



Adsorption Kinetics for the Removal of Hexavalent Chromium from Aqueous Solution by Acid Activated Coal Fly Ash (CFA)

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ABSTRACT

The adsorption of hexavalent chromium, present in effluents of various industries such as electroplating, tannery, etc., on Coal Fly Ash (CFA) has been investigated in the present study. Parameters like contact time, adsorbent dose, pH and initial chromium ion concentration were studied in kinetic batch experiments at 25°C. Among all the parameters, pH of the solution was most effective for chromium removal. The adsorption of hexavalent chromium on CFA was found to be maximum at low pH. The adsorption data fit well with Langmuir and Freundlich isotherm models. The Langmuir adsorption isotherm to the systems yielded maximum adsorption capacity of 19.77 mg/g at the solution pH of 2. Results showed that the pseudo second order kinetic model best correlate with the experimental data.

INTRODUCTION

Hexavalent chromium is present in the effluents produced from electroplating, cement, dyeing, fertilizer and leather tanning industries and causes severe environmental and public health problems (Sharma 2001, Hu et al. 2003). The National Toxicology Program (NTP) and The International Agency for Research on Cancer (IARC) reported that hexavalent chromium is toxic to animals and humans and it is known to be carcinogenic (Oguz 2005 & Patterson 1985) (Table 1, EPA 1990).

Thus, treatment of the effluent to reduce/remove the pollutant before discharging into the environment becomes inevitable. Different methods such as reduction and precipitation (Philipot et al. 1984), ion exchange (Jorgensen 1979), electrolysis, solvent extraction (Patterson 1978) and electrochemical precipitation (Huang et al. 1975) have been suggested for the removal of hexavalent chromium. Most of these methods suffer from drawbacks such as high capital and operational costs or the disposal of residual metal sludge. Many reports have appeared on the development of low cost adsorbents developed from cheaper and readily available materials (Table 2).

In this study, a method for the efficient utilization of Coal Fly Ash (CFA) and evaluation of its potential for the removal of hexavalent chromium was investigated. The conditions required for the activation of CFA, adsorption properties, adsorption isotherms and rate of adsorption for the removal of hexavalent chromium were studied.

MATERIALS AND METHODS

The CFA sample used in this work was obtained from an

840 MW thermal power plant located at Mettur in Tamil Nadu, India. The sample used was pretreated in a high gradient magnetic separator to remove Fe_2O_3 and TiO_2 . The CFA was washed with water and dried at 120°C for 6 h. The activation was carried out with concentrated H_2SO_4 (98% w/w) in 1:1 weight ratio and kept in an oven at a temperature of 150°C for 24 h. Again, it is washed with distilled water to remove free acid.

Hexavalent chromium stock solution was prepared by dissolving 28.29 g of AR grade $\text{K}_2\text{Cr}_2\text{O}_7$ in 1000 mL distilled water. Standard solutions of different concentrations from 50 to 250 mg/L were prepared by diluting the stock solution. 0.5 N HCl and 0.5 N NaOH solutions were used for pH adjustments.

Kinetic batch experiments were carried out in 250 mL Borosil glass stoppered bottle by agitating a pre-weighed amount of CFA at the speed of 180 rpm with different concentrations of aqueous chromium solutions at 25°C in Orbital Shaking Incubator (RIS-24BL). The solution was then filtered at preset time intervals and equilibrium concentration of hexavalent chromium in the solution was determined by reacting with 1,5-diphenyl carbazide and the adsorption was measured in the ELICO-make double beam bio UV-visible spectrophotometer at 540 nm.

The % chromium removal at any instant time was determined by the following equation.

$$\text{Chromium removal \%} = \frac{q_o - q_e}{q_o} \times 100 \quad \dots(1)$$

Where q_o and q_e are the concentration of chromium at

Table 1: Present and tolerable limit of Cr (VI) in industrial and potable water.

	Industrial waste water, mg/L	Tolerance Limit	
		Inland surface water, mg/L	Potable water, mg/L
Hexavalent Chromium	0.5 to 270	0.1	0.05

initial condition and at any instant of time respectively.

RESULTS AND DISCUSSION

Effect of contact time on hexavalent chromium adsorption: Contact time is one of the effective parameters in batch adsorption process. In this stage, the other parameters such as temperature (25°C), adsorbent dose (10 g/L), pH (2), initial chromium concentration (100 mg/L) and agitation speed (180 rpm) were kept constant. The effect of contact time on hexavalent chromium adsorption efficiency is showed in Fig. 1. The adsorption rate initially increases rapidly and the optimal removal efficiency was reached in about 10 h to 84.5%. There was no significant change in equilibrium concentration after 12 h upto 20 h. Therefore, the contact time of 10 h could be considered for the adsorption of hexavalent chromium for entire batch process. The rate of adsorption of hexavalent chromium is faster in the initial periods and has less effect in the later half of the process. The decrease in the rate of adsorption in the later stages can be explained as intra particle diffusion becomes predominant and may be due to the slow pore diffusion of the hexavalent chromium into the bulk of the adsorbent.

Effect of pH on hexavalent chromium adsorption: The experiments of this stage were done under the conditions of constant temperature (25°C), adsorbent dose (10g/L), initial chromium concentration (100 mg/L), agitation speed (180 rpm) and contact time (10 h). pH of the solution was changed and the chromium removal was investigated. It is evident from Fig. 2 that the percentage of adsorption is higher (84.5%) at lower pH (2) and the removal efficiency decreased with increase of pH. To explain the behaviour of hexavalent chromium adsorption with varying pH, it is necessary to examine various mechanisms such as electrostatic attraction/repulsion, chemical interaction and ion exchange, which are responsible for adsorption on adsorbent surface. The most prevalent form of hexavalent chromium in aqueous solution was acid chromate (HCrO_4^-), chromate (CrO_4^{2-}), dichromate ($\text{Cr}_2\text{O}_7^{2-}$) and other Cr oxyanions (Donmez et al. 1999). It was evident that at low pH, acid chromate ions (HCrO_4^-) were the dominant species. As the pH increased, there was a little decrease in percentage of adsorption and when pH is further increased, a sharp decrease in percentage of adsorption was

Table 2: Adsorbent capacity of various adsorbents.

Adsorbent	Adsorption capacity, mg/g	References
Activated carbon (Filtrisorb-400)	57.7	(Huang et al. 1977)
Saw dust	39.7	(Sharma et al. 1994)
Banana peel	21.0	(Annadurai et al. 2002)
Acid Activated CFA	19.8	Present Study
Sago waste	16.1	(Kadirvelu et al. 2005)
Sugarcane baggage	13.4	(Sharma et al. 1994)
Coir pith	6.72	(Namasivayam et al. 2002)
Biomass residual slurry	5.87	(Namasivayam et al. 1995)
Waste tea	1.55	(Orhan et al. 1993)
Walnut shell	1.33	(Orhan et al. 1993)

observed. This might be due to the weakening of electrostatic force of attraction between the oppositely charged adsorbate and adsorbent which ultimately lead to the reduction in sorption capacity. The pH at point zero charge (pzc) was found to be 9.0. This is in agreement with these experimental observations showing a very low adsorption at $\text{pH} > 9$.

Effect of adsorbent dose on hexavalent chromium adsorption: The effect of CFA amount on the adsorption of hexavalent chromium is shown in Fig. 3. The percentage removal increases from 21.3 to 91.1% by increasing the adsorbent amount from 1 to 25 g/L respectively. The adsorption capacity dropped from 21.3 to 3.64 mg/g by increasing the adsorbent amount from 1 to 25 g/L. The hexavalent chromium removal efficiency increased with increase in adsorbent dose, since contact surface of adsorbent particles increased and it would be more probable for HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ ions to be adsorbed on adsorption sites (Morschedzadeh et al. 2007). However, the decrease in adsorption capacity by increasing the adsorbent amount is basically due to the sites remaining unsaturated during the adsorption process.

Effect of initial concentration on hexavalent chromium adsorption: Fig. 4 predicts the effect of initial concentration on the percentage removal of hexavalent chromium and the adsorption capacity of CFA. The percentage removal decreases from 86.2 to 64.52% and the adsorption capacity increases from 4.31 to 16.13 mg/g with increase in the initial chromium concentration from 50 to 250 mg/L respectively. The decrease in the percentage removal of hexavalent chromium can be explained with the fact that all the adsorbents have a limited number of active sites, which would have become saturated above a certain concentration. The increase in the adsorption capacity with increase in the initial concentration may be due to the higher adsorption rate and the utilization of all the active sites available for the adsorption at higher concentration.

Adsorption isotherm: Adsorption studies were carried out

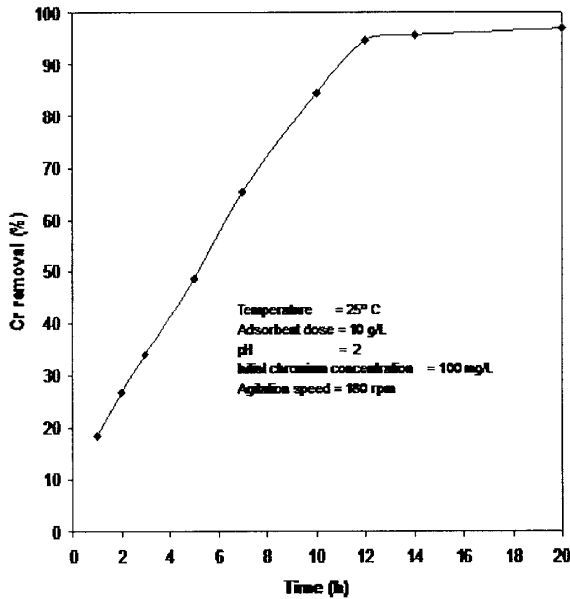


Fig. 1: Effect of contact time on adsorption process efficiency.

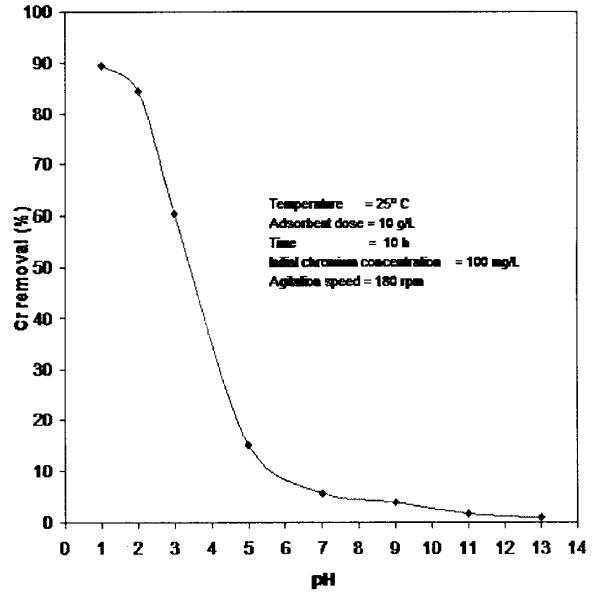


Fig. 2: Effect of pH on adsorption process efficiency.

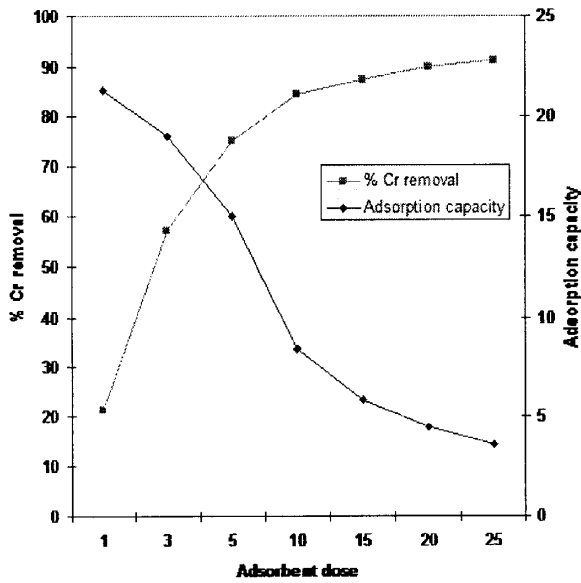


Fig. 3: Effect of adsorbent dose on chromium removal.

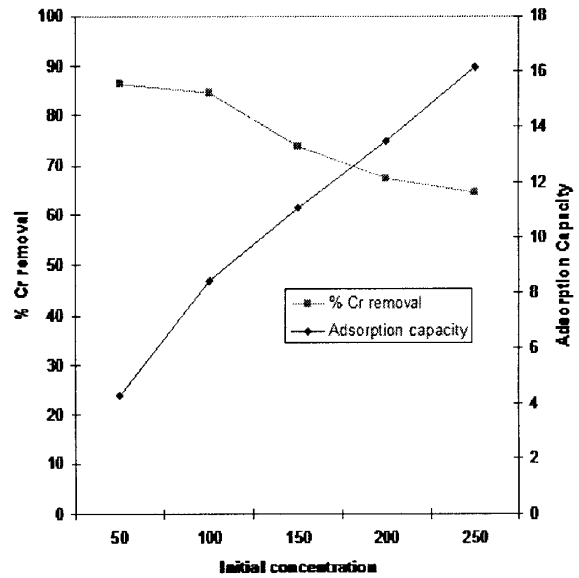


Fig. 4: Effect of initial concentration on chromium removal.

with a fixed initial adsorbent dose (10 mg/L) and varying adsorbate concentration (50-250 mg/L) and applicability of the data to the Langmuir and Freundlich adsorption isotherms were tested.

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{1}{q_m} C_e \quad \dots(2)$$

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad \dots(3)$$

Where, C_e is the equilibrium concentration and q_e is the

amount adsorbed per gram of adsorbent at equilibrium; q_m and b are the Langmuir constants related to the adsorption capacity and energy of adsorption respectively; K_f and n are Freundlich constants representing the adsorption capacity and intensity of adsorption respectively.

It was found that the data obtained fitted well into the Langmuir adsorption isotherm as shown in Fig. 5. The regression constants are tabulated in Table 3. The correlation coefficient ($R^2 = 0.9637$) indicated a good agreement between the parameters. The adsorption capacity (q_m) can be as high

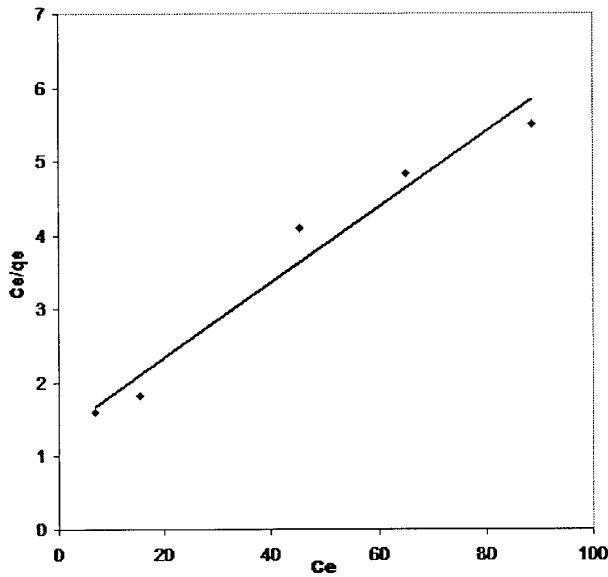


Fig. 5: Langmuir isotherm for the adsorption of hexavalent chromium on CFA.

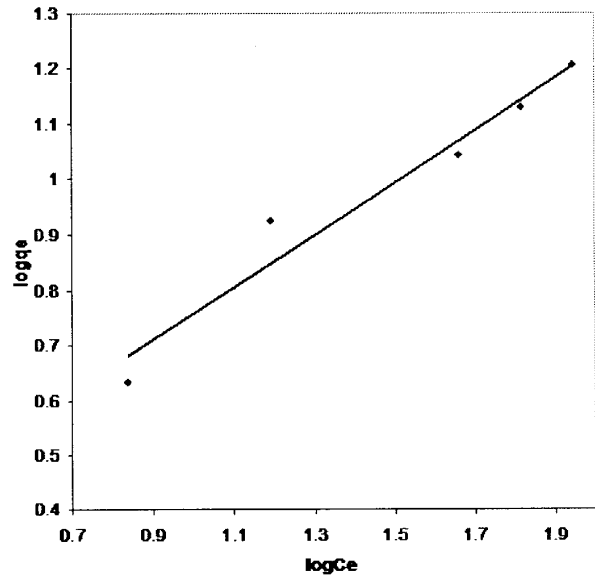


Fig. 6: Freundlich isotherm for the adsorption of hexavalent chromium on CFA.

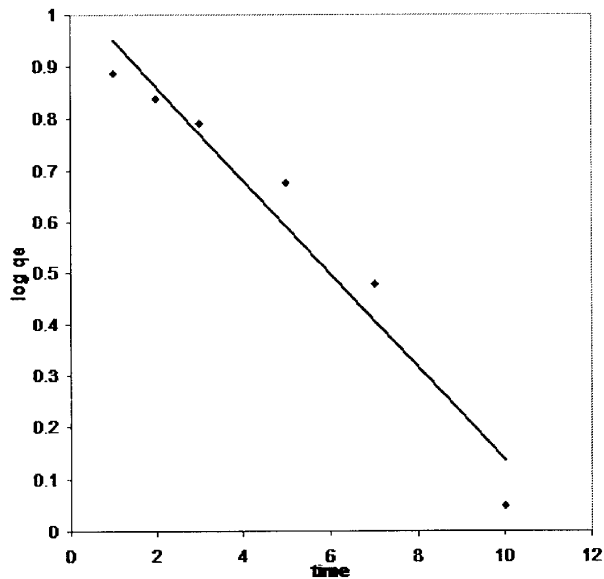


Fig. 7: Pseudo-first-order kinetics for the adsorption of hexavalent chromium on CFA.

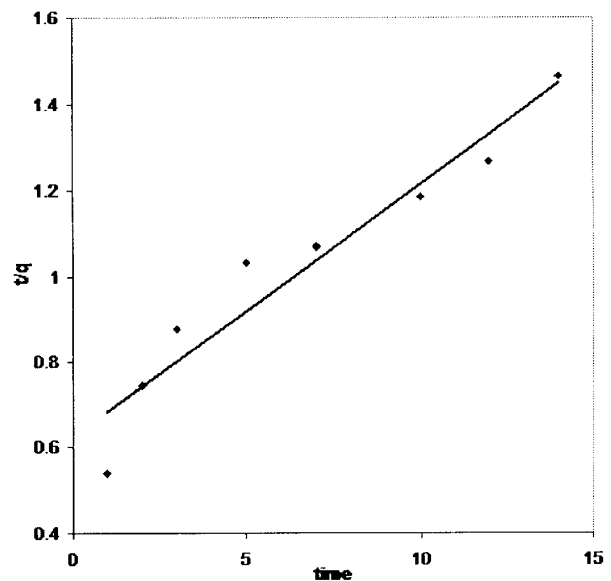


Fig. 8: Pseudo-second-order kinetics for the adsorption of hexavalent chromium on CFA.

as 19.77 mg/g. The essential features of Langmuir adsorption isotherm can be expressed in terms of a dimensionless constant called separation factor or equilibrium parameter (R_L), which is defined by the following relationship (Hall et al. 1966 & Malik 2004):

$$R_L = \frac{1}{(1 + bC_0)} \quad \dots(4)$$

R_L value for the present study was found to be 0.342. From the R_L value, it is confirmed that the system is desir-

able under the conditions used in this study (Table 4).

The same data were also fitted with the Freundlich equation and shown in Fig. 6. As shown in Table 3 for Freundlich isotherm, n is equal to 2.118. The situation $n > 1$ is most common and may be due to a distribution of surface sites or any factor that causes a decrease in adsorbent-adsorbate interaction with increasing surface density (Reed et al. 1993) and the values of n within the range of 2-10 represent good adsorption (McKay et al. 1980, Ozer et al. 2006).

Table 3: Isotherm constants for adsorption of hexavalent chromium on CFA.

Langmuir Isotherm			Freundlich Isotherm		
Constants		Correlation Coefficient	Constants	Correlation Coefficient	
q_m (mg/g)	b (L/mg)	(R^2)	K_F	n	(R^2)
19.77	0.0385	0.9637	1.9284	2.12	0.9539

Table 4: Characteristics of adsorption of Langmuir isotherms (Malik 2004, McKay et al. 1982).

S.No.	Separation factor, R_L	Characteristics of Adsorption
1	$R_L > 1$	Unfavourable
2	$R_L = 1$	Linear
3	$0 < R_L < 1$	Favourable
4	$R_L = 0$	Irreversible

Table 5: Kinetic constants for adsorption of hexavalent chromium on CFA.

Pseudo first order			Pseudo second order		
Constants		Correlation Coefficient	Constants		Correlation Coefficient
q_m (mg/g)	K_1	(R^2)	q_m (mg/g)	K_2	(R^2)
11.033	0.2089	0.9498	17.007	0.0055	0.9261

Adsorption kinetics: In order to define the adsorption kinetics, the kinetic parameters for the adsorption process were studied for contact time ranging from 1 h to 20 h by monitoring the removal percentage of hexavalent chromium ions. The data were then regressed against the Lagergren equation, which represents a first order kinetics equation (Namasivayam et al. 1995) and against a pseudo second order kinetics equation (Ho et al. 1995).

$$\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303} \quad \dots(5)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad \dots(6)$$

Where, q_e and q_t are the adsorption capacities at equilibrium and at time t , respectively (mg.g^{-1}); K_1 and K_2 are the rate constants of pseudo first-order adsorption (l.min^{-1}) and the rate constant of pseudo second-order adsorption ($\text{g.mg}^{-1}.\text{min}^{-1}$).

The slopes and intercepts of these curves were used to determine the values of K_1 and K_2 as well as the equilibrium capacity (q_m) (Fig. 7, Fig. 8). The results (Table 5) show that

the adsorption process follows pseudo second-order model.

CONCLUSION

CFA has a great potential to remove hexavalent chromium from wastewaters. The removal of hexavalent chromium depends on adsorbent dose, pH, contact time and initial chromium ion concentration. Among all the selected parameters pH of the solution was most effective on chromium removal. The results showed that the highest adsorption of chromium on CFA (84.5%) was at lower solution pH of 2. The adsorption data fitted well to the Langmuir adsorption isotherm with the adsorption capacity of 19.77 mg/g. The adsorption of chromium on CFA could be well described with the pseudo second order kinetics model with a correlation coefficient (R^2) of 0.9261.

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