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REMOVAL OF HEXAVALENT CHROMIUM BY ADSORPTION ONTO FIRECLAY AND IMPREGNATED FIRECLAY

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ABSTRACT

The removal of hexavalent chromium from its aqueous solutions by adsorption onto fireclay (FC) and impregnated fireclay (IFC) has been studied at 30°C. The adsorption process follows the Langmuir-type adsorption behavior, and the extent of adsorption is more for impregnated fireclay. It is found that electrostatic and H-bonding interactions play a key role in binding the adsorbate molecules to the adsorbent surface. The adsorption process is affected greatly by variation in pH and temperature of the system. Low pH and high temperature favor the adsorption process.

Various kinetic and adsorption parameters such as rate constant for adsorption, intraparticle diffusion rate constant, diffusion coefficient, and adsorption capacity have been evaluated to reflect the experimental findings.

Key Words: Adsorption; Fireclay; Impregnated fireclay; Hexavalent chromium.

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INTRODUCTION

Hexavalent chromium, one of the inorganic pollutants with well-known toxicity (1), is used extensively in industries such as electroplating, tanning, anodizing, and chrome mining. Strong exposure of chromium may cause cancer in the digestive tract and lungs (2). The chromium compounds may cause epigastric pain, nausea, vomiting, severe diarrhea, and hemorrhage (3). Therefore, it is essential to remove Cr(VI) from industrial effluents before it is mixed with drinking water sources. Conventional methods for the removal of Cr(VI) from wastewater include chemical precipation, ion exchange, electrolysis, and reverse osmosis (4,5). However, owing to the operational difficulties and cost of the treatment, attempts have been made to develop new methods. One among them is the adsorption on low-cost adsorbents. Some of the adsorbents used in the removal of hexavalent chromium include rice husk carbon (6), saw dust (7), fly ash (8), bituminous coal (9), wood charcoal (10), starch-based products (11), kendu fruit gum dust (12), lignite coal (13), and drumstick gum dust (14). In this connection, this paper describes the removal of hexavalent chromium from its aqueous solutions by adsorption onto fireclay and impregnated fireclay. The impregnation by Al^{3+} and Fe^{3+} ions on the fireclay results in the accomodation of these ions on the surface of silica in tetrahedral coordination. The purpose of impregnation is simply to increase the removal efficiency of fireclay.

EXPERIMENTAL

Fireclay was obtained from Bagharaji village of district Jabalpur in the state of Madhya Pradesh and was fractionated into different fractions of varying particle sizes (100–290 μm) by passing through standard sieves of mesh sizes 52, 100, and 150, having geometrical mean particle diameter of 290, 150, and 100 μm, respectively. The surface area of the adsorbent was determined by a three-point N_2 gas adsorption method. The porosity and density of the adsorbent were determined by using a mercury porosimeter and specific gravity bottle, respectively. The clay was analyzed by Indian standard methods of chemical analysis of fireclay and silica refractory materials (15). The characteristics of the adsorbents are: Al_2O_3, 23%; SiO_2, 68%; Fe_2O_3, 1.3%; TiO_2, 1.1%; CaO, 1.1%; loss on ignition, 5.1%; porosity, 0.34 specific gravity, 1.38 g dm^{-3}; mean particle size, 13.7×10^{-3} cm; and surface area, 9.64 m^2 g^{-1}. The particle size and the surface area are given for the particle passed through 150 μm mesh sized sieve, because these particles were used only for the whole investigation.

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Impregnation with Fe^{3+} Ions

The fireclay retained on the sieve with mesh size number 150 (with the mean particle diameter 150 μm) was impregnated with 0.1 M ferric chloride solution. This fraction was selected due to its high particle distribution. For impregnation, 100 g of adsorbent was added to 500 mL of 0.001 M NaOH solution and left for 24 h. Then it was filtered, and residue was washed three times with distilled water to remove excess NaOH. Then this residue was added to 500 mL of 0.1 M solution of ferric chloride with stirring, left for 24 h, and then filtered, washed with distilled water, and dried at room temperature. Finally it was dried at 100°C for 2 h.

Similarly, impregnation was done with Al^{3+} ions by aluminium nitrate solution. The fireclay samples, impregnated with Fe^{3+} and Al^{3+} ions, were denoted as IFCFe and IFCA1, respectively.

Kinetics of Adsorption

All the reagents used were of analytical grade (BDH). Solution of hexavalent chromium was prepared by dissolving potassium dichromate in doubly distilled water. The final pH was adjusted with 0.1 M H_2SO_4 and 0.1 M NaOH solution.

Batch adsorption experiments were carried out by shaking 1.0 g of the adsorbent with 50 mL of the aqueous solution of potassium dichromate at pH 2.0, in a temperature-controlled shaking water bath. Continuous mixing was provided during the experimental period with a constant agitation speed of 120 rpm. The remaining concentration of Cr(VI) in each sample, after adsorption at different time intervals, was determined spectrophotometrically (16).

Here it is worth mentioning that the SO_4^{2-} ions present in the system due to addition of the H_2SO_4 may adsorb on the positively charged surface and hence may influence the adsorption of $Cr_2O_7^{2-}$ ions. In order to confirm this, the H_2SO_4 was added to the distilled water to make the same pH, and this solution (not containing $K_2Cr_2O_7$) was agitated with the adsorbent under similar experimental conditions. The amount of SO_4^{2-} ions adsorbed was determined by the gravimetric analysis of the supernatant. It was found that a very negligible amount of SO_4^{2-} ions was adsorbed on the fireclay. Therefore, it may be predicted that the probability of interference caused by the presence of SO_4^{2-} ions is very low.

RESULTS AND DISCUSSION

It is clear from the analysis of fireclay that its main constituents are Al_2O_3 and SiO_2, whereas other constituents are present in traces. So it is expected that the silica and alumina content of fireclay should play a major role in the removal of hexavalent chromium.

Sorption Dynamics

Adsorption Isotherm

The uptake of Cr(VI) by FC and IFC with time has been analyzed with the help of Langmuir model. The modified form of Langmuir equation may be given as

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

where C_e is the equilibrium concentration (mg dm^{-3}) of Cr(VI), Q_o is the adsorption capacity (mg g^{-1}), and b is the adsorption energy (dm^3 mg^{-1}).

The plots of C_e/q_e versus C_e (Fig. 1) were found to be linear, thus suggesting the possibility of Langmuir type adsorption behavior for Cr(VI)-FC system. However, many adsorption systems that are not Langmuirion also provide straight lines. The values of Q_o and b were determined from the slope and intercepts of the straight-line plots and have been summarized in Table 1.

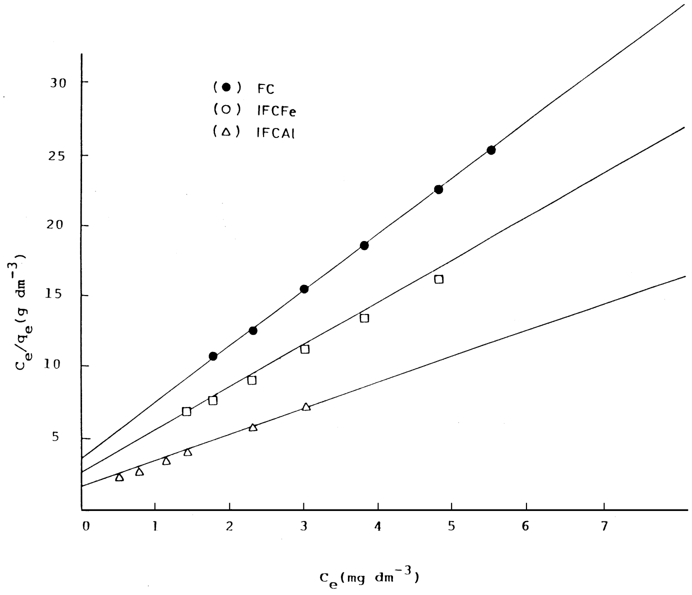

Figure 1. Langmuir plot for adsorption of Cr(VI) onto fireclay and impregnated fireclay at 30°C. [Cr(VI)] = 6 mg dm^{-3}; particle size = 150 μm; pH = 2.0.

Table 1. Values of Rate Constants and Langmuir Constant for Fireclay and Impregnated Fireclay. Particle Size = 150 μm; pH = 2.0; Temperature = 30°C

	Rate Constants		Langmuir Constants			
			Graphical Values		Regression Values	
Adsorbents	Adsorption Coefficient K_{ad} (min^{-1})	Intraparticle Diffusion Rate Constant k_{id} ($mg\ g^{-1}\ min^{-0.5}$)	Q_o ($mg\ g^{-1}$)	b ($dm^3\ mg^{-1}$)	Q_o ($mg\ g^{-1}$)	b ($dm^3\ mg^{-1}$)
FC	0.0318	0.0232	0.235	1.37	0.234	1.36
IFCFe	0.0396	0.0289	0.307	1.82	0.305	1.84
IFCAI	0.0467	0.0354	0.389	2.23	0.383	2.26

The validity of the Langmuir isotherm was further confirmed by the regression analysis of the equilibrium date and are represented in the form of simple straight-line equations:

$$\frac{C_e}{q_e} = 4.2735\ C_e + 3.1426\ \textit{for FC} \tag{2}$$

$$\frac{C_e}{q_e} = 3.2786\ C_e + 1.7818\ \textit{for IFCFe} \tag{3}$$

$$\frac{C_e}{q_e} = 2.6246\ C_e + 1.1665\ \textit{for IFCAl} \tag{4}$$

By comparing these linear equations with Langmuir equation, the values of Q_o and b have been determined (Table 1) and are in good agreement with graphical values.

Rate Constant Study

The kinetics of sorption of Cr(VI) on FC and IFC was studied on the basis of the Lagergren (17) equation:

$$\ln(q_e - q) = \ln q_e - K_{ad}\cdot t$$

or

$$\ln\left(l - \frac{q}{q_e}\right) = -K_{ad}t \tag{5}$$

where q ($mg\ g^{-1}$) is the amount of chromium(VI) sorbed at time "t," q_e ($mg\ g^{-1}$) is the amount sorbed at equilibrium, and K_{ad} (min^{-1}) is the rate constant of sorption. The rate constant of sorption of Cr(VI) on FC and IFC, as determined from the slope of the straight line plots of $\ln(1 - q/q_e)$ vs t (Fig. 2) are given in Table 1.

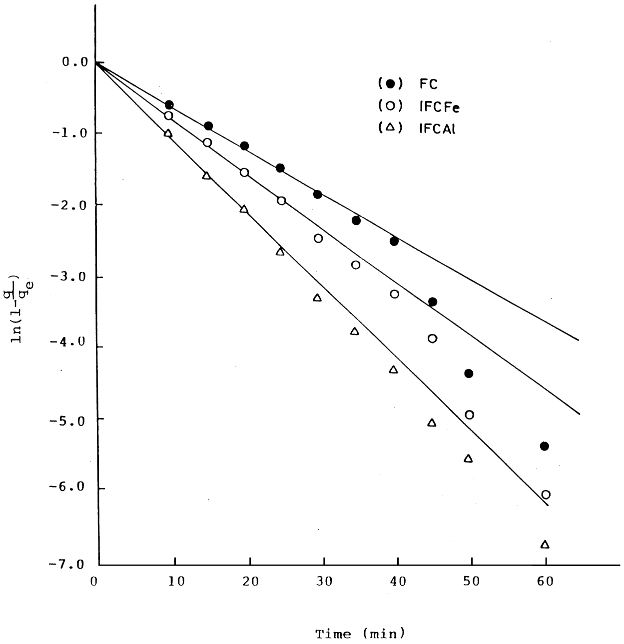

Figure 2. First-order reversible kinetic fit of Cr(VI) uptake by fireclay and impregnated fire clay at 30°C. [Cr(VI)] = 6 mg dm^{-3}; particle size = 150 μm; pH = 2.0.

Study of Diffusion Rate Constant

Due to the porous nature of the adsorbents (FC and IFC), pore diffusion is also expected in addition to surface adsorption. The rate constants of intraparticle transport (K_{id}) were calculated from the slopes of the linear plots (Fig. 3 and Table 1) between amount sorbed per unit weight of sorbent (q) versus $t^{0.5}$ as suggested by Weber and Morris (18).

$$q = K_{id}\, t^{0.5} \tag{6}$$

where K_{id} is the intraparticle diffusion rate constant (mg g^{-1} min$^{-0.5}$).

The pore diffusion coefficients for the intraparticle transport of Cr(VI) were calculated assuming spherical geometry of the sorbent (19) using following equation (20).

$$t_{1/2} = \frac{0.03\, r_o^2}{\overline{D}} \tag{7}$$

where r_o is the radius of the sorbent, $\overline{D}$ is the pore diffusion coefficient (cm^{2}s^{-1}) and $t_{1/2}$ is the time for half sorption. The values of $\overline{D}$ have been summarized in Table 2.

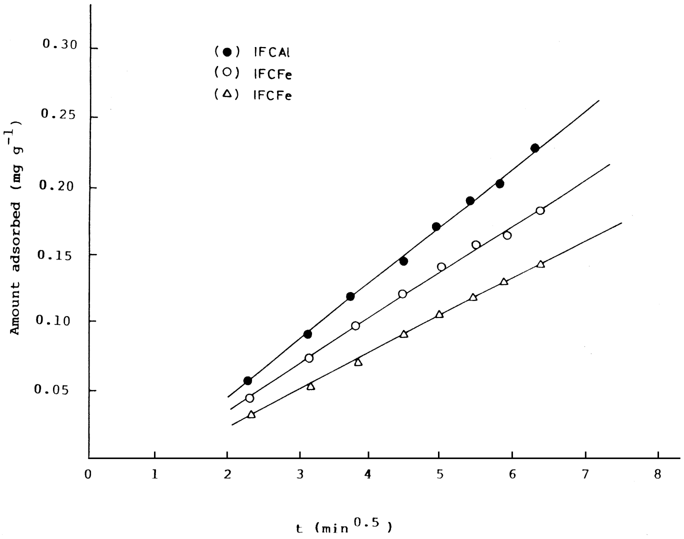

Figure 3. Variation of amount adsorbed of Cr(VI) by fireclay and impregnated fireclay with square root of time at 30°C. [Cr(VI)] = 6 mg dm^{-3}; pH = 2.0; particle size = 150 μm.

Effect of Particle Size

The chemical analysis of fireclay shows that it is an alumino-siliceous material containing oxides of calcium, iron, and titanium with other minor constituents. Chemical analysis of the different sized particles of fireclay shows that the amounts of major constituents alumina and silica increases as the particle size decreases. The silica and alumina content of FC plays a major role in the removal of Cr(VI) because of strong electrostatioc interaction between $Cr_2O_7^{2-}$ ions and the protonated aluminol ($AlOH_2^+$) and silanol ($SiOH_2^+$) groups present on the ad-

Table 2. Values of Diffusion Coefficients and Mass Transfer Coefficients for Fire Clay and Impreganted Fire Clay; [Cr(VI)] = 6 mg dm^{-3}; Particle Size = 150 μm; pH = 2.0; Temperature = 30°C

Adsorbent	Diffusion Coefficient $\overline{D}$ (cm^{2}s^{-1}) × 10^{10}	Mass Transfer Coefficient β_1 (cm s^{-1}) × 10^5
FC	11.70	1.45
IFCFe	12.87	2.23
IFCAI	14.04	3.16

sorbent surface, as the experiments have been carried out in acidic medium (pH = 2.0). Moreover, the surface area also increases as the particle size decreases. The effect has been well depicted in Fig. 4, which clearly shows that the efficiency of removal decreases in the following order:

FC (100 μm) > FC (150 μm) > FC (290 μm)

This is in agreement with the statement (based on mathematical considerations) that if the mechanism of uptake is simply one of adsorption on a specific external site, then the rate should vary reciprocally with the first power of the diameter, whereas in intraparticle diffusion the rate should vary with the reciprocal of the square of the diameter (18). However, in order to explain the kinetic parameters, the rate-limiting step must be known. The determined values of the pore diffusion coefficients are of the order of 10^{-10}, and these low values suggest that the pore diffusion is the rate-limiting step (21). The kinetic parameters for the different sized fractions of fireclay (Table 3) can be summarized as follows:

K_{ad}, K_{id} (100 μm) > K_{ad}, K_{id} (150 μm) > K_{ad}, K_{id} (290 μm)

and $\overline{D}$ (100 μ*m*) < $\overline{D}$ (150 μm) < $\overline{D}$ (290 μm).

The variation in $\overline{D}$ is the reverse of K_{id} and K_{ad} because of the effect of particle size ($\overline{D} \propto r_o^2$).

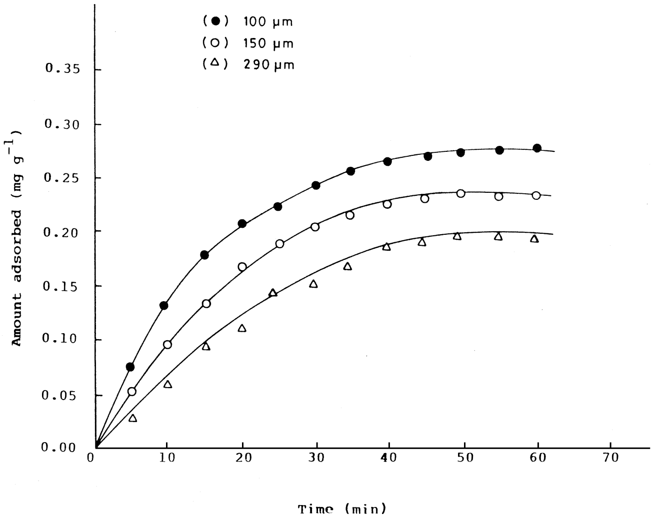

Figure 4. Sorption kinetics of Cr(VI) on fireclay at various particle sizes. [Cr(VI)] = 6 mg dm^{-3}; pH = 2.0; temperature = 30°C.

Table 3. Sorption Kinetic Parameters for Different Particle Sizes of Fireclay; [Cr(VI)] = 6 mg dm^{-3}; pH = 2.0; Temperature = 30°C

Adsorbent	Particle Size (μm)	K_{ad} (min^{-1})	K_{id} (mg g^{-1} $min^{-0.5}$)	$\overline{D}$ (cm^2s^{-1}) $\times 10^{10}$
FC	100 μm	0.0425	0.0262	6.25
FC	150 μm	0.0318	0.0232	11.70
FC	290 μm	0.0268	0.0204	26.25

Effect of Impregnation by Fe^{3+} and Al^{3+} Ions

It is clear from Table 1 that removal rate of Cr(VI) is higher by IFC as compared to FC. This is probably caused by the strong electrostatic interaction between $Cr_2O_7^{2-}$ ions and newly developed Lewis acid sties (Al^{3+} and Fe^{3+}) on impregnated fireclay. Moreover, the complexation between the lone pair of electrons of oxygen atoms in $Cr_2O_7^{2-}$ ions and Al^{3+} and Fe^{3+} ions is also possible. The development of acidity is probably a result of the accomodation of Al^{3+} and Fe^{3+} ions on the surface of silica in tetrahedral coordination, leaving the surface charged (22). The surface acidity of IFC is also confirmed by the acidic nature of its extract. The removal rate of Cr(VI) is greater for IFAI than for IFCFe because the effectiveness of coagulation followed by the sorption has the sequence (23).

$$Al^{3+} > Fe^{3+} > Cu^{2+} > Zn^{2+} > Ni^{2+} > Co^{2+}$$

On the basis of this discussion, it can be said that the kinetic parameters K_{ad}, K_{id}, and D decrease in the following order:

$$[K_{ad}, K_{id} \text{ and } \overline{D}]_{IFCAL} > [K_{ad}, K_{id} \text{ and } \overline{D}]_{IFCFe} > [K_{ad}, K_{id} \text{ and } \overline{D}]_{FC}$$

Mass Transfer Analysis

The removal of Cr(VI) by adsorption on FC and IFC is assumed to occur by a three-step model given below:

1) Mass transfer of Cr(VI) from its aqueous solution to the adsorbent surface
2) Intraparticle diffusion or migration of Cr(VI) within the pores of the adsorbent
3) Adsorption of Cr(VI) at interior sites of the adsorbents

The mass transfer analysis of Cr(VI) during the process involving these steps was studied by using the diffusion mode (24) given following:

$$\ln\left[\frac{C_t}{C_o} - \frac{1}{1 + mK_{ad}}\right] = \ln\frac{m\,K_{ad}}{1 + mK_{ad}} - \frac{1 + m\,K_{ad}}{mK_{ad}}\,\beta_1 S_s t \tag{8}$$

The values of m and S_s were determined using the following equations (25).

$$m = \frac{w}{v} \tag{9}$$

and

$$S_s = \frac{6\,m}{d_p P_p\,(1 - \xi_p)} \tag{10}$$

where m is mass of the adsorbents per unit volume of particle-free adsorbate solutions (g dm^{-3}), w is weight of adsorbents (g), v is volume of particle-free adsorbate solution (dm^3), d_p is particle diameter (cm), P_p is density of adsorbents (g dm^{-3}), ξ_p is porosity of adsorbent particles and C_t is concentration (mg dm^{-3}) of Cr(VI) at time t.

The values of mass transfer coefficient (β_1) were determined from the slopes and intercept of the straight line plots (Fig. 5) for FC and IFC. The linear nature of the plots suggests the validity of the diffusion model of equation for

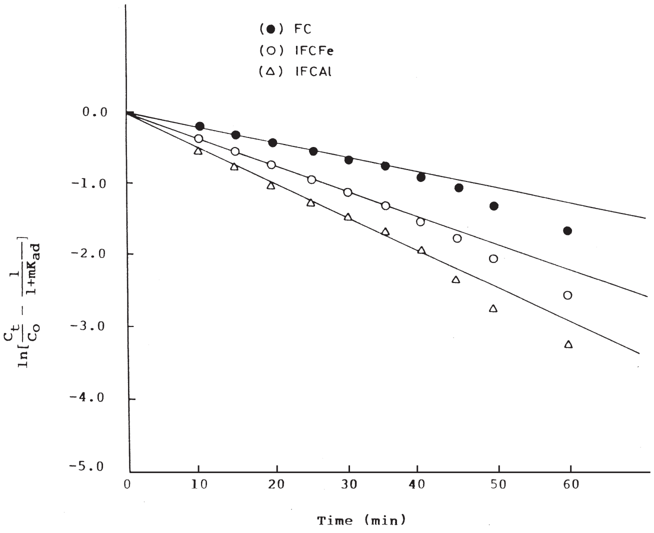

Figure 5. Plot for mass transfer of Cr(VI) on fireclay and impregnated fireclay at 30°C. [Cr(VI)] = 6 dm^{-3}; pH = 2.0; particle size = 150 μm.

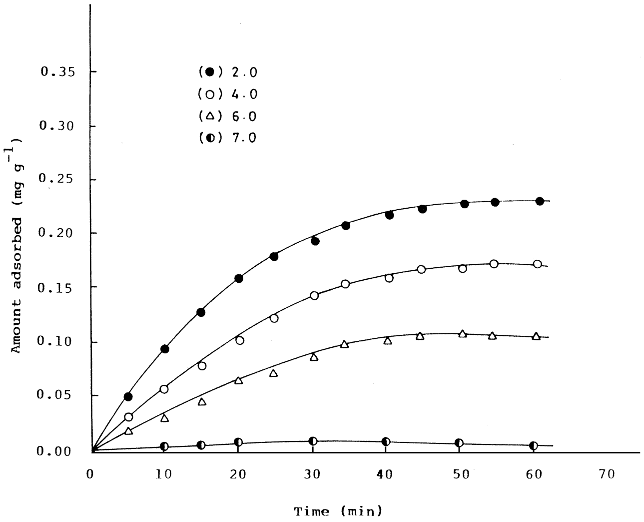

Figure 6a. Sorption kinetics of Cr(VI) on fireclay at different pH values. [Cr(VI)] = 6 mg dm^{-3}; particle size = 150 μm; temperature 30°C.

Cr(VI)-FC and Cr(VI)-IFC systems. The deviation of some points from linearity near saturation is due to the varying extent of mass transfer at the initial and final stages of adsorption. Here one more point to be noted is that the Langmuir and the mass transfer analysis have provided good fits that may be contributed to the fact that the concentrations of hexavalent chromium are significantly low, and hence Langmuir isotherm may be treated as a linear one. The values of the mass transfer coefficients (Table 2) suggest that the velocity of mass transport of Cr(VI) from bulk to the surface of fireclay is rapid enough to use FC and IFC for the treatment of water and wastewaters enriched in Cr(VI).

Effect of pH

The pH of the adsorption medium affects the extent of adsorption significantly as it changes the charge profile of the adsorbent surface that finally results in the alteration in the kinetic behavior of the sorption process. In the present study pH of the Cr(VI)-FC system was varied from 2.0 to 7.0, and it was found that the amount of sorbate decreased with increase in pH (Fig. 6a). The observed experimental finding may be explained as following.

It is believed that the overall separation of Cr(VI) from an aqueous solution is governed by two factors, namely surface adsorption and pore diffusion (26).

When pH of the system is 2.0 (which is quite below the PZC of fireclay (pH_{pzc} = 6.1), the adsorbent surface contains a large number of protonated aluminol ($AlOH_2^+$) and silanol ($SiOH_2^+$) groups that bind electrostatically with the $Cr^2O_7^{2-}$ ions to cause the adsorption to take place.

When pH of the adsorbate solution is increased, the number of protonated aluminol and silanol groups decreases and hence the extent of adsorption also decreases, and it becomes minimum at the pH 6.0, which is almost the point of zero charge for the present system. However, whatever adsorption takes place, it may be due to weak H-bondings interactions between $Cr_2O_7^{2-}$ ions and unprotonated AlOH and SiOH groups.

Finally, when pH of the adsorption medium is 7.0 ($pH > pH_{pzc}$), the adsorbent surface contains AlO^- and SiO^- groups and hence due to electrostatic repulsion between $Cr_2O_7^{2-}$ and negatively charged groups on the adsorbent, the extent of adsorption is extremely poor.

Here one more interesting point to consider is the conversion of $Cr_2O_7^{2-}$ into Cr^{3+} due to change in pH of the system towards strongly acidic region. For instance, Huang and Wu (27) observed that in the presence of activated carbon there was appreciable conversion of $Cr_2O_7^{2-}$ into Cr^{3+} in the pH range 2–6. Moreover, in the absence of adsorbent, no such conversion was observed. This, in fact, was the case of the reduction of hexavalent chromium into trivalent state by activated carbon. In the present study, chances of such reduction are almost nil because the adsorbent fireclay does not contain an appreciable amount of reducing species that could convert chromium into trivalent state in acidic range. It is clear from the chemical analysis that mineral matter content of fireclay is nearly 95% whereas carbonaceous matter is only 5%. Hence, this data supports the statement that the chances of presence of Cr^{3+} ions are very low.

Table 4 summarizes the sorption kinetic parameters for Cr(VI)-FC system at different pH of the medium. Thus, the removal at different pH values decreases as follows:

$$\text{pH } 2 > \text{pH } 4 > \text{pH } 6 > \text{pH } 7$$

The kinetic parameters K_{ad}, K_{id}, and $\overline{D}$ have been summarized in Table 4.

Table 4. Sorption Kinetic Parameters at Different pH Values; [Cr(VI)] = 6 mg dm^{-3}; Particle size = 150 μm; Temperature = 30°C

pH	K_{ad} (min^{-1})	K_{id} ($mg\ g^{-1}\ min^{-0.5}$)	$\overline{D}$ ($cm^2 s^{-1}$) × 10^{10}
2.0	0.0318	0.0232	11.70
4.0	0.0218	0.0173	9.62
6.0	0.0104	0.0098	5.28

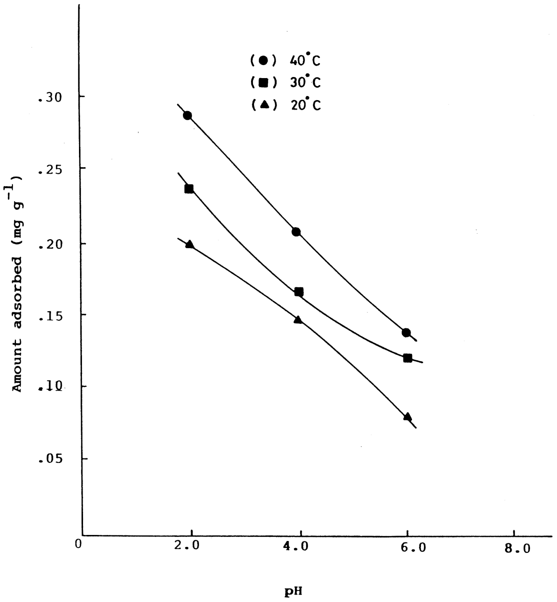

Figure 6b. Variation in amount of Cr(VI) adsorbed onto fireclay with pH of the adsorption medium at various temperatures.

In an attempt to correlate the pH and temperature of the adsorption system with amount of Cr(VI) adsorbed, pH effect was studied at 20°, 30°, and 40°C. The results have been depicted in Fig. 6b, which clearly shows that for a given pH, the amount of Cr(VI) adsorbed increases with rise in temperature. While discussing the pH effect, it has been mentioned that electrostatic and H-bonding interactions between the adsorbate molecules and adsorbent surface play a major role in causing the adsorption to take place. Hence, it is expected that a rise in temperature should weaken these interactions due to increase in the kinetic energy of adsorbate molecules. Therefore, it may be expected that the extent of adsorption should decrease with rise in temperature. But results obtained are rather surprising as an increase in amount of Cr(VI) adsorbed has been noticed. The observed experimental finding may be explained by the fact that with the increase in temperature, the number of active centers available for sorption must have increased as observed in the case of adsorption of Ni onto fireclay (28). Moreover, as diffusion is an endothermic process, the increase in uptake of Cr(VI) may also be due to an enhanced rate of intraparticle diffusion of sorbate (29). An increase in pore diffusivity of adsorbate with temperature has also been reported in the case of removal of Cr(VI) by its adsorption onto fly ash (26).

Finally, it may be concluded that the observed increase in amount of Cr(VI) adsorbed is due to fact that the increase in pore diffusivity of sorbate and in number of active sites are more effective and pronounced as compared to the decrease in extent of electrostatic and H-bonding interactions.

Effect of Concentration of Sorbate

The rate of removal of Cr(VI) is observed to increase as the concentration of Cr(VI) in the solution increases (Fig. 7). This is in agreement with the findings that the rate of uptake of sorbate is found to increase nonlinearly with increasing concentration of solute (18). This is seen in Table 5 where the intraparticle diffusion rate constant K_{id}, diffusion coefficient $\overline{D}$ increase with a rise in concentration.

The increase in rate of adsorption and amount adsorbed with concentration is indicative of a system controlled by intraparticle transport (30).

However, the sorption rate constant K_{ad}, determined using the Lagergren rate equation, varies in the reverse manner, because at high concentrations the

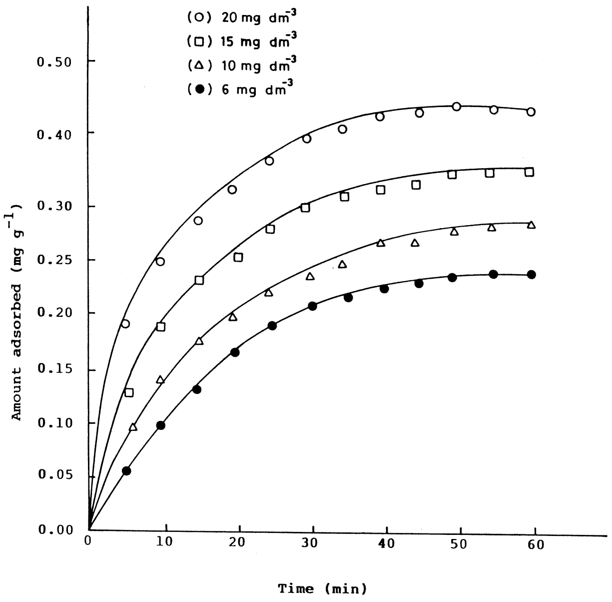

Figure 7. Sorption kinetics of Cr(VI) on fireclay at different initial concentrations of sorbate pH = 2.0; temperature = 30°C; particle size = 150 μm.

Table 5. Sorption Kinetic Parameters at Different Concentrations of Cr(VI) in the Solution; Particle Size = 150 μm; pH = 2.0; Temperature = 30°C

Concentration (mg dm^{-3})	K_{ad} (min^{-1})	K_{id} (mg g^{-1} min$^{-0.5}$)	$\overline{D}$ (cm^{2}s^{-1}) × 10^{10}
6	0.0318	0.0232	11.70
10	0.0284	0.0262	13.69
15	0.0189	0.0298	16.06
20	0.0112	0.0335	18.79

fractional adsorption is low (31). This reverse variation in k_{ad} is probably due to lower fractional sorption value (low-percentage sorption) at higher concentrations. Thus, k_{ad} values vary in the reverse order, that is

$$K_{ad}(6\text{ mg}) < K_{ad}(10\ mg) < K_{ad}(15\text{ mg}) < K_{ad}(20\ mg)$$

CONCLUSION

The present investigation shows that the fireclay and the impregnated fireclay can be employed as an effective adsorbent for the removal of hexavalent chromium from the wastewater. The pH of the medium is the controlling master parameter of this separation process. The process follows the Langmuir type adsorption behavior and is mainly governed by the electrostatic interactions between the $Cr_2O_7^{2-}$ ions and the protonated adsorbent surface. The experimental results suggest that fireclay has great efficiency in removing Cr(VI) from water. The data thus obtained may be helpful to environmental sanitary engineers for designing and establishing a continous treatment plant for water and wastewaters enriched in Cr(VI). The cost of removal will be quite low, as the adsorbent is quite cheap and easily available in large quantities.

REFERENCES

1. Galvin, J. B.; Dberg, S. G. Toxicity Nature of Hexavalent Chromium to Alveolax Macrophage in Vivo in Vitro. Env. Res. **1984,** *33*, 7.
2. Kaufaman, D. B. Acute Potassium Dichromate Poisoning in Man. Am. J. Diseases Childeren. **1970,** *119*, 374.
3. Browning, E. *Chromium in Toxicity of Industrial Metals*. 2nd Ed. Butterworths and Co.: London, 1969; Chapter 12.
4. Marshal, S. *Metal and Inorganic Waste Reclaiming Encyclopedia*; Wayers Beta Corp.: Park-Ridge, New Jersey, 1980.

5. Patterson, J. W. *Industrial Waste Water Treatment Technology*; Ann Arbor Science Pub. Inc.: Ann Arbor, Mich., 1985; 53.
6. Srinivasan, K.; Balasubramanium, N.; Ramakrishna, T. V. Ind. J. Env. Health. **1988,** *30*, 376.
7. Srivastava, H. C.; Mathur, R. P.; Mehrotra, I. Env. Technol. Lett. **1986,** *7*, 55.
8. Dasmahapatra, G. P.; Pal, T. K.; Bhadra, A.; Bhattacharya, B. Studies on Separation Characteristics of Hexavalent Chromium from Aqueous Solutions by Fly Ash. Sep. Sci. Technol. **1996,** *31*, 2001–09.
9. Nagesh, N.; Krishnaiah, A. Ind. J. Env. Health. **1989,** *31*, 304.
10. Deepak, D.; and Gupta, A. K. Hexavalent Chromium Removal from Wastewater. Ind. J. Env. Health. **1991,** *33*, 297–305.
11. Tare, V.; Chaudhary, S. Water Res. **1987,** *21*, 1109.
12. Samantaroy, S.; Mohanty, A. K.; Mishra, M. Removal of Hexavalent Chromium by Kendu Fruit Gum Dust. Appl. Poly. Sci. **1997,** *66*, 1485–1494.
13. Kanon, N.; Vanangamudi, A. A Study on Removal of Chromium(VI) by Adsorption on Lignite Coal. Ind. J. Env. Prot. **1991,** *11*, 241–245.
14. Samantaroy, S.; Mohanty, A. K.; Mishra, M. Studies on Removal of Hexavalent Chromium by Drumstick Gum Dust. *IUPAC International Symposium on Advances in Polymer Science and Technology*; MACRO-98: Chennai, 1998; 1061–1064.
15. Indian Standard Methods of Chemical Analysis of Fire Clay and Refractory Materials, 1960; IS:1527.
16. APHA. *Standard Methods for Examination of Water and Waste Water*, 17th Ed.; American Public Health Association: New York, 1989.
17. Lagergren, S.; Bil, K. Svenskar Vatens Kapsakad Handl. **1898,** 24.
18. Weber, W. J.; Morris, J. C. Kinetics of Adsorption on Carbon from Solution J. Sanit. Eng. Div., ASCE, **1963,** *89* (SA2), 31–39.
19. Helfferch, F. *Ion Exchange*; McGraw Hill Book Co. Inc.: New York, 1962.
20. Bhattacharya, A. K.; Venkobachar, C. Removal of Cadmium (II) by Low Cast Adsorbents. J. Envir. Eng., **1984,** *110*, 110–22.
21. Michelson, L. D.; Gideon, P. G.; Pace, E. G.; Kutal, L. H. Removal of Soluble Mercury from Waste Water by Complexing Techniques. US Dept. Industry, Office of Water Research and Technology, Bull No. 74, 1975.
22. Wells, A. F. *Structural Inorganic Chemistry*, 2nd Ed.; Clarendon Press: Oxford, 1950; 101.
23. Khan, S. U. Interaction between Humic Acid Fraction of Soils and Certain Metallic Cations, Soil Sci. Soc. Am. Proc. **1969,** *33*, 851–54.
24. Mckay, G.; Otterburn, M. S.; Sweeny, A. G. Surface Mass Transfer Process during Colour Removal from Effluent Using Silica. Wat. Res. **1981,** *15*, 327–31.
25. Yadav, K. P.; Pandey, K. K.; Tyagi, B. S.; Singh, V. N. Fly Ash for the Treatment of Cd (II) Rich Effluents. J. Environ. Technol. Lett. **1987,** *8* (5), 225–34.

26. Dasmahapatra, G. P.; Pal, T. K.; Bhattacharya, B. Evaluation of Thermodynamic Parameters for Separation of Hexavalent Chromium by Fly Ash. Sep. Scie. Technol. **1996.** *31* (20), 2843–853.
27. Huang, C. P.; Wu, M. H. The Removal of Chromium (VI) from Dilute Aqueous Solution by Activated Carbon, Water Res., **1977,** *11*, 673–679.
28. Bajpai, S. K. Effect of Temperature on Removal of Ni(II) from Aqueous Solution by Adsorption onto Fire Clay. Asian J. Chem. **1999,** *11* (1), 171–80.
29. Singh, B. K.; Rawat, N. S. Comparative Sorption Kinetic Studies of Phenolic Compounds on Fly Ash and Impregnated Fly Ash. J. Chem. Technol. Biotech. **1994,** *61*, 57–65.
30. Zogoroski, J. S.; Faust, S. D.; Hags, J. H., Jr. The Kinetics of Adsorption by Granular Activated Carbon. J. Colloid Interface Sci. **1976,** *55* (2), 329–41.
31. Mckay, G. Adsorption of Dye Stuff from Aqueous Solutions with Activated Carbon—1. Equilibrium and Contact Time Studies. J. Chem. Technol. Biotechnol. **1982,** *32* (11), 759–72.

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