

Fluoride adsorption studies of montmorillonite clay

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Batch adsorption studies were conducted to determine the effects of contact time and temperature on fluoride removal by montmorillonite clay at neutral pH. The adsorption of fluoride was studied at four different temperatures, *viz.* 30, 40, 50 and 60°C. The kinetics of adsorption as well as adsorption isotherms at different temperatures were studied. Adsorption obeyed both Langmuir and Freundlich isotherm models. The percentage of fluoride removed increased with time and reached an optimum level at 50th min. The material with particle size of 75 microns registered maximum percentage of fluoride adsorption, compared to the other particle sizes. Thermodynamic studies revealed that the adsorption of fluoride by montmorillonite is an endothermic process, showing increase in sorption at higher temperature. The negative values of ΔG° indicate the spontaneity of the sorption process. Adsorption takes place on the surface as well as through intraparticle diffusion pattern of the adsorbent material. SEM studies revealed the morphological characteristics of the untreated sorbents as well as the changes in the treated sorbents. X-ray diffraction studies also confirmed the deposition of fluoride on the surface of the clay material. FTIR studies showed the involvement of hydroxyl group present on the surface in the adsorption interaction.

Keywords: Adsorption, fluoride removal, montmorillonite clay, Langmuir isotherm, Freundlich isotherm

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Water intended for consumption must be free from disease organisms, toxic substances and excessive amounts of minerals and organic matter. Water contains numerous trace elements and several studies indicate that precipitation and adsorption can be used to control the problem of water pollution¹⁻⁴. Excess fluoride in drinking water causes harmful effects such as dental fluorosis and/or skeletal fluorosis⁵. The maximum allowable level of fluoride in drinking water has been set at a concentration of 1 mg/L by the World Health Organisation (WHO)⁶. Prevalence of fluorosis in an endemic area is attributed to levels of excess fluoride in drinking water⁷. One of the most important preventive measures of fluorosis is provision of drinking water containing fluoride within tolerance limits⁸. Methods tried for defluoridation of water belong to three basic types *viz.*, adsorption, ion-exchange and precipitation methods. The different materials used for defluoridation include activated carbon, bone charcoal, tricalcium phosphate, synthetic ion exchangers, activated alumina, alum and lime. A

comprehensive review on the subject is presented elsewhere^{9,10}.

Montmorillonite clay has been found to remove fluoride by adsorbing over its surface. This material has been widely used in medicine, paint, cosmetics, detergent and purification of water¹¹. Montmorillonites are dioctahedral smectite clay mineral with layer charges predominantly in octahedral sites. Its composition is $(\text{Na}, \text{Ca})_{0.33} (\text{Al}, \text{Mg})_2 \text{Si}_4\text{O}_{10} (\text{OH})_2 \cdot n\text{H}_2\text{O}$. The layer charge is $0.5 < x < 1.2$. The structure of montmorillonite is given in Fig. 1. The unit layer is composed of three tetrahedral-octahedral-tetrahedral (T-O-T) sheets¹². The crystal structure of this clay mineral was first proposed by Pauling and this was ascertained by the X-ray diffraction technique¹³. In the present studies, the effects of contact time and temperature on the defluoridation property of montmorillonite have been experimentally verified in neutral pH. The mechanism of adsorption is explained using the Langmuir and Freundlich isotherms. Further the nature and morphology of the adsorbent are discussed on the basis of results of SEM, X-ray diffraction and FTIR studies.

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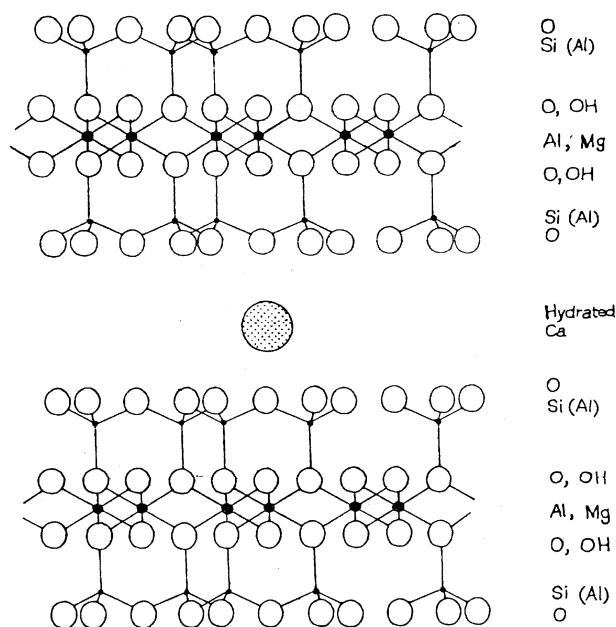


Fig. 1—Crystal structure of montmorillonite

Experimental Procedure

Materials and methods

The montmorillonite clay was obtained from the Department of Geology, V.O.C. College, Tuticorin, India. The sample was sieved to the particle size of 75 microns and was used without any pretreatment. The physico-chemical properties of this material are given in Table 1. Stock solution of sodium fluoride containing 3 mg/L was prepared and this was used in the defluoridation experiments. The batch adsorption experiments at room temperature and at higher temperatures were performed by mixing 7g of montmorillonite with 100 mL of sodium fluoride solution containing 3 mg/L of fluoride in a temperature controlled mechanical shaker (Remi model, RSB 12-LXCM-1927). The mixing was regulated at 125 rpm and the duration of each experiment was 50 min. The time required for attaining the equilibrium was determined by studying the adsorption of fluoride as a function of time. The residual fluoride concentration in each sample was determined using the ion selective electrode, fluoride electrode, 'Orion ion analyser' model 94-09 USA¹⁴. The experiments were carried out in neutral medium. The pH of the solution was measured with Elico pH analyzer (model LI 126). The kinetic and thermodynamic parameters of the adsorption experiments were determined by conducting the experiments at 30, 40, 50 and 60°C. The rate

Table 1—Physico-chemical characterization of montmorillonite

Constituents	% by Weight
SiO ₂	58.25
Al ₂ O ₃	27.50
MgO	3.10
CaO	3.78
Na ₂ O	1.44
Colour	White
Crystal system	monoclinic (010)
Cell dimension	A b c β
	5.17 8.94 9.95 99°5'
Hardness	1-2
Specific gravity	2.0-2.7
Surface area (m ² /g)	750
Density (g/m ³)	2-3

Source: Department of Geology, V.O.C College, Tuticorin, Tamil Nadu

constants were calculated using conventional rate equations¹⁵. X-ray diffraction patterns of the untreated and fluoride treated clay samples were obtained to study the crystal nature and adsorption behaviour. XRD studies were carried out using Philips PW 1051 diffractometer with K-Alpha 1 radiation. Similarly, the raw and treated clay samples were also scanned using SEM, in order to examine the possible morphological changes in the surface. FTIR measurements were taken using Perkin-Elmer/1600 series at ambient conditions using KBr as diluent to determine the specific functional groups on the clay adsorbents and their mode of adsorption.

Results and Discussion

Effect of contact time

Figure 2 shows the percentage of defluoridation of montmorillonite with time. The adsorption rate of fluoride for the initial 100 min was studied. The percentage of fluoride removed increased linearly in the early stages up to 50th min and thereafter remained static. This means that the montmorillonite requires a minimum contact time of 50 min for the removal of the maximum amount of fluoride. The optimum percentage of fluoride removed at the 50th min is found to be 82 as seen in Fig. 2. High rate of adsorption is due to the availability of more specific surface area on the adsorbent as adsorption process is dependent on the surface morphology. The adsorption rate of fluoride by the montmorillonite is interpreted in terms of the adherence of fluoride on the active

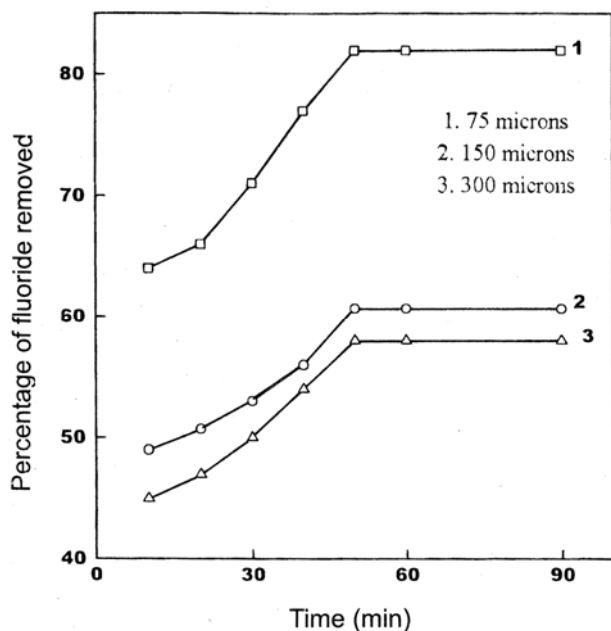


Fig. 2—Percentage of fluoride removed as a function of time

sites of the adsorbent as well as its intraparticle diffusion within the pores of the adsorbent. Fig. 3 explains the extent of adsorption of fluoride as a function of square-root of time at room temperature. As seen from Fig. 3, the plot is linear for a wide range of contact time but does not pass through the origin, which indicates that the mechanism of fluoride removal on the clay is both by surface adsorption and through intraparticle diffusion. A similar type of intraparticle diffusion study of polio virus has been reported onto silicate minerals¹⁶.

Effect of particle size

The defluoridation experiments were conducted using montmorillonite with three different particle sizes *viz.*, 75, 150 and 300 microns. As the adsorption process is a surface phenomenon, the defluoridation efficiency of the sample with 75 microns registered high defluoridation efficiency due to larger surface area. The percentage of fluoride removed by the samples with different particle sizes are given in Table 2. As the material with particle size of 75 microns registered higher percentage of fluoride removal, this was chosen for further experiments. Higher percentage of adsorption by montmorillonite with smaller particle size is due to the availability of more specific surface area on the adsorbent surface. All the forthcoming discussions are based on the experimental results using this sample.

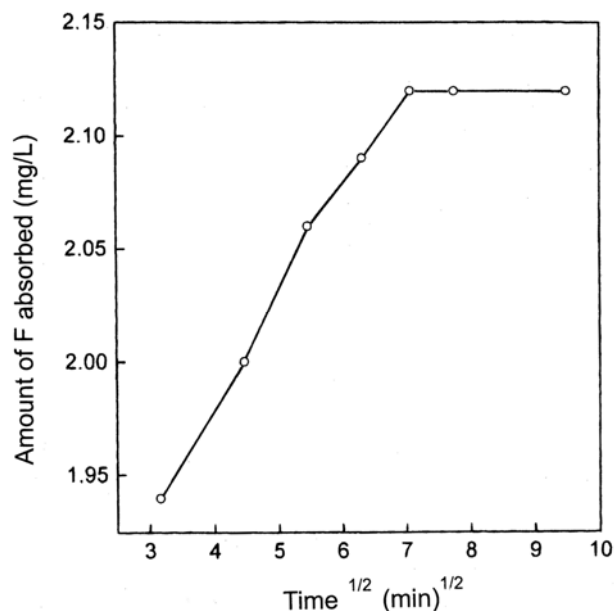


Fig. 3—Plot for intraparticle diffusion at room temperature

Table 2—Effect of particle size on the percentage of fluoride removal of montmorillonite

S.No.	Particle size (microns)	% of fluoride removed
1	75	82.0
2	150	60.6
3	300	58.3

Effect of dose of adsorbent

Actual dosage of the montmorillonite, which has the optimum fluoride adsorption after the required contact time of 50 min, was experimentally verified. The concentration of fluoride was fixed as 3 mg/L while the doses of the adsorbent were varied from 3 to 10 g. The percentage of fluoride removed by different doses of montmorillonite is given in Fig. 4. The fluoride adsorption increased exponentially with the increasing amount of the adsorbent as higher doses of the adsorbent provided more active sites. The dose of adsorbent having the optimum fluoride removal efficiency was found to be 7 g. Further addition of higher doses of the adsorbents did not result in considerable increase in defluoridation. This is due to the overlapping of the active sites at higher concentrations of the adsorbents, thus reducing the net surface area^{17,18}. Hence, 7 g of the montmorillonite was taken as the dose possessing the optimum fluoride removal efficiency and this was fixed as the dose of the material for further experiments.

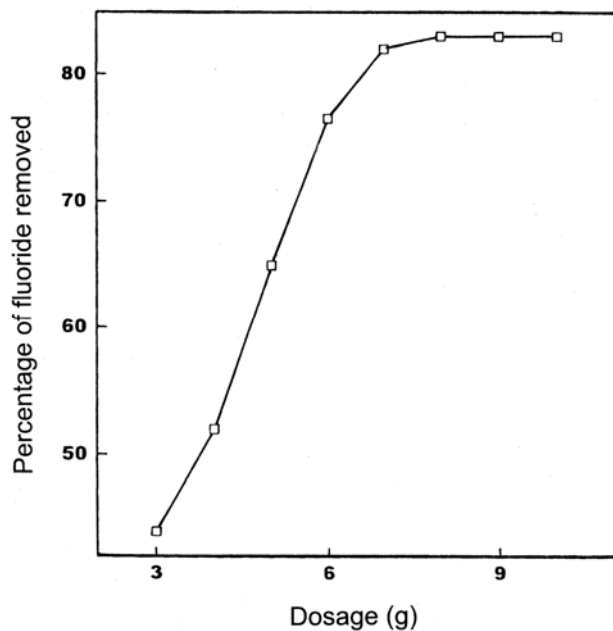


Fig. 4—Effect of adsorbent dose on the removal of fluoride by montmorillonite

Effect of pH

Defluoridation studies were carried out in the pH range of 2-12. The plot of the percentage of fluoride removed by montmorillonite at the pH range 2-12 is given in Fig. 5. Montmorillonite possesses appreciable defluoridating efficiency throughout the pH range studied. The percentage of fluoride removed at pH 2 is 97.0 and it has been observed that the same decreases with increase in pH. For example, at pH 7, the percentage of fluoride removed is 82, while at pH 10 it is about 60 and at pH 12 the fluoride removed is 56 per cent. The influence of pH on the pronounced adsorption of fluoride on the surface of the material at low pH ranges leads to the assumption that chemisorption dominates in this range and chemisorption along with physisorption occurs at higher pH ranges.

The pH of the solution is an important variable and it controls the adsorption of the fluoride at the montmorillonite – solution interface. Such interface on acid-base dissociation develops positive and negative charges of the surface^{19,20}. Montmorillonite is made up of metal oxides which are hydrolysed in aqueous solution. The decrease in the adsorption of fluoride on its surface reflects a reduction in the quantity of the positive charges. The zero point of charge (PPZC) of montmorillonite is at 2.5²¹. The percentage of fluoride removal is 97 at low pH i.e. at pH 2. It is due to the availability of more H⁺ ions in

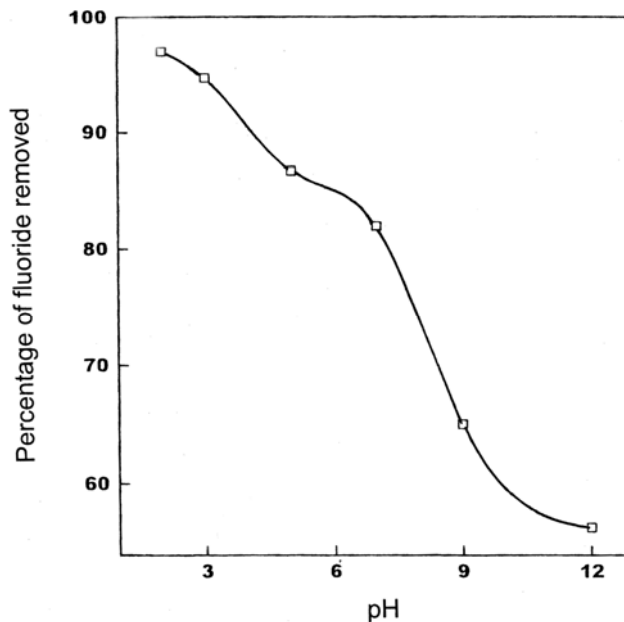
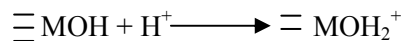
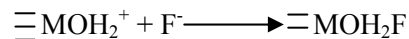


Fig. 5—Effect of pH on the removal of fluoride by montmorillonite

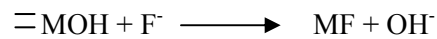
the surface of the adsorbent and thereby greater adsorption of the fluoride. Hence, fluoride adsorption increases at low pH levels as more of the surface sites are positively charged. In solution, the ionisation of sodium fluoride increases and hence the concentration of negatively charged fluoride ions. The adsorption of fluoride onto the surface of the material is due to the development of positively charged surface sites according to the following reactions²².



Where 'M' is a metal ion in the mineral lattice. The positively charged sites are available for fluoride exchange as



Further, anion exchange may also occur by displacement of the hydroxyl species as



The reduction in the percentage of adsorption of fluoride at higher pH levels is due to the increasing electrostatic repulsion between the negatively charged surface sites of the adsorbent and fluoride ions.

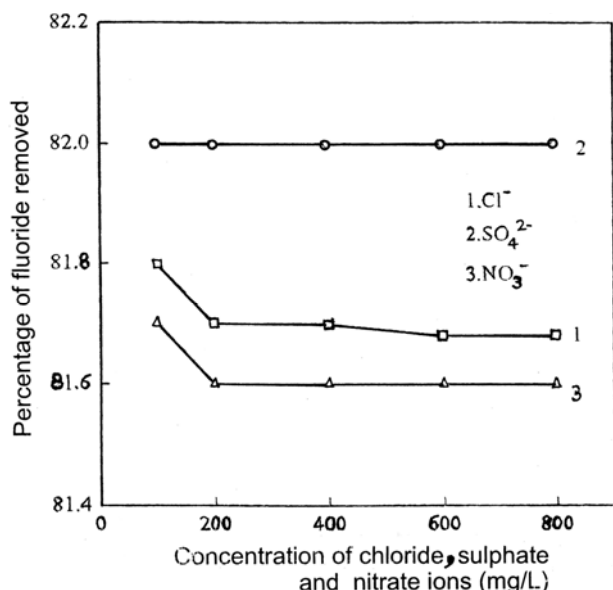


Fig. 6—Effect of common anions on the removal of fluoride by montmorillonite

Effect of co-ions

The defluoridation property of montmorillonite was experimentally verified in presence of excess amounts of common anions like Cl^- , SO_4^{2-} , NO_3^- and HCO_3^- . Fig. 6 explains the influence of common anions on the percentage of fluoride removed by montmorillonite. No significant influence on defluoridation efficiency of the material is observed in presence of Cl^- , SO_4^{2-} , and NO_3^- . However, in presence of excess HCO_3^- the defluoridation efficiency was found to decrease from 82 to 58% as shown in Fig. 7. A similar interfering role on the defluoridation efficiency by the bicarbonate ions was reported in the case of defluoridation property of the alumina-gibbsite²³. This specificity in the case of bicarbonate ions is due to the competition of bicarbonate ions with fluoride ions for the active site on the surface of the adsorbent.

Effect of temperature

The temperature dependence of fluoride adsorption by montmorillonite was studied over a range of 30–60°C. The percentage of adsorption of fluoride ions at 50th min was found to be 82.0, 92.6, 94.0 and 95.3, respectively at 30, 40, 50 and 60°C. The plot of time against fluoride adsorbed by the material at the four different temperatures is given in Fig. 8. The increase in the percentage of fluoride adsorption at higher temperatures confirms the endothermic nature of the process. The first, sharp portion of the curve corresponds to the external surface adsorption stage or

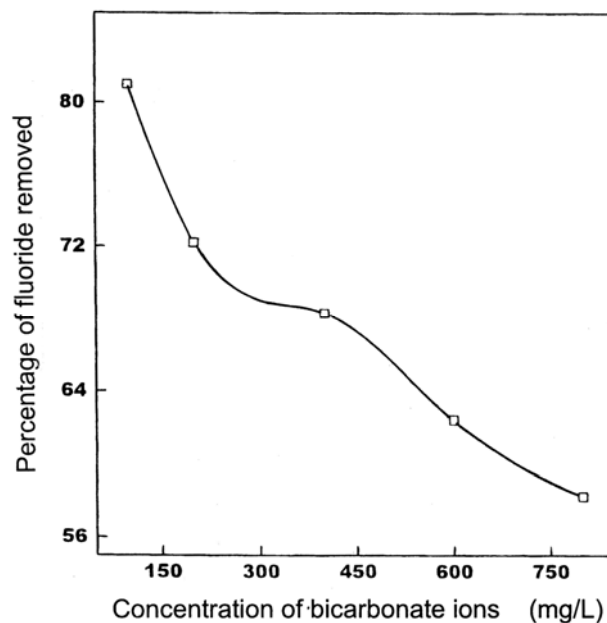


Fig. 7—Effect of bicarbonate on the percentage of fluoride removed

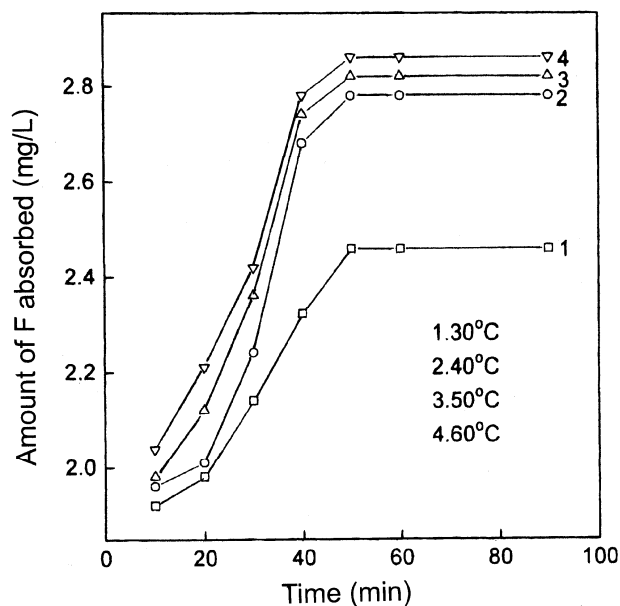


Fig. 8—Amount of fluoride adsorbed with time at different temperatures

instantaneous adsorption stage²⁴. The second, gradual linear portion follows the gradual adsorption stage and the final, linear portion represent the equilibrium stage²⁵. In this model, the clay mineral is treated as being surrounded by a boundary layer film of water molecules through which the fluoride ions must diffuse prior to adsorption on the clay surface. The

second portion of the figure indicates predominantly intra particle diffusion, where the diffusive transport of fluoride occurs through the internal pores of the adsorbent. The third portion of the curve shows the decrease in the rate of diffusion, reaching equilibrium²⁶. The observation about the enhanced fluoride adsorption rate by the adsorbent at higher temperatures are in perfect agreement with earlier findings²⁷⁻²⁹.

Adsorption isotherm

The adsorption of fluoride obeyed the Langmuir and Freundlich adsorption isotherms. The Langmuir constants Q° and b were obtained from the linear regression analysis of the Langmuir equation

$$\frac{C_e}{q_e} = \frac{1}{Q^\circ b} + \frac{C_e}{Q^\circ} \quad \dots (1)$$

where Q° and b are Langmuir constants related to adsorption capacity and energy of adsorption respectively. The linear plots (Fig. 9) of C_e/q_e versus C_e shows that the adsorption follows Langmuir isotherm model. The values of Q° and b were calculated from the slopes and intercepts of the plots respectively and are presented in Table 3. The increasing trends observed in Q° and b confirm the enhanced adsorption at higher temperature.

The Freundlich equation is widely used to explain the adsorption of pollutants from an aqueous medium empirically³⁰. The expression of Freundlich equation is given as

$$\log q_e = \log k_f + 1/n \log C_e \quad \dots (2)$$

where k and n are adsorption capacity and intensity of adsorption. Fig. 10 shows the linear plots of the $\log q_e$ versus $\log C_e$ indicating that the adsorption follows Freundlich isotherm. The values of Freundlich constants k and n are given in Table 3. The values of $n > 1$ indicate favorable adsorption conditions. The values of the exponent, n between 1 and 10 represent the beneficial adsorption and this agrees well with the observation of Traybal³¹.

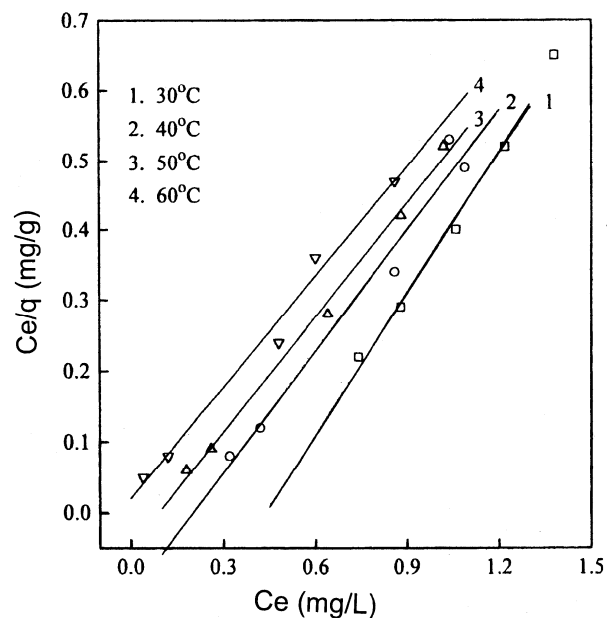


Fig. 9—Effect of temperature: Langmuir's plots

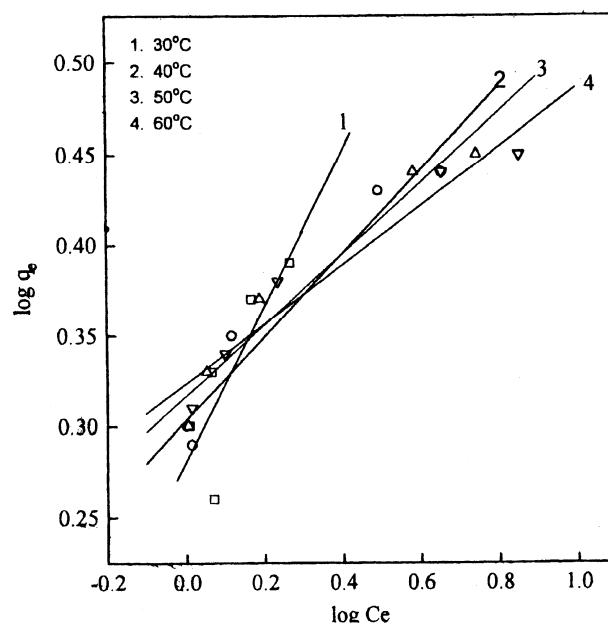


Fig. 10—Effect of temperature: Freundlich's plots

Table 3—Langmuir and Freundlich isotherm constants at different temperatures

Temperature °C	Q° mg/g	b dm ³ /mg	r	k	n	r
30	1.485	4.202	0.995	0.279	2.351	0.829
40	1.836	10.753	0.997	0.304	4.371	0.978
50	1.873	12.658	0.996	0.313	5.308	0.972
60	1.910	16.129	0.993	0.325	6.050	0.967

Adsorption kinetics

The rate constants for adsorption, K_{ad} for the removal of fluoride by montmorillonite at the four temperatures were determined using the following first order expression by Lagergren.

$$\text{Log}(q_e - q) = \text{Log} q_e - (K_{ad}/2.303) \times t \quad \dots (3)$$

where, q_e and q are the amounts of fluoride adsorbed at equilibrium and at any time interval 't' respectively. The straight line plots of $\log(q_e - q)$ versus t indicate the applicability of the above equation. The Lagergren plots of the reactions at the four temperatures are given in Fig. 11. The values of K_{ad} at four different temperatures were calculated from the slopes of the respective linear plots and are given in Table 4 along with the thermodynamic parameters.

The equilibrium constant K_0 , for the sorption reactions was determined by the method suggested by Khan and Singh³² by plotting $\ln(q_e/C_e)$ versus q_e and extrapolating to zero q_e (Fig. 12). The endothermic nature of adsorption is indicated by an increase in K_0 with rise in temperature. The values are given in Table 4. The standard free energy (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were calculated using the following equations.

$$\Delta G^\circ = -RT \ln K_0 \quad \dots (4)$$

$$\ln K_0 = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad \dots (5)$$

A plot of $\ln K_0$ versus $1/T$ was found to be linear as indicated in Fig. 13. ΔH° and ΔS° were determined from the slope and intercept of the plots and the values are presented in Table 4. The negative values of ΔG° indicate the feasibility of the process and also the spontaneity of adsorption process. The value of ΔH° is positive (12.81 KJ/mole) and this indicates that the adsorption is endothermic. The positive value of ΔS° shows the increased randomness of the solid/solution interface during the adsorption of fluoride on montmorillonite.

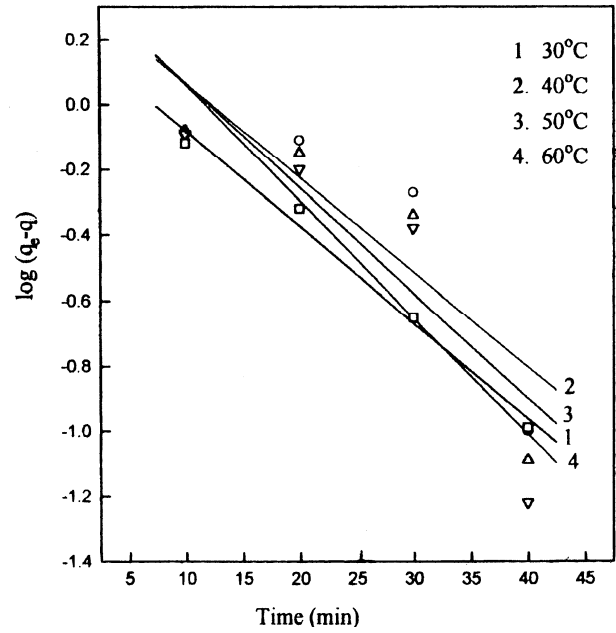


Fig. 11—Effect of temperature: Lagergren plots

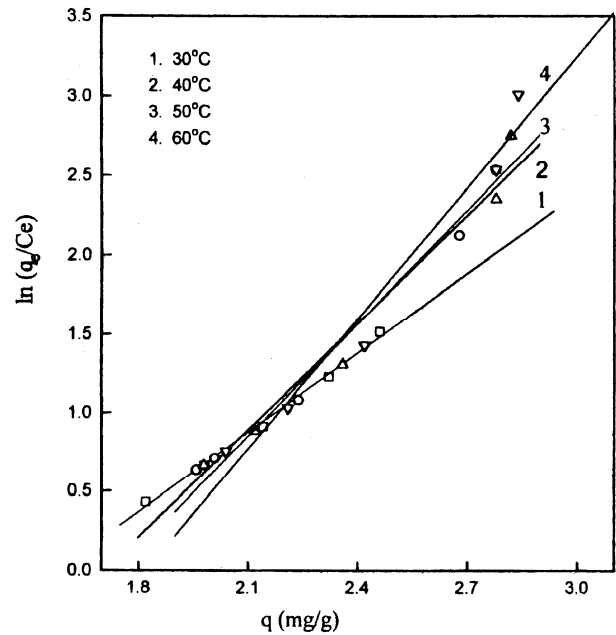


Fig. 12—Plots of $\ln q_e/C_e$ versus q_e for the adsorption of fluoride on montmorillonite clay

Table 4—Kinetic and thermodynamic parameters at different temperatures

Temperature °C	$K_{ad} \text{ min}^{-1}$	K_0	$\Delta G^\circ \text{ KJ/mole}$	$\Delta H^\circ \text{ KJ/mole}$	$\Delta S^\circ \text{ KJ/mole}$
30	2.8×10^{-2}	1.684	-1312.90	12.81	46.99
40	2.9×10^{-2}	2.269	-2132.15	-	-
50	3.0×10^{-2}	2.390	-2339.79	-	-
60	3.5×10^{-2}	2.754	-2804.70	-	-

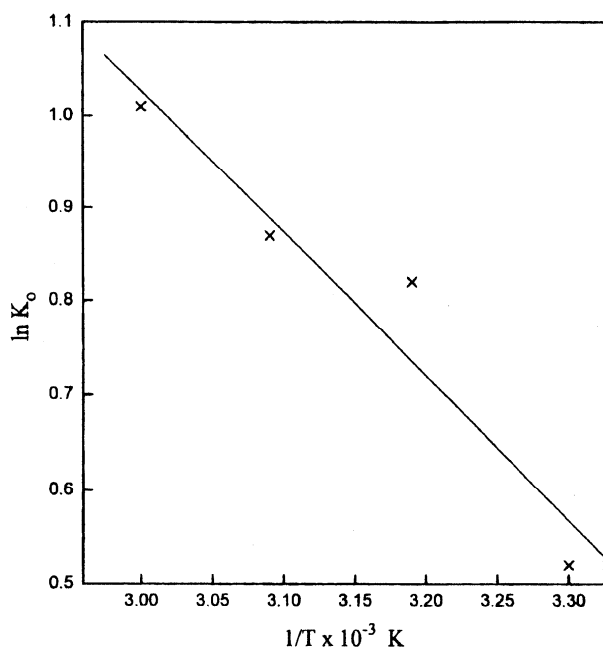


Fig. 13—Plot of $\ln K_0$ versus $1/T$ for the adsorption of fluoride on montmorillonite clay

Intraparticle diffusion studies

In batch reactors, due to rapid agitation, there is a possibility that the adsorbate ions can diffuse from solution into the adsorbent pores and this may form the controlling step³³. This possibility was explored by plotting the amount of fluoride adsorbed versus $t^{1/2}$ for different temperatures (Fig. 14). All the plots have the same general features, initial curved portion followed by linear portion and a plateau. The initial curved portion is attributed to the bulk diffusion and subsequent linear portion to the intraparticle diffusion. This means that for adsorption at the outer surface of the adsorbent there is also possibility of intraparticle diffusion from the outer surface into the pores of the material. The rate constants K_p for the intraparticle diffusion process at the four temperatures, calculated from the slopes of the linear curves, are given in Table 5. An increase in the K_p values with temperature indicates enhanced adsorption rate at higher temperature.

Instrumental studies

For understanding the nature of fluoride sorption X-ray, FTIR and SEM studies were performed using the raw and treated adsorbents. Powder X-ray diffraction studies were carried out on the raw and fluoride treated montmorillonite samples. XRD patterns of the treated adsorbents showed significant changes. The XRD data of the treated

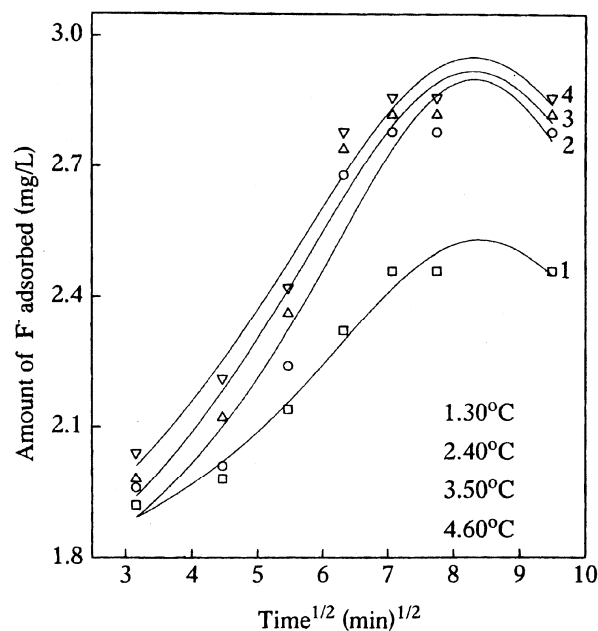


Fig. 14—Plots for constants for pore diffusion at different temperatures

Table 5—Effect of temperature on adsorption rate of pore diffusion

Temperature °C	K_p (mg/g/min ^{1/2})
30	0.143
40	0.232
50	0.234
60	0.236

montmorillonite provided evidence of slight modification over the crystal cleavages. The intensity of the peak due to the hkl plane 010, the monoclinic crystal system of montmorillonite disappeared after the fluoride adsorption on its surface. This is possible due to the lattice dislocation in the crystal system. The X-ray diffraction patterns of raw and fluoride treated material are given in Figs 15 and 16. This shows the strong adsorption of fluoride on the surface of the adsorbent. Adsorption of fluoride has resulted in several changes like the disappearance of some bands, shifts and decrease in the percentage of transmittance in the IR spectra of the solid surfaces in the range 4000-637 cm^{-1} . FTIR analysis of the sorbent surface before and after the sorption reaction has provided information regarding the surface groups that might have participated and also about the surface sites at which sorption might have taken place (Fig. 17a, b). The shift of stretching frequency, corresponding to

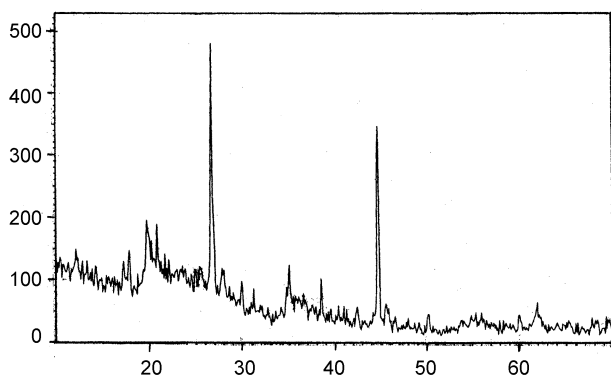


Fig. 15—X-ray diffraction pattern of pure montmorillonite clay

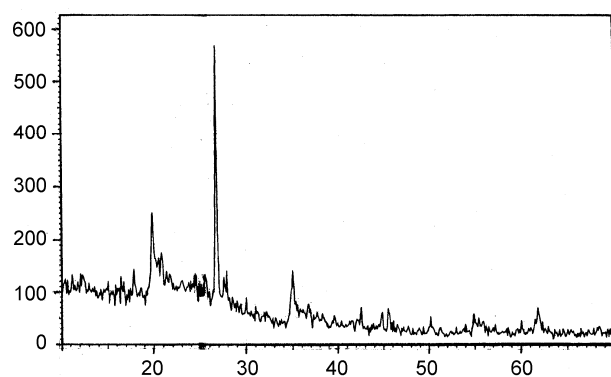


Fig. 16—X-ray diffraction pattern of fluoride adsorbed montmorillonite clay

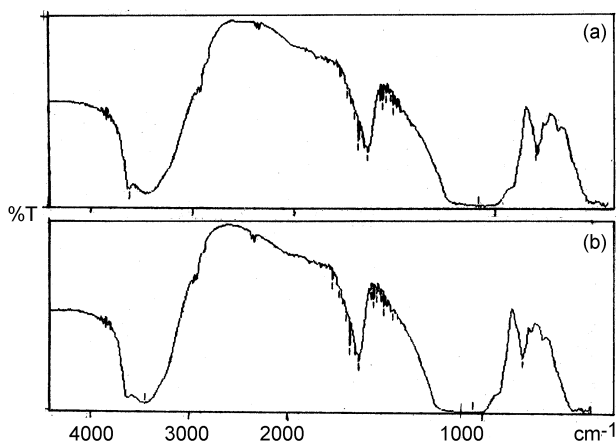


Fig. 17 —FTIR spectra of inloaded montmorillonite clay (a)—before treatment; (b)—after treatment

the presence of -OH groups from 3626 to 3451 cm^{-1} is assigned to the involvement of hydroxyl groups in the fluoride adsorption by montmorillonite. Similar observations have been made by Boehm *et al.*³⁴. The SEM analysis of the raw and treated montmorillonite

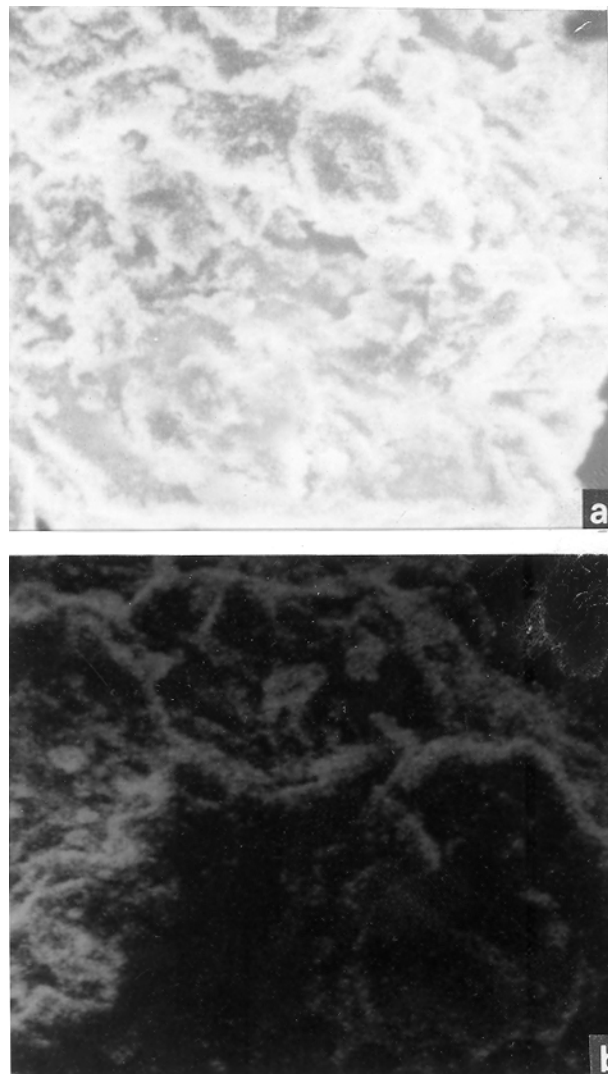


Fig. 18—SEM image of the surface of montmorillonite (a)—before defluoridation; (b)—after defluoridation

samples confirmed a layer of fluoride ions over its surface. The SEM photographs are provided in Fig. 18a, b.

Conclusion

The results of the present investigation reveal some important observations of fluoride adsorption mechanism. The adsorbent exhibits an increase in the adsorption rate at higher temperatures and this confirms the endothermic nature of the process. Though, the adsorption process follows both Langmuir and Freundlich models, the preferred mode of isotherm seems to be the Langmuir model. The adsorption mechanism also follows the intraparticle diffusion pattern and surface adsorption. XRD studies

show changes in the crystalline nature of the adsorbent due to adsorption of fluoride on its surface. SEM studies visualized the formation of the fluoride layer over the surface. FTIR studies indicate the participation of the surface sites of the sorbent in the adsorption interaction.

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