

# Kinetic parameters for the removal of lead and chromium from wastewater using activated carbon developed from fertilizer waste material

S.K. Srivastava, V.K. Gupta and Dinesh Mohan

*Chemistry Department, University of Roorkee, Roorkee - 247 667, U.P., India*

Received 19 October 1995; revised 28 May 1996

The waste slurry generated in fertilizer plants in India has been converted into a cheap carbonaceous adsorbent material. The prepared adsorbent has been characterised and used for the removal of lead and chromium metals. The kinetics of adsorption and the extent of adsorption at equilibrium are dependent on the physical and chemical characteristics of the adsorbate, adsorbent and experimental system. Results of laboratory scale studies conducted to delineate the effect of such parameters on the kinetics of adsorption of metal ions are reported. Parameters evaluated include: hydronium ion concentration, temperature, initial adsorbate concentration, size of adsorbent, and amount of adsorbent. On the basis of these studies the various physical parameters such as effective diffusion coefficient, activation energies and entropy of activation are evaluated, as these provide some information regarding the mechanistic aspects. Mass transfer coefficient values suggest a rapid transport of the adsorbate from bulk to solid phase.

**Keywords:** Activated carbon, lead, chromium, adsorption, adsorbent, wastewater treatment, low cost adsorbent.

## 1 Introduction

Industrial waste containing heavy metals is extremely pernicious due to the fact that these are environmentally persistent and toxic. Unlike most organic pollutants, heavy metals are generally refractory and can not be degraded or readily detoxified biologically. Safe and effective disposal of heavy metal containing wastewater is always a challenging task for the industries due in part to the fact that the cost-effective treatment alternatives are not readily available. Numerous techniques exist to remove toxic metal ions from aqueous solutions. The process of adsorption is by far the most versatile and widely used method. Efforts made to develop low cost materials, as possible media, for metal removal from aqueous solutions, including natural and industrial wastewater, are quite well documented. Such materials range from industrial waste products, e.g. waste rubber tyres, blast furnace slag, to agricultural products like wool, rice, straw, coconut husk, saw dust etc.

In an endeavour to prepare efficient and cheap adsorbent materials, the scavenging properties of a variety of substances, viz., granular activated carbon [1], fly ash [2], mixed adsorbent [3], moss [4,5], waste biomass [6], zeolites [7,8], goethite [9], metal oxides [10,11], lignin [12], clays [13,14], waste tea leaves [15] etc., are reported in the literature. Numerous other efforts made in this direction are described in a review article by Pollard et al. [16].

Fertilizer plants generate a waste slurry due to liquid fuel combustion and this has been causing a disposal

problem. Efforts made to convert the waste slurry into a cheap carbonaceous adsorbent and utilization of the product for the removal of metal ions and phenols has already been reported [17–19]. The research summarized herein was part of the investigations conducted to evaluate the efficacy of the adsorbent material in removing metal ions from aqueous solutions. The results of experiments designed to show the influence of chemical and physical parameters associated with the adsorbate, adsorbent and experimental system on the rate of adsorption of metal ions from aqueous solutions are presented herein.

## 2 Material and methods

The reagents used were all AR grade chemicals. Stock solutions of the test species were made by dilution with doubly distilled water. Salts used were potassium dichromate for Cr(VI) and lead nitrate for Pb(II).

### 2.1 Equipment

pH measurements were made with a pH meter, model pH 821 ECIL, India. Atomic absorption spectra were recorded on an atomic absorption/emission spectrophotometer model 750 (Instrumentation Labs, U.S.A.). X-ray measurements were done by Philips X-ray diffractometer employing nickel filtered Cu-K $\alpha$  radiation. The surface area of the sample was recorded by a surface area analyser model QS-7 Quantasorb surface analyser.

Porosity and density of the adsorbent were determined by a mercury porosimeter and specific gravity bottle, respectively. The constituents of carbon were analysed following the routine methods of chemical analysis.

## 2.2 Material development

The raw material, a waste product from National Fertilizer Limited (NFL), was in the form of small, spherical, black, greasy granules. As reported earlier [17] the waste was treated with hydrogen peroxide to oxidize the adhering organic material and then heated to 200°C in air until the emission of black soot stopped. The heated product was cooled and activated in air.

Activation, in presence of air, was performed in an ordinary furnace, at 450°C, for 1 hr. The temperature and time were optimized by observing the surface properties of carbon obtained by activating the raw material for different intervals of time and at varying temperatures. The capacity of samples, activated to different temperatures and time periods, for taking up a variety of toxic materials was explored (by isotherms) and the conditions of activation were optimized to obtain samples exhibiting the best sorption capacity. The product obtained at a temperature higher or lower than 450°C exhibited poor adsorption capacity [17], probably due to a collapse of pore network and surface functional groups (at higher temperature).

The material was then treated with 1.0M HCl solution to remove the ash content and then washed with distilled water. It was dried at 100°C for 24 hr and sieved before use, so that all the tests could be performed on a reasonably uniform particle size (100–150 mesh). Finally, the product was stored in a vacuum desiccator until required.

## 2.3 Kinetic studies

For the adsorption rate study, the batch technique was selected because of its simplicity. A number of stoppered pyrex glass tubes (50 ml capacity) containing known concentrations were placed in a thermostat-cum-shaking assembly. When the desired temperature was reached a known amount of adsorbent (0.01 g) was added into each tube and the solutions were agitated by mechanical shaking. At predecided intervals of time, the solutions of the specified tubes were separated from the sorbent material and analysed to determine the uptake of metal ions. Equilibrium was attained in about 6–8 hours.

# 3 Results and discussion

## 3.1 Characterization

One gram of carbonaceous material was stirred with

100 ml of deionized water (pH 6.8) for 2 hr and left for 24 hr in an air-tight stoppered conical flask. A lowering of pH was observed. According to Steenberg's classification [20] the material under investigation may be termed as "L" carbon. The surface area of the sample as determined by the BET method was 629 m<sup>2</sup> g<sup>-1</sup>. The X-ray diffraction spectrum pattern of the sample does not show any peak, thereby indicating the amorphous nature of the product. The chemical analysis of the product gave carbon, aluminium, and iron contents as 92.0%, 0.4% and 0.6% respectively with LOI = 7%. The amount of silica and ash is negligibly small. Infrared spectroscopic analysis of the carbonaceous adsorbent points to the existence of carboxylic, phenolic, hydroxylic and quinone type carboxylic groups on the surface. The band at 1710 cm<sup>-1</sup> corresponds to a normal carbonyl group [21], while the one at 1605 cm<sup>-1</sup> may be attributed to conjugated hydrogen bonded carbonyl groups as suggested by Hallum and Drushel [22]. The density and porosity of the sample, as determined by the standard methods, were found to be 1.30 g/cm<sup>3</sup> and 78.0 respectively.

## 3.2 Kinetic studies

Kinetic studies are essential for a successful application of the adsorption process in wastewater treatment. It is desirable to have a quantitative understanding of the process, which reflects the mechanism of the rate controlling step and sometimes sheds significant light on the internal physical structure of the adsorbent material. Certain properties of the adsorbent and adsorbate can be helpful in indirectly determining the nature of the rate limiting steps. These factors include the particle size of the adsorbent, concentration of adsorbate, degree of mixing, affinity of adsorbate for adsorbent, and diffusion coefficients of the adsorbate in bulk solution and within the pores of the adsorbent. Results of laboratory scale studies conducted to delineate the effect of such parameters on the kinetics of adsorption of Pb<sup>2+</sup> and Cr<sup>6+</sup> (as dichromate ions) on carbonaceous material developed from fertilizer waste material are given below.

## 3.3 Effect of hydrogen ion concentration

The change in adsorption of the two metal ions over a pH range of 2–6 has been studied. The negative surface charge density of the carbonaceous adsorbent may not undergo much change with changing hydrogen ion concentration. The improved adsorption of Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> on carbonaceous adsorbent at low pH may be due to the neutralisation of negative surface charge by an excess of hydrogen ions, thereby facilitating the diffusion of dichromate ions and their uptake on the carbon surface. A significant reduction in the adsorption of Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> at higher pH is possibly due to the abundance of OH<sup>-</sup> ions, resulting in an increased hindrance to the diffusing metal

ions. Thus the optimum pH chosen for the removal of  $\text{Cr}_2\text{O}_7^{2-}$  is 2.0. In the case of lead, the adsorbing ion is positively charged and the sorption on the carbon surface may solely be electrostatic in nature and therefore does not change much with increasing hydrogen ion concentration (figure 1).

### 3.4 Time of contact

Some preliminary investigations on the rate of removal of  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{Pb}^{2+}$  on the adsorbent developed from fertilizer waste material indicate the process to be quite rapid and typically 50 to 80 percent of the ultimate adsorption occurs within the first hour of contact. The initial rapid adsorption subsequently gives way to a very slow approach to equilibrium and in 24 hr time saturation is reached.

### 3.5 Effect of the amount of adsorbent

The effect of the amount of adsorbent material on the rate of uptake of  $\text{Pb}^{2+}$  and  $\text{Cr}_2\text{O}_7^{2-}$  is shown in figure 2(a, b). It is observed that the rate of removal of adsorbate increases with increasing amount of adsorbent material. There is a substantial increase in sorption when the carbon dose increases from 0.5 to 1.0 g/l while the increase in removal efficiency, on introducing an additional 0.5 g/l carbon, is not so significant. Keeping this in view, the amount of carbon taken in all subsequent kinetic studies is 1.0 g/l. Further, the time taken for fifty percent of the total adsorption ( $t_{50}$ ) decreases with increasing amount of adsorbent and this reflects that the rate of adsorption is dependent on the amount of carbon present in the reactor.

### 3.6 Effect of particle size of adsorbent

Many experiments were performed to evaluate the influ-

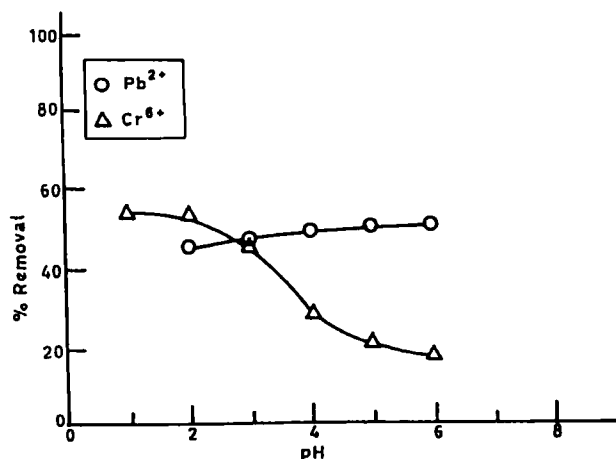


Figure 1. Effect of pH on the adsorption of metal ions on activated carbon.

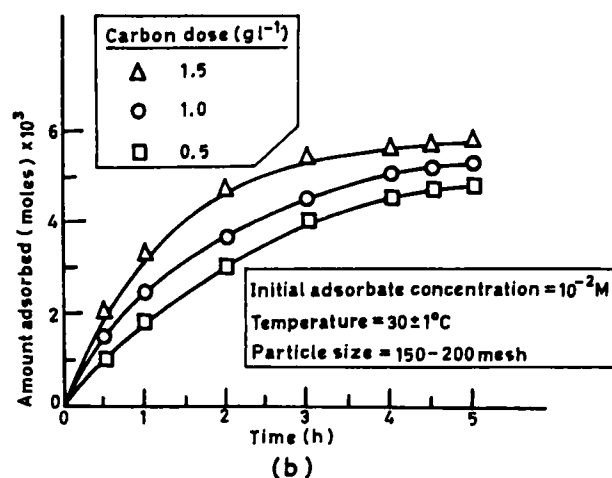
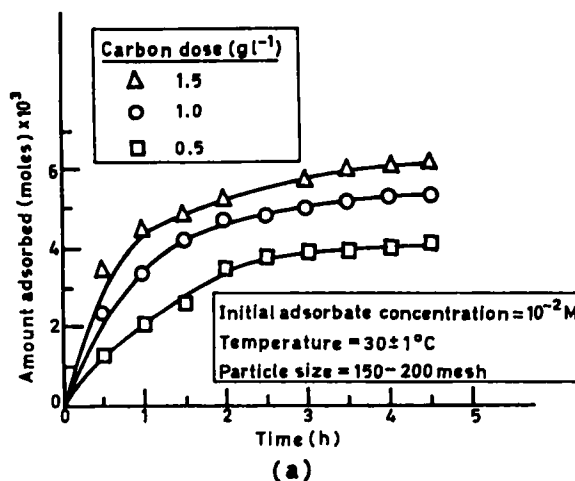


Figure 2. Effect of amount of activated carbon on the rate of uptake of (a)  $\text{Cr}^{6+}$ , (b)  $\text{Pb}^{2+}$ .

ence of the size of adsorbent particles on the kinetics of adsorption of  $\text{Pb}^{2+}$  and  $\text{Cr}_2\text{O}_7^{2-}$  on activated carbon. The results are graphically presented in figure 3(a, b). The rate of removal of  $\text{Pb}^{2+}$  and  $\text{Cr}_2\text{O}_7^{2-}$  increases with decrease in size of the adsorbent particles and the time required for 50% of the total adsorption is also less with particles of smaller size. This relationship clearly demonstrates the advantage of powdered adsorbent over the granular form from a kinetic viewpoint provided it does not hamper the flow rate in a column. This also gives some idea of the rate limiting step of the process as according to diffusion theory such a dependence is normally expected where external transport limits the rate of adsorption [23].

### 3.7 Effect of temperature

The adsorption of  $\text{Pb}^{2+}$  and  $\text{Cr}_2\text{O}_7^{2-}$  on carbon is an exothermic process and hence the rate of removal of adsorbate decreases with increasing temperature as shown in figure 4(a, b). This is further confirmed by the

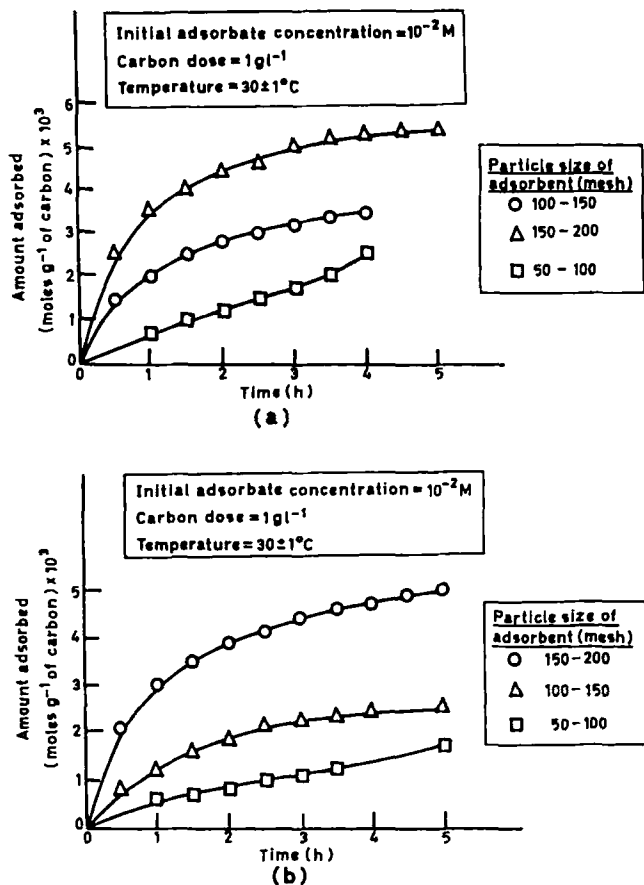


Figure 3. Effect of particle size of activated carbon on the rate of uptake of (a) Cr<sup>6+</sup>, (b) Pb<sup>2+</sup>.

fact that the time required for fifty percent completion of adsorption increases with a rise in temperature. The removal of the metals, in the first one hour of the process, goes down with enhancing temperature.

### 3.8 Effect of initial adsorbate concentration

For a strictly adsorptive reaction, the rate varies directly with the concentration of the adsorbate. The amount of Pb<sup>2+</sup> and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> removed in the first hour of contact increases as the concentration of the metal ions increases. It is further observed that the time required for fifty percent of the ultimate adsorption is independent of the initial adsorbate concentration (figure 5(a, b)).

It is quite well established that the rate of exchange adsorption is controlled by diffusion either through a hydrostatic boundary layer called **film diffusion control** or through the pores of the resin matrix called **particle diffusion control**. The rate of ion-exchange or exchange adsorption is mainly controlled by film-diffusion under conditions of small resin particle, dilute solution and mild stirring. It is controlled by particle diffusion under conditions of large particles, high concentration of solution and vigorous stirring. More practically, it is controlled by both processes.

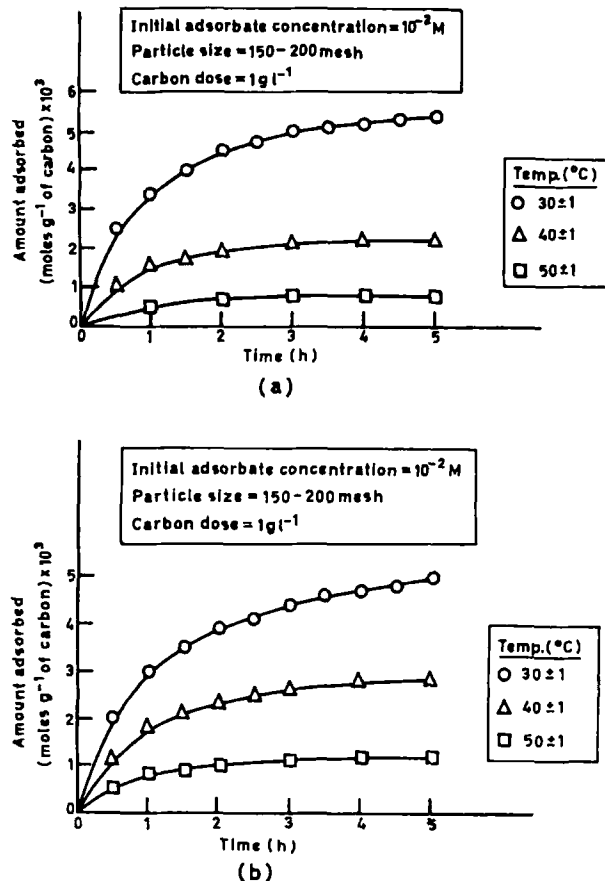


Figure 4. Effect of temperature on the rate of uptake of (a) Cr<sup>6+</sup>, (b) Pb<sup>2+</sup> by activated carbon.

Thus, in order to properly interpret the experimental data, it is necessary to determine which of the steps in the adsorption process governs the overall removal rate under the specified experimental conditions.

The three consecutive steps in the adsorption of an organic/inorganic compound by a porous adsorbent are:

- (I) Transport of the ingoing ion to the external surface of the adsorbent (film diffusion).
- (II) Transport of the adsorbate within the pores of the adsorbent except for a small amount of adsorption which occurs on the external surface (particle diffusion).
- (III) Adsorption of the ingoing ion (adsorbate) on the interior surface of the adsorbent.

It is generally accepted that process (III) is very rapid and does not represent the rate limiting step in the uptake of an inorganic compound. For the remaining two steps in the overall transport, three distinct cases occur:

- Case 1: external transport > internal transport.  
Case 2: external transport < internal transport.

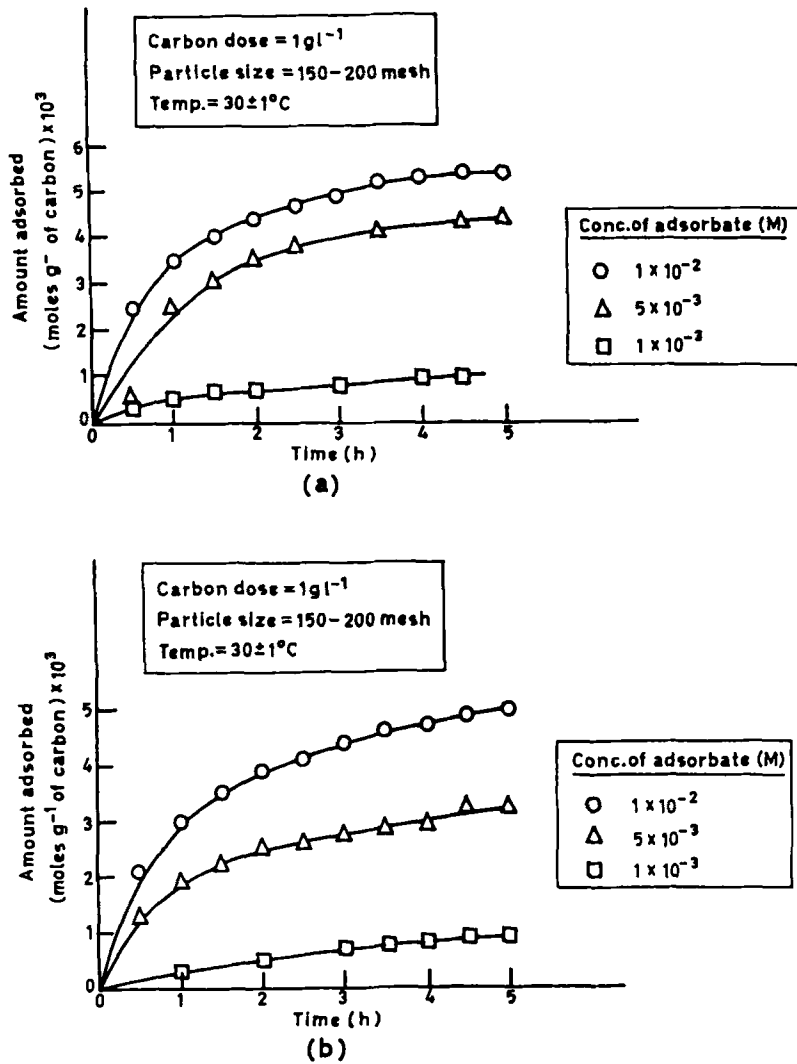


Figure 5. Effect of adsorbate concentration on the rate of uptake of (a) Cr<sup>6+</sup>, (b) Pb<sup>2+</sup> by activated carbon.

Case 3: external transport  $\approx$  internal transport.

$$B = \frac{\pi^2 D_i}{r_0^2} = \text{time constant}, \quad (3)$$

In cases 1 and 2, the rate is governed by particle and film diffusion respectively, whereas in case 3, the transport of ions to the boundary may not be possible at a significant rate and in all the three cases there may be a liquid film with a concentration gradient surrounding the sorbent particles.

To properly interpret the experimental findings, a quantitative treatment of the data is based on the model suggested by Helfferich [22]. Various parameters are calculated using the expressions (1)–(4) given by Boyd et al. [23]:

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left[\frac{-D_i t \pi^2 n^2}{r_0^2}\right] \quad (1)$$

$$= 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp[-n^2 B t], \quad (2)$$

where  $F$  = fractional attainment of equilibrium at time  $t$ ,

$D_i$  = effective diffusion coefficient,  
 $r_0$  = radius of the adsorbent particle assumed to be spherical,  
 $n = 1, 2, 3, \dots$  are the integers defining the infinite series solution obtained for a Fourier type of analysis.

A good approximation coefficient  $D_i$  can be calculated for an adsorption using the series.

The fractional attainment of equilibrium can be determined by

$$F = \frac{q}{q_e}, \quad (4)$$

where  $q$  = amount adsorbed after time  $t$ ,  
 $q_e$  = amount adsorbed after infinite time or at equilibrium.

For every observed value of  $F$ , corresponding  $Bt$  values as derived from equation (2) are obtained from

Reichenberg's table [24]. The linearity of  $Bt$  versus  $t$  plots are employed to distinguish between the film diffusion and particle diffusion controlled rates of adsorption.  $Bt$  versus time plots for the sorption of  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{Pb}^{2+}$  on activated carbon, developed from the fertilizer waste material, are linear and pass through the origin at and above a value of  $5 \times 10^{-3} \text{M}$  (figure 6(a, b)). However, at lower concentration the plots deviate from linearity. Also, the diffusion coefficient is dependent on the concentration of adsorbate and this reflects that the film diffusion may also be operative.

However, an increase in the sorption rate of  $\text{Pb}^{2+}$  and  $\text{Cr}^{6+}$  at higher temperature and decreasing particle size of the adsorbent (figures 7(a, b) and 8(a, b)) support the particle diffusion mechanism. This is further verified by drawing Mckay plots [24] ( $\log(1 - F)$  versus time) for the adsorbates at varying adsorbate concentrations. At low concentrations, the linear plots indicate a purely film diffusion controlled process (figure 9; only the case of  $\text{Cr}^{6+}$  is given), whereas at higher concentrations ( $\geq 5 \times 10^{-3} \text{M}$ ) the process is initially film diffusion controlled but in a later stage the particle diffusion mechanism becomes operative.

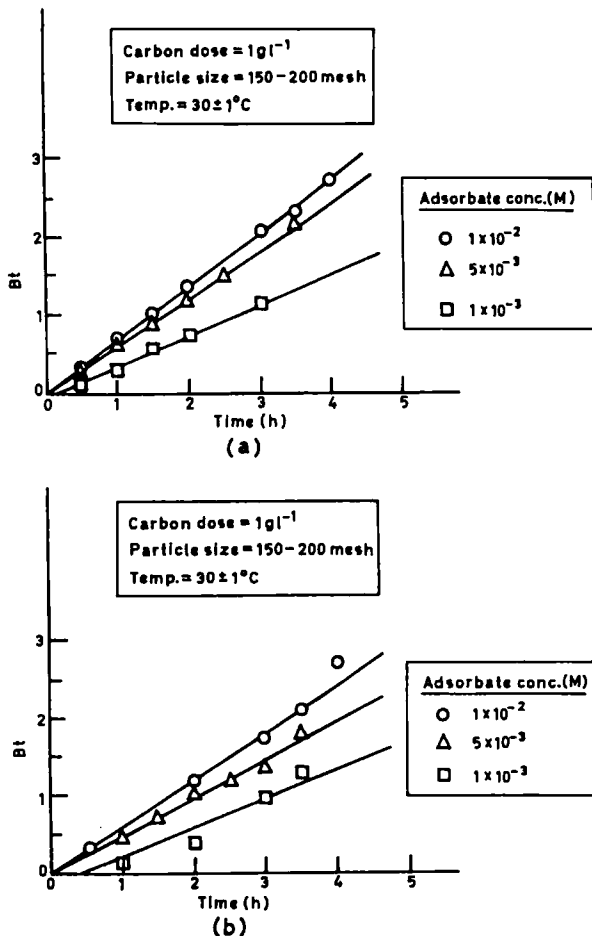


Figure 6.  $Bt$  vs. time plots at various adsorbate concentrations of (a)  $\text{Cr}^{6+}$ , (b)  $\text{Pb}^{2+}$  for activated carbon.

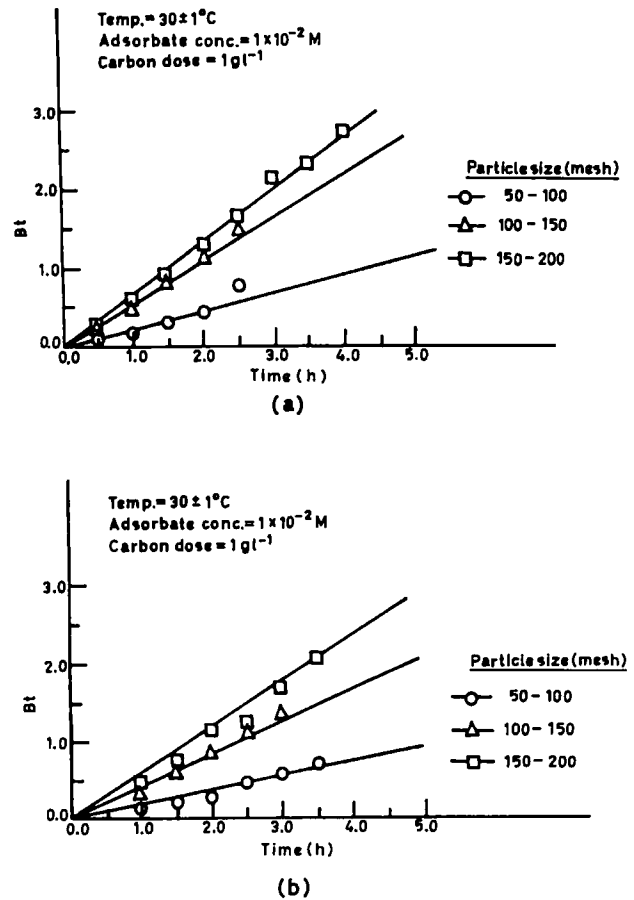


Figure 7.  $Bt$  vs. time plots of (a)  $\text{Cr}^{6+}$  and (b)  $\text{Pb}^{2+}$  at different particle sizes for activated carbon.

Figure 9(a, b) shows a change in rate of adsorption with change in temperature. The  $D_i$  values at 30, 40 and 50°C are given in table 1. The increased mobility of ions and a decrease in retarding forces acting on the diffusing ion results in the enhancement of  $D_i$  with the temperature (figure 10). Diffusion coefficient values for the two metal ions follow the same order in which these get adsorbed on the carbonaceous material. A comparison of these values on different adsorbates is worthwhile in visualizing the efficiency of the material under study. The effective diffusion coefficient values, observed in these investigations, are greater than those reported in case of hydrous ferric oxide [11] and clay montmorillonite [12] ( $10^{-18} \text{m}^2\text{sec}^{-1}$ ) and less than those for minerals like iron (III) antimonate [25] ( $10^{-12} \text{m}^2\text{sec}^{-1}$ ). This leads to the inference that the channels in the adsorbent, activated carbon generated from fertilizer waste slurry, are wider than those of hydrous oxides and narrower as compared to the minerals mentioned above.

The linear behaviour of  $\log D_i$  versus  $(1/T)$  (figure 10) plots permits the use of the Arrhenius equation and the energy of activation  $E_a$  and  $D_0$  values of the process are evaluated and reported in table 1.

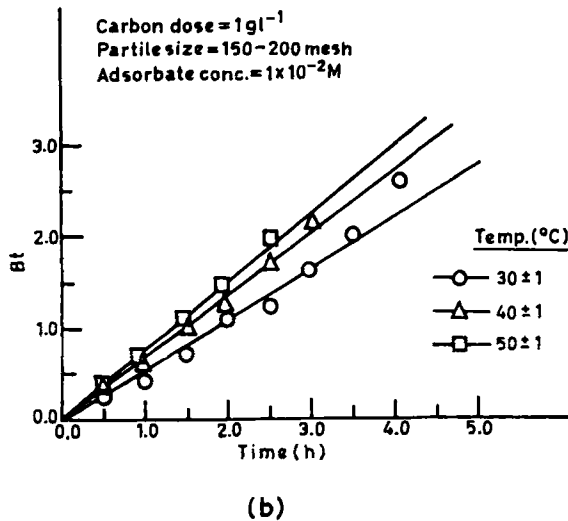
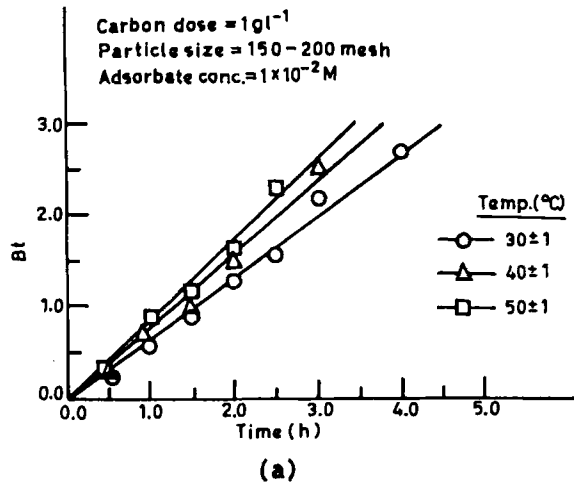


Figure 8.  $Bt$  vs. time plots of (a)  $\text{Cr}^{6+}$  and (b)  $\text{Pb}^{2+}$  at different temperatures for activated carbon.

$$D_i = D_0 \exp\left[\frac{-E_a}{RT}\right]. \quad (5)$$

The pre-exponential constant  $D_0$  (analogous to the Arrhenius frequency factor) gives the entropy of activation  $\Delta S^\ddagger$  as

$$D_0 = 2.72d^2 \left[\frac{kT}{h}\right] \exp\left[\frac{\Delta S^\ddagger}{R}\right], \quad (6)$$

where  $k$  = Boltzmann constant,  
 $h$  = Planck's constant,  
 $R$  = gas constant,  
 $T$  = temperature in Kelvin,  
 $d$  = distance between two active sites of the adsorbent which is conventionally taken as  $5 \text{ \AA}$ .

The values of  $E_a$  and  $\Delta S^\ddagger$  are given in table 1.

It is found that values of activation energy ( $E_a$ ) are higher from chromium than for lead. The negative values of entropies of activation ( $\Delta S^\ddagger$ ) obtained for the

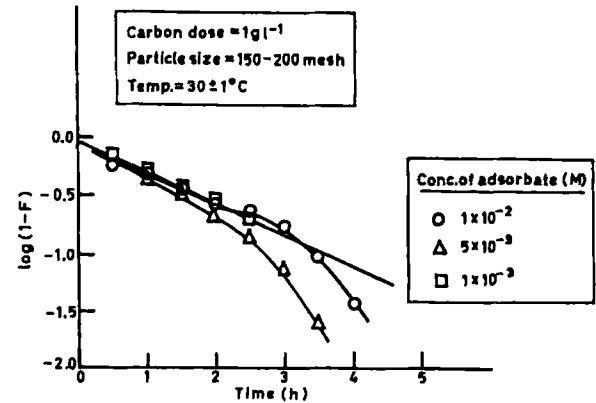


Figure 9. McKay plots of  $\text{Cr}^{6+}$  at various adsorbate concentrations for activated carbon.

adsorption of  $\text{Pb}^{2+}$  and  $\text{Cr}^{6+}$  are not uncommon in ion-exchange processes. Rawat and coworkers [25,26] have reported the negative  $\Delta S^\ddagger$  values for the exchange of metal ions in antimonates. This is analogous to the behaviour of bivalent ions migrating through  $\gamma$ -zeolites as observed by Freeman and Stamires [27]. The values reflect that no significant change occurs in the internal structure of the adsorbent during the adsorption of metal ions.

The removal of  $\text{Pb}^{2+}$  and  $\text{Cr}^{6+}$  at different concentrations (figure 5(a, b)) of adsorbent takes place in two phases. The first phase of solute uptake, the "immediate solute removal", obtained within the first two hours, is followed by "subsequent removal of solute" and this continues for a longer period of time. Thus the initial external/surface mass transfer is followed by a slower rate of internal diffusion within the carbonaceous material itself. The values of external mass transfer coefficients ( $\beta_L$ ) responsible for slowing the rate of uptake have been determined using the following mathematical mass transfer model suggested by McKay et al. [28]:

$$\ln\left[\frac{C_t}{C_0} - \frac{1}{mk}\right] = \ln\left[\frac{mk}{1+mk}\right] - \frac{1+mk}{mk} \times \beta_L S_S t, \quad (7)$$

$$m = \frac{W}{V}, \quad (8)$$

$$S_S = \frac{6m}{(1-\epsilon_p)d_p\rho_p}, \quad (9)$$

where  $C_t$  is the concentration of adsorbate (mg/l) after time  $t$ ;  $C_0$  the initial concentration of adsorbate (mg/l);  $m$  is the mass of adsorbent per unit volume of particle free adsorbate solution (g/l);  $K$  (lg) the Langmuir constant obtained by multiplying adsorption capacity  $Q_0$  and adsorption energy ( $b$ );  $\beta_L$  the mass transfer coefficient ( $\text{cm sec}^{-1}$ ); and  $S_S$  is the outer surface of the adsorbent per unit volume of particle free slurry ( $\text{cm}^{-1}$ ). The values of  $m$  and  $S_S$  are calculated using equations (8) and (9), where  $W$  is the weight of adsorbent (g),  $V$  the volume

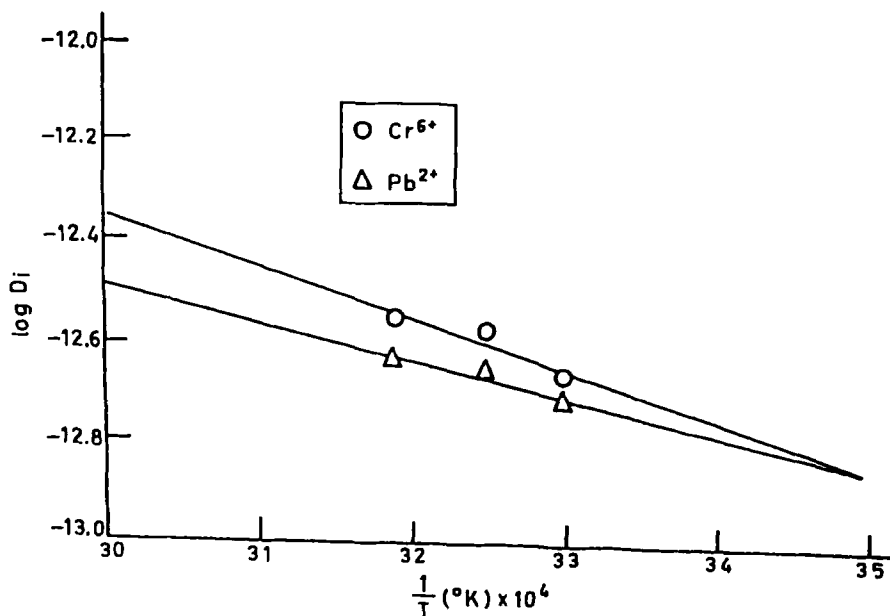


Figure 10.  $\log D_i$  vs.  $1/T$  plots of  $Pb^{2+}$  and  $Cr^{6+}$  for activated carbon.

of particle free adsorbate solution ( $l$ ),  $d_p$ , the particle diameter (cm),  $\rho_p$  the density of adsorbent ( $g\ cm^{-1}$ ) and  $\epsilon_p$  is the porosity of adsorbent material.

At  $t \rightarrow 0$ , surface mass transfer will predominate, consequently a plot of  $\ln[(C_t/C_0) - 1/(1 + mk)]$  versus time yields a straight line with intercept  $mk/(1 + mk)$  and slope  $((1 + mk)/mk)\beta_L S_S$ , from which the surface mass transfer coefficient has been evaluated. The linear nature of the plots (figure 11) for the systems under investigation indicate the applicability of the diffusion model. The values of mass transfer coefficients ( $\beta_L$ ) for the sorption of  $Pb^{2+}$  and  $Cr^{6+}$  on carbon at  $30^\circ C$  were calculated and are reported in table 2. Mass transfer coefficients of  $Pb^{2+}$  and  $Cr^{6+}$  suggest the velocity of the adsorbate transport from bulk to solid phase to be quite rapid.

The adsorption of  $Pb^{2+}$  and  $Cr^{6+}$  from liquid to solid phase can be considered as a reversible reaction with an equilibrium established between two phases. Expression (10) (Lagergren expression [29]), a first order rate expression, has been applied for the determination of the specific rate constant of adsorption for carbon-metal ions systems:

$$\log(q_e - q) = \log q_e - \frac{K_{ad}}{2.303} t, \quad (10)$$

where  $q_e$  and  $q$  are the amounts of adsorbate species adsorbed by one gram of adsorbent (moles  $g^{-1}$ ) at equilibrium and at time  $t$  respectively and  $K_{ad}$  is the specific rate constant of adsorption ( $min^{-1}$ ). The straight line plots of  $\log(q_e - q)$  versus time at  $30^\circ C$  (figure 12) show the applicability of the first order rate expression of Lagergren and the values are given in table 2.

#### 4 Cost estimation

The uptake of  $Pb^{2+}$  and  $Cr^{6+}$  on carbonaceous material developed from fertilizer waste material is quite comparable to other commercially available adsorbents as shown in table 3 [12,15,30-32].

In India the cheapest variety of commercially available carbon costs \$ 250 per ton. The fertilizer waste is available at \$ 5.0 a ton and considering the total expenses for transport, chemicals, electrical energy etc., the finished product would cost approximately \$ 20 per ton.

Table 1  
Effective diffusion coefficients ( $D_i$ ) values,  $D_0$ ,  $E_a$  and  $\Delta S^\#$  values for the adsorption of metal ions on carbon.

Metal ions	Effective diffusion coefficient ( $m^2 sec^{-1}$ )			$D_0$ ( $m^2 sec^{-1}$ )	$E_a$ ( $kJ\ mol^{-1}$ )	$-\Delta S^\#$ ( $JK^{-1} mol^{-1}$ )
	$30^\circ C$	$40^\circ C$	$50^\circ C$			
$Pb^{2+}$	$1.96 \times 10^{-13}$	$2.25 \times 10^{-13}$	$2.31 \times 10^{-13}$	$2.41 \times 10^{-13}$	24.2	138.60
$Cr^{6+}$	$2.15 \times 10^{-13}$	$2.63 \times 10^{-13}$	$2.85 \times 10^{-13}$	$3.00 \times 10^{-13}$	31.8	136.88



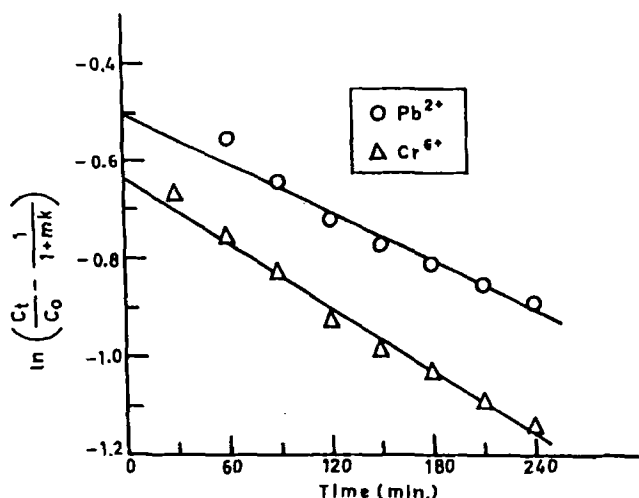


Figure 11. Plots of  $\ln((C_t/C_0) - 1/(1+mk))$  vs. time for the mass transfer of  $Pb^{2+}$  and  $Cr^{6+}$  at  $30^\circ C$  on activated carbon.

Recovery of metal ions and the chemical regeneration of columns (without dismantling the same), if possible, may further bring down the cost factor.

## 5 Treatment of effluent

The findings mentioned above show the possibility of using the carbonaceous material for the treatment of lead and chromium bearing wastewater. Experiments with actual waste material from a metal finishing plant provide some fruitful results. A typical run containing  $Cu = 10.0$ ;  $Zn = 3.0$ ;  $Cd = 4.0$ ;  $Fe = 2.0$ ;  $Ni = 58.0$ ;  $Pb = 12.0$ ;  $Cr = 9.0$  mg/l and  $Cu = 2.0$ ;  $Zn = 10.0$ ;  $Cd = 1.0$ ;  $Pb = 8.0$ ;  $Cr = 11.0$ ;  $Ni = 5.0$  mg/l was treated with the prepared adsorbent. Increase in adsorbent dose enhanced the separation of lead and chromium and a complete removal of the two metal ions,  $Pb(II)$  and  $Cr(VI)$  from 50 ml of wastewater at  $pH = 2.0$  (for  $Cr^{6+}$ ) and at 4.0 (for  $Pb^{2+}$ ) was possible at an adsorbent dose of 3.0 g/l.

## 6 Conclusions

The carbonaceous material developed from fertilizer waste is an effective adsorbent for the removal of  $Pb^{2+}$

Table 2  
Mass transfer coefficients ( $\beta_L$ ) and rate constant of adsorption ( $K_{ad}$ ) for activated carbon-metal ions systems.

Metal ions	$\beta_L$ ( $cm\ sec^{-1}$ )	$K_{ad}$ ( $min^{-1}$ )
$Pb^{2+}$	$1.24 \times 10^{-6}$	$0.94 \times 10^{-2}$
$Cr^{6+}$	$1.56 \times 10^{-6}$	$0.92 \times 10^{-2}$

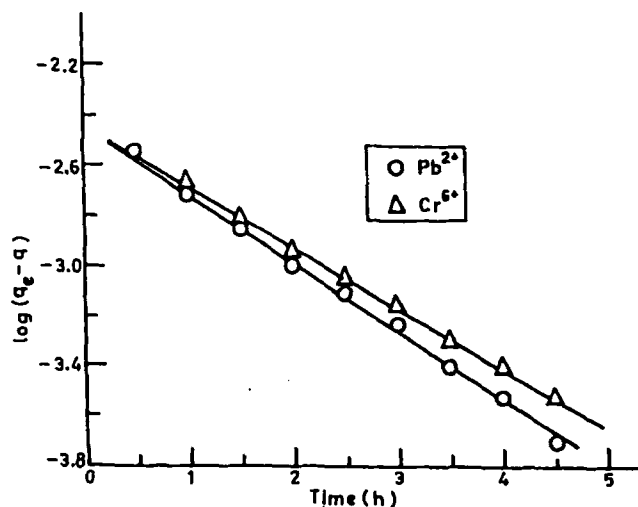


Figure 12. Lagergren plot for adsorption of  $Pb^{2+}$  and  $Cr^{6+}$  at  $30^\circ C$  on activated carbon.

and  $Cr^{6+}$  from aqueous solutions and wastewater. The removal of these two metal ions by the adsorbent material takes place via particle diffusion mechanism and the thermodynamic parameters reflect the feasibility of the process. The kinetics of  $Pb^{2+}$  and  $Cr^{6+}$  is an exothermic process. Quantitative removal of  $Pb(II)$  and  $Cr(VI)$  from 50 ml of metal finishing wastewater required 300 mg of adsorbent.

## Acknowledgement

One of the authors, Dinesh Mohan, is grateful to the Council of Scientific and Industrial Research (CSIR), New Delhi for providing financial assistance.

Table 3  
Adsorption capacities of activated carbon vis-à-vis other low-cost adsorbents.

Adsorbents	$Q^0$ (mg metal $g^{-1}$ of different adsorbents) for $Pb^{2+}$ and $Cr^{6+}$	
	$Pb^{2+}$	$Cr^{6+}$
Sphagnum moss peat	—	119
Waste tea leaves	125.85	—
Human hairs	80.7	1.1
Activated carbon (calgon filtrosorb-400)	—	3265.39
Lignin	2536.00	—
Mixed adsorbent (fly ash + china clay + wallastonite)	192.09	—
Waste tyre rubber	0.238	—
Moss	79.91	—
Activated carbon (developed from fertilizer waste material) under investigation	1213.80	1618.0

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