

Evaluation of removal efficiency of fluoride from aqueous solution using quick lime

M. Islam, R.K. Patel*

Department of Chemistry, National Institute of Technology, Rourkela 769008, India

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Abstract

Several methods are available to remove fluoride from the aqueous environment but they are not feasible in all places and conditions due to various reasons. In the present work, F^- has been removed by using activated and ordinary quick lime. The removal of fluoride was 80.6% and the final concentration was 9.7 mg/L at optimum condition from the synthetic solution having initial fluoride concentration of 50 mg/L. Adsorption kinetic study revealed that the adsorption process followed first order kinetics. And the removal process followed Langmuir adsorption isotherm. The SEM micrographs and XRD studies revealed that the removal of fluoride was mainly due to chemisorption and precipitation. However, they can be suitably used to remove fluoride from industrial effluent where the concentration is high. But this method cannot be employed to treat water for domestic purpose, since it cannot bring fluoride within permissible limit and also increases the pH of treated water.

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Keywords: Fluoride; Quick lime; Adsorption kinetics; Adsorption isotherms; Thermodynamic parameter

1. Introduction

Fluoride related health hazards are a major environmental problem in many regions of the world. Literature review reveals that, India is among the 25 nations around the globe, where health problem occurs due to the consumption of fluoride-contaminated water. In India, 17 states have been identified as epidemic for fluorosis and Orissa is one of them. The fluoride contamination in Orissa is wide spread, where 10 district out of 30 have excess of fluoride in ground water. Fluoride is a necessary micronutrient both for human and animal depending on the total amount ingested. More than 60% of our fluoride demand is fulfilled by the consumption of drinking water. Thus fluoride present in the drinking water can have beneficial or detrimental effect depending on its concentration and consumption of total amount [1]. Excess of fluoride (>1.5 mg/L) in drinking water is harmful to the human health [2]. The physiological effects of fluoride upon human health have been studied since the early part of 20th century. Several reports and studies [3] established both the risk of high fluoride dosing and the benefits of minimal

exposure [4,5]. A low dose of fluoride was deemed responsible for inhibiting dental caries while a higher daily dose was linked to permanent tooth and skeletal fluorosis [6].

Fluoride has two sources. It can appear “naturally” in water or it can appear as a toxic waste. Even where it does appear without any help from industry, it can cause problem. The earliest problems associated with toxic wastes involved those businesses manufacturing aluminum with the resulting wastes usually being sodium fluoride. In Britain, today, the most frequently used toxic waste product used for fluoridation comes from the phosphate fertilizer industry.

Various treatment technologies, based on the principle of precipitation, ion exchange, electrolysis, membrane and adsorption process have been proposed and is tested for removal efficiency of excess of fluoride from drinking water as well as industrial effluent [7–11]. Adsorption process involves the passage of the water through a contact bed where fluoride is removed by ion exchange or surface chemical reaction [12]. Adsorption on activated alumina, alum, charcoal, ash [13–18], ion exchange [19–21] and the membrane processes such as reverse osmosis, nanofiltration, electrodialysis and donnan dialysis [22–25] are studied. The most commonly adopted method in India, Nalgonda technique of community defluoridation is based on precipitation process. The process involves addition of aluminium sulphate

* Corresponding author. Tel.: +91 6612462652; fax: +91 6612462999.
E-mail address: rkpatel@nitrkl.ac.in (R.K. Patel).

with lime and sometimes bleaching powder, lime is added 5% by weight [26]. The process is not very efficient. The major limitations of Nalgonda technique are daily addition of chemicals, large amount of sludge production, least effective with water having high total dissolved solid and high hardness. Moreover, it converts a large portion of soluble ionic fluoride into soluble aluminum complex and practically removes only a small portion of it (18–33%). Therefore, this technique is erroneous [26]. Residual aluminum ranging from 2.01 to 6.86 mg/L was also reported in Nalgonda technique [27], which is dangerous to human health as aluminum is a neurotoxin, concentration as low as 0.08 mg/L in drinking water has been reported to cause Alzheimer's disease [28–30] and is a strong carcinogenic agent [31–34].

Among these technologies fluoride adsorption by quick lime appeared to be an interesting process. The use of quick lime as adsorbent to remove fluoride has not been clarified. It is already been used to remove other pollutants from water, especially arsenic [35]. Most of the available materials for defluoridation are expensive and technically non-feasible. Hence, the need to find locally available defluoridation media for safe and easy use at both household and community levels is desirable. The objective of the present research was to carry out kinetic study, study of thermodynamic parameters to know the feasibility and adsorption isotherms to understand the adsorption process in a better way. The effect of various parameters such as, temperature, adsorbent dose, initial fluoride concentration and time was also studied.

2. Experimental

2.1. Collection and processing of adsorbent materials

Quick lime samples for the present research were collected from dolomite mines area, Birmitrapur, Orissa. These samples were ground to powder by mortar pastel. The powder sample was sieved to <150 μm and then it was stored in air-tight bottles for further studies.

2.2. Thermal activation of adsorbent materials

The preliminary adsorption studies of various adsorbent showed that thermal treatment of adsorbent significantly enhances the adsorbing capacity by increasing the porosity and surface area. And hence the quick lime samples were thermally treated at a temperature of 450 $^{\circ}\text{C}$ for 4 h before adsorption studies were carried out. An accurately weighed quantity of quick lime was calcined in a preheated muffle furnace. The weight of quick lime sample after calcination was taken and was used to calculate loss of water and other volatiles (if any).

2.3. Chemical analysis of quick lime

Chemical analysis for the determination of percentage of calcium present in the sample of quick lime was done by flame photometer. Accurately weighed quantity of quick lime was dissolved in dilute hydrochloric acid. After proper dilution, cal-

cium ion (Ca^{2+}) present in the solution was measured by ELICO CL361 flame photometer. And then the percentage of calcium ion was calculated.

2.4. Chemicals used

Stock solution of fluoride was prepared by dissolving 2.21 g of sodium fluoride in 1 L distilled water. The measuring cylinder, volumetric flask and conical flask used were of PVC. The sodium fluoride used was of analytical grade (Merck, Germany). The required concentration of fluoride solution was prepared by serial dilution of 1000 mg/L fluoride solution.

2.5. Batch experiments

The fluoride adsorption experiments from its aqueous solution on thermally activated quick lime samples were carried out using standard 10 and 50 mg/L fluoride solution in absence of any other competing ions and also in presence of certain competing ions such as phosphate (PO_4^{3-}), sulphate (SO_4^{2-}) and nitrate (NO_3^-). The adsorption experiments were carried out by adding 0.1–1.0 g of adsorbent in 100 mL of synthetic fluoride solution in 250 mL PVC conical flask with stopper. Stoppers were provided to avoid change in concentration due to evaporation. All the experiments were carried out at ambient temperature ($25 \pm 2^{\circ}\text{C}$). Although the reaction of CaO with water is exothermic in nature but the mass of adsorbent was very less as compared to volume of synthetic solution (maximum 1 g/100 mL) and due to high specific heat capacity of water the temperature remained in the range of $25 \pm 2^{\circ}\text{C}$. After continuous stirring in magnetic stirrer at about 400 rpm for a predetermined time interval, the solid was separated by filtration through Whatman 42 filter paper and the remaining fluoride was estimated by Orion ion selective electrode and Orion 720 A+ ion analyzer. Total ionic strength adjusting buffer (TISAB-III) solution was added to both samples and standards in the ratio 1:10. TISAB-III contains 300 g sodium citrate·2H₂O (FW = 294.10), 22 g of 1,2-cyclohexanediamine-*N,N,N',N'*-tetraacetic acid (CDTA) and 60 g of NaCl in a volume of 1000 mL (pH 5–5.5). TISAB-III solution regulates the ionic strength of samples and standard solutions, adjust the pH and also avoid interferences by polyvalent cations such as Al(III), Fe(III) and Si(IV), which are able to complex or precipitates with fluoride and reduce the free fluoride concentration in the solution [36] CDTA forms stable complexes with polyvalent metal cations (e.g. Al(III), Fe(III) and Si(IV)) which are more stable than metal–fluoride complexes (AlF_6^{3-} , FeF_6^{3-} , etc.) in solution. The CDTA preferentially complexes with polyvalent cations present in water and/or aqueous solution (e.g. Si^{4+} , Al^{3+} and Fe^{3+}) [37]. The electrode is selective for the fluoride ion over other common anions by several orders of magnitude.

2.6. Desorption experiments

The reusability of used quick lime sample mainly depends on the ease with which fluoride gets desorbed from loaded quick lime sample. For this 100 mL solution of Sodium fluoride of

50 mg/L concentration was treated with 0.5 g of quick lime and was kept for a contact time of 24 h. The contents of the flask was then filtered and separated. The filtered adsorbent was then retreated with 100 mL of distilled water and was kept for contact time of 24 h. The residual fluoride concentration was measured.

All analytical grade chemicals were used in the investigation. The study was carried out at room temperature ($25 \pm 2^\circ\text{C}$).

3. Results and discussion

3.1. Preliminary adsorption experiment

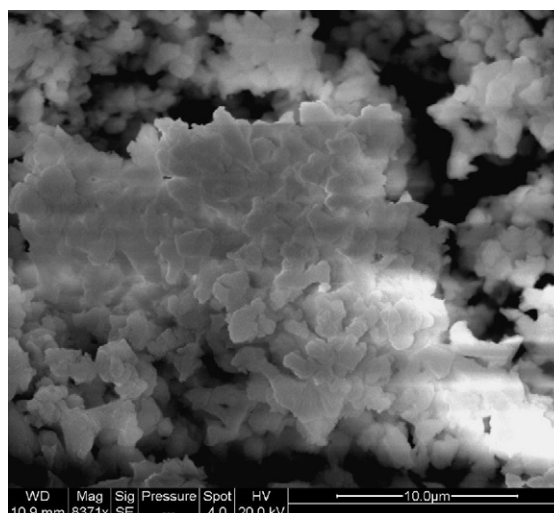
The adsorption data are represented in Table 1. The thermal pretreatment of hydrous metal oxide strongly influences the adsorption of fluoride ion [38,39]. So, it would be interesting to know the role of calcinations on their adsorption capacities. The preliminary adsorption experiments under identical sets of experimental conditions were carried out using untreated and thermally treated (at 450°C for 4 h) quick lime samples, which indicates that the thermally activated samples have much higher more than two times F^- sorption capacity compared to untreated samples. Surface area of untreated and thermally treated quick lime samples were determined by BET method. The surface area of untreated sample was found to be $4.19\text{ m}^2/\text{g}$ while that of thermally treated sample was $11.75\text{ m}^2/\text{g}$. The above data shows that the surface area was increased appreciably by heat treatment. SEM micrographs of quick lime before and after thermal activation and after adsorption is presented in Fig. 1. The SEM micrograph clearly shows the surface modification, which takes place due to calcination. The SEM micrograph of fluoride-loaded quick lime shows small spherical fluoride ion adsorbed over the surface of adsorbent. Calcinations leads to surface modifications, structural transformation and loss of structural water molecules, which ultimately affect the adsorption of fluoride ions. The structural water may be present in the form of water of crystallization, hydration of oxides or hydroxyl groups. The percentage of calcium (Ca^{2+}) present in the sample was found to be 66.61%, percentage of non-volatile matter after calcination was found to be 96.2% and the water content contributes only 3.8%.

3.2. Effect of adsorbent dose

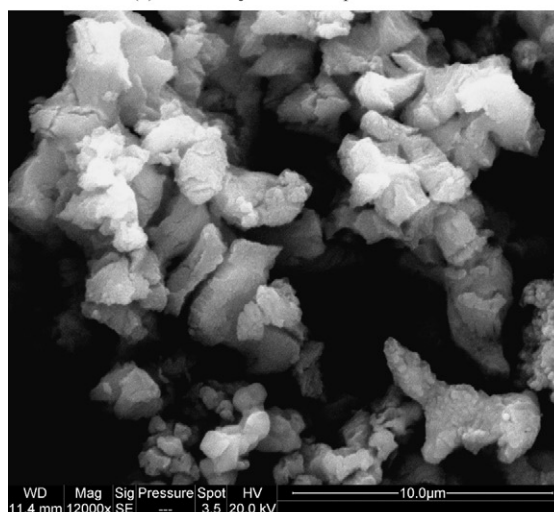
The effect of adsorbent dose on the removal of fluoride was studied at ambient temperature ($25 \pm 2^\circ\text{C}$) and contact time

Table 1
Percentage removal of fluoride using untreated and thermally treated quick lime with initial concentration of 50 mg/L

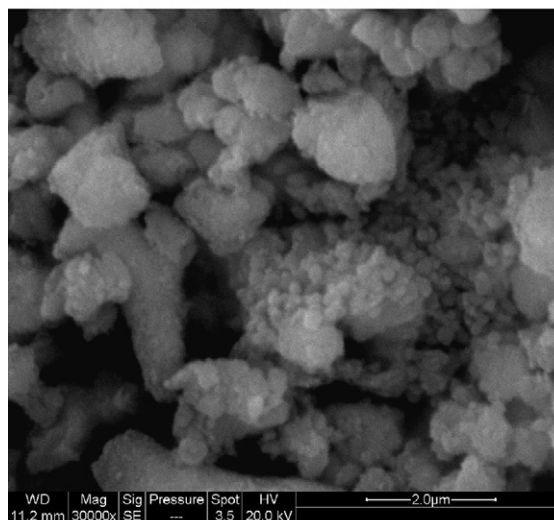
Weight of adsorbent (g/100 mL)	Fluoride adsorbed in percentage	
	Untreated	Thermally treated
0.1	8.5	19.6
0.2	20.1	41.8
0.3	28.1	60.4
0.4	35.2	79.8
0.5	35.7	80.5



(a) Thermally untreated quicklime



(b) Thermally treated quicklime



(c) Fluoride loaded quicklime

Fig. 1. SEM micrographs of quick lime (a) before thermal activation (magnification: 8371 \times), (b) after thermal activation (magnification: 12,000 \times) and (c) fluoride adsorbed quick lime (magnification: 30,000 \times).

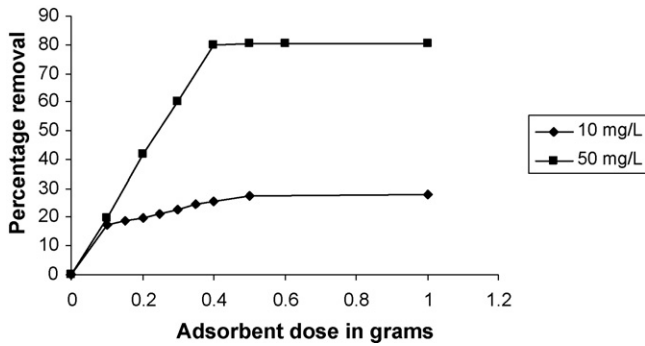


Fig. 2. Adsorbent dose vs. percentage removal of fluoride with initial concentration of 10 and 50 mg/L.

of 75 min for initial fluoride concentration of 10 and 50 mg/L. The results are presented in Fig. 2. It is evident from the figure that the removal of fluoride increased from 17.2% to 27.5% for 0.1–1.0 g/100 mL of thermally activated quick lime (initial fluoride concentration of 10 mg/L). And the removal of fluoride of initial concentration of 50 mg/L, increased from 19.6% to 80.6% for 0.1–1.0 g/100 mL of thermally activated quick lime. However, it is observed that after dosage of 0.5 g/100 mL, there was no significant change in percentage removal of fluoride. It may be due to the overlapping of active sites at higher dosage. There is decrease in the effective surface area resulting in the conglomeration of exchanger particles [40]. So, 0.5 mg/100 mL was considered as optimum dose and was used for further study. Since quick lime is basic in nature and study at varying pH could not be carried out, the pH of solution (concentration 50 mg/L) before and after the addition of quick lime was measured for different adsorbent doses (Fig. 3). The initial pH of the synthetic solution was found to be 6.61, but after treatment the pH was increased and was in the range of 12.55 to 12.77. The pH for optimum dose (i.e. 0.5 g/L) was found to be 12.71. It is concluded from the above data that pH of the synthetic solution after the treatment process was carried out, was always more than 12.

3.3. Effect of contact time

The percentage of fluoride adsorbed for initial fluoride concentration of 50 mg/L keeping other parameter constant is presented in Fig. 4. It is evident that the adsorption process is very

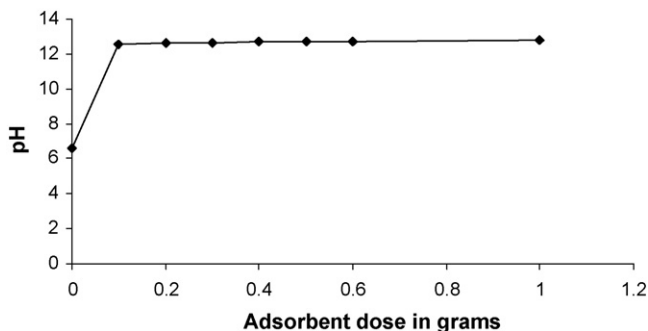


Fig. 3. Adsorbent dose vs. pH of synthetic solution with initial concentration of 50 mg/L.

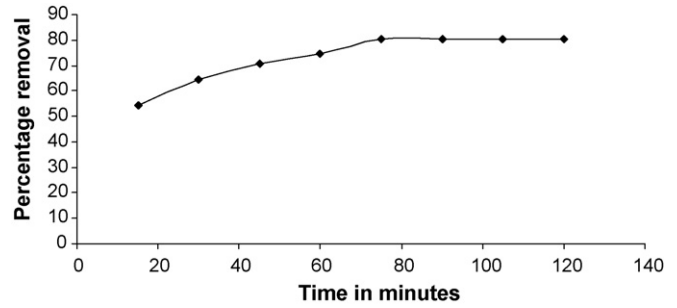


Fig. 4. Time vs. percentage removal of fluoride with initial concentration of 50 mg/L.

fast and most of the fluoride ion is adsorbed in the first 15 min and equilibrium was established, almost after 75 min. The change in the rate of removal might be due to the fact that initially all adsorbent sites were vacant and the solute concentration gradient was high. Later, the fluoride uptake rate by adsorbent was decreased significantly, due to the decrease in number of adsorption sites as well as fluoride concentration. Decreased removal rate, particularly, towards the end of experiments, indicates the possible monolayer formation of fluoride ion on the outer surface.

3.4. Adsorption kinetics

Adsorption of fluoride ion was rapid for the first 15 min and its rate gradually slowed down as the equilibrium approached. The rate constant K_{ad} for sorption of fluoride was studied by Lagergren rate equation [41,46]:

$$\log(q_e - q) = \log q_e - K_{ad} \left(\frac{t}{2.303} \right) \quad (1)$$

where q_e and q (both in mg/g) are the amounts of fluoride adsorbed at equilibrium and at time ' t ', respectively. Straight line plots of $\log(q_e - q)$ versus ' t ' at different times indicates the validity of Lagergren rate equation. The plot of $\log(q_e - q)$ versus ' t ' were straight line with $r^2 > 0.99$, indicates the validity of Lagergren equation of first order kinetics (Fig. 5). The adsorption rate constant (K_{ad}), calculated from the slope of the above plot was found to be 0.0328 min^{-1} for initial fluoride concentration of 50 mg/L under experimental condition.

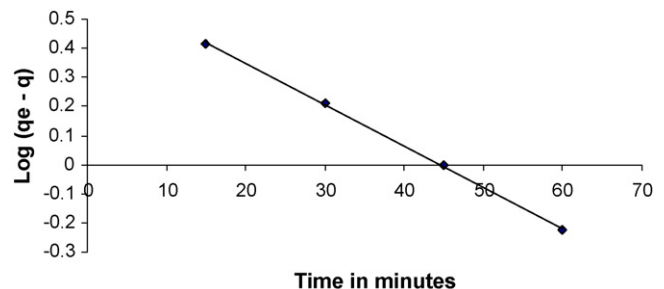


Fig. 5. Adsorption kinetics, time vs. $\log(q_e - q)$ with initial fluoride concentration of 50 mg/L.

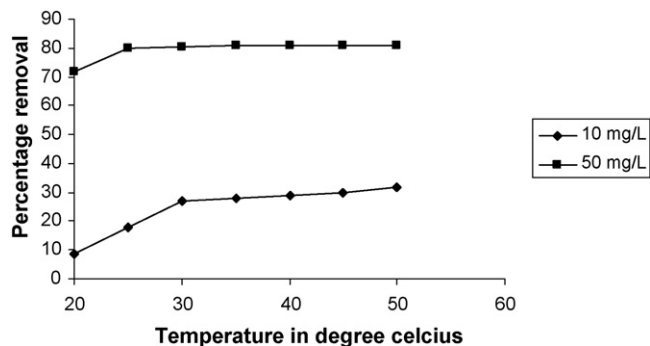


Fig. 6. Temperature vs. percentage removal of fluoride with initial concentration of 10 and 50 mg/L.

3.5. Effect of temperature

The effect of temperature on the adsorption of fluoride with initial concentration 10 and 50 mg/L was studied using optimum adsorbent dose (0.5 g/100 mL). The results are represented as percentage removal of fluoride versus temperature (Fig. 6). The percentage removal of fluoride with initial concentration 10 mg/L, increased from 8.9% to 32.0% for 20–50 °C temperature. And the percentage removal of fluoride of initial concentration 50 mg/L, increased from 71.6% to 80.9% for 20–50 °C temperature. However, it can be clearly seen from the figure that the removal of fluoride sharply increased till 30 °C (for initial fluoride concentration of 10 mg/L) and 25 °C (for initial concentration of 50 mg/L). And it is also noted that the percentage removal increased continuously, first sharply and then slowly, which indicates that the adsorption process was endothermic in nature, though the reaction of quick lime with water is exothermic in nature.

This was further supported by calculating thermodynamic parameters. The change in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) of adsorption were calculated using the following equations [42–44]:

$$\log K_C = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \quad (2)$$

$$\Delta G = \Delta H - T\Delta S \quad (3)$$

where ΔS and ΔH are the changes in entropy and enthalpy of adsorption, respectively. A plot of $\log K_C$ versus $1/T$ for initial fluoride concentration of 10 and 50 mg/L was linear. Values of ΔH and ΔS were evaluated from the slope and intercept of van't Hoff plots and represented in Table 2. The positive value of entropy (ΔS) indicates increase in randomness of the ongoing process and hence a good affinity of fluoride with quick lime. Negative value of ΔG at each temperature indicates the feasibility

Table 2
Thermodynamic parameters using synthetic fluoride solution of 10 and 50 mg/L

Initial fluoride concentration (mg/L)	ΔH (J/mol)	ΔS (J/(K mol))	ΔG (kJ/mol)						R^2
			25 °C	30 °C	35 °C	40 °C	45 °C	50 °C	
10	9151.61	65.93	-10.49	-10.83	-11.16	-11.49	-11.82	-12.15	0.962
50	879.67	58.79	-16.64	-16.93	-17.23	-17.52	-17.82	-18.11	0.987

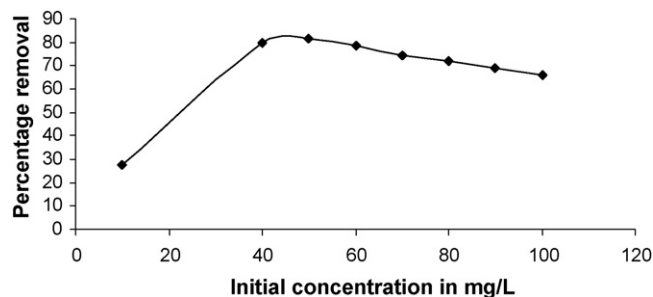


Fig. 7. Initial fluoride concentration vs. percentage removal.

ity and spontaneity of ongoing adsorption. A decrease in values of ΔG with the increase in temperature suggests more adsorption of fluoride at higher temperature. The endothermic nature of the process was once again confirmed by the positive value of enthalpy (ΔH). Positive value of enthalpy (ΔH) suggests that entropy is responsible for making the ΔG value negative. So, the adsorption process is spontaneous, since the entropy contribution is much larger than that of enthalpy.

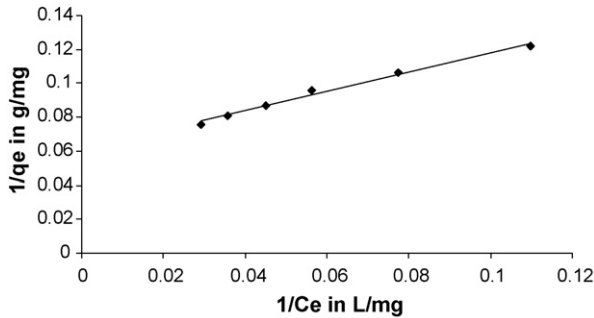
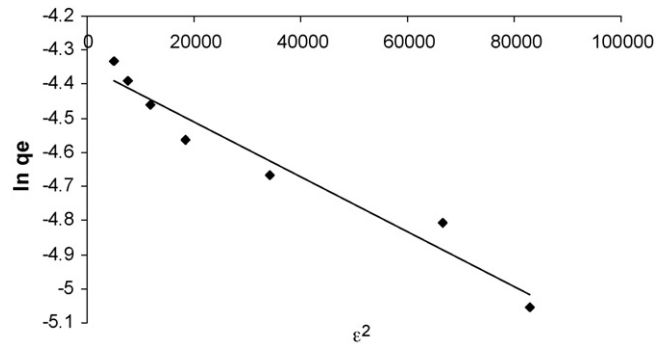
3.6. Effect of initial fluoride concentration

The adsorption of fluoride onto quick lime was studied by varying initial fluoride concentration using optimum adsorbent dose (0.5 g/100 mL) at ambient temperature (25 ± 2 °C) for a contact time of 75 min. The results are represented in graphical form as percentage removal versus initial fluoride concentration (Fig. 7). The initial fluoride concentration was increased from 10 to 100 mg/L and the corresponding removal gradually increased from 27.5% (initial concentration of 10 mg/L) and achieved a maximum value of 81.78% (initial concentration of 50 mg/L) and then it is gradually decreased to 65.8% (initial concentration of 100 mg/L). However, it is clear from the above figure that, maximum removal takes place when the initial concentration is high (i.e. 50 mg/L) and removal is very less at lower concentrations.

3.7. Adsorption isotherm

The adsorption data were fitted to linearly transformed Langmuir isotherm. The linearised Langmuir equation, which is valid for monolayer sorption onto a surface with finite number of identical sites, is given by [41,42]:

$$\frac{1}{q_e} = \frac{1}{q_0 b C_e} + \frac{1}{q_0} \quad (4)$$

Fig. 8. Langmuir adsorption isotherm, $1/C_e$ vs. $1/q_e$.Fig. 9. DR adsorption isotherm, $\ln q_e$ vs. ε^2 .

where q_0 is the maximum amount of the fluoride ion per weight of activated quick lime to form a complete monolayer on the surface (adsorption capacity), C_e denotes equilibrium adsorbate concentration in solution, q_e is the amount adsorbed per unit mass of adsorbent, and b is the binding energy constant. The linear plot of $1/C_e$ versus $1/q_e$ (Fig. 8) indicates the applicability of Langmuir adsorption isotherm. The values of Langmuir parameters, q_0 and b are 16.67 mg/g and 0.1457 L/mg, respectively.

In order to predict the adsorption efficiency of the adsorption process, the dimensionless equilibrium parameter was determined by using the following equation [45]:

$$r = \frac{1}{1 + bC_0} \quad (5)$$

where C_0 is the initial concentration. Values of $r < 1$ represent favorable adsorption. The r -value for initial concentration of 50 mg/L was found to be 0.1207. The value indicated a favorable system.

It is known that the Langmuir and Freundlich adsorption isotherm constant do not give any idea about the adsorption mechanism. In order to understand the adsorption type, equilibrium data were tested with Dubinin–Radushkevich (DR) isotherm [6].

The linearized DR equation can be written as:

$$\ln q_e = \ln q_m - K\varepsilon^2 \quad (6)$$

where ε is the Polanyi potential, and is equal to $RT \ln(1 + 1/C_e)$, q_e the amount of fluoride adsorbed per unit mass of adsorbent, q_m the theoretical adsorption capacity, C_e the equilibrium concentration of fluoride, K the constant related to adsorption energy, R the universal gas constant and T is the temperature in K.

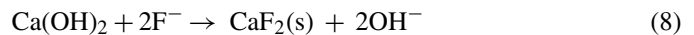
Fig. 9 shows the plot of $\ln q_e$ against ε^2 , which was almost linear with correlation coefficient, $r^2 = 0.954$. DR isotherm constants K and q_m were calculated from the slope and intercept of the plot, respectively. The value of K was found to be $2.012 \times 10^{-3} \text{ mol}^2 \text{ kJ}^{-2}$ and that of q_m was 0.012941 g/g.

The mean free energy of adsorption (E) was calculated from the constant K using the relation [45]:

$$E = (-2K)^{-1/2} \quad (7)$$

It is defined as the free energy change when 1 mol of ion is transferred to the surface of the solid from infinity in solution.

The value of E was found to be $15.76 \text{ kJ mol}^{-1}$. The value of E is very useful in estimating the type of adsorption and if the value is less than 8 kJ mol^{-1} , then the adsorption is physical in nature and if it is in between 8 and 16 kJ mol^{-1} , then the adsorption is due to exchange of ions [45]. The value found in the present study was in between 8 and 16 kJ mol^{-1} so the adsorption can be best explained as exchange of ions. When quick lime is added to water, it is converted into calcium hydroxide. A part of which goes into the solution and the remaining is left as solid. The portion which goes into solution reacts with F^- to form CaF_2 , which is insoluble and is left as precipitate. The major portion of calcium hydroxide does not go into solution. So there is adsorption of fluoride by surface chemical reaction, in which hydroxide ions of calcium hydroxide are replaced by fluoride ions with the formation of CaF_2 . Both of the above process can be represented by the following equation:



This was further confirmed by taxing XRD of quick lime, before and after the adsorption process was carried out (Fig. 10). The thermally activated quick lime, before the adsorption was carried out, mainly contained the phases of calcium oxide and low intensity peaks for calcium hydroxide. But the adsorbent retrieved after adsorption, contained phases of calcium hydroxide and calcium fluoride. The XRD of quick lime before thermal activation was also taken, it also contained phases of calcium oxide and calcium hydroxide. This shows that, if quick lime sample is kept exposed for some time, then gradually it gets converted to calcium hydroxide. For this reason, thermal activation was done just before the experiment was carried out.

3.8. Effect of competitive ions

Drinking water and waste water contains many anions. Therefore, it was thought worthwhile to study the effect of competitive ions like sulphate, nitrate and phosphate on the adsorption of fluoride. Varying concentration of these solutions was prepared from their potassium salts. The initial concentration of fluoride was fixed at 50 mg/L while the initial concentration of other anions varied from 10 to 80 mg/L. The results of these studies are given in Fig. 11. It is clear from the figure that presence of these anions reduced the adsorption of fluoride apprecia-

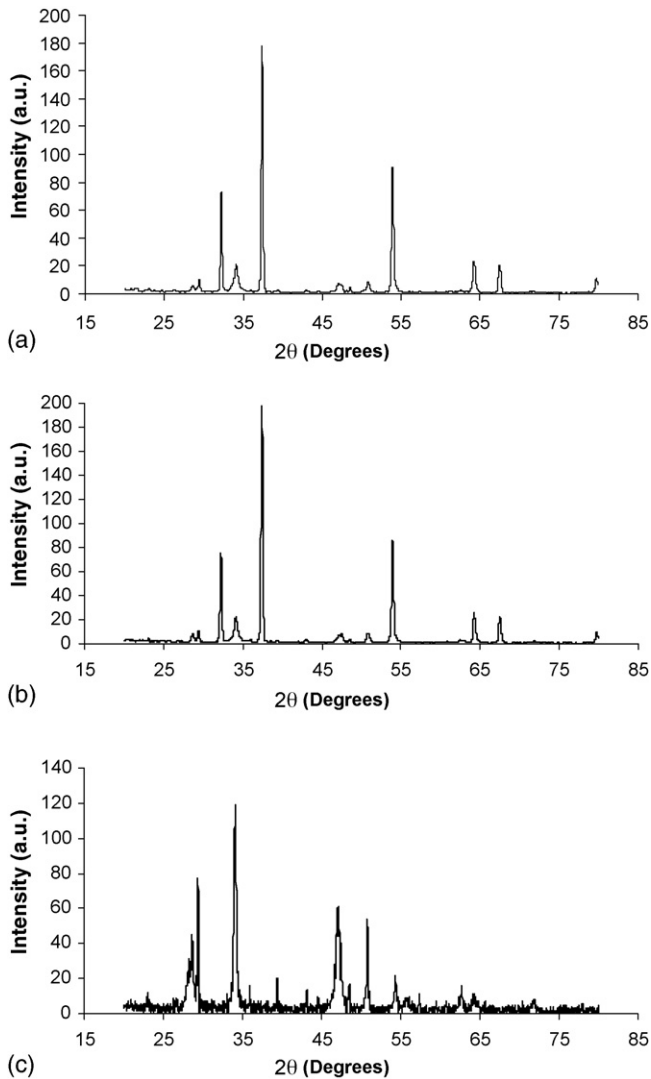


Fig. 10. XRD patterns of quick lime: (a) before thermal activation, (b) after thermal activation and (c) fluoride adsorbed quick lime.

bly with increase in initial concentration of different anions. The anions reduced the fluoride adsorption in the order, phosphate > sulphate > nitrate. These results were in well agreement with those reported in literatures [6,46].

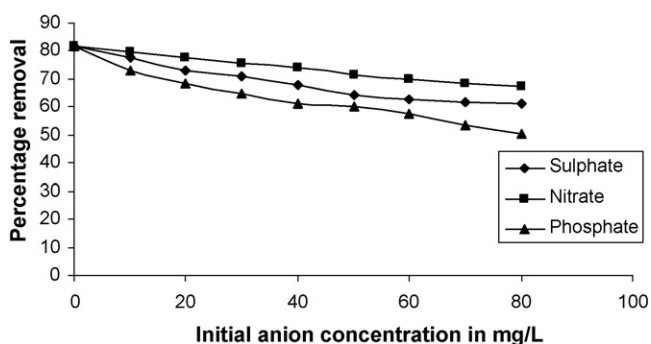


Fig. 11. Percentage removal vs. initial anion concentration of solution with initial fluoride concentration of 50 mg/L.

3.9. Desorption study

In order to know the nature of adsorption, i.e. physical, chemical or both, the desorption study was carried out, the regeneration study at varying pH could not be done since the adsorbent is a base. The desorption of the adsorbed fluoride on quick lime resulted about 6%. Thereby indicating the process of adsorption predominantly chemical in nature.

Amount adsorbed = 40.31 mg/L,

amount desorbed = 2.34 mg/L,

percentage desorption = 5.805%

4. Conclusion

From the above studies, it is indicated that the adsorption process is chemisorption along with precipitation. Removal efficiency was found to be maximum when the initial fluoride concentration was high, hence this technique of removal may be suitably employed to treat industrial effluent where the concentration of fluoride is high. But the removal of fluoride using quick lime cannot be used for domestic purpose, since it cannot bring fluoride concentration within permissible limit, and also increases the pH of the treated water. However, these methods can be optimized further by adding to other binding materials and can be formed into column, the study of which is in progress.

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