

Equilibrium, kinetic and thermodynamic studies of adsorption of fluoride onto plaster of Paris

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Received 30 August 2005; received in revised form 24 June 2006; accepted 26 June 2006

Available online 1 July 2006

Abstract

Batch sorption system using plaster of Paris as an adsorbent was investigated to remove fluoride ions from aqueous solutions. The system variables studied include initial concentration of the sorbate, agitation time, adsorbent dose, pH, co-ions and temperature. The experimental data fitted well to the Freundlich and Langmuir isotherms. Thermodynamic parameters such as ΔH° , ΔS° and ΔG° were calculated indicating that the adsorption was a spontaneous and exothermic. Kinetic studies reveal that the adsorption is first order. A mechanism involving three stages (external surface adsorption, intraparticle diffusion and final equilibrium) has been proposed for the adsorption of F^- onto plaster of Paris. XRD patterns of the adsorbent were recorded to get a better insight into the mechanism of adsorption process.

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Keywords: Adsorption; Defluoridation; Isotherms; Plaster of Paris

1. Introduction

Endemic skeletal fluorosis continues to be a public health problem in several parts of the world where drinking water contains naturally occurring soluble fluoride much above the permissible limit of 1.5 mg L^{-1} [1]. Current methods used to remove fluoride from water can be divided into two categories: precipitation and adsorption. Precipitation of fluoride with calcium and aluminium salts has been used to remove fluoride from industrial wastewater. Typically, lime is used as a calcium source and the Ca(II) ions released interact with fluoride and form CaF_2 precipitate. The aluminium salts interact with fluoride in water and form AlF_n^{3-n} and $\text{Al(OH)}_{3-m}\text{F}_m$, etc. [2]. Adsorption is another technique, in which fluoride is adsorbed onto a membrane, or a fixed bed packed with resin or other mineral particles.

Many techniques have been reported, such as reverse osmosis, electro-dialysis, Donnan dialysis, ion exchange, limestone reactor and activated alumina column [3]. The efficiency of this technique mainly depends on adsorbents. Recent attention of researchers has been devoted to the study of low cost, but

effective materials [4]. The objective of the present endeavor, therefore, is to study the adsorption behavior of fluoride onto plaster of Paris; chemically it is calcium sulfate hemi-hydrate and a non-toxic colorless powder with high porosity.

1.1. Adsorption isotherms

The adsorption isotherms generally used for the design of adsorption system. The Langmuir [5] and Freundlich [6] equations are commonly used for describing the adsorption isotherm. The linear equation of Langmuir and Freundlich are represented as follows (Eqs. (1) and (2), respectively):

$$\frac{C_e}{Q_e} = \frac{C_e}{Q^0} + \frac{1}{Q^0 b} \quad (1)$$

$$\log Q_e = \frac{1}{n \log C_e} + \log K \quad (2)$$

where Q_e and C_e has the usual meanings and Q^0 and b are the Langmuir constants, indicating the adsorption capacity and energy of adsorption, respectively. K and n are the empirical constants of the Freundlich isotherm measuring the adsorption capacity and intensity of adsorption, respectively.

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The essential characteristics of the Langmuir equation can be described by a dimensionless equilibrium parameter, R_L , which is defined by Hall et al. [7], as:

$$R_L = \frac{1}{1 + bC_0} \quad (3)$$

where b is the Langmuir constant (L mg^{-1}) and C_0 is the initial fluoride ion concentration (mg L^{-1}). The value of R_L indicates the shape of the isotherms to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

1.2. Kinetic modeling

Kinetics of sorption describes the solute uptake rate which in turn governs the residence time of sorption reaction. It must be remembered that the two important physico-chemical aspects for parameter evaluation of sorption process as unit operation are the kinetics and the equilibria. Hence in the present study, the kinetics of fluoride removal has been carried out to understand the behavior of the adsorbent employed.

The sorption of fluoride from a liquid phase to solid phase may be expressed as (Eq. (4)):



where k_1 is the forward rate constant and k_2 is the backward rate constant. A represents fluoride remaining in the solution and B represents fluoride retained on the surface of the adsorbent. Since the reaction in both directions is of first order, the rate constant of adsorption, k_{ad} , was determined using the following rate expression given by Natarajan and Khalaf [8], Eq. (5):

$$\log \left(\frac{C_0}{C_t} \right) = \left(\frac{k_{ad}}{2.303} \right) t \quad (5)$$

where C_0 and C_t are the concentration in mg L^{-1} of fluoride initially and at time t , respectively.

The intraparticle diffusion equation [9] can be described as:

$$Q_e = k_p t^{0.5} + C \quad (6)$$

where Q_e is the amount of fluoride adsorbed per unit mass of the adsorbent (mg g^{-1}) at time t and k_p is the intraparticle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{-0.5}$).

1.3. Thermodynamic parameters

The standard free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were calculated from the variation of the thermodynamic equilibrium constant K_0 . K_0 for the adsorption process was determined by the reported method [10]. The thermodynamic parameters were calculated using the following equations:

$$\ln K_0 = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (7)$$

$$\Delta G^\circ = -RT \ln K_0 \quad (8)$$

ΔH° and ΔS° were determined from the slope and intercept of the plot of $\ln K_0$ versus $1/T$.

2. Experimental

2.1. Materials

All the reagents and the adsorbent, plaster of Paris, used were of commercially available high purity Analar grade (SRL, India/sd-fine, India). Stock solutions of fluoride were prepared by dissolving sodium fluoride in doubly distilled water.

2.2. Methodology

The concentration of fluoride was measured using a fluoride ion-selective electrode (Orion USA, Model 94-09). pH measurements were made with Systronic digital pH meter. The zero point charge of the adsorbent (pH_{ZPC}) was calculated as described in the literature [11]. The particle size of the adsorbent was determined using the Carl Zeiss Light microscope (Axiostar Plus) as reported earlier [12]. The XRD patterns of the adsorbent, before and after treatment with fluoride ions, were recorded at the Regional Research Laboratory, Thiruvananthapuram, South India.

2.3. Batch adsorption experiments

Adsorption experiments were performed by agitating 1 g of adsorbent with 50 ml of fluoride solution of desired concentrations at $30 \pm 1^\circ \text{C}$ in different stoppered bottles in a shaking thermostat machine (Tempo, India). The shaking speed was 120 strokes/min, throughout the study. At the end of predetermined time intervals, the sorbate was filtered and the concentration of fluoride was determined. All experiments were carried out twice. Adsorbed fluoride concentrations were the means of the duplicate experimental results. Experimental variables considered were: (i) initial concentration of fluoride ions, 2–10 mg L^{-1} ; (ii) contact time between adsorbent and the fluoride solution, 5–45 min; (iii) pH 3–11; (iv) dosage of the adsorbent, 0.1–1.5 g/50 ml; (v) temperature, 30–50 $^\circ \text{C}$ and (vi) co-ions, Cl^- , SO_4^{2-} , NO_3^- and HCO_3^- .

2.4. X-ray diffraction (XRD) studies

Adsorption reaction may lead to changes in molecular and crystalline structure of the adsorbent and hence an understanding of the molecular and crystalline structures of the adsorbent and the resulting changes thereof would provide valuable information regarding adsorption reaction. Hence, XRD patterns of the adsorbent before and after treatment with fluoride ions have been studied.

2.5. Data analysis

The experimental data were analyzed using Microcal Origin (version 6) computer software. The goodness of fit was discussed

using coefficient of determination, r^2 and standard deviation, S.D.

2.6. Error analysis

In the single-component isotherm studies, the optimization procedure requires an error function to be defined in order to be able to evaluate the fit of the isotherm to the experimental equilibrium data. In this study, linear coefficients of determination and a non-linear χ^2 test, as described in the literature [13], were used.

The χ^2 test statistic is basically the sum of the squares of the differences between the experimental data and data obtained by calculating from models, with each squared difference divided by the corresponding data obtained by calculating from models. The equivalent mathematical statement is:

$$\chi^2 = \sum \frac{(Q_e - Q_{e,m})^2}{Q_{e,m}} \quad (9)$$

where $Q_{e,m}$ is the equilibrium capacity obtained by calculating from the model (mg g^{-1}) and Q_e is the experimental data of the equilibrium capacity (mg g^{-1}). If data from the model are similar to the experimental data, χ^2 will be a small number; if they are different, χ^2 will be a large number. Therefore, it is necessary to also analyze the data set using the χ^2 test to confirm the best-fit isotherm for the sorption system.

3. Results and discussion

3.1. Sorbent characterization

The particle size of the adsorbent employed in the present study is 0.43 mm. The zero point charge (pH_{ZPC}) of the adsorbent was found to be 6.72.

3.2. Effect of agitation time and initial concentration

Fig. 1 shows the effect of agitation time and initial concentration on the adsorption of fluoride ions on the adsorbent. It is clear from the figure that the uptake of fluoride ions increases slowly with the lapse of time and reaches to saturation in 20 min, which is fixed as the optimum contact time for other experiments. The equilibrium time was independent of initial fluoride ions concentration. The results in Table 1 revealed that, the amount adsorbed increases while the percentage removal decreases with the increase in initial concentration of fluoride

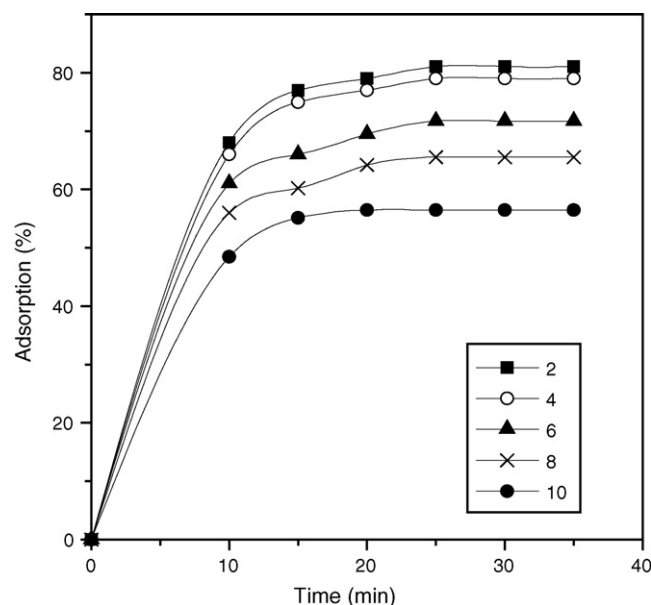


Fig. 1. Effect of agitation time and initial concentration (mg L^{-1}) for the adsorption of fluoride onto plaster of Paris.

ions. This indicates that there exists a reduction in immediate solute adsorption owing to the lack of available active sites on the adsorbent surface, compared with the relatively large number of active sites required for the high initial concentration of fluoride [10].

The percentage uptake is highly dependent on initial concentration of fluoride ions in the solution and it decrease, at a fixed concentration of fluoride, with increase in temperature. This may be due to the fact that with increase in temperature the rate of adsorption may decrease, i.e., the adsorption process is exothermic in nature. Further, the fluoride ions uptake versus time curves are single, smooth and continuous leading to saturation, suggesting the possible monolayer coverage of fluoride ions on the surface of the adsorbent [14].

3.3. Effect of adsorbent dosage

Fig. 2 shows the amount of fluoride removed as a function of adsorbent dosages at 4 mg L^{-1} of initial fluoride concentration and at 30°C . Adsorbent dosages was varied from 100 mg to 1.5 g/50 ml and equilibrated for 45 min. From the result it is evident that optimum adsorbent dosage of 1 g/50 ml is required for maximum removal of fluoride. It is interesting to note that, in

Table 1
Equilibrium parameters for the adsorption of fluoride onto plaster of Paris

| $[\text{F}^-]_0$ | C_e (mg L^{-1}) | | | Q_e (mg g^{-1}) | | | Fluoride removed (%) | | |
|------------------|------------------------------|--------------------|--------------------|------------------------------|--------------------|--------------------|----------------------|--------------------|--------------------|
| | 30°C | 40°C | 50°C | 30°C | 40°C | 50°C | 30°C | 40°C | 50°C |
| 2 | 0.380 | 0.435 | 0.531 | 0.081 | 0.078 | 0.073 | 81 | 78 | 73 |
| 4 | 0.838 | 0.915 | 1.28 | 0.158 | 0.154 | 0.136 | 79 | 77 | 68 |
| 6 | 1.70 | 1.83 | 2.56 | 0.215 | 0.209 | 0.172 | 72 | 70 | 57 |
| 8 | 2.76 | 3.20 | 3.67 | 0.262 | 0.240 | 0.217 | 66 | 60 | 54 |
| 10 | 4.35 | 5.28 | 5.47 | 0.283 | 0.256 | 0.227 | 57 | 47 | 45 |

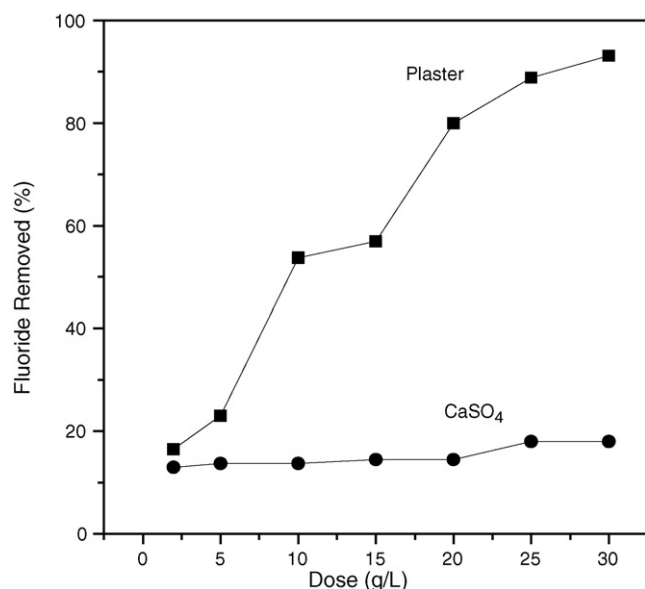


Fig. 2. Effect of dose on adsorption.

the same range of dosage calcium sulfate dihydrate, as adsorbent, exhibits comparatively very low fluoride removal capacity.

3.4. Adsorption isotherms

Langmuir adsorption equation was applied to quantify the adsorption capacity of the chosen adsorbent for the removal of fluoride ions from water. The adsorption isotherms were studied at 30, 40 and 50 °C. The linear plots (Fig. 3) of C_e/Q_e versus C_e at different temperatures indicate the applicability of the Langmuir adsorption isotherm. The value of isotherm constants and other statistical parameters were given in Table 2. The results

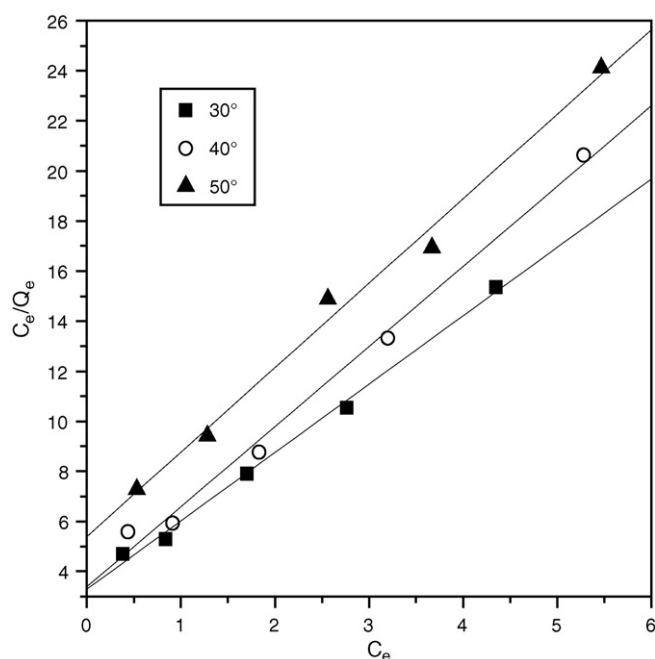


Fig. 3. Linear Langmuir adsorption isotherms at 30, 40 and 50 °C.

Table 2
Langmuir and Freundlich isotherm constants

| Isotherm | Statistical parameter/ constants | Temperature | | |
|------------|----------------------------------|----------------------|-----------------------|----------------------|
| | | 30 °C | 40 °C | 50 °C |
| Freundlich | r^2 | 0.945 | 0.895 | 0.964 |
| | S.D. | 0.06 | 0.08 | 0.04 |
| | χ^2 | 9.8×10^{-3} | 15.8×10^{-3} | 4.5×10^{-3} |
| | K | 0.151 | 0.137 | 0.108 |
| | n | 1.96 | 2.16 | 2.03 |
| Langmuir | r^2 | 0.996 | 0.992 | 0.990 |
| | S.D. | 0.34 | 0.64 | 0.74 |
| | χ^2 | 0.782 | 0.715 | 0.784 |
| | Q^0 | 0.366 | 0.313 | 0.297 |
| | b | 0.830 | 0.721 | 0.624 |

indicate that the adsorption capacity decreased with increasing temperature. The plots in Fig. 3 shows that the Langmuir equation provides an accurate description of the experimental data, which is further confirmed by the extremely high values of the coefficient of determination.

The R_L values computed for the present system are provided in Table 3. The R_L values between 0 and 1 indicate favorable adsorption for all the initial concentrations and temperatures studied. The R_L values indicated that the adsorption was more favorable for higher initial fluoride concentrations than the lower ones. Further, the sorption process become less favorable with increasing temperature [14].

The adsorption data have been fitted to the Freundlich isotherm. The linear plots of $\log Q_e$ versus $\log C_e$ (Fig. 4) at different temperatures indicate the applicability of Freundlich adsorption isotherm. The results (Table 2) indicates that the adsorption capacity (measured by K) of the adsorbent decreases with increase in temperature. Further the value of intensity of adsorption (n) is greater than unity signifies that the forces within the surface layer are attractive [15].

The Langmuir model deals with monolayer coverage and constant adsorption energy while Freundlich equation deals with physicochemical adsorption on heterogeneous surfaces [16]. The applicability of both these isotherms to plaster of Paris, in the present study, implies that both monolayer adsorption and heterogeneous surfaces conditions exist under the experimental conditions used. The adsorption properties of plaster of Paris are thus likely to be complex, involve more than one mechanism [17].

Table 3
Equilibrium parameter, R_L

| Fluoride concentration (mg L ⁻¹) | Temperature | | |
|--|-------------|-------|-------|
| | 30 °C | 40 °C | 50 °C |
| 2 | 0.373 | 0.409 | 0.445 |
| 4 | 0.229 | 0.256 | 0.286 |
| 6 | 0.166 | 0.188 | 0.211 |
| 8 | 0.130 | 0.148 | 0.167 |
| 10 | 0.106 | 0.122 | 0.138 |

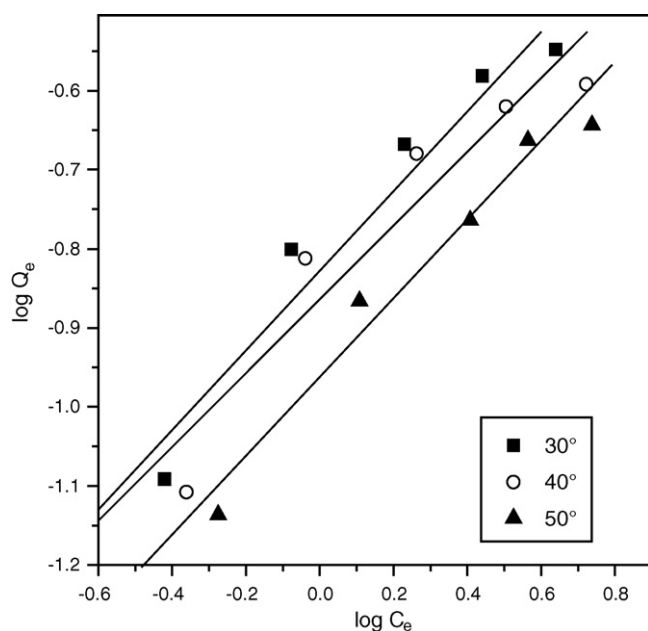


Fig. 4. Linear Freundlich adsorption isotherms.

3.5. Non-linear analysis

The chi-square statistic, χ^2 and coefficient of determination, r^2 were obtained and are shown in Table 2. The Freundlich isotherm exhibited lower χ^2 values than the Langmuir. Therefore, drawing conclusion from the non-linear chi-square analysis, the Freundlich isotherm was best fitting isotherm followed by the Langmuir isotherm [13].

3.6. XRD studies

The XRD patterns of the adsorbent before and after treatment with fluoride ion solution are shown in Fig. 5 and the data are given in Table 4. It is evident from the XRD study that the crystal structure of the adsorbent showed significant changes after the adsorption of fluoride ions. This suggests that the uptake of fluoride ions by the adsorbent is by chemisorption, in the form of precipitation of fluorite (CaF_2) at pH 5.5–7.0, with the alteration in the crystal structure of the adsorbent [18,19]. The possibility of CaF_2 formation by reaction of fluoride with soluble or exchangeable calcium present in

Table 4

X-ray diffraction data for the adsorbent before and after treatment with fluoride ions

| <i>d</i> -spacing (Å) | Relative intensity (%) | Angle, 2θ (°) | Peak height (counts) |
|-----------------------|------------------------|----------------------|----------------------|
| Before adsorption | | | |
| 7.53332 | 37.21 | 11.73746 | 705.00 |
| 5.96343 | 68.23 | 14.84296 | 1292.80 |
| 3.45203 | 58.48 | 25.78682 | 1108.07 |
| 2.99106 | 100.00 | 29.84681 | 1894.89 |
| 2.80008 | 32.98 | 31.93506 | 625.01 |
| 1.84333 | 26.32 | 49.40080 | 498.74 |
| After adsorption | | | |
| 7.58988 | 100.00 | 11.64970 | 7378.76 |
| 4.27548 | 33.64 | 20.75842 | 2481.86 |
| 3.79554 | 14.68 | 23.41828 | 1083.31 |
| 3.06182 | 38.55 | 29.14156 | 2844.29 |
| 2.86925 | 5.73 | 31.14539 | 423.09 |
| 2.68119 | 4.66 | 33.39165 | 343.52 |

soil at near neutral pH has been reported by earlier workers [20].

3.7. Thermodynamic parameters

The standard free energy change, enthalpy and entropy changes along with equilibrium constants were given in Table 5. The exothermic nature of adsorption is indicated by a decrease in K_0 with rise in temperature. The results in Table 5 indicate that ΔG° values increase with increasing initial fluoride concentration. The ΔG° values are negative (except for initial fluoride concentration of 10 mg L^{-1} at 40 and 50°C) which mean that the reaction is spontaneous, while the positive ΔG° values indicate non-spontaneous reactions. The values of enthalpy of a sorption process may be used to distinguish between chemical and physical sorption [21]. For chemical sorption, enthalpy values range from 83 to 830 kJ mol^{-1} , while for physical sorption they range from 8 to 25 kJ mol^{-1} . On the basis of the above distinction, fluoride ion sorption by plaster of Paris could be a physical process, however, higher values of enthalpy change in consonance with XRD data favours chemisorption. Negative values of ΔH° suggest that the process is exothermic, so a decrease of temperature encourages fluoride ion adsorption. As indicated in Table 5, ΔS° values for the adsorption process are negative. The values are expected for ΔS° , because during adsorption the degree of internal freedom of the system are decreased [21].

Table 5

Equilibrium constant and thermodynamic parameters for the adsorption of fluoride onto plaster of Paris

| $[\text{F}^-]_0$ | K_0 | | | $-\Delta G^\circ (\text{kJ mol}^{-1})$ | | | $-\Delta H^\circ (\text{kJ mol}^{-1})$ | $-\Delta S^\circ (\text{J K}^{-1} \text{mol}^{-1})$ |
|------------------|-------|-------|-------|--|--------|--------|--|---|
| | 30 °C | 40 °C | 50 °C | 30 °C | 40 °C | 50 °C | | |
| 2 | 4.263 | 3.598 | 2.766 | 3.653 | 3.332 | 2.732 | 17.55 | 45.73 |
| 4 | 3.773 | 3.372 | 2.125 | 3.345 | 3.163 | 2.024 | 23.19 | 65.03 |
| 6 | 2.529 | 2.279 | 1.344 | 2.337 | 2.144 | 0.794 | 25.53 | 75.94 |
| 8 | 1.899 | 1.500 | 1.180 | 1.616 | 1.055 | 0.444 | 19.35 | 58.50 |
| 10 | 1.299 | 0.894 | 0.828 | 0.659 | −0.292 | −0.507 | 18.44 | 59.08 |

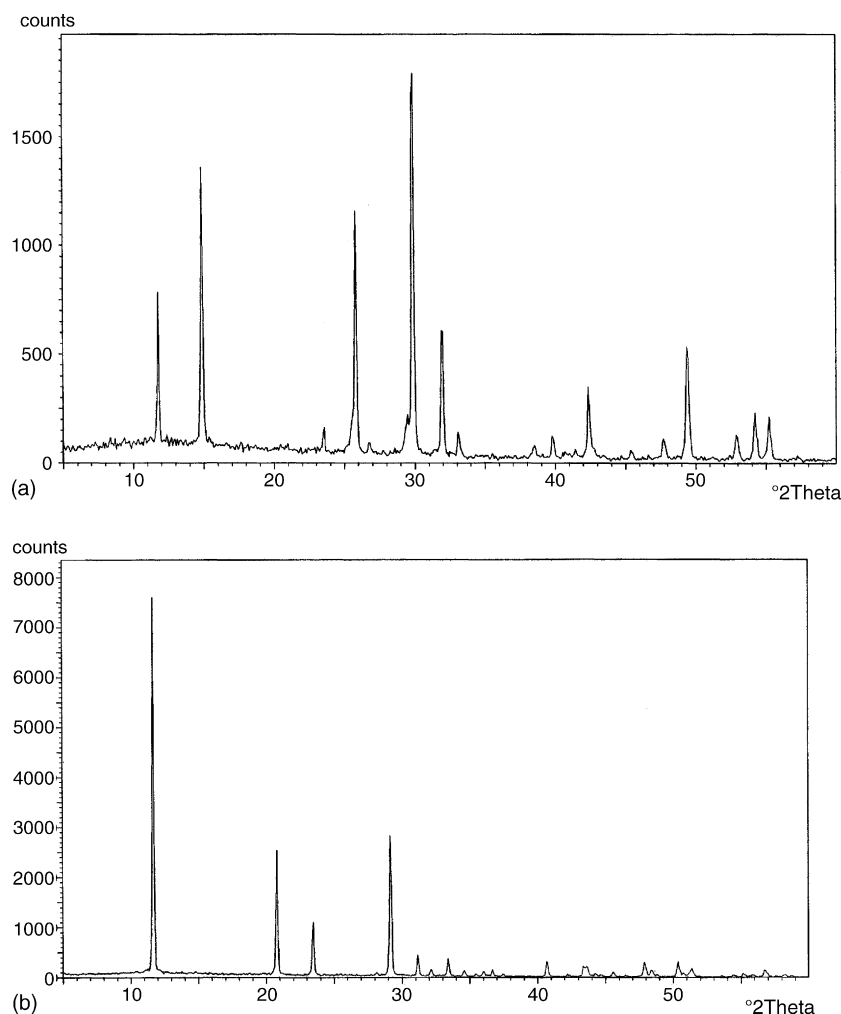


Fig. 5. (a) XRD pattern of the adsorbent before adsorption. (b) XRD pattern of the adsorbent loaded with fluoride ions.

3.8. Effect of pH

The effect of initial pH of the fluoride solution on the amount of fluoride ions adsorbed was studied. The percent removal of fluoride at pH values 3, 5, 7, 9, 11 and 13 are 80.7, 83.5, 79, 83.2, 82.4 and 20%, respectively. The results indicate that the adsorbent exhibits a commendable defluoridation capacity in wide range of pH. The value of zero point charge (pH_{ZPC} 6.72) suggests the presence of some weakly acidic groups on the surface of the adsorbent. Hence, the defluoridation capacity of the adsorbent is appreciable in acidic range. However, at very high pH the defluoridation capacity decreases sharply. This may be due to the competition between hydroxide and fluoride ions in this pH range [22].

3.9. Effect of co-ions

The effect of added co-ions viz. Cl^- , NO_3^- , SO_4^{2-} and HCO_3^- on the percentage of adsorption is depicted in Fig. 6. The results indicate that addition of co-ion decrease the amount of fluoride ions removed to a greater extent. This is due to the

competition between the anions and fluoride ions for the active sites on the adsorbent [22].

3.10. Kinetics of adsorption

Linear plots ($r > 0.99$, figure not shown) of $\log(C_0/C_t)$ versus t suggest the applicability of the Natarajan and Khalaf equation. The rate constants were calculated from the slope and are presented in Table 6. The forward (k_1) and backward (k_2) rate constants were calculated as described in the literature [23] and are also furnished in Table 6. It is evident, from the results, that the forward rate constant is much higher than the backward rate constant suggesting that the rate of adsorption is clearly dominant.

The values of k_{ad} was found to decrease with increase in the initial concentration of fluoride from 2 to 10 mg L^{-1} . An examination of the effect of fluoride ion concentration on the k_{ad} helps to describe the mechanism of removal taking place. In cases of strict surface adsorption, a variation of rate should be proportional to the first power of concentration. However, when pore diffusion limits the adsorption process, the relationships

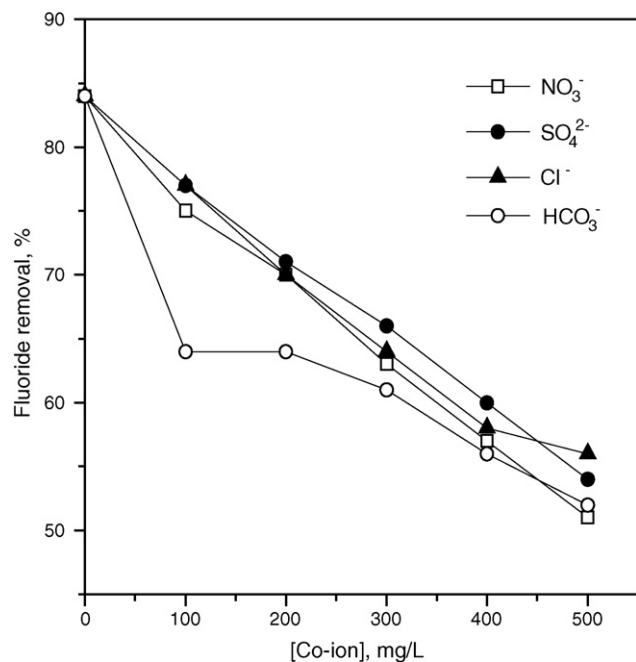


Fig. 6. Effect of added co-ions on the fluoride removal.

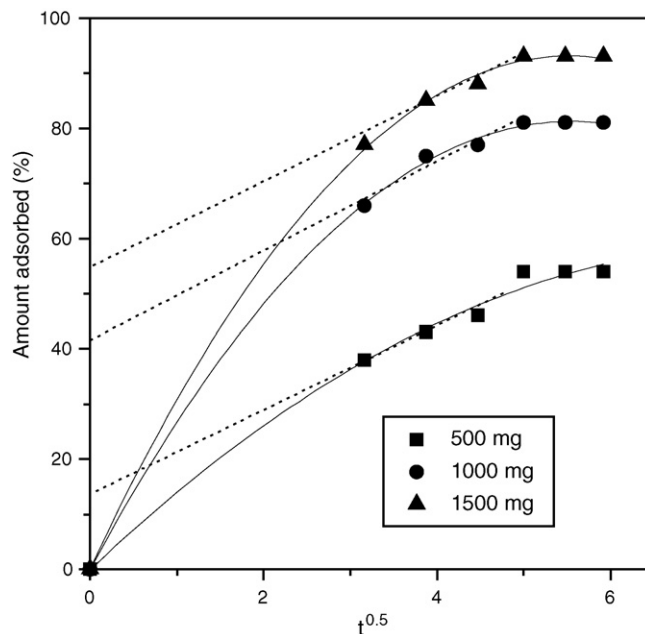


Fig. 7. Intraparticle diffusion plot for the adsorption of fluoride on plaster of Paris at different doses.

between initial solute concentration and the rate of reaction will not be linear. Hence, it seems likely that pore diffusion limits the overall rate of fluoride adsorption [24].

The contact time experimental results can be used to study the rate determining step in the adsorption process, as shown by Weber and Morris [9]. Since, the particles are vigorously agitated during the adsorption period, it is probably reasonable to assume that mass transfer from the bulk liquid to the particle external surface does not limit the rate. One might then postulate that the rate determining step may be either film or intraparticle diffusion. As they act in series, the slower of the two will be the rate-determining step.

In a rapidly stirred batch reactor, the adsorbate species are most probably transported from the bulk of the solution to the solid phase through intraparticle diffusion, which is often the rate-limiting step in many sorption process [25]. Applying the intraparticle diffusion model tests the presence of intraparticle diffusion process in the present adsorption system.

The plot of Q_e versus $t^{0.5}$ is shown in Fig. 7. The initial curved portions represent the boundary layer diffusion [26]. The

value of intraparticle diffusion rate constant k_p , calculated from the slopes of the linear portion of the curves, for 500, 1000 and 1500 mg/50 ml of the adsorbent doses are 6.14, 7.78 and 8.37, respectively. The value of k_p increase with the dose of the adsorbent, as more active binding sites are available for fluoride ions to diffusion into it.

3.11. Time dependence of the fraction of adsorption

The plots of Y_t versus $t^{0.5}$ (Fig. 8) for different doses have three stage shapes. The first, sharp portion of the curves corresponds to the external surface adsorption stage or instantaneous adsorption stage. The second, gradual linear portion corresponds

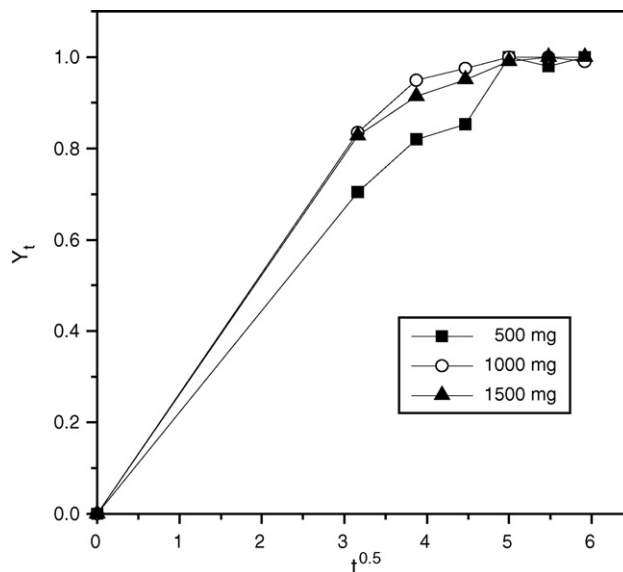
Fig. 8. Plot of Y_t vs. $t^{0.5}$.

Table 6

Rate constants for the adsorption of fluoride (k_{ad} , $\times 10^3 \text{ min}^{-1}$) and rate constants for the forward (k_1 , $\times 10^3 \text{ min}^{-1}$) and reverse (k_2 , $\times 10^3 \text{ min}^{-1}$) processes

| [F ⁻] ₀ | k_{ad} | | | Temperature | | | | | |
|--------------------------------|----------|-------|-------|-------------|-------|-------|-------|-------|-------|
| | 30 °C | 40 °C | 50 °C | 30 °C | | 40 °C | | 50 °C | |
| | | | | k_1 | k_2 | k_1 | k_2 | k_1 | k_2 |
| 2 | 16.69 | 10.02 | 6.56 | 13.52 | 3.17 | 7.48 | 2.18 | 4.82 | 1.74 |
| 4 | 13.64 | 8.35 | 5.79 | 10.78 | 2.86 | 6.44 | 1.91 | 3.94 | 1.85 |
| 6 | 11.03 | 6.71 | 5.54 | 7.90 | 3.13 | 4.66 | 2.05 | 3.18 | 2.36 |
| 8 | 8.08 | 6.23 | 3.18 | 5.29 | 2.79 | 3.74 | 2.49 | 1.72 | 1.46 |
| 10 | 5.33 | 3.03 | 2.22 | 3.01 | 2.32 | 1.43 | 1.59 | 1.01 | 1.21 |

to intraparticle diffusion and the final, linear portion represents the equilibrium stage [26]. In this model, the adsorbent is treated as being surrounded by a boundary layer film of water molecules through which the fluoride ions must diffuse prior to adsorption. The second portion of the curve indicates the intraparticle diffusion, which is predominant in the rate-controlling step where the diffusive transport of fluoride ions occurs through the internal pores of the adsorbent. As the bulk and surface fluoride ion concentrations start to decrease, the third section of Fig. 8 shows a decrease in the rate of diffusion reaching a point of equilibrium [26].

3.12. Test with field samples

The utility of the adsorbent has been tested by treating natural water samples collected from tube well water sources located at Myladumparai (sample 1) and Kadamalaikundu (sample 2) of Theni District, Tamil Nadu, South India. Compositions (all in mg L⁻¹ except pH) of the waters are, respectively, pH: 7.1, 7.4; total alkalinity: 500, 495; total hardness: 800, 500; total dissolved solids: 1960, 1950; NO₃⁻: 15, 28; Cl⁻: 500, 550; F⁻: 2.1, 1.6; SO₄²⁻: 140, 150. The percentage removal of fluoride at 30 °C, by the adsorbent from samples 1 and 2 were found to be 68 and 72, respectively, which is in close agreement with the results mentioned above.

4. Conclusion

In batch adsorption studies, data show that plaster of Paris has considerable potential for the removal of fluoride ions from aqueous solutions. Wide range of pH and low temperature ranges were found as the optimum conditions for maximum fluoride adsorption by the adsorbent. The results gained from this study were extremely well described by the theoretical Freundlich and Langmuir isotherms. Values of equilibrium parameter, R_L , indicated the F⁻/plaster of Paris system was favorable. The thermodynamics of the system pointed out the system was spontaneous and exothermic. The higher enthalpy change for the

adsorption process and XRD studies indicate that the adsorption occurs through chemisorption. On the basis of the kinetic studies a mechanism involving three stages has been proposed for the adsorption of F⁻ onto the plaster of Paris in which the pore diffusion is the rate-limiting step.

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