Adsorption of fluoride ions onto naturally occurring earth materials

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ABSTRACT: Batch sorption system using two naturally occurring earth materials (EM) as adsorbents was investigated to remove fluoride ions from aqueous solution. 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 isotherm. The amount of fluoride ions adsorbed per unit mass of the adsorbent was found to be 0.011 and 0.007 mg/g, at 30°C from 4 mg/L fluoride solution, for EM1 and EM2 respectively. Thermodynamic parameters such as ΔH^o, ΔS^o and ΔG^o were calculated which indicates that the removal of fluoride ions is an endothermic process. Kinetic studies reveal that the adsorption follows reversible first order kinetics. X-ray diffraction patterns of the adsorbents before and after adsorption and Dubinin-Radushkevick (D-R) isotherm indicate that the adsorption of fluoride ions onto these materials is a physisorption process. @ JASEM

The removal of fluoride from water is one of the most important issues due to the effect on human health and environment. Fluoride in drinking water may be beneficial or detrimental depending on its concentration (WHO 2004). The optimum fluoride level in drinking water for general good health set by World Health Organization (WHO) is considered to be less than 1.5 mg/l. During recent past removal of fluoride from water has been paid more attention in literature by the different technologies (Saha 1993; Chaturvedi *et al.*, 1990; Sivasamy *et al.*, 2001; Ku *et al.*, 2002; Gopal *et al.*, 2007). Current treatment methods can be divided into two categories viz. precipitation and adsorption. Precipitation of fluoride with calcium and aluminium salts has been used to remove fluoride from industrial waste water. Typically lime is used as a calcium source and Ca(II) ions released from calcium salt interact with fluoride and form CaF_2 precipitate. The aluminium salts interact with fluoride in water and form AlF_n^{3+} and $Al(OH)_{3-m}F_m$ etc. The final concentration of fluoride in the water treated using this method greatly depends on the solubility of CaF_2 and aluminium complexes (Saha, 1993). Adsorption is another technique; wherein many adsorbents have been investigated for the removal of fluoride, (Chaturvedi *et al.*, 1990; Sivasamy *et al.*, 2001; Ku *et al.*, 2002; Gopal *et al.*, 2007; Wei *et al.*, 2007).

Certain habitations of the Andipatti revenue block (which is a fluoride endemic region) of Theni district in Tamil Nadu, South India are free from fluoride in their ground waters. Therefore, an attempt has been made to investigate the ability of the earth materials, (EM1 and EM2) taken from those habitations, to adsorb fluoride ions from aqueous solution and to shed some light on the mechanism of interaction between the soil and fluoride ions.

MATERIALS AND METHODS

All the reagents used were of commercially available high purity analar grade (Merck or Sd-fine, India). Stock solution of fluoride was prepared by dissolving sodium fluoride in doubly distilled water. Naturally available earth materials were collected from Kanavilakku (EM1) and Bodidhasanpatty (EM2) of Andipatti block in Theni district, pulverized, sieved and used as adsorbents. These materials were examined by geologists and found as kankar, which is a deposit often nodules of $CaCO_3$ formed in soils of semi aerid regions, similar to calcrete and cap rocks. It is a yellowish hard and kankery bed and is the combination of $CaCO_3$ (~60%) with silica (~20%) granules.

Adsorption experiments were carried out by batch sorption method. The concentration of fluoride ions and pH were measured using ion-selective meter (Eutech Cyberscan 2100). The XRD patterns of the adsorbent before and after adsorption were recorded at the National Institute for Science and Technology, Thiruvananthapuram, India. The zero point charge (pH_{ZPC}) of the adsorbents was determined by pH drift method (Jia *et al.*, 2002) and it was found to be 6.86 and 6.92 for EM1 and EM2 respectively indicating that the adsorbents were neutral. Experimental variables considered were initial concentration of fluoride ions 2-10 mg/l; contact time between adsorbent and the fluoride solution 5-60 min; pH 3-11; dosage of the adsorbent 1-10 g/50 ml; temperature 30-50⁰ C and co-ions viz. chloride, sulphate, nitrate and bicarbonate ions.

The experimental data were analyzed using Microcal Origin (version 6.0) computer software. The goodness of fit was discussed using correlation coefficient, r, and standard deviation, sd.

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RESULT AND DISCUSSION

Effect of contact time and initial concentration: The amount of fluoride adsorbed per unit mass of the adsorbent (Q_e, mg/g) onto the two earth materials were studied and the results indicated that the amount of fluoride adsorbed increased with an increase in the initial sorbate concentration and also with rise in temperature. The amount of fluoride removed per unit mass of the adsorbent is 0.03 mg/g for EM1 and 0.022 mg/g for EM2. The variation of Q_e with temperature suggested that the adsorption is an endothermic process. However, this increase is only marginal. This may be due to the fact that as the adsorbents are crystalline in nature, with rise in temperature the pores present in the adsorbents may be enlarged to a very lesser extent leading to a marginal increase in uptake of fluoride ions. The changes in the rate of removal of fluoride may be due to the fact that, initially, all adsorbent sites were vacant and solute gradient was high. A decreasing removal rate particularly towards the end of the experiment indicated possible monolayer of fluoride ions on the outer surface and/or pores of the adsorbent (Parab *et al*., 2005; Munoz *et al*., 2006; Saxena *et al*., 2006).

Table 1. Statistical parameters and isotherm constants for the removal of fluoride by earth materials

Isotherm	Statistical parameter/ constants	EM1	EM2
Freundlich	r	0.996	0.992
	sd	0.024	0.031
	n	1.32	1.47
	K	0.006	0.007
Langmuir	r	0.910	0.891
	sd	18	22
Q^0 (mg/g)	0.067	0.058	
b (L/mg)	0.084	0.128	
D-R Isotherm	r	0.917	0.906
	sd	0.24	0.24
	β (x 10^{-7})	-5.19	3.73
	E (kJ/ mol)	0.98	1.16

Effect of dose: The amount of fluoride removed as a function of adsorbent dosage (1-10 g/50 ml) at 4 mg/l of initial fluoride concentration. The results indicated that the removal of fluoride increased with increase in dosages, as expected. From the result it was evident that an optimum dosage of 6 g/50 ml and 8 g/50ml are required for appreciable removal of fluoride ions for EM1 and EM2 respectively, and hence these amounts were employed as a dose for further studies.

Equilibrium isotherms: The Langmuir (Langmuir, 1918) and Freundlich (Freundlich, 1906) isotherm models were examined, in this study, to describe the adsorption equilibrium. Langmuir isotherm constants were calculated and are listed in Table 1 along with the statistical results of these plots. From the results, it was evident that the correlation of the experimental data via the Langmuir isotherm was poor. The adsorption data have been fitted to the Freundlich isotherm. The statistical parameters and other isotherm constants are also collected in Table 1. The linearity of the figure shows the applicability of the Freundlich adsorption isotherm. The applicability the Freundlich adsorption isotherm suggested that the uptake of fluoride ions by the earth materials might be due to physicochemical adsorption on heterogeneous surfaces. The results indicated that the adsorption capacity (measured by K) of the adsorbents increased with an 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 (Raichur *et al*., 2001; Krishnan *et al*., 2002). The Dubinin-Radushkevick (D-R) (Ghazy and Ragab, 2007) isotherm was used to determine the nature of the adsorption process *viz*. physisorption or chemisorption. The statistical results along with other isotherm constants are given in Table 1. The mean sorption energy values range from 0 to 8 kJ mol^{-1} is for physical adsorption and from 9 to 16 kJ mol^{-1} for chemical adsorption (Ghazy and Ragab, 2007; Sari *et al*., 2007). It is evident from the results that, in the present study, the mean sorption energy are in between the 0-2 kJ mol^{-1} which indicates that the earth materials trap the fluoride ions by physisorption.
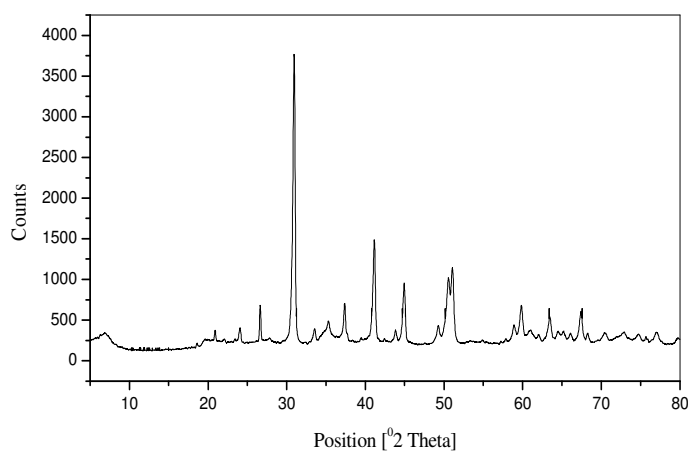
(a)

Thermodynamic parameters. The thermodynamic parameters such as standard free energy, enthalpy and entropy changes were calculated from the temperature dependence of equilibrium constant as explained earlier (Kadirvelu *et al.*, 2002; Stephen Inbaraj and Sulochana 2002). The values of enthalpy change (7-22 kJ mol^{-1}) were positive indicating the endothermic nature of the process. Further, the magnitude of the enthalpy changes suggested that the adsorption is a physical process. The positive ΔG^0 (0.21-2.11 kJ mol^{-1}) values indicate that the adsorption process was non spontaneous. The ΔS^0

values (16-77) for the adsorption process are positive. This indicated the prevalence of a high degree of disorderliness at the solid solution interface during the adsorption of fluoride onto the adsorbents (Gopal and Elango 2007; Doula *et al.*, 2000). This may be due to the fact that adsorbed water molecules which are displaced by the adsorbate species gain more translational entropy than is lost by the adsorbate molecules. Thus, allowing the prevalence of randomness in the system (Namasivayam and Yamuna 1995).
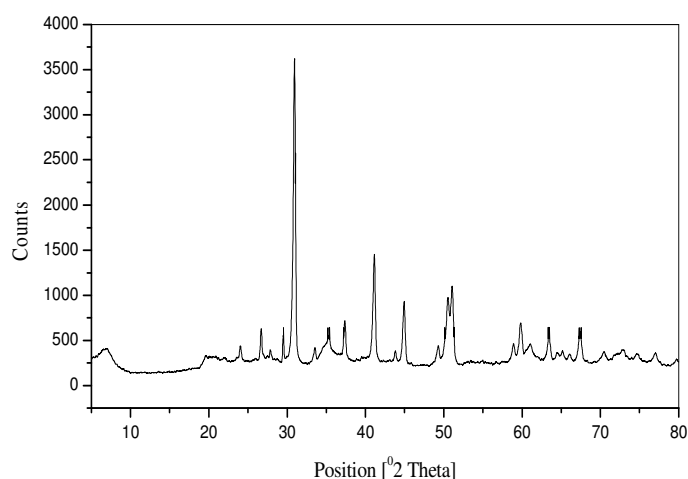

(b)

Fig 1. XRD pattern of EM1 (a) before adsorption (b) after the treatment with fluoride

Effect of pH: To study the influence of solution pH on the removal of fluoride ions, test mixtures containing 4 mg/l of fluoride solution and a known

amount of the adsorbents (6g /50 ml for EM1 and 8g /50 ml for EM2) were adjusted to various initial *p*H values, agitated for the equilibrium time and analyzed

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for residual fluoride ion concentrations. It is evident from the results that there is no significant change in the amount of fluoride adsorbed in the pH range 3 - 9. However, at higher pH (=11), there was an appreciable reduction in the amount adsorbed. This may be due to the fact that, at this pH, OH⁻ ions may compete effectively with fluoride ions for the active sites causing a decrease in the amount of fluoride removed (Gopal and Elango 2007).
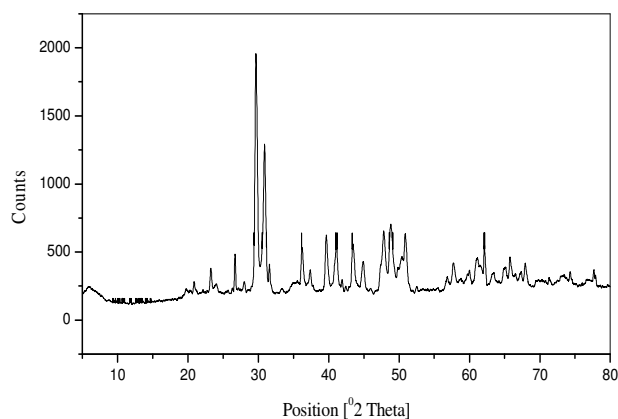

(a)

Effect of co-ions: The effect of added co-ions viz. Cl⁻, NO_3^-, SO_4^{2-} and HCO_3^- on the amount of fluoride adsorbed is studied and the results indicated that the addition of co-ions, in the concentration ranges investigated, has no appreciable effect on the amount of fluoride ions removed by these adsorbents.

Kinetic modeling: The rate constant for the adsorption, k_{ad} was determined using the Natarajan-Khalaf equation as described earlier (Kannan and Vanangamudi 1991). The rate constants for the adsorption and forward and reverse processes were calculated from the plot. The results indicated that the k_{ad} values increases with increase in temperature suggesting endothermic nature of the adsorption process. Further, an examination of the effect of fluoride ion concentration on the k_{ad} values 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 relationship between initial solute concentration and the rate of reaction will not be linear. Hence, in the present study, it seems likely that pore diffusion limits the overall rate of fluoride adsorption (Rengaraj *et al*., 1999; Weber 1963). Further, the values of k_{-1} were found to be larger than that of k_1 suggesting desorption is dominant over adsorption which lead to lower amount of fluoride adsorption, as observed.
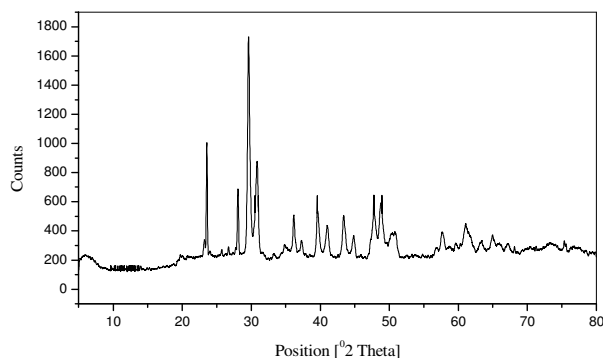
(b)

Fig 2. XRD pattern of EM1 (a) before adsorption (b) after the treatment with fluoride

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Intra-particle diffusion: In adsorption studies, it is necessary to determine the rate limiting step. Therefore, the results obtained from the experiments were used to study the rate-limiting step in the adsorption process. In order to show the existence of intra-particle diffusion in the adsorption process, the amount of fluoride sorbed at time t, was plotted against square root of time. The linear portion of the curves does not pass through the origin indicating that the mechanism of fluoride removal by EM1 and EM2 is complex and both, the surface adsorption as well as intra-particle diffusion contribute to the rate determining step (Rengaraj *et al*., 1999; Shabudeen *et al*., 2006). The intra-particle diffusion rate constant, k_p, values were obtained from the slop of the linear portions of the curves and were found to be 4.62×10^{-3}, 4.64×10^{-3} and 4.65×10^{-3} mg/g min$^{0.5}$ for EM1 at 30^0, 40^0 and 50^0C, respectively. For EM2 the values were 3.48×10^{-3}, 3.83×10^{-3} and 4.71×10^{-3} mg/g min$^{0.5}$ at 30^0, 40^0 and 50^0C, respectively. The general increase in k_p values with an increase in temperature may be due to the enlargement of pores present in the adsorbents with rise in temperature.

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 (Namasivayam and Yamuna 1995). Hence, the X-ray diffraction (XRD) patterns of the EM1 and EM2 before and after adsorption were recorded and are shown in Fig. 1 and 2, respectively. It was evident from the XRD patterns that the crystal structure of the adsorbents showed no significant changes after the adsorption of fluoride ions. This suggests that the uptake of fluoride ions by the adsorbent was by physisorption (Vemkata Mohan *et al*., 2001).

Conclusion: The removal of fluoride ions by the two naturally occurring earth materials was found to be endothermic and a non-spontaneous process. The results of isotherm, thermodynamic and XRD studies revealed that the adsorption of fluoride ions onto these materials under investigation was through physisorption. Though the amounts of fluoride ions adsorbed by these adsorbents were low, the results of the present study would definitely add on to the knowledge of the mechanism of interaction of fluoride ions with soils in the natural environment.

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