

Removal of fluoride from aqueous solution using graphite: A kinetic and thermodynamic study

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Batch sorption system using various grades of graphite as adsorbents 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 which indicated that the adsorption was endothermic and a physical process. Kinetic studies reveal that the adsorption follows reversible first order kinetics. XRD patterns of the adsorbent before and after adsorption were recorded to get a better insight into the mechanism of the adsorption process.

Keywords: Adsorption, Fluoride, Graphite, Kinetics, Thermodynamics

The removal of fluoride from water is one of the most important issues due to its ill-effects on human health and environment. Fluoride in drinking water may be beneficial or detrimental depends on its concentration¹. The optimum fluoride level in drinking water for general good health set by World Health Organization (WHO) is below 1.5 mg/L. During recent past removal of fluoride from water has been attempted using different technologies²⁻⁶. 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 wastewater. Typically lime is used as a calcium source and Ca(II) ions released from calcium salt interact with fluoride and precipitate CaF₂. The aluminium salts interact with fluoride in water and form AlF_n³⁻ⁿ 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 CaF₂ and aluminium complexes². Adsorption is another technique; wherein many adsorbents have been investigated for the removal of fluoride³⁻¹⁰.

Literature survey reveals that activated carbon, prepared from various materials, has been used by various researchers for the removal of fluoride from aqueous solution^{9,10}. However, no such study has been reported so far, with graphite (an allotropic form of carbon) as an adsorbent to remove fluoride ions from water. The main objective, therefore, of the present work is to study the equilibrium, kinetic and

thermodynamic aspects of the adsorption of fluoride onto various grades of commercially available graphite with an aim to understand the mechanism of the adsorption process and to explore the possibility of using graphite as a medium for fluoride removal since it is available in plenty, practically insoluble in water and non toxic in nature. Further, its attritional loss during regeneration may be very less than other adsorbents due to its crystalline nature.

Experimental Procedure

Materials

All the reagents used were of commercially available higher purity Analar grade (Merck or Sd-fine, India). Stock solutions of fluoride were prepared by dissolving sodium fluoride in doubly distilled water. Commercially available three grades of graphite were used as adsorbents as received. The point of zero charge (pH_{ZPC}) of the adsorbents was determined by reported method¹¹. The characteristics of the adsorbents used (given by the makers) are presented in Table 1.

Methodology

The concentration of fluoride and pH were measured using ion-selective meter (Eutech Cyberscan 2100). The XRD pattern of the adsorbent before and after adsorption was recorded at Regional Research Laboratory, Thiruvananthapuram. The surface area measurements were carried out at Anna University, Chennai.

Table 1 — Important characteristics of the adsorbents

Parameter	Adsorbent		
	G1	G2	G3
Moisture (%)	0.80	0.81	0.52
Ash content (%)	1.61	4.18	0.60
Carbon content (%)	98.73	95.20	98.30
Particle size (200 mesh)	80	93	87
Surface area (m ² /g) ^a	818	578	571
pH _{ZPC} ^a	7.34	6.89	7.28

^aExperimentally measured quantities; all other parameters were makers specifications

Batch adsorption experiments

Adsorption experiments were performed by agitating 250 mg of adsorbent with 50 mL of fluoride solution of desired concentration at 30±0.5°C in different stoppered bottles in a shaking thermostat machine. The shaking speed was 120 strokes/min throughout the study. At the end of predetermined time intervals, the sorbet was filtered and the concentration of fluoride was determined. All experiments were carried out twice and the adsorbed fluoride concentrations given were the means of duplicate experimental results.

Experimental variables were: initial concentration of fluoride ions 2-10 mg/L; contact time between adsorbent and the fluoride solution 10-60 min; pH 3-11; dosage of the adsorbent 50-1000 mg/50 mL; temperature 30-50°C and co-ions *viz.* chloride, sulphate, nitrate and bicarbonate.

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*.

Results and Discussion

Effect of contact time and initial concentration

The amount of fluoride adsorbed per unit mass of the adsorbent (Q_e , mg/g) for the different grades of graphite studied as a function of initial fluoride ion concentration at 30°C is shown in Fig. 1. Similar trend in Q_e versus fluoride ion concentration was observed at 40 and 50°C also. The results indicate that the amount of fluoride adsorbed increases with increase in initial sorbate concentration and also with rise in temperature. The variation of Q_e with temperature suggests that the adsorption is an endothermic process. However, this increase is only marginal. This may be due to the fact that with rise in temperature the enlargement of pores in the adsorbent may vary to a lesser extent as it is crystalline in nature.

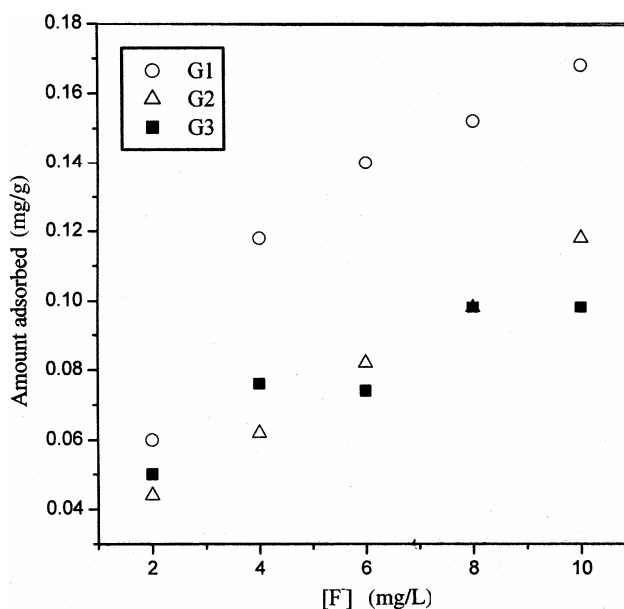


Fig. 1 — Amount of fluoride adsorbed as a function of initial fluoride ion concentration

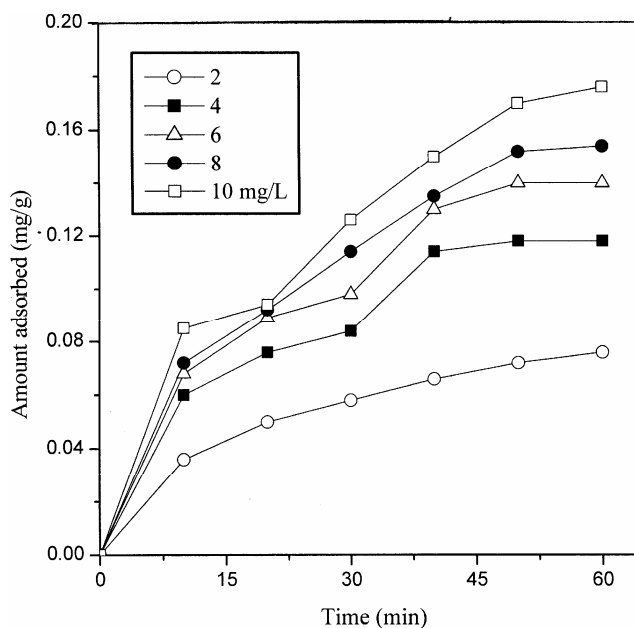


Fig. 2 — Effect of agitation time on the adsorption of fluoride ion onto G1

The variation of Q_e with contact time for different initial concentrations of fluoride is shown in Fig. 2. It has also been observed that the amount of fluoride adsorbed per gram of the adsorbent increased with time up to 40 min and then the curve become flattened indicating the attainment of equilibrium. It is also seen that the equilibrium time is independent of initial concentration of fluoride. 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 adsorbent¹²⁻¹⁴.

Effect of adsorbent dosage

The amount of fluoride removed as a function of adsorbent dosage (50-1000 mg/50 mL) at 4 mg/L of initial fluoride concentration and at 30°C is given in Fig. 3. The result indicates that the removal of fluoride increases with increase in dosages and this was attributed to increased carbon surface area and availability of more adsorption sites. From the result it is evident that optimum dosage of 250 mg/50 mL is required for appreciable removal of fluoride ions and hence this amount is employed as a dose for further studies.

Adsorption isotherm

The distribution of solute between the solid and the solution interface at equilibrium has been described by the Freundlich¹⁵ and Langmuir¹⁶ equations. These two models are widely used, the former being purely empirical and the latter assuming that maximum adsorption occurs when the surface is covered by adsorbate. The Freundlich equation is commonly presented as:

$$\log Q_e = \log K + 1/n \log C_e \quad \dots(1)$$

where *K* and *n* are temperature dependent Freundlich constants, *C_e* the equilibrium concentration (mg/L) and *Q_e* is the amount adsorbed at equilibrium (mg/g). The experimental results were plotted as log *Q_e* against log *C_e* (Fig. 4) and the statistical results along with the Freundlich constants were collected in Table 2. The results indicate that the values of adsorption capacity, *K* decrease in the order G3>G1>G2. The higher adsorption capacity of G3 and G1 may be due to their comparatively higher carbon content and lower particle size (Table 2). Further, the values of intensity of adsorption, *n* are greater than one which indicates that the adsorption is favourable^{17,18}.

To quantify the adsorption capacity of the adsorbent for the removal of fluoride from aqueous solutions, Langmuir equation is also applied in the following form.

$$C_e/Q_e = 1/Q_o b + C_e/Q_o \quad \dots(2)$$

where, *C_e* and *Q_e* has usual meanings, and *Q_o* and *b* are the Langmuir constants related to the capacity and energy of adsorption, respectively. The linear plot of

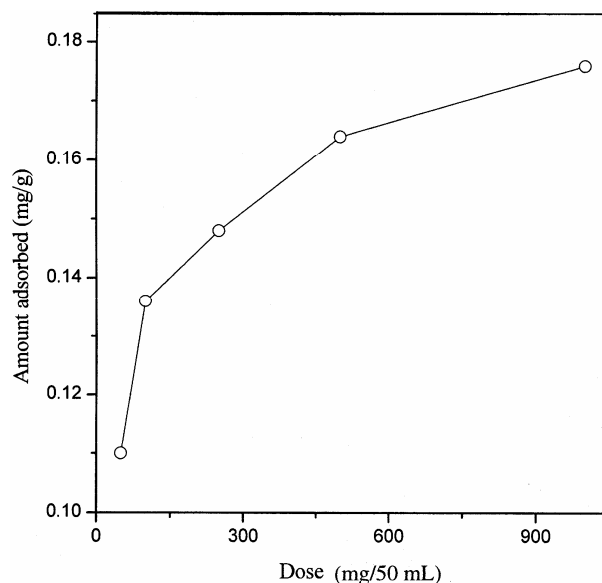


Fig. 3 — Effect of dose on the adsorption of fluoride ion onto G1 [F]=4 mg/L; Temp=30°C; pH=7; Agitation time=60 min

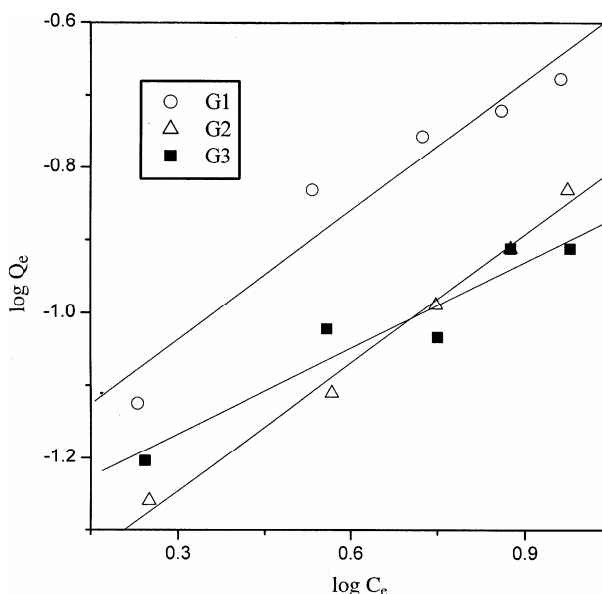


Fig. 4 — Freundlich adsorption isotherms for the adsorption of fluoride ion onto graphite

Table 2 — Langmuir and Freundlich isotherm constants

Isotherm	Statistical parameter/ constants	Adsorbent		
		G1	G2	G3
Langmuir	r	0.97	0.96	0.98
	sd	0.80	4.09	5.16
	Q _o	3.13	0.25	0.16
	b	0.07	0.14	0.36
Freundlich	r	0.97	0.99	0.96
	sd	0.06	0.02	0.04
	n	1.68	1.70	2.53
	K	0.06	0.04	0.09

C_e/Q_e versus C_e (Fig. 5) indicates the applicability of Langmuir adsorption isotherm. The values of Q_0 and b were calculated from the slope and the intercept of the linear plots and are also listed in Table 2. In order to predict the adsorption efficiency of the adsorption process, the dimensionless equilibrium parameter was determined by using the following equation.

$$R_L = 1 / (1 + bC_0) \quad \dots(3)$$

where C_0 is the initial concentration and b is the Langmuir isotherm constant. The values of R_L (Table 3) were found to be between 0 and 1 which confirms that the ongoing adsorption process is favourable^{19,20}.

Thermodynamic parameters

The standard free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) were calculated from the variation of the equilibrium

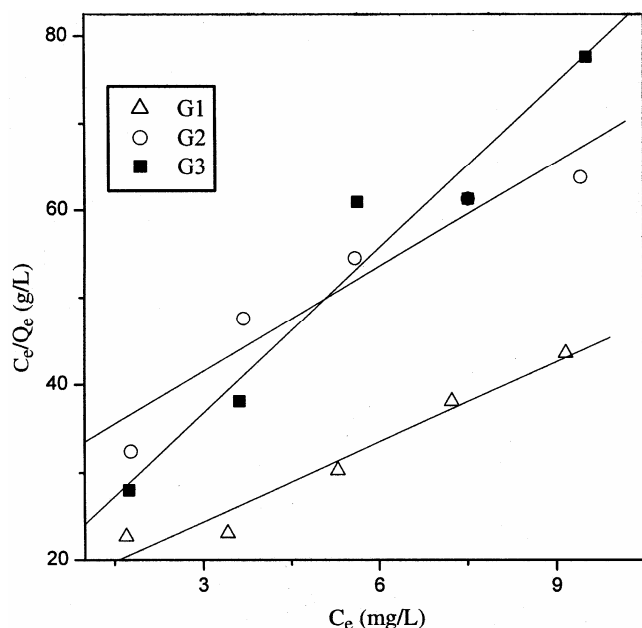


Fig. 5 — Langmuir adsorption isotherms for the adsorption of fluoride ion onto graphite constant with temperature as described elsewhere²¹. The equilibrium constant was calculated using the following equation²¹.

$$K_0 = C_{Ac}/C_e \quad \dots(4)$$

where, C_{Ac} is the concentration (mg/L) of fluoride in the solid phase at equilibrium and C_e is the equilibrium concentration. The values of the equilibrium constant were found to be in the range of 0.052 to 0.258. The endothermic nature of adsorption is indicated by increase in K_0 with rise in temperature. The ΔG^0 values (3.64 to 7.47 kJ mol⁻¹) are positive which mean that the reaction is non-spontaneous. The value of enthalpy of a sorption process may be used to distinguish between chemical and physical sorption²². The enthalpy changes, at different initial fluoride ion concentrations, for the adsorption process under investigation were found to be in the order of 3.99 to 24.57 kJ mol⁻¹. 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 discussion it is concluded that fluoride ion sorption by graphite is a physical process. Positive values of ΔH^0 suggest that the adsorption process is endothermic. At all initial fluoride ion concentrations, the ΔS^0 values for the adsorption process are positive ($0.5 < \Delta S^0 < 65.4 \text{ JK}^{-1} \text{ mol}^{-1}$). This indicates the prevalence of a high degree of disorderliness at the solid solution interface during the adsorption of fluoride onto graphite. 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 system²³.

Table 3 — Equilibrium parameter, R_L

[F] (mg/L)	Adsorbent								
	G1			G2			G3		
	30°	40°	50°C	30°	40°	50°C	30°	40°	50°C
2	0.88	0.87	0.87	0.58	0.42	0.50	0.79	0.72	0.65
4	0.79	0.78	0.77	0.41	0.27	0.33	0.65	0.56	0.48
6	0.71	0.70	0.69	0.32	0.20	0.25	0.55	0.46	0.38
8	0.65	0.64	0.63	0.26	0.15	0.20	0.48	0.39	0.31
10	0.60	0.59	0.57	0.22	0.13	0.16	0.42	0.34	0.27

Effect of pH

The pH of the aqueous solution is an important variable which controls the adsorption at the water-adsorbent interfaces. Therefore, the adsorption of fluoride onto the graphite was examined at different initial pH values ranging from 3 to 13 and the results are depicted in Fig. 6. The results indicate that the adsorbent exhibits a commendable defluoridation capacity in wide range of pH. This behaviour can be explained on the basis of zero point charge (7.34, 6.89 and 7.28 for G1, G2 and G3 respectively) of the adsorbents. At higher pH above this point, the OH⁻ ions compete effectively with fluoride ions causing a decrease in the amount of fluoride removed. At a lower pH below this zero point charge, the surface of the adsorbent gets positively charged, which enhances the adsorption of negatively charged fluoride ions through electrostatic force of attraction²⁴⁻²⁶.

Effect of co-ions

The effect of added co-ions viz. Cl⁻, NO₃⁻, SO₄²⁻ and HCO₃⁻ on the amount of fluoride adsorbed is given in Table 4. The results indicate that the addition of co-ions, in the concentration range investigated, has no appreciable effect on the amount of fluoride ions removed. However, increase in the concentration of bicarbonate ions slightly decreases the adsorption. This may due to the competition between bicarbonate and fluoride ions for the active sites on the adsorbent. Similar observation was made in the adsorption of fluoride onto activated alumina²⁷ and magnesia²⁸.

Kinetic of adsorption

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 behaviour of the adsorbent employed.

The sorption of fluoride from a liquid phase to solid phase may be expressed as Eq. (5).



where k_1 is the forward rate constant and k_{-1} is the backward rate constant. 'A' represents fluoride remaining in the solution and 'B' represents fluoride

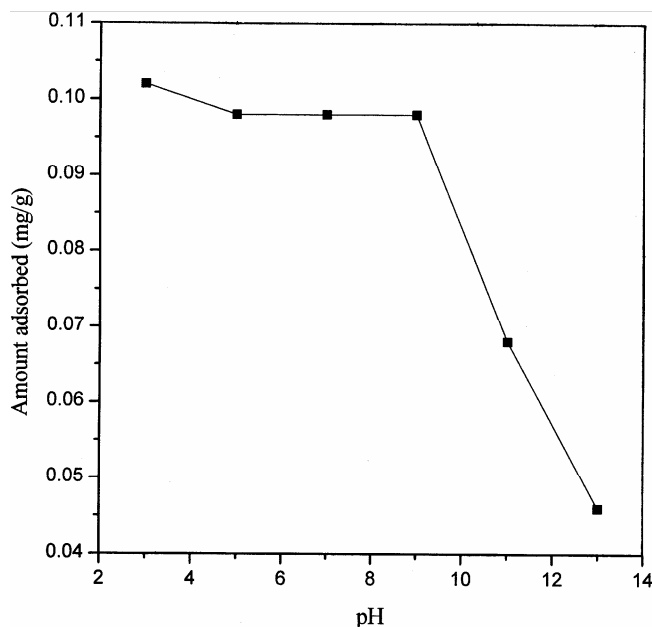


Fig. 6 — Effect of pH on the adsorption of fluoride ion onto G1 [F]=4 mg/L; Temp=30°C; Contact time=60 min

Table 4 — Effect of co-ions on the amount of fluoride adsorbed (mg/g) by G1

Co-ion	Concentration of co-ion (mg/L)				
	100	200	300	400	500
Chloride	0.14	0.12	0.11	0.12	0.12
Sulphate	0.96	0.92	0.11	0.10	0.11
Nitrate	0.12	0.11	0.10	0.11	0.10
Bicarbonate	0.12	0.08	0.07	0.06	0.05

retained on the surface of the adsorbent. Since the reaction in both directions is of first order, the rate constants of adsorption k_{ad} were determined using the following expression given by Natarajan and Khalaf²⁹, Eq. (6).

$$\log(C_0/C_t) = (k_{ad}/2.303) t \quad \dots(6)$$

where C_0 and C_t are the concentration in mg/L of fluoride initially and at time t , respectively. Linear plots ($r > 99$) of $\log(C_0/C_t)$ versus t suggest the applicability of Natarajan-Khalaf equation. A representative plot is shown in Fig. 7. The rate constants were calculated from the slope and the values are collected in Table 5. The results indicate that the rate constant k_{ad} varies non-linearly with increase in the concentration of fluoride ions. 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 fluoride concentration and rate of reaction will not be linear. It

shows that pore diffusion limits the overall rate of fluoride adsorption^{30,31}. The rate constants for the forward (k_1) and backward (k_{-1}) processes are calculated using the following equation as described in the literature³².

$$k_{ad} = k_1 + k_{-1} = k_1 [1 + 1/K_o] \quad \dots(7)$$

$K_o = k_1/k_{-1}$ where K_o is the equilibrium constant. The values thus computed are also collected in Table 5. It is evident from the results that the forward rate constant is much lower than the backward rate constant suggesting that the rate of desorption is clearly dominant and consequently the adsorption is non-spontaneous as it is evidenced from free energy

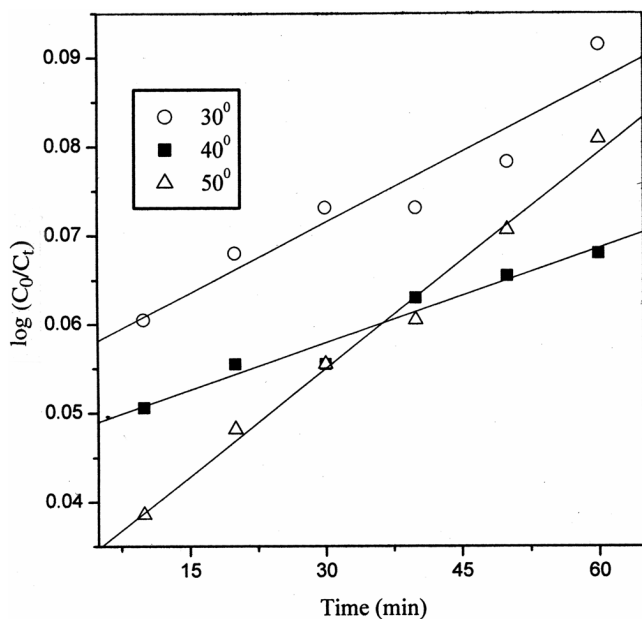


Fig. 7 — Natarajan-Khalaf plot for the adsorption of fluoride ion onto G1
change values. It is interesting to compare the kinetic results available in literature for the removal of fluoride by newspaper carbon³³, where adsorption is clearly dominant over desorption.

Intra-particle diffusion study

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. Since the particles were vigorously agitated during the experiments, it is reasonable to assume that the mass transfer from the bulk liquid to the particle external surface did not limit the rate. One might, then postulate that the rate limiting step might be film or intra-particle diffusion which was tested by plotting a graph between amount of fluoride adsorbed and square root of time (Fig. 8). The double nature of these plots may be explained as the initial curve portions are attributed to boundary layer diffusion effect, while the final linear portions are due to intra-particle diffusion effect^{34, 35}.

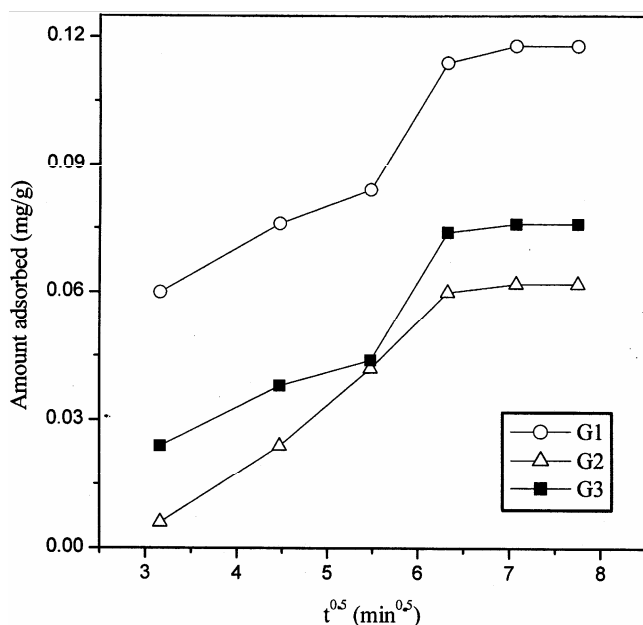


Fig. 8 — Intraparticle diffusion plot for the adsorption of fluoride ion onto graphite

The rate constants for intra-particle diffusion, k_p for the removal of fluoride by the three adsorbents were determined from the slopes of the linear portion of the respective plots. The values of k_p ($\text{mg g}^{-1} \text{min}^{-0.5}$) are 0.0005, 0.007 and 0.003 for G1, G2 and G3 at 30°C respectively. Further, the linear portions of the curves

do not pass the origin in Fig. 8. This indicates that mechanism of removal of fluoride is complex and both the surface adsorption and intra-particle diffusion may contribute to the rate-determining step^{30,36}. The amount of fluoride adsorbed per unit mass of the adsorbent varies in the order $G1 > G3 > G2$ while the intra-particle diffusion rate varies in the order $G2 > G3 > G1$. Thus, the mechanism of adsorption of fluoride onto graphite involves surface adsorption as well as intra-particle diffusion. Further, the lower rate of adsorption over desorption exhibited by graphite may be due to its lower porosity (0.7-53%) than that of activated carbons (>95%)³⁷.

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 adsorption of fluoride ions have been studied.

As a representative case the XRD patterns of the G1 before and after treatment with fluoride ions are shown in Fig. 9a and 9b respectively. It is evident from the figure that the XRD pattern of G1 loaded with fluoride ions exhibits no variation in the crystal

Table 5 — Rate constants for the adsorption of fluoride and the rate constants for forward (k_1) and reverse (k_{-1}) processes

[F] (mg/L)	$10^4 k_{ad}$			$10^4 k_1$			$10^4 k_{-1}$		
	30°	40°	50°C	30°	40°	50°C	30°	40°	50°C
Adsorption onto G1									
2	22.1	56.0	51.0	0.6	18.5	20.9	21.5	37.5	30.1
4	30.0	31.0	61.9	0.7	10.8	24.9	29.3	20.2	37.0
6	23.0	8.4	29.8	1.8	0.9	4.3	21.2	7.5	25.5
8	29.9	28.6	76.0	2.6	4.7	11.4	27.3	23.9	64.6
10	20.3	13.4	18.0	1.3	1.5	2.2	19.0	11.9	15.8
Adsorption onto G2									
2	12.3	8.2	18.6	1.9	1.3	3.1	10.4	6.9	15.5
4	17.8	8.7	18.4	2.7	1.31	2.9	15.1	7.4	15.5
6	4.9	6.7	11.4	0.6	0.8	1.5	4.3	5.9	9.9
8	15.1	16.5	10.3	1.4	1.6	1.1	13.7	14.9	9.2
10	0.103	0.591	0.201	0.9	5.4	1.9	9.4	53.7	18.1
Adsorption onto G3									
2	64.5	19.9	37.5	8.1	3.7	7.7	56.4	16.2	29.8
4	8.7	19.3	6.9	0.8	1.9	0.8	7.9	17.4	6.1
6	71.3	13.7	59.9	4.4	1.1	5.1	66.9	12.6	54.8
8	8.0	7.1	15.7	0.5	0.5	1.1	7.5	6.6	14.6
10	13.4	15.9	17.5	0.7	0.9	1.2	12.7	15.0	16.3

structure and this suggests that the fluoride ions might diffuse into micropores and sorbs mostly by physisorption without altering the structure of the adsorbent³⁸. The above observation corroborated well with batch sorption experiments and thermodynamic results.

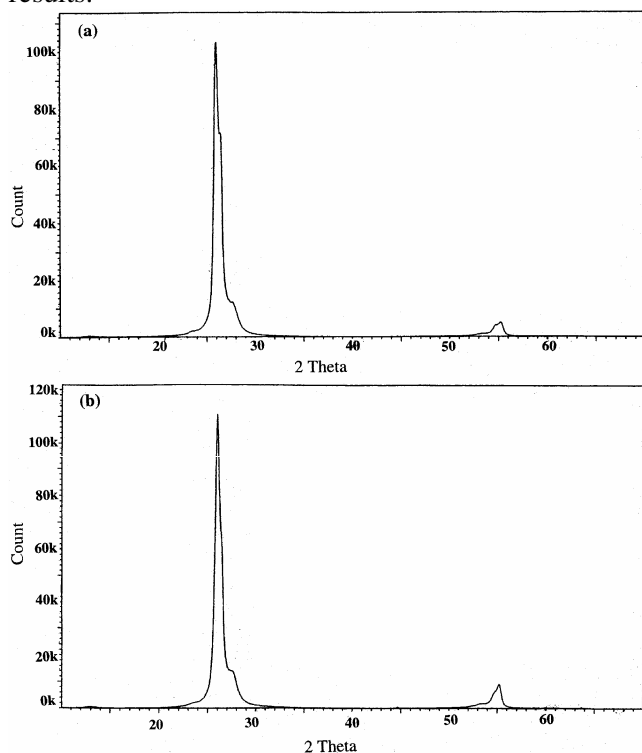


Fig. 9 — XRD pattern of G1 (a) before adsorption and (b) loaded with fluoride ions

Table 6 — Langmuir isotherm parameters for adsorption of fluoride from aqueous solution on different adsorbents

Adsorbent	Langmuir constants		Reference
	Q_0 (mg/g)	b (mg/g)	
Activated alumina	2.41	0.31	39
Fluorspar	1.79	0.091	8
Activated quartz	1.16	0.086	8
Hydroxy apatite	4.54	2.44	8
Calcite	0.39	0.023	8
Quartz	0.19	0.12	8
Titanium rich bauxite	3.70	0.29	40
Plaster of Paris	0.366	0.830	31
NPC	2.732	0.028	6
G1	3.13	0.07	Present work
G2	0.25	0.14	Present work
G3	0.16	0.36	Present work

Adsorption isotherms for fluoride in aqueous solution were compared for different adsorbents and the values of Langmuir constants for the adsorption of fluoride by different adsorbents reported in literature with graphite are summarized in Table 6. Although direct comparison of graphite with other adsorbents is difficult, owing to the different applied experimental conditions, it was found, in general, that the adsorption capacity of graphite for fluoride is comparable with that of other adsorbents.

Conclusion

In batch adsorption studies, data show that various grades of graphite have potential for the removal of fluoride ions from aqueous solutions. Lower range of pH and high temperature ranges were found as the optimum conditions for maximum fluoride adsorption by the adsorbents. The results gained from this study were well described by the Langmuir and Freundlich isotherms. The thermodynamics of the system pointed out the adsorption process was endothermic. On the basis of the kinetic and XRD studies a mechanism in which surface adsorption as well as intra-particle diffusion as rate limiting step has been proposed for the physisorption of fluoride ions onto graphite.

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