DEFLUORIDATION OF WATER BY ADSORPTION ON FLY ASH

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Abstract. The ability of fly ash to remove fluoride from water and wastewaters has been studied at different concentrations, times, temperatures and pH of the solution. The rate constants of adsorption, intraparticle transport, mass transfer coefficients and thermodynamic parameters have been calculated at 30, 40, and 50 °C. The empirical model has been tested at various concentration for the present system. The removal of fluoride is favorable at low concentration, high temperature and acidic pH.

1. Introduction

Wastewaters from fertilizers, glass and ceramic, phosphatic and rubber industries are enriched in fluoride and needs formidable treatment. The highest limit of fluoride in general drinking water is from 0.5 to 1.5 mg L^{-1} (Barnett *et al.*, 1969). It has been observed that with the intake of fluoride above the permissible limit causes skeletal abnormalities and dental fluorosis (Chaturvedi *et al.*, 1988). Long term ingestion of excessive fluoride has a chronic effect on kidney (Waldbott, 1973). Previous investigations show that the fluoride content of water can be reduced to the desired limit by precipitation and adsorption (Choi and Kenneth, 1979). Adsorption involves the contact of the fluoride containing water with an appropriate adsorbent. Recent research demonstrates the feasibility of waste products to decontaminate wastewaters containing metal ions and other toxic pollutants. Fly ash has been successfully used by several investigators (Yadava, *et al.*, 1987; Panday *et al.*, 1985) for the removal of metal ions from water and wastewaters. The present investigation is undertaken to test the use of fly ash for fluoride removal from water and wastewaters instead of costly adsorbents such as activated carbon, activated alumina, activated bauxite, etc. Adsorption techniques have been found to be useful means for controlling the extent of water pollution due to metallic species (McKay *et al.*, 1980; Singh *et al.*, 1984; Panday *et al.*, 1984, 1985).

2. Materials and Methods

Fly ash was obtained from Obera Thermal Power Plant, Mirzapur (U.P.). The adsorbent was sieved through 53 μm and used as such without any pretreatment. The surface area was determined by a 'three point', N_2 gas adsorption method

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using model 85–7 Quantasorb surface area analyzer (Quantachrome Corp., U.S.A.). The mean particle size was measured by HIAC - 320, Model 8002971 (Royco Inst. Division, U.S.A.). The porosity and density were determined by mercury porosimetry and specific gravity bottle, respectively. The constituents of fly ash were analyzed by using Indian Standard Methods (1960). Standard fluoride solution was prepared by dissolving 221.0 mg anhydrous sodium fluoride in 1000 mL deionized - distilled water (fluoride concentration: 100 mg L^{-1}). The experimental solutions of desired concentrations were prepared by appropriate dilutions. The desired pH of the solution was maintained using 0.5 M NaOH and HCl. Different polythene bottles containing 1.0 g fly ash and 50 mL fluoride solution of desired concentration and pH were agitated in a shaking incubator at constant temperature for different time intervals. The speed of agitation (125 rpm) was kept constant for each run throughout the experiment to ensure equal mixing. After predetermined time interval, the adsorbent and adsorbate were separated by centrifugation (at 12000 rev) for 5 min and supernatant liquid was analyzed spectrophotometrically for residual fluoride content by SPADNS method (Choi and Kenneth, 1979).

3. Results and Discussions

3.1. CHARACTERIZATION OF ADSORBENT

SiO_2 and Al_2O_3 are the major constituents of fly ash (Table I) and other oxides are present in trace amounts. It is thus expected that fluoride will be mostly adsorbed either by any or by a combined influence of the major oxides present in the adsorbent.

3.2. EFFECT OF CONCENTRATION AND CONTACT TIME

Removal of fluoride by adsorption on fly ash increases with time upto 120 min, thereafter, it becomes constant. With the increase in the initial fluoride concentration from 5 to 15 mg L^{-1}, the amount adsorbed increases from 0.2240 to 0.6150 mg

TABLE I

Characterisation of fly ash

Constituent	% by weight
SiO_2	56.04
Al_2O_3	25.90
CaO	2.22
Fe_2O_3	1.26
MgO	0.94
Loss of ignition	13.64
Mean particle size	46×10^{-4} cm
Surface area	5.77 $m^2 g^{-1}$
Density	3.42 g cm^{-3}
Porosity	0.38
pH_{ZPC}	2.40

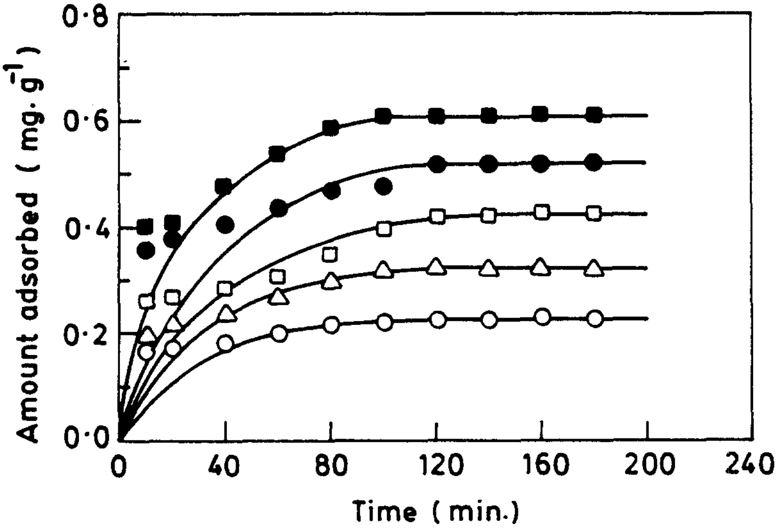


Fig. 1. Effect of concentration on removal of fluoride by fly ash, (o) 5 mg L^{-1}, (Δ) 7.5 mg L^{-1}, (□) 10 mg L^{-1}, (●) 12.5 mg L^{-1}, (■) 15 mg L^{-1}. Conditions: 30 °C Temperature, 6.5 pH.

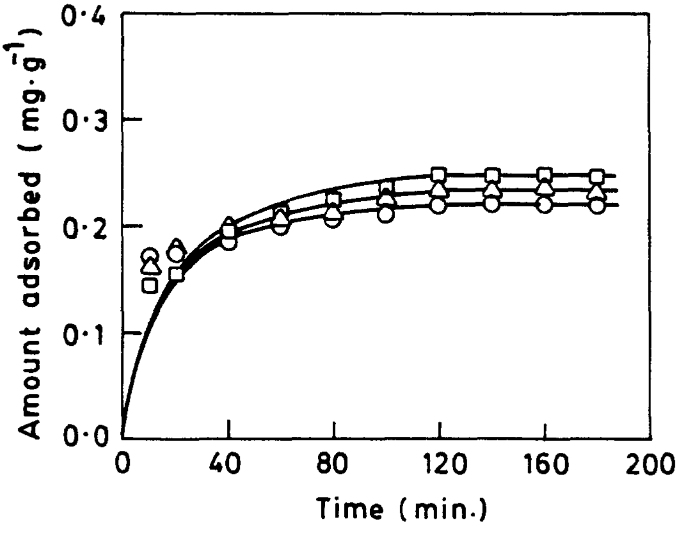


Fig. 2. Effect of temperature on removal of fluoride by fly ash, (o) 30 °C, (Δ) 40 °C, (□) 50 °C, Conditions: 10 mg L^{-1} concentration, 6.5 pH.

g^{-1} (Figure 1) while percentage of adsorption decreases from 89.6 to 82% at 30 °C and 6.5 pH. It is thus clear that defluoridation is highly concentration dependent.

3.3. EFFECT OF TEMPERATURE

With an increase in temperature from 30 to 50 °C, using 10 mg L^{-1} of fluoride solution, the adsorption of fluoride increases from 0.4280 mg g^{-1} (85.60%) to 0.4700 mg g^{-1} (94%) at 6.5 pH (Figure 2). This shows the endothermic nature of the adsorption process (Malcolm *et al.*, 1978; Panday *et al.*, 1985).

3.4. ADSORPTION DYNAMICS

3.4.1. *Determination of Rate Constant of Adsorption and Intraparticle Diffusion*

The rate of fluoride uptake by fly ash has been discussed in the light of the adherence of fluoride on the active surface sites of adsorbent as well as its intraparticle diffusion within the pores of adsorbent. The removal of fluoride by adsorption on fly ash follows first order rate expression (Lagergren and Bil, 1898):

$$\log(q_e\text{-}q) = \log q_e - \frac{K}{2.303}\, t \tag{1}$$

where, q_e is the amount adsorbed (mg g^{-1}) at equilibrium and q is the amount adsorbed (mg g^{-1}) at time t. The values of rate constants of adsorption K were calculated from slope of the linear plots of log $(q_e\text{-}q)$ *vs* t (Figure 3) and found to be 1.8145×10^{-2}, 4.0052×10^{-2} and 5.3146×10^{-2} min^{-1} at 30, 40 and 50 °C, respectively.

In a batch process, there is also the possibility of transport of fluoride from bulk into the pores of the adsorbent due to a rapid stirring.

The rate constants of intraparticle diffusion at different temperatures were determined by the slopes of the plots of amount adsorbed *vs* square root of time $(\text{min})^{1/2}$ (Figure 4) and found to be 6.3830×10^{-3}, 9.6492×10^{-3} and 14.4230×10^{-3} mg g^{-1} $\text{min}^{-1/2}$ at 30, 40, and 50 °C, respectively.

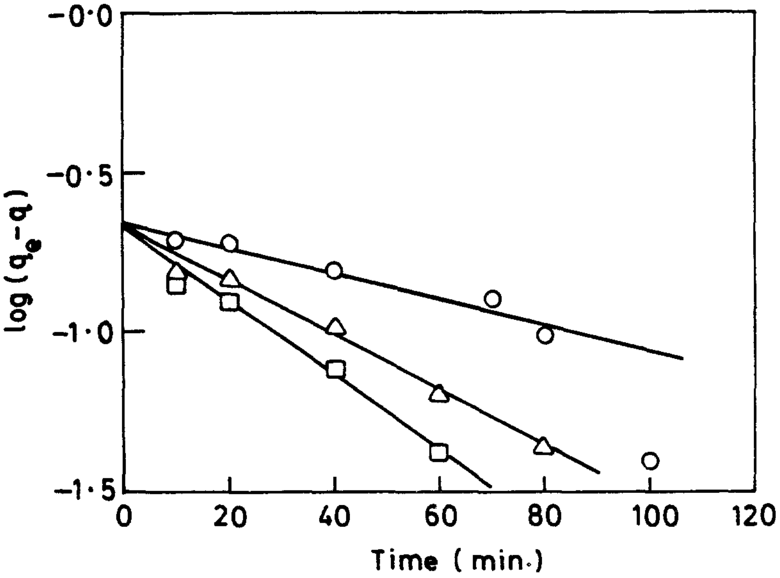


Fig. 3. Plots for rate constants of adsorption at different temperatures. (o) 30 °C, (Δ) 40 °C, (□) 50 °C, Conditions: 10 mg L^{-1} concentration, 6.5 pH.

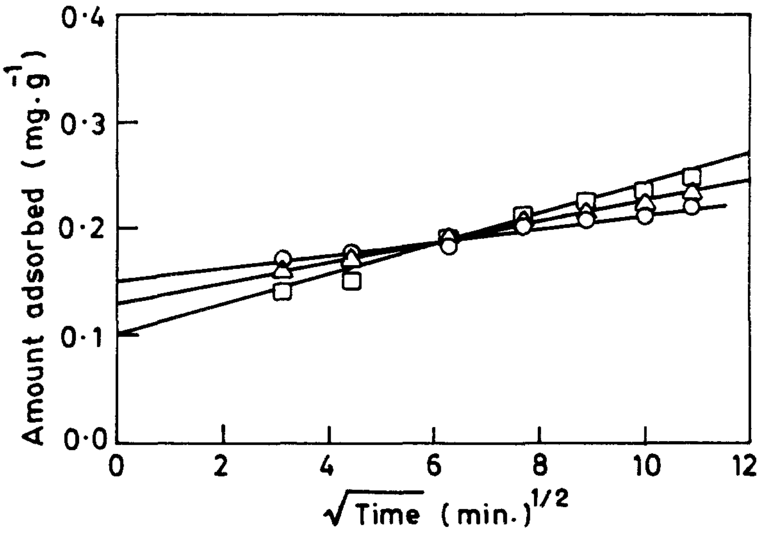


Fig. 4. Intraparticle diffusion plot for the adsorption of fluoride on fly ash, (o) 30 °C, (Δ) 40 °C, (□) 50 °C. Conditions: 10 mg L^{-1} concentration, 6.5 pH.

3.4.2. *Determination of Mass Transfer Coefficients*

The mass transfer coefficient, β_1 for the adsorption of fluoride on fly ash was determined using the following relationship (McKay *et al.*, 1981):

$$\ln\left(\frac{C_t}{C_0}-\frac{1}{1+mK}\right)=\ln\frac{mK}{1+mK}-\frac{1+\mathrm{mK}}{mK}\beta_1 S_s t \tag{2}$$

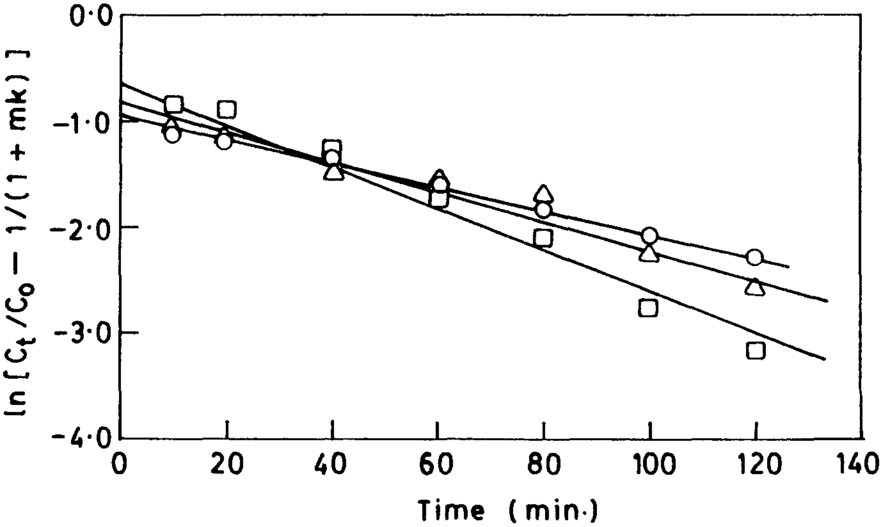


Fig. 5. Mass transfer plot (McKay *et al.*, 1981) for the adsorption of fluoride on fly ash, (o) 30 °C, (Δ) 40 °C, (□) 50 °C. Conditions: 10 mg L^{-1} concentration, 6.5 pH.

TABLE II

Mass transfer coefficients and Langmuir constants at different temperatures

Temperature (°C)	β_l (cm S^{-1})	Q^0 (mg g^{-1})	b (L mg^{-1})	K (L g^{-1})
30	1.26×10^{-4}	20.00	0.54	10.81
40	1.38×10^{-4}	20.43	0.75	27.14
50	1.42×10^{-4}	23.33	1.32	30.76

where, C_0 is the initial concentration of fluoride (mg L^{-1}), C_t the fluoride concentration (mg L^{-1}) after time t; m the mass of fly ash per unit volume of particle free solution (g L^{-1}), K (L g^{-1}) the product of Langmuir constants Q^0 and b and S_s the outer surface of adsorbent per unit volume of particle free slurry (cm^{-1}). The value of mass transfer coefficients were calculated from the slopes and intercepts of the straight line plots of ln $[(C_t/C_0) - 1/(1+mK)]$ *vs* t (Figure 5) and tabulated in Table II). Table II shows that the values of mass transfer coefficients increase with the increase in temperature. Thus, high temperature favors the removal of fluoride from water.

3.5. Adsorption isotherm

The distribution of fluoride between the solid-solution interface at equilibrium has been described by the Langmuir equation (Panday *et al.* 1984):

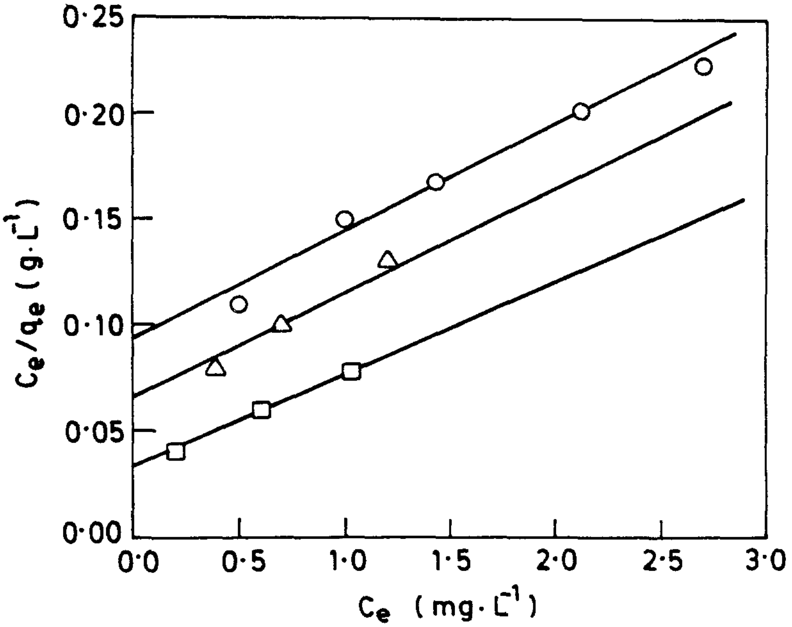


Fig. 6. Langmuir plot for the removal of fluoride by fly ash (o) 30 °C, (Δ) 40 °C, (□) 50 °C. Conditions: 6.5 pH.

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0}. \tag{3}$$

The constant Q^0 signifies the adsorption capacity and b is related with the energy of adsorption. The values of Q^0 and b were calculated from the slopes and intercepts of the linear plots C_e/q_e *vs* C_e (Figure 6) and shown in Table II. Plots of C_e/q_e *vs* C_e give straight lines at different temperatures suggesting applicability of the Langmuir isotherm for the present system. It is clear from the Table II that the adsorption capacity of fly ash removal of fluoride increases with rise of solution temperature.

3.6. EMPIRICAL MODEL

The following empirical mathematical relationship (Prakash *et al.*, 1987; Yadava *et al.*, 1988) has been tested with the help of kinetic data obtained from the batch adsorption technique at various fluoride concentrations:

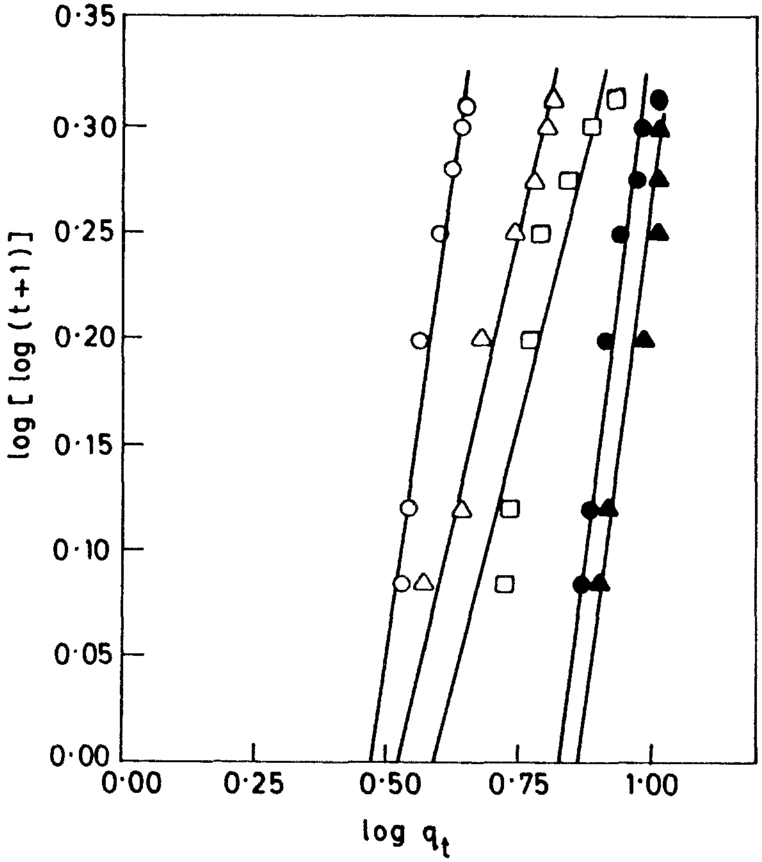


Fig. 7. Kinetics of fluoride removal by adsorption on fly ash. Conditions: (o) 5 mg L^{-1}, (Δ) 7.5 mg L^{-1}, (□) 10 mg L^{-1}, (●) 12.5 mg L^{-1}, (■) 15 mg L^{-1}; 30 °C Temperature, 6.5 pH.

$$\mathrm{Log}(t+1) = K(q_t)^{\mathrm{A}} \tag{4}$$

in which q_t is the amount adsorbed mg L^{-1} of fluoride in solution at time t, t is the time in minutes, K and A signify empirical constants. The values of K and A depend on C_0. The straight line plots of log $(t+1)$ *vs* $\log(q_t)^A$ (Figure 7) suggesting the suitability of the model at various concentrations for the present system. The values of K and A have been determined from the slopes and intercepts of the straight line plots from Figure 7 and the values of K and A at various concentrations are shown in Figure 8.

The percentage removal of fluoride with time can be found using

$$\left(\frac{q_t}{C_0} \times 100\right) = \frac{100}{C_0}\,\frac{\log_{10}(t+1)^{1/\mathrm{A}}}{K} \tag{5}$$

where C_0 is initial concentration of adsorbate. The rate of removal of fluoride with time can be found using:

$$\frac{\mathrm{d}_c}{\mathrm{d}_t} = \frac{\mathrm{d}}{\mathrm{d}_t}\,\frac{\log_{10}(t+1)^{1/\mathrm{A}}}{K}. \tag{6}$$

The value of K increases with increase in initial concentration (Figure 8) while

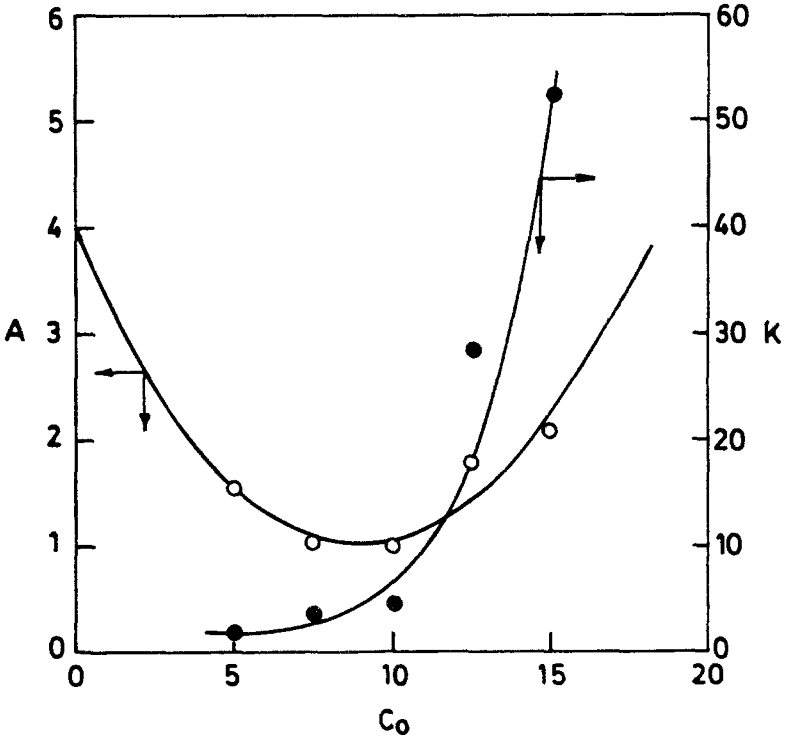


Fig. 8. Variation of K and A with C_0. Conditions: 30 °C temperature, 6.5 pH.

the behavior of A is quite different with the concentration range studied. The value of A decreases with increase in initial concentration upto 10 mg L^{-1} and then again increases with increase in concentration (Figure 8).

3.7. DETERMINATION OF THERMODYNAMIC PARAMETERS

The thermodynamic parameters for the adsorption of fluoride on fly ash have been calculated at different temperatures using the following relationships (Jain *et al.*, 1979):

$$\Delta G^0 = -RT \ln K \tag{7}$$

$$\Delta H^0 = R\left(\frac{T_2\ T_1}{T_2 - T_1}\right) \ln \frac{K''}{K'} \tag{8}$$

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} \tag{9}$$

where, K, K', and K'' are the equilibrium constants at temperature T, T_1 and T_2, respectively. The values of ΔG^0, ΔH^0, and ΔS^0 were placed in Table III. The negative value of free energy change (ΔG^0) indicates that the process of adsorption is spontaneous i.e., the adsorptive forces are quite strong to overcome the potential barrier. It is also evident from the Table III that the enthalpy changes (ΔH^0) are positive for the present system, suggesting the process to be endothermic. Further, positive values of ΔS^0 suggests the increased randomness at the solid-solution interface during the adsorption of fluoride on fly ash.

3.8. EFFECT OF pH

The removal of fluoride by adsorption on fly ash was found to increase from 79 to 94% (Figure 9) with the change in pH of the fluoride solution (10 mg L^{-1}) from 2.0 to 6.5 at 30 °C. Such type of changes are particularly observed in the case of adsorption of strong hydrolyozable cations (James and Healy, 1972). Fly ash contains metal oxides which are hydroxylated in aqueous solution. Such an interface on acid base dissociation develops positive and negative charges on the surface (Panday *et al.*, 1983; Chaturvedi *et al.*, 1988) as follows:

TABLE III

Thermodynamic parameters at different temperatures

Temperature (°C)	$-\Delta G^0$ (kcal mol^{-1})	ΔH^0 (kcal mol^{-1})	ΔS^0 (e.u.)
30	1.2970	6.491	17.141
40	1.5530	6.919	17.143
50	2.0396	–	–

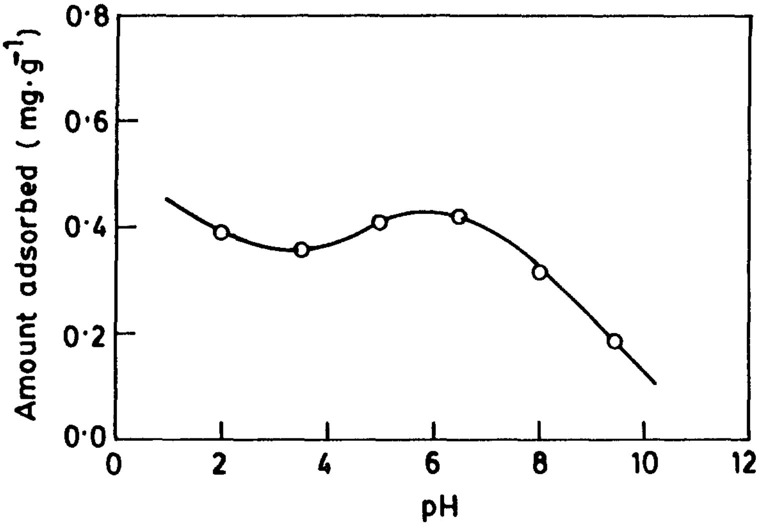
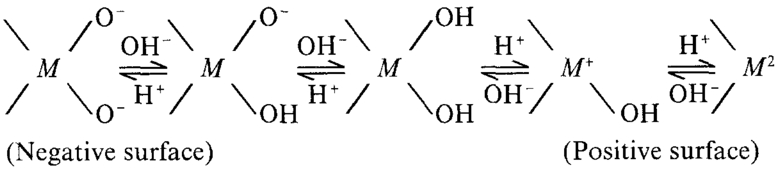


Fig. 9. Effect of pH on the removal of fluoride by fly ash. Conditions: 10 mg L^{-1} concentration and 30 °C temperature.



(10)

where *M* represents Al, Si, Ca, etc. The change in removal of fluoride with pH may also be explained in the light of electrophoretic mobility results. The pH_{ZPC} for fly ash is 2.4, while for alumina and silica pH_{ZPC} are reported to be 8.2 and 2.3, respectively. The change in solubility of alumina with pH shows a maximum near the neutral pH range (Yadava *et al.*, 1987).

4. Conclusion

The present investigation thus indicates the ability of fly ash to remove fluoride from water in a simple and economic way. The data thus obtained may be helpful for designing and fabricating a treatment plant for the defluoridation of water and wastewaters.

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