pH_0 of the solutions were then accurately noted. CFA (1 g) was added to each flask and securely capped, immediately. The suspension was then manually agitated. The pH values of the supernatant liquid were noted. The difference between the initial (pH_0) and final pH (pH_f) values ($\Delta pH = pH_0 - pH_f$) were plotted against the pH_0. The point of intersection of the resulting curve at pH_0 gave the PZC.

2.3. Preparation of fluoride stock solution and standards

All the reagents used were of AR grade. A synthetic fluoride stock solution was prepared by dissolving 221 mg anhydrous sodium fluoride in 1,000 mL distilled water in volumetric flask. Fluoride standard solution was prepared by diluting 100 mL stock solution to 1,000 mL distilled water in volumetric flask. This 1 mL solution contains 0.1 mg of fluoride. The adjustments for pH were done using HCl or NaOH.

2.4. Equipments

Orion EA 940 expandable ion analyzer (USA) was used for pH measurements and fluoride measurements. An IHC 3280 Orbital shaking incubator (REMI, India) was used for all adsorption experiments. TC650 S Multiple Centrifuge (MULTISPIN, India) was used to separate the supernatant.

2.5. Batch study

Batch adsorbent experiments were carried out in 250 mL conical flasks with 50 mL working volume with a concentration of 10 mg/L. A weighed amount (100 mg/50 mL) of adsorbent was added to the solution. The flasks were agitated at a constant speed of 150 rpm in a shaker. The influence of pH (2–12), contact time (5–240 min), adsorbent dose (5–300 mg), temperature (30, 40 and 50˚C), and agitation speed (100, 150, and 200 rpm) was evaluated during the present study. Samples were collected from the flasks at predominant time intervals for analyzing the residual ion concentration in the solution. The residual amount of fluoride ion in each flask was investigated using Orion EA 940 expandable ion analyzer. The amount of fluoride adsorbed per unit of CFA was calculated according to a mass balance on the fluoride ion concentration Eq. (1).

$$q_e = \frac{(C_i - C_e)}{m} V \tag{1}$$

where C_i and C_e (mg/L) are the liquid phase concentrations of fluoride at initial and equilibrium, respectively, q_e is the amount of adsorbate adsorbed per unit weight of adsorbent at equilibrium (mg/g), V the volume of the solution (l), and m is the mass of adsorbent used (g).

3. Results and discussion

3.1. Characterization of adsorbent

The physicochemical properties of the adsorbent was characterized, the values are shown in Table 1. The results of the PZC of the CFA (PZC = 8.8) is represented in Fig. 1. From Fig. 1 it was observed that at pH less than 8.8, the surface of the CFA is predominated by positive charges while at pH greater than 8.8, the surface is predominated by negative charges [20].

Table 1
Properties of CFA

Properties	Values
Size	100–150 µm
pH	8.97
Specific gravity	1.951
Moisture content	0.51%
Loss on ignition	0.45%
Point of zero charge	8.8

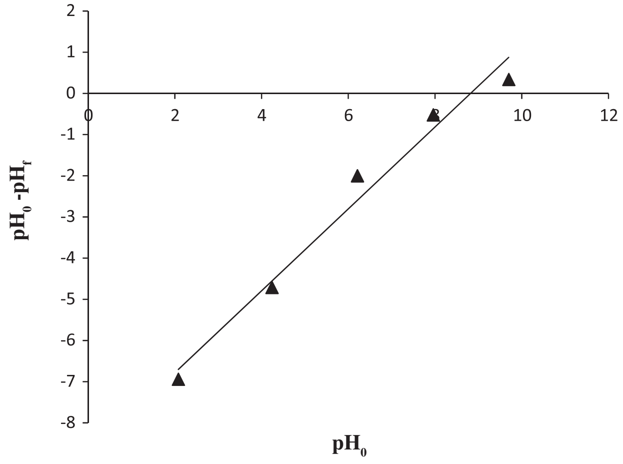

Fig. 1. PZC of CFA.

3.2. Effects of initial concentration and contact time

Adsorption experiments were conducted to study the effect of the initial concentration of fluoride ions in the solution on the rate of adsorption of CFA. It was observed that fluoride uptake is rapid for the first 10 min and there after it proceeds at a slower rate and finally attains saturation (Fig. 2). This may be explained by a rapid adsorption on the outer surface, followed by slower adsorption inside the pores [21]. Such short times coupled with high removals at the initial stage of adsorption indicate a high degree of affinity for the fluoride pointing towards chemisorption [22]. Then, the reduction in removal rate is due to reduction of active sites of adsorbent and the formation of repulsive forces between the fluoride on the solid surface and in the bulk phase [23]. The time required to attain the state of equilibrium (saturation) is termed as equilibrium time, and the amount of fluoride adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under those operation conditions [24]. At

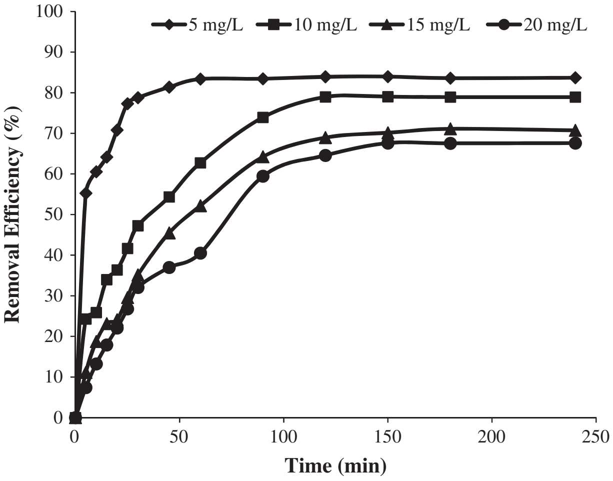

Fig. 2. Effect of initial concentration on fluoride removal by CFA.

this point, the amount of fluoride being adsorbed onto the adsorbent was in a state of dynamic equilibrium with the amount of fluoride desorbed from the adsorbent [22].

The influence of initial fluoride concentration in equilibrium uptake is also presented in Fig. 2. As the initial fluoride ion concentration increases from 5, 10, 15, and 20 mg/L, the equilibrium removal of fluoride decrease. The equilibrium time decreases in the order of 150, 150, 120, and 60 min for 20, 15, 10, and 5 mg/L solution, respectively. This may be due to the fact that at lower concentrations, almost all the molecules were adsorbed very quickly on the outer surface, but further increases in initial concentrations led to fast saturation of adsorbent surface, and thus most of the fluoride ions adsorption took place slowly inside the pores [25].

3.3. Effect of adsorbent dosage

The effect of adsorbent dose on fluoride removal was analyzed by varying the dosage of CFA and the results are shown in the Fig. 3. From Fig. 3, it is clear that the fluoride removal efficiency increases with the increase in the adsorbent dose to a certain extent after which it remains more or less constant. This may be due to the increase in availability of surface active sites resulting from the increased dose of adsorbent and conglomeration of the adsorbent, especially at higher dose [26]. The maximum fluoride ion uptake was observed to be 80% for 3 g/L of adsorbent dosage.

3.4. Effect of variation in pH

The pH of the aqueous solution is a controlling factor in the adsorption process. Thus, the role of hydrogen

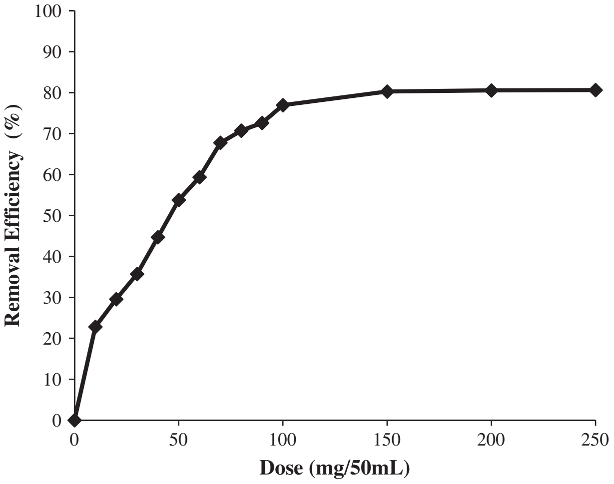

Fig. 3. Effect of dose on fluoride removal by CFA.

ion concentration was examined at pH values of 2–12. This was adjusted by adding 0.1 N HCl or 0.1 M NaOH with 50 mL of standard solution of 10 mg/L of fluoride for optimum contact time with an optimum dose of CFA adsorbent. The influence of pH on the sorption rate is shown in Fig. 4. It is observed that the extent of removal of fluoride ions decreases with the increase in pH of the solution and that was investigated as 80% at pH 7.5. Efficiency gradually increases up to pH 7.5, then decreases with increase in pH of the solution. In this case, the result may be due to the neutralization of the negative charges at the surface of the treated fly ash by greater hydrogen ion concentration at neutral pH value [27]. This could be explained due to the change in surface charge of the adsorbent. The PZC was a concept relating to the phenomenon of adsorption. When the solution pH was below the PZC, the fluoride anions

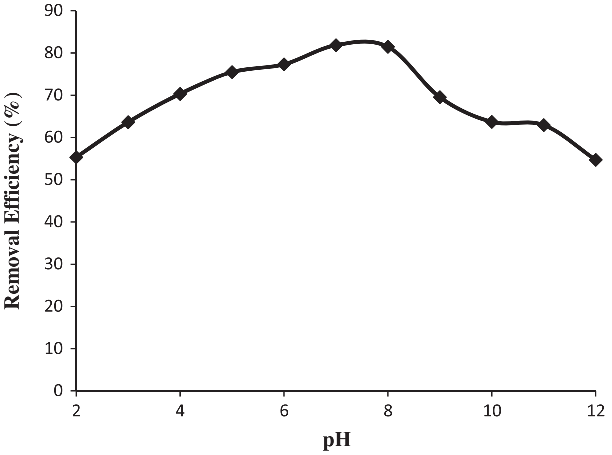

Fig. 4. Variation of removal efficiency with variation in pH.

were attracted to the positively charged surface of the CFA, caused by the protonation of the CFA hydroxyl groups, thus favoring fluoride accumulation onto the surface [15]. Furthermore, the surface charge of CFA became more positively charged while decreasing the pH. Hence, more fluoride ions were attracted to the surface causing an increase in the adsorption capacity of CFA. At pH above the PZC, adsorption of fluoride anions were very slight because the CFA surface was negatively charged, due to the deprotonation of CFA hydroxyl groups, causing a mutual repulsion between fluoride anions and the CFA surface.

3.5. Effect of variation in temperature

The adsorption studies were carried out at three different temperatures 30, 40, and 50˚C, and the results of these experiments are shown in Fig. 5. The adsorption capacity increases with the increase in temperature, indicating that the adsorption is an endothermic process. Ten percent of additional fluoride was removed with the increase of temperature from 30 to 50˚C. This increase in fluoride uptakes at higher temperature is due to increased penetration of adsorbate inside micropores at higher temperatures or the creation of new active sites [28]. This may also be due to the decrease in the boundary layer thickness surrounding the sorbent, so that the mass transfer resistance of adsorbate in the boundary layer is decreased [29].

3.6. Effect of variation in agitation speed

It is well known that agitation is one of the important parameters governing an adsorption process since it influences the distribution of the solute in the bulk solution and the formation of external boundary film [30]. The effect of agitation on the adsorption of fluoride by CFA was studied at different agitation speed (100, 150, and 200 rpm) as shown in Fig. 6. It was also observed that percentage of fluoride sorption increased with increase in agitation speed. This may be explained by the fact that increasing the agitation speed reduced the film boundary layer surrounding particles, thereby increasing the external film transfer coefficient, and hence, the adsorption capacity [31]. The degree of agitation reduced the boundary layer resistance and increased the mobility of the system [31]. It may happen in four steps [32]: (i) migration of adsorbate molecules from the bulk solution to the surface of the adsorbent, (ii) diffusion through the boundary layer to the surface of adsorbent, (iii) adsorption at a site, and (iv) intraparticle diffusion into the interior of the adsorbent. Due to this, the adsorbate is forced towards the adsorbent surface and leads to an increase in the diffusion of adsorbate into the surface of the adsorbent.

3.7. Adsorption isotherms

The study of adsorption isotherm has been of important and significant in the wastewater treatment by batch adsorption technique as they provide an approximate estimation of the adsorption capacity of the adsorbent [33]. The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state [34]. The adsorption isotherm models were used to characterize the interaction of fluoride with sorbents. The experimental

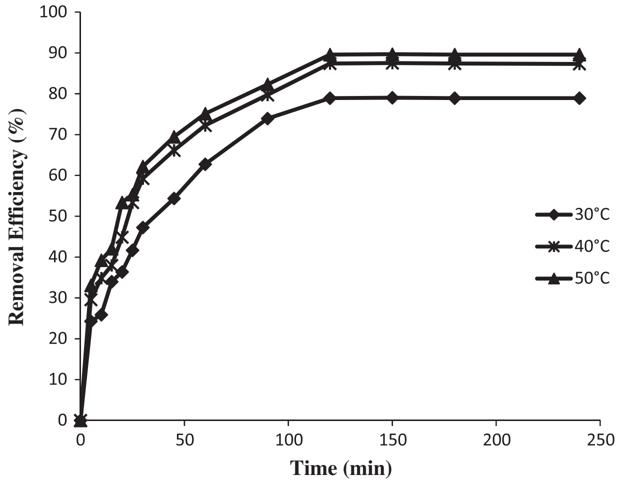

Fig. 5. Variation of fluoride removal efficiency of CFA with variation in temperature.

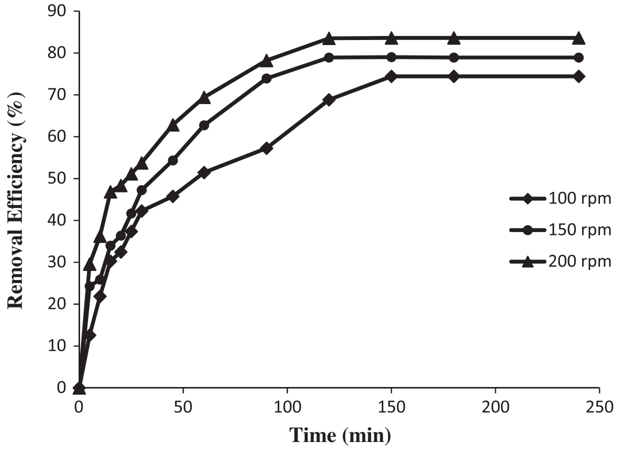

Fig. 6. Effect of agitation speed on fluoride removal by CFA.

values are fitted with Freundlich, Langmuir, and Temkin isotherm models.

3.7.1. Langmuir isotherm

Langmuir's isotherm model suggests that uptake occurs on homogeneous surface by monolayer sorption without interaction between sorbed molecules [34]. This model is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, with no lateral interaction between the sorbed molecules [35]. The Langmuir isotherm model [36] can be represented in the form of equation as Eq. (2).

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} b} \frac{1}{C_e} \tag{2}$$

where q_e is the amount of adsorbate adsorbed per unit weight of adsorbent at equilibrium (mg/g), $q_{\max}$ is the maximum adsorption capacity (mg/g), b is the Langmuir constant that relates to the energy of adsorption (L/mg), and C_e is the equilibrium concentration of adsorbate in solution (mg/L).

A linear plot (Fig. 7) is obtained for the sorbent when $1/q_e$ is plotted against $1/C_e$ which gives $q_{\max}$ and b values from the slope and intercept, respectively, and the calculated results are listed in Table 2. The experimental data fits well to Langmuir isotherm. This indicates that CFA surface is homogeneous in nature. Fluoride ions made monolayer coverage on CFA surface. The adsorption activation energy between CFA and sorbed fluoride molecules is equal. The monolayer adsorption capacity of CFA is found as 10.86 mg/g.

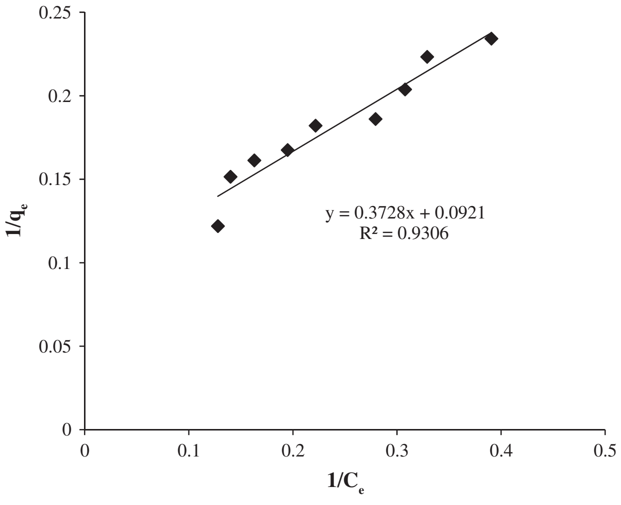

Fig. 7. Langmuir isotherm model for fluoride removal.

In order to find out the further feasibility of the isotherm, the essential characteristics of the Langmuir isotherm can be described by an equilibrium parameter R_L as in Eq. (3) [37].

$$R_L = \frac{1}{1 + bC_0} \tag{3}$$

where C_0 is the initial concentration of fluoride in mg/l and R_L indicates the nature of the adsorption process, as given below [38]:

- $R_L > 1$ Unfavorable
- $R_L = 1$ Linear
- $0 < R_L < 1$ Favorable
- $R_L = 0$ Irreversible

R_L value calculated (Table 2) for the Langmuir isotherm from the present study lies within 0 and 1, which indicates a favorable adsorption process.

3.7.2. Freundlich isotherm

Freundlich isotherm is more accurate by considering an exponential distribution of enthalpies for low coverage of adsorbed species [39]. It is an improvement over Langmuir isotherm by including physical adsorption of species. The equation is a special case for heterogeneous surface species. The Freundlich equation is an empirical equation that is very useful as it accurately describes much adsorption data [40]. The Freundlich equation (Eq. 4) is expressed as:

$$\log q_e = \log K_f + \frac{\log C_e}{n} \tag{4}$$

where K_f and n are the constants depending on temperature, the adsorbent, and the substance to be

Table 2
Isotherms constants for fluoride removal by CFA

Isotherm models	Regression values	Constants
Langmuir isotherm	$R^2 = 0.93$	$q_{\max} = 10.86$ (mg/g); $b = 0.247$; $R_L = 0.288$
Freundlich isotherm	$R^2 = 0.92$	$K_f = 9.75$ (mg/g); $n = 0.884$
Temkin isotherm model	$R^2 = 0.90$	$A_T = 1.135$ (1/mg); $B_T = 3.451$ (J/mg)

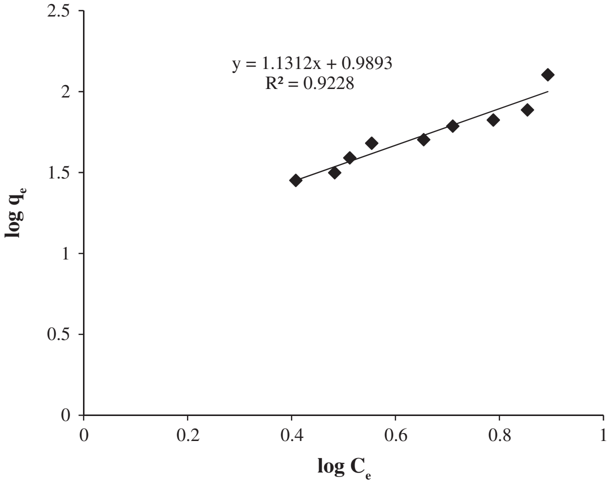

Fig. 8. Freundlich isotherm model for fluoride removal.

adsorbed. The values of $1/n$ and K_f for the sorbent are calculated from the slope and the intercept of the linear plot (Fig. 8) of ln q_e vs. ln C_e and are listed in Table 2. The value of $1/n$ does not lie between 0 and 1 and the n value not in the range of 1–10 confirms the unfavorable conditions for adsorption [41]. A value of $1/n$ below one indicates a normal Langmuir isotherm while $1/n$ above one is indicative of cooperative adsorption [42]. This indicates that even at equal R^2 values, Langmuir isotherm fits well than Freundlich isotherm. This may be due to homogeneous distribution of active sites onto CFA surface, since the Langmuir equation assumes that the surface is homogenous [35].

3.7.3. Temkin isotherm

The Temkin isotherm model assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent–adsorbate interactions, and adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy [43]. The Temkin isotherm Eq. (5) is given as:

$$q_e = B_T(\ln A_T + \ln C_e) \tag{5}$$

where A_T (L/g) is the equilibrium binding constant, corresponding to the maximum binding energy, and constant B_T is related to the heat of adsorption.

A linear plot (Fig. 9) of q_e vs. ln C_e enables the determination of the isotherm constants B_T and A_T from the slope and intercept of the straight line plot. The constant values are given in Table 2.

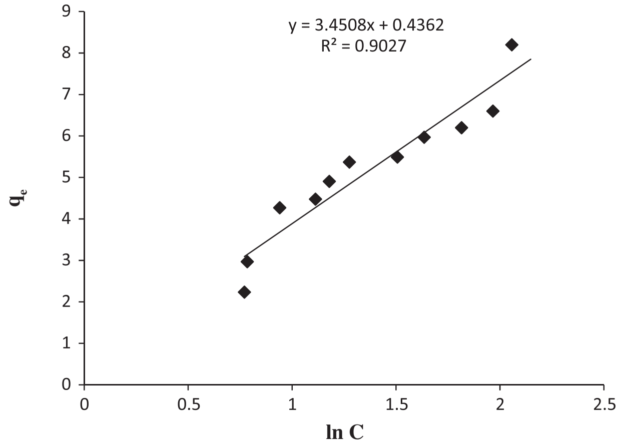

Fig. 9. Temkin isotherm model for fluoride removal.

3.8. Kinetic Studies

The kinetics of fluoride adsorption was modeled using pseudo–first-order and pseudo-second-order kinetic models. The conformity between the experimental data and the model-predicted values were expressed by the correlation coefficient (R^2 values close to or equal to 1).

3.8.1. Pseudo-first-order equation

The Lagergren's pseudo-first-order equation Eq. (6) is generally expressed as [44]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{6}$$

where q_e and q_t are adsorption capacities at equilibrium and at time t, respectively. k_1 is the rate constant of pseudo-first-order adsorption. The values of ln (q_e–q_t) were linearly correlated with t. The plot of ln (q_e–q_t) vs. t should give a linear relationship from which k_1 and q_e can be determined as the slope and the intercept, respectively, which are shown in Fig. 10 and the calculated values are given in Table 3. It was found that the calculated q_e values did not agree with the experimental q_e values even at higher R^2 values. This suggests that the adsorption of fluoride did not follow first-order kinetics [45].

3.8.2. Pseudo-second-order equation

The second-order Lagergren equation Eq. (7) was given by Ho and McKay [46]. It is expressed as:

$$\frac{1}{q_t} = \frac{1}{k_2 q_{e^2}} + \frac{1}{q_e} t \tag{7}$$

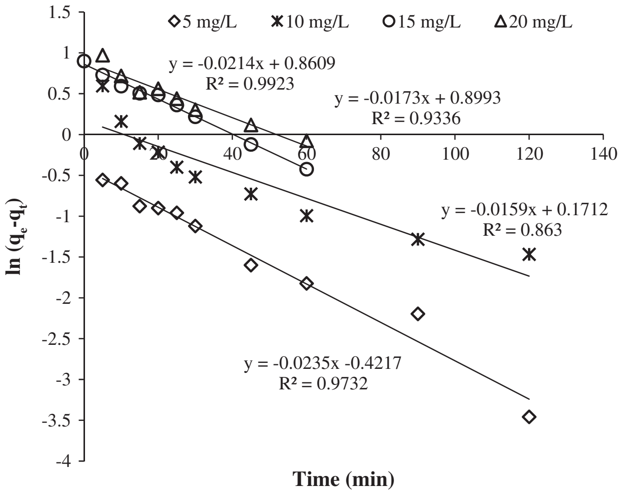

Fig. 10. Lagergren's pseudo-first-order kinetics of fluoride adsorption by CFA.

where k_2 is the rate constant of pseudo-second-order adsorption expressed in g/mg/min. The plot (Fig. 11) of $1/q_t$ and t should give a linear relationship and the values are listed in Table 3. By comparing the theoretical and experimental q_e values, it can be seen from Table 3 that the pseudo-second-order model best represented the adsorption kinetics, suggesting that the adsorption process was controlled by chemisorption [45].

3.8.3. Intraparticle diffusion model

As the above kinetic models were not able to identify the diffusion mechanism, intraparticle diffusion model based on the theory proposed by Weber and Morris [47] was tested. It is an empirically found functional relationship, common to the most adsorption processes, where uptake varies almost proportionally with $t^{1/2}$ rather than with the contact time t as in Eq. (8).

$$q_t = kt^{0.5} + C \tag{8}$$

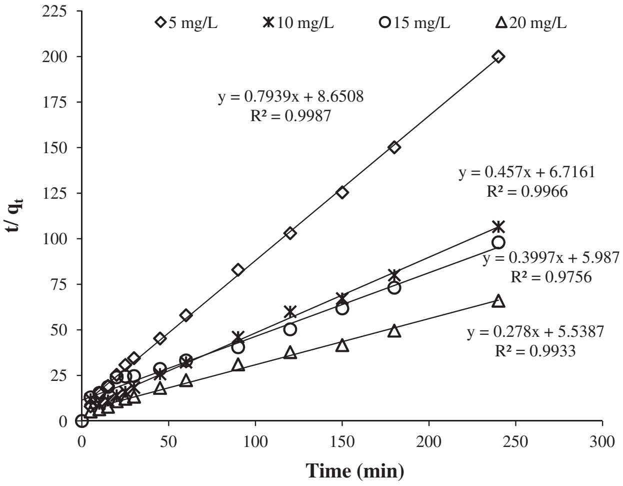

Fig. 11. Pseudo-second-order kinetics of fluoride adsorption by CFA.

where q_t is the amount of fluoride adsorbed at time t, C is the intercept, and k is the intraparticle diffusion rate constant (mg/g min$^{0.5}$) which can be evaluated from the slope of the linear plot of q_t vs. $t^{0.5}$.

The intraparticle diffusion model for the adsorption of the fluoride at 25°C is shown in Fig. 12. If intraparticle diffusion occurs, then q_t vs. $t^{1/2}$ will be linear and if the plot passes through the origin, then the rate limiting process is only due to the intraparticle diffusion. Otherwise, some other mechanism along with intraparticle diffusion is also involved [48]. As seen from Fig. 12, the plots were not linear over the whole time range, implying that more than one process affected the adsorption. For intraparticle diffusion plots, the first sharper region is the instantaneous adsorption or external surface adsorption [45]. The second region is the gradual adsorption stage where intraparticle diffusion is the rate limiting [45]. In some cases, the third region exists, which is the final equilibrium stage where intraparticle diffusion starts to slow down due to the extremely low adsorbate concentrations left in the solutions [48]. Referring to Fig. 12, for all initial concentrations, the first stage was

Table 3
Kinetic coefficient values for the different initial fluoride concentrations

Fluoride ion concentration (mg/L)	Theoretical, q_e (mg/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
		q_e (mg/g)	k_1 (1/min)	R^2	q_e (mg/g)	k_2 (g/mg/min)	R^2
5	1.19	0.65	0.023	0.97	1.26	0.073	0.99
10	2.23	1.18	0.016	0.86	2.18	0.031	0.99
15	2.46	2.36	0.016	0.99	2.50	0.026	0.97
20	3.60	2.45	0.017	0.93	3.59	0.014	0.98

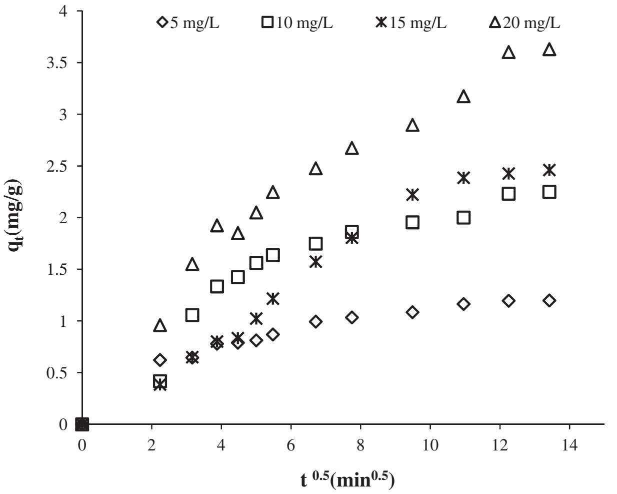

Fig. 12. Intraparticle diffusion model of fluoride adsorption by CFA.

completed within the first 40 min and the second stage of intraparticle diffusion control was then attained. The different stages of rates of adsorption observed indicated that the adsorption rate was initially faster and then slowed down when the time increased.

3.9. Comparison of various adsorbents

Table 4 compares the adsorption capacity of different types of adsorbents used for removal of fluoride. The value of $q_{\max}$ in this study is larger than those in most of previous works. This suggests that fluoride could be easily adsorbed on CFA. The results indicated that the CFA can be considered a promising adsorbent for the removal of fluoride from aqueous solution.

Table 4
Comparison of adsorption capacities of various adsorbents for fluoride uptake

Adsorbents	$q_{\max}$(mg/g)	Reference
Manganese-oxide—coated-alumina	2.58	Maliyekkal et al. [16]
Commercial ion-exchange resin	0.097	Meenakshi and Viswanathan [41]
Magnesia-loaded fly ash	6	Xu et al. [1]
Pumice	0.85	Malakootian et al. [49]
Cynodon dactylon	4.702	Alagumuthu et al. [50]
Rice husk	0.82	Vivek Vardhan and Karthikeyan [51]
Acid-activated kaolinite	1.287	Gogoi and Baruah [52]
Calcium treated fly ash	10.86	Present study

3.10. Real field applications

Batch equilibrium experiments were carried out for finding the capacity of CFA to treat fluoride containing groundwater. The groundwater was collected from Salem District (Tamil Nadu, India) and physico chemical characteristics of the water were analyzed according to standard methods. The physico-chemical characteristics of the water are given in Table 5. Fifty mL of the water sample ($F^- = 2.76$ mg/L) were taken in several conical flasks and various dosage of CFA up to 100 mg were added to it. Residual concentrations of fluoride were analyzed after 150 min of contact time and the results are shown in Fig. 13. Then, 69.5% fluoride was removed for the CFA dosage of 100 mg/50 mL after 150 min of contact time. This was very less than the value obtained from the aqueous

Table 5
Physico-chemical characteristics of groundwater

Sl. no.	Properties	Values
1	pH	7.12
2	Electrical conductivity	612 μS
3	Dissolved solids	316 mg/L
4	Sulfate	200 mg/L
5	Fluoride	2.76 mg/L
6	Alkalinity	62.5 mg/L
7	Chloride	49.98 mg/L

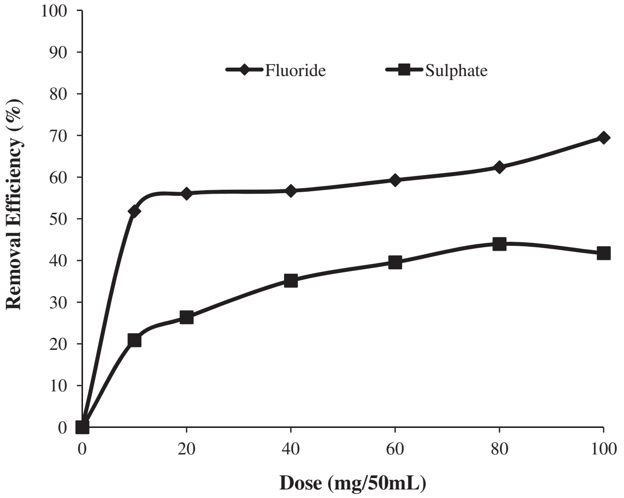

Fig. 13. Removal of fluoride and sulfate from groundwater.

solution. This is mainly due to selective sorption occurred during the experiments. Aqueous solution of fluoride contains only fluoride as anions, while the real field water contains several anions other than fluoride. The other anions in the real field water also adsorbed by CFA and the effective active sites for fluoride sorption are very less than that in aqueous solution. In order to confirm the selective sorption capacity of CFA, residual sulfate concentrations in the real field water after the sorption process were also checked. The results are also shown in Fig. 13. Forty three percent of sulfate was removed by CFA after 150 min of contact time. Even the percentage removal of sulfate is less than that of fluoride; uptake of sulfate (43 mg/g) is very much higher than that of fluoride uptake (0.96 mg/g). This indicates that CFA has higher affinity towards sulfate than that of fluoride. Experimental results also showed that CFA is not only a good adsorbent for fluoride removal; it is also good for removing other anions like sulfate from groundwater.

4. Conclusions

The CFA employed in the adsorption processes is efficient in removing fluoride from aqueous solution. More than 80% of fluoride was removed from its 10 mg/L solution, at an equilibrium contact time of 120 min and CFA dosage of 3 g/L. The maximum removal rate was observed at pH = 7, this shows that the adsorption is enhanced in neutral solution. The removal efficiency increased with increase in the temperature indicating that the process is endothermic and spontaneous in nature. Adsorption equilibrium was better described by the Langmuir isotherm model. The monolayer adsorption capacity of CFA for fluoride was found to be 10.86 mg/g. Kinetic examination of the equilibrium data showed that the adsorption of fluoride ions onto CFA followed the pseudo-second-order kinetic model well, indicating that the process follows chemisorption. The intraparticle diffusion model suggests that it is a multi-step adsorption process and shows that some other mechanism along with intraparticle diffusion is also involved. Real field water treatment using CFA indicates that CFA is not only a good adsorbent for removing fluoride from water; it is also a good adsorbent for removing other anions from groundwater.

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