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Evaluation of Thermodynamic Parameters for Separation of Hexavalent Chromium by Fly Ash

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ABSTRACT

Kinetics and thermodynamic parameters of Cr^{6+} separation by fly ash from aqueous solution has been evaluated. It was found that the separation process is partly diffusion controlled and endothermic in nature. The mass transfer coefficient increases with an increase in temperature. The activation energy and change of enthalpy were also evaluated and found to be 17.5 kJ/mol and 14.47 kcal/mol, respectively. The free energy of the process was small but positive, and it decreases with an increase of temperature. The change of entropy was found to be small and remains unchanged over the 30 to 50°C temperature range. This process follows the Langmuir isotherm model where Q_0 and b were also determined at different temperatures.

Key Word. Fly ash; Hexavalent chromium; Enthalpy; Entropy; Activation energy; Mass transfer coefficient; Langmuir isotherm; Free energy; Pore diffusion

INTRODUCTION

Hexavalent chromium is a major pollutant which originates from electroplating, tanning, anodizing, chrome mining, etc. Although the most

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widely used method for controlling hexavalent chromium pollution is by reducting it to the trivalent state by reacting it with ferrous sulfate or sodium bisulfite followed by its precipitation as chromium(III) hydroxide (1). However, this method of treatment has its own limitation due to the formation of an enormous quantity of sludge as well as an increase in the dissolve solid content of the treated effluent. Separation of waste metal from effluent by surface adsorption by using active adsorbents like alumina (2), activated carbon (3), and ferric oxide (4, 5) is gaining importance since it does not produce sludge. The adsorbed metal could be reused after its recovery through backwashing the column and simultaneously regenerating the column. The possibility of utilizing fly ash as an adsorbing medium for the separation of chromium is well documented in our previous studies (6). However, the main objective of the present study is to evaluate such thermodynamic parameter as activation energy (ΔE), enthalpy (ΔH), entropy (ΔS), and free energy (ΔG) for separation of Cr^{6+} by fly ash.

EXPERIMENTAL METHODOLOGY

All the reagent used were obtained from BDH and are of AR grade. Cr^{6+} solution was prepared by dissolving potassium dichromate. The pH was adjusted with 0.1 N H_2SO_4 or 0.1 N NaOH. Two grams of fly ash was added to 50 mL of Cr^{6+} solution in a connical flask with a stopcork. The temperature was kept constant and the solution was stirred continuously at 120 rpm. To study the degree of separation, a number of aliquot were withdrawn, filtered, washed, and ultimately the concentration of Cr^{6+} was estimated spectrophotometrically (7) at 540 nm. The separation of Cr^{6+} by fly ash was carried out at pH 2.0 while varying the temperature from 30 to 50°C. Isotherms were plotted.

RESULT AND DISCUSSION

Molecules are often diffused into the interior of a porous adsorbent in an adsorption experiment. The rate process of such a pore diffusion usually depends on t^x, where $x \leq 0.5$, instead of t itself. In the present investigation it was found that a plot of c_t/c_0 against $t^{0.5}$ is linear. This observation is in good agreement with Grover and Narayanswamy (8). The rate constant of pore diffusion (k') was determined according to the following equation (9):

$$c_t/c_0 = k't^{0.5} \qquad (1)$$

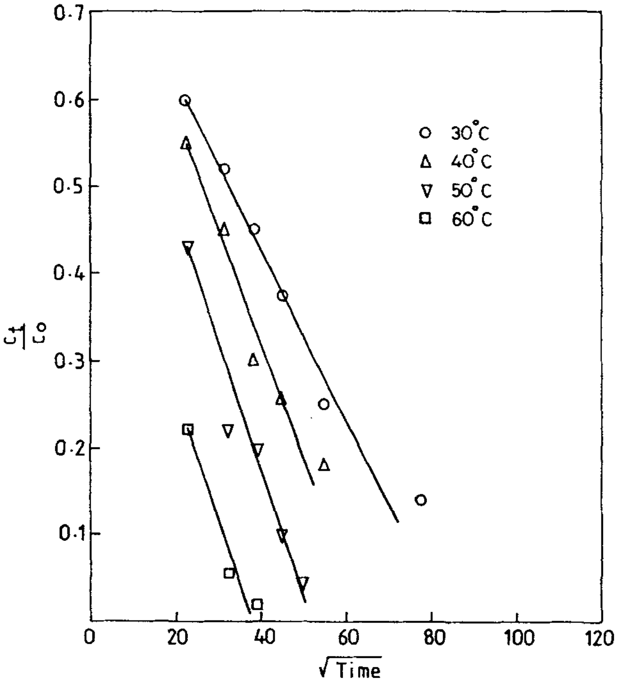


FIG. 1 Variation of fraction of Cr^{6+} adsorbed by fly ash with square root of time at pH 2.0.

The variation of the fraction of chromium(VI) adsorbed with square root of time at different temperatures is shown in Fig. 1, and values of the pore diffusion constant are listed in Table 1.

Very often the pore diffusion constant was utilized by earlier investigators (9, 10) for determination of the activation energy of the separation

TABLE 1
Pore Diffusion Constant, Mass Transfer Coefficient, and Langmuir Constant at Different Temperatures for Cr^{6+} Separation by Fly Ash at pH 2.0

Temperature (°C)	k' ($\min^{-1/2}$)	β_l (cm^{-1})	Q_0 ($mg \cdot g^{-1}$)	b ($l\ mg^{-1}$)
30	0.93×10^{-2}	2.0×10^{-5}	0.20	0.14
40	1.27×10^{-2}	2.68×10^{-5}	0.19	0.28
50	1.46×10^{-2}	2.96×10^{-5}	0.16	0.49

process at a solid–liquid interface. Transfer of Cr^{6+} from an aqueous solution to solid a fly-ash surface or pores can be accepted as a activated adsorption phenomenon. The extent of activation energy of the process is determined by the Arrhenius equation:

$$\ln k' = \ln A - E/RT \tag{2}$$

Plotting ln k' against $1/T$ gives a linear plot (Fig. 2), from which the activation energy is found to be 17.5 kJ/mol.

The mass transfer coefficient for the separation process of Cr^{6+} was determined according to

$$\ln\left(\frac{c_t}{c_0} - \frac{1}{1 + mk}\right) = \ln\frac{mk}{1 + mk} - \frac{1 + mk}{mk}\beta_l S_s t \tag{3}$$

Plotting the left-hand side of Eq. (3) against t gives a straight line for various temperatures (Fig. 3). The mass transfer coefficient β_l was determined from the slope of the curve. The values of m and S_s were calculated from

$$m = w/v \tag{4}$$

$$S_s = \frac{6m}{d_p\rho_p(1 - \xi_p)} \tag{5}$$

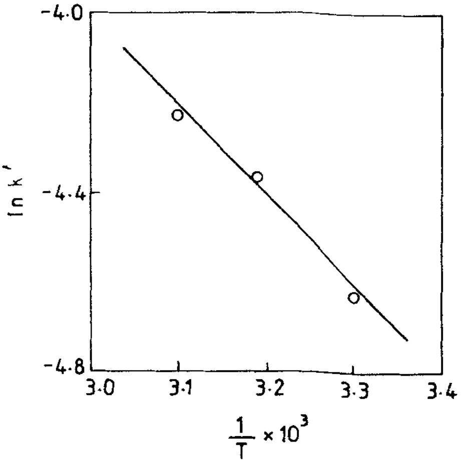


FIG. 2 Variation of pore diffusion constant of Cr^{6+} with reciprocal of temperature (Arrhenius plot).

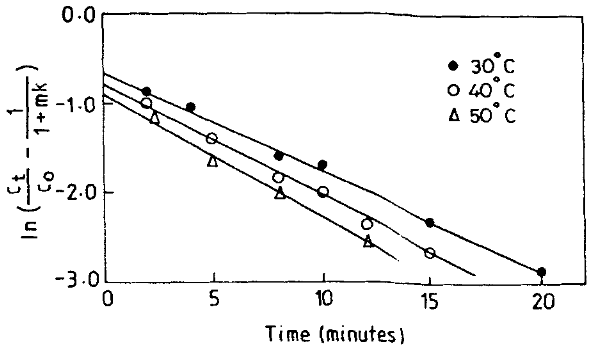


FIG. 3 Variation of ln (c_t/c_0 − 1/1 + mK) with time in a batch Cr^{6+} separation experiment at pH 2.0.

The values of the mass transfer coefficient are shown in Table 1. They suggests that the velocity of mass transfer of chromium(VI) from bulk to the surface of fly ash is rapid enough to use the adsorbent for the separation of chromium(VI) from contaminated wastewater. A similar observation was reported by Grover et al. (8). Moreover, the product of β_1 and S_s is proportional to the overall rate constant ($\beta_1 S_s \alpha k$).

Separation Isotherm

The uptake of chromium(VI) by fly ash with time has been analyzed with the help of the Langmuir model. The modified Langmuir model used in this study is

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \tag{6}$$

Figure 4 is a plot of C_e/q_e against C_e. The straight line at different temperatures reveals the adaptability of the Langmuir isotherm. The values of Q_0 and b, two constants of the Langmuir isotherm, are presented in Table 1. The constant Q_0 signifies the adsorption capacity and b is related to the energy of adsorption. Since the value of Q_0 decreases from 0.2 to 0.166 with an increase of temperature from 30 to 50°C, the rate of surface adsorption decreases with an increase of temperature.

Thermodynamic parameter like enthalpy (ΔH), free energy (ΔG), and entropy (ΔS) for chromium(VI) separation by fly ash were calculated using following equations:

$$\ln b = \ln b' - \Delta H/RT \tag{7}$$

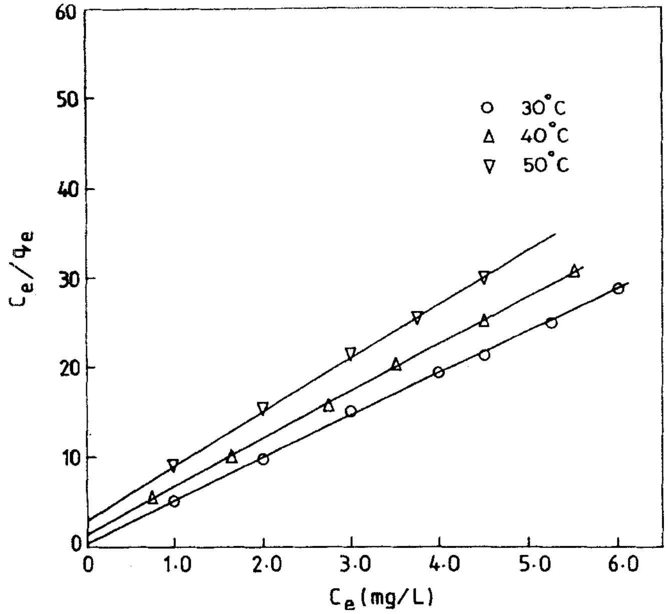


FIG. 4 Langmuir isotherm plot for Cr^{6+} adsorption by fly ash.

$$\ln(1/b) = \Delta G/RT \tag{8}$$

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

The enthalpy change, ΔH, is determined graphically by plotting ln b against $1/T$, which gives a straight line (Fig. 5). ΔH was found to be 14.47 kcal/mol. The values of ΔG and ΔS were computed numerically and are presented in Table 2. ΔG is very small and positive. Its values decreases with an increase of temperature, which indicates that better separation is obtained at higher temperature, which is supported by earlier investigations (10, 11). The positive values of entropy may be due to some structural changes in both the adsorbate and adsorbent during the separation process.

Proposed Mechanism of Separation Process

It is believed that the overall separation of chromium(VI) from an aqueous solution is governed by three factors: surface adsorption, pore diffusion and ion exchange. Due to surface activity (pH_{zpc}), fly ash particles

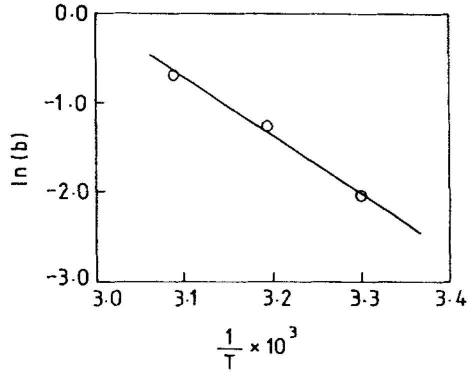


FIG. 5 Variation of ln(*b*) with reciprocal of temperature for Cr^{6+} separation by fly ash.

are capable of adsorbing adsorbate molecules on the surface, and the contribution of surface adsorption to the overall separation capacity decreases with an increase of temperature due to an increase in the kinetic movement of the adsorbate ion. This effect is predominant in the case of chromate ion due to its large size in comparison to such cationic ions as Zn^{2+}, Cu^{+}, and Pb^{2+}. It is further confirmed in Fig. 6 that the uptake of chromium(VI) by fly ash increases steadily to a maximum, then remains constant at a particular temperature. However, a slight decrease in adsorption capacity has also been observed at higher temperature (60°C) when the separation was carried out for a prolonged period of time.

Favorable separation in acidic pH may be explained on the basis of an ion-exchange mechanism. The oxides of metals present in the adsorbent form aqua complexes with water and develop a charged surface through amphoteric dissociation at varying pH:

TABLE 2
Thermodynamic Parameters for Cr^{6+} Separation by Fly Ash at Different Temperatures

Temperature (°C)	ΔG (Kcal·mol^{-1})	ΔS (cal·mol^{-1}·degree^{-1})
30	1.18	38.9
40	0.78	38.8
50	0.44	38.7

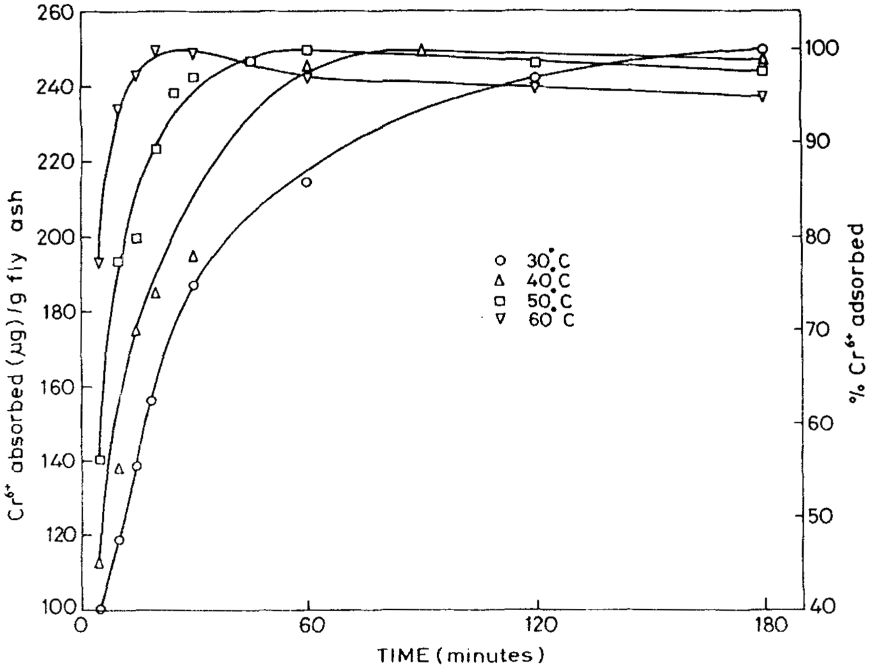
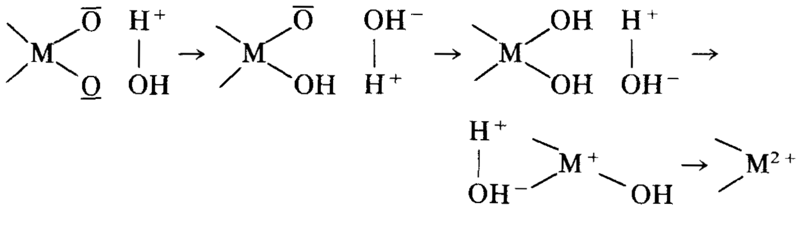


FIG. 6 Variation of Cr^{6+} separation of fly ash with time at different temperatures.



A positive charge develops on the surface of the oxides of the adsorbent in acidic medium. Thus the fly ash surface attracts the negatively charged chromate ion more effectively due to strong electrostatic attraction.

As observed earlier in our study, pore diffusivity of adsorbate increases with an increase of temperature. This is faciliated for fly ash when it is treated with acidic solution. Figure 7 represents the release of Ca^{2+} and Mg^{2+} ions to the aqueous solution when exchanged with Cr^{6+} in fly ash at different time interval. It was found that the initial release of Ca^{2+} and Mg^{2+} ions is much less than the quantity of Cr^{6+} uptake, but in the later

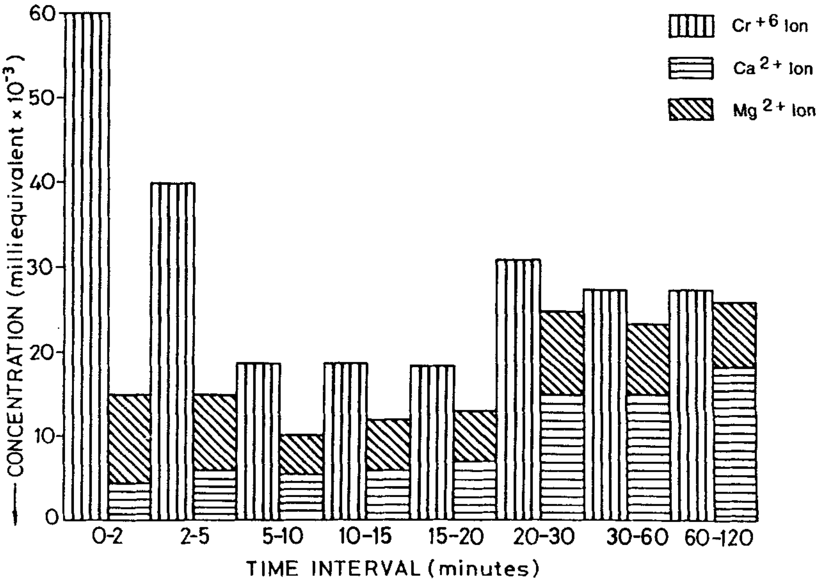


FIG. 7 Bar chart showing Cr^{6+} absorption in different time intervals and corresponding release of Ca^{2+} and Mg^{2+} ions in a batch experiment.

stage the release of Ca^{2+} and Mg^{2+} ion is almost equal to Cr^{6+} uptake. This may be explained by the fact that in the later stage of separation, pore diffusion predominates after saturation of the surface adsorption.

CONCLUSION

In the present study the separation of Cr^{6+} by fly ash has been found to be satisfactory. Such thermodynamic parameters as enthalpy (ΔH), entropy (ΔS), free energy (ΔG), and the mass transfer coefficient (β_l) as evaluated in this study will be of immense help in designing a commercial process.

NOMENCLATURE

t	time (min)
c_t	concentration of Cr^{6+} at time t ($mg \cdot L^{-1}$)
c_0	initial concentration of Cr^{6+} ($mg \cdot L^{-1}$)
k'	rate constant of pore diffusion ($min^{-1/2}$)
E	activation energy ($kJ \cdot mol^{-1}$)

T	solution temperature (K)
m	mass of fly-ash particle per unit volume of particle-free slurry ($g \cdot L^{-1}$)
k	rate constant of adsorption (min^{-1})
β_1	mass transfer coefficient ($cm \cdot s^{-1}$)
S_s	outer surface of fly-ash particles per unit volume of particle-free slurry (cm^{-1})
w	weight of adsorbent (g)
v	volume of particle-free solution (L)
d_p	particle diameter (cm)
ρ_p	density of fly-ash particle ($g \cdot L^{-1}$)
ξ_p	porosity of fly-ash particle ($cm \cdot cm^{-1}$)
C_e	equilibrium concentration of Cr^{6+} in solution ($mg \cdot L^{-1}$)
q_e	amount of Cr^{6+} adsorbed at equilibrium ($mg \cdot g \cdot L^{-1}$)
Q_0	Langmuir constant related to the adsorption capacity ($mg \cdot g \cdot L^{-1}$)
b	Langmuir constant related to the energy adsorption ($L \cdot mg^{-1}$)
ΔH	enthalpy change for adsorption of Cr^{6+} on fly ash ($kcal \cdot mol^{-1}$)
ΔG	free energy change of adsorption of Cr^{6+} on fly ash ($kcal \cdot mol^{-1}$)
ΔS	entropy change for adsorption of Cr^{6+} on fly ash ($cal \cdot mol^{-1}$)

REFERENCES

1. S. P. Pande, D. N. Kulkarni, and D. M. Dharmadhikari, "The Impact of Chromite Mining on the Environment and Appropriate Solution—A Case Study," *Impact Min. Environ.*, pp. 245–252 (1994).
2. S. S. Bokade, V. P. Thergaonkar, and A. M. Deshkar, "Spoiled Alumina as an Absorbent," *Indian J. Environ., Health*, *32*(4), 383–388 (1990).
3. A. R. Bowers and C. P. Huang, "Activated Carbon Processes for the Treatment of Chromium(VI)-Containing Industrial Waste Waters," *Prog. Water Technol.*, *12*, 629–650 (1980).
4. J. M. Zachara, D. C. Girvin, R. L. Schmidt, and C. R. Thomas, "Chromate Adsorption on Amorphous Iron Hydroxide in the Presence of Major Ground Water Ions," *Environ. Sci. Technol.*, *21*, 289–594 (1987).
5. T. Aoki and M. Munemori, "Recovery of Chromium(VI) from Waste Waters with Iron(III) Hydroxide," *Water Res.*, *16*, 797–799 (1982).
6. G. P. Dasmahapatra, T. K. Pal, A. Bhadra, and B. Bhattacharya, "Studies on Separation Characteristics of Hexavalent Chromium from Aqueous Solution by Fly Ash," *Sep. Sci. Technol.*, *31*, 2001–2009 (1996).
7. *APHA Standard Methods for Examination of Water and Waste Water*, 17th ed., American Public Health Association, New York, NY, 1989.
8. M. Grover and M. S. Narayanswamy, "Removal of Hexavalent Chromium by Absorption on Fly-ash," *IE(I) J.—EN 63*, 36–39 (1982).
9. W. J. Weber and C. J. Morris, "Kinetics of Adsorption of Carbon from Solution," *J. Sanit. Eng. Div., Am. Soc. Civ. Eng.*, *89*(SA2), 31 (1963).

10. A. N. Singh, D. P. Singh, and V. N. Singh, "Fly-ash for the Treatment of Zn(II) Rich Effluent," *Environmentalist*, *11*(3), 217–224 (1991).
11. K. K. Pandey, G. Prasad, and V. N. Singh, "Removal of Cr(VI) from Aqueous Solutions by Adsorption on Fly-ash Wollastonite," *J. Chem. Technol. Biotechnol.*, *34A*, 367–374 (1984).

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