

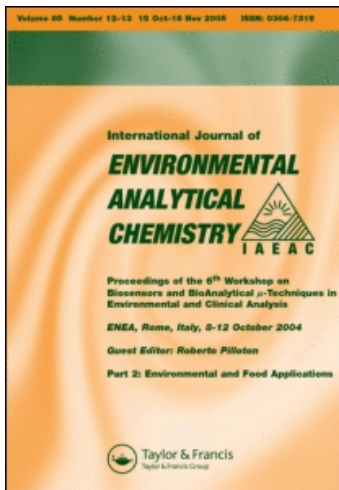
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International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713640455>

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To cite this Article Sharma, Y. C. , Prasad, G. and Rupainwar, D. C.(1991) 'Treatment of Cadmium(I)-Rich Effluents (Kinetic Modelling and Mass Transfer)', *International Journal of Environmental Analytical Chemistry*, 45: 1, 11 – 18

To link to this Article: DOI: 10.1080/03067319108232933

URL: <http://dx.doi.org/10.1080/03067319108232933>

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TREATMENT OF CADMIUM(II)-RICH EFFLUENTS (KINETIC MODELLING AND MASS TRANSFER)

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(Received 15 September 1990; in final form 10 January 1991)

Removal of Cd(II) by sorption on China clay has been investigated. Removal increased from 41.0 to 80.3% by decreasing the cadmium concentration from 2.0×10^{-4} M to 0.5×10^{-4} M at pH = 6.5 and 30°C. Kinetic modelling of the process has been done using Lagergren's first-order rate equation. The rate of adsorption at pH = 6.5 and 30°C was found to be $5.0 \times 10^{-2} \text{ min}^{-1}$. The process of removal involves intraparticle diffusion. Mass transfer parameters have been calculated; the process is exothermic in nature. Studies with representative wastewater samples from plating units have also been undertaken.

KEY WORDS: Effluents, Cd(II), adsorption, kinetic modelling, mass transfer.

INTRODUCTION

Heavy metals are toxic to the ecosystem and their pollution effect poses a possible human health risk causing cancer of various sites of the body.¹ From the beginning of the nineteenth century, due to the arrival of the industrial revolution in the world, cadmium contamination has increased about five times due to increased use.² This heavy metal has been well documented as a cumulative toxicant with a biological half-life of 16–33 years in man.³ Ingestion of cadmium to human body results in a very painful disease, *itai-itai*¹. An epidemiological study on Japanese farmers concludes that an allowable concentration limit for cadmium would probably not exist with respect to man,³ whereas the European Community has fixed the threshold limit value (TLV) for cadmium in drinking water as 0.1 mg L^{-1} .⁴ Moreover, freshwater biota which plays an important role in aquatic food chains has been found to be very sensitive to this metal ion and it is noteworthy that these show survival risks even in the $\mu\text{g L}^{-1}$ range.^{5,6} Various established research agencies have compiled important reviews on cadmium.^{7–9}

Adsorption on activated carbon has been a popular technique for removal of heavy metals and other water and wastewater pollutants,^{10–13} but its high cost limits its application at industrial levels in a developing country like India. The present research paper has been addressed to the use of China clay, a locally available cheap clay mineral, for the removal of Cd(II) by adsorption. The effect of retention time and concentration on the removal of Cd(II) has been studied. The dynamics of adsorption and the mass transfer at various temperatures have also been studied.

MATERIALS AND METHODS

The chemicals used in the experiments were of analytical reagent grade and were obtained from B.D.H., Bombay (India). China clay was obtained from Bihar, India. The details about the determination of particle size, surface area, etc. have been published elsewhere.¹⁰ Stock solutions of cadmium were prepared by dissolving appropriate quantities of pure cadmium metal in distilled water and 1 M HCl.¹¹ Stock suspensions of the adsorbent (40 g L^{-1}) were prepared several weeks prior to the experiments to ensure complete hydration of the solid surface. The batch adsorption experiments were conducted by first adding appropriate quantities of distilled water, NaClO_4 solution ($I = 10^{-2} \text{ M}$) and metal solutions (10^{-4} M) to a set of 250-ml polythene bottles. China clay, the adsorbent (20 g L^{-1}) was then added to the stock solution, the pH of the solutions was adjusted as desired by adding 1 M HCl or 1M NaOH. After pH adjustment, the sample bottles were shaken in a thermostatted shaker at the desired temperature until saturation. After equilibrium, the adsorbent was removed by centrifugation. The supernatant was analysed for Cd(II) by atomic absorption spectrophotometry, using a Perkin-Elmer model 250 apparatus.¹¹ Desorption studies were also carried out in the presence of pH 2.0 solution. Similar batch adsorption experiments were carried out with the waste-water sample collected at an electroplating unit in Mirzapur.

RESULTS AND DISCUSSION

Chemical characterization of the adsorbent

Chemical characterization of China clay has been published elsewhere.¹⁰ Silica (46.2%) and alumina (38.4%) are the major constituents of china clay; trace amounts of the oxides of iron, calcium etc. are also present in it.

Effect of retention time and concentration on the removal of Cadmium

From Figure 1 it is clear that the uptake of cadmium increased initially and acquired saturation in 80 min. The plots are single and smooth indicating monolayer coverage of the adsorption for the present system. The time required to attain equilibrium is independent of the concentration of Cd(II) which reveals the concentration-independent nature of Cd(II) removal. The uptake increased from 41.0 to 80.3% by decreasing the initial concentration of Cd(II) from 2.0×10^{-4} to $0.5 \times 10^{-4} \text{ M}$ at pH 6.5 and 30°C . The finding that uptake is greater at lower concentrations is industrially useful.¹²

Kinetic modelling

Kinetic modelling of the process was carried out using Lagergren's model:³

$$\log(q_e - q) = \log q_e - \frac{k_{ad}}{2.303 \cdot t} \quad (1)$$

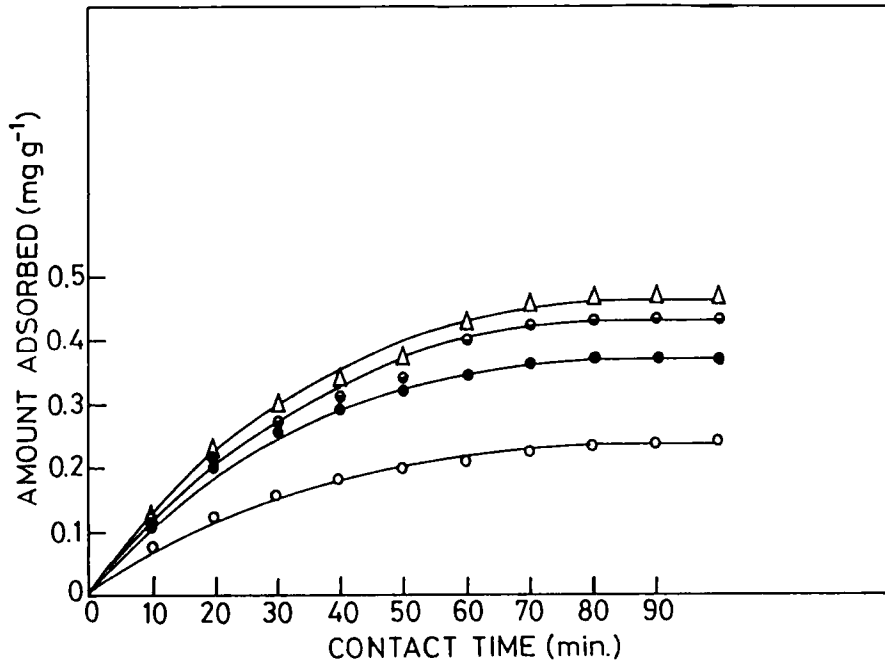


Figure 1 Effect of retention time and concentration on the removal of Cd(II) by sorption on China clay concentrations (\circ) 0.5×10^{-4} M, (\bullet) 1.0×10^{-4} M (\odot) 1.5×10^{-4} M and (\triangle) 2.0×10^{-4} M, temperature, 30°C , pH 6.5, ionic strength, 1.0×10^{-2} M NaClO_4 .

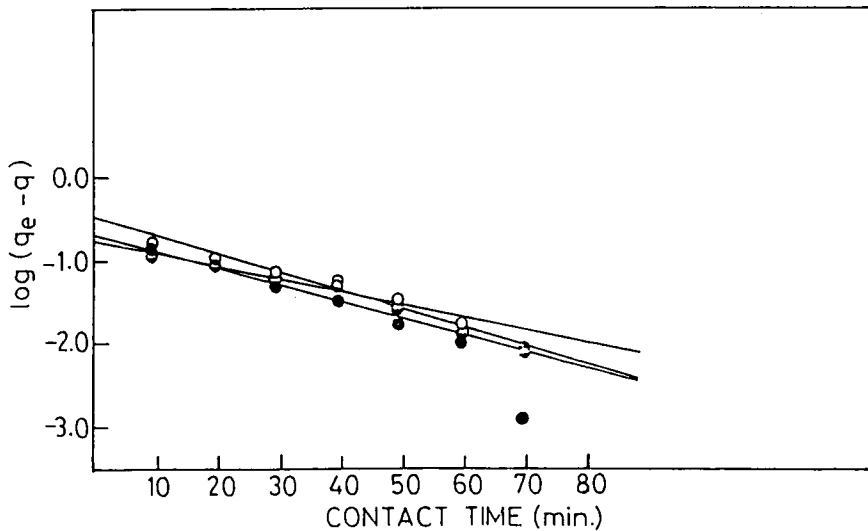


Figure 2 Dynamic modelling of Cd(II) uptake by China clay, concentration 0.5×10^{-4} M, Temperatures: (\circ) 30°C , (\bullet) 40°C (\odot) 50°C ; pH 6.5; ionic strength, 1.0×10^{-2} M NaClO_4 .

Table 1 Kinetic modelling parameters of the process of Cd(II) removal

Temperature (°C)	k_{ad} (min^{-1})	k_p ($\text{min}^{-1/2}$)
30	0.051	0.020
40	0.045	0.015
50	0.034	0.009

where q_e and q (both in mg g^{-1}) are the amounts of Cd(II) adsorbed at equilibrium and at time t respectively and $k_{ad}(\text{min}^{-1})$ is the rate constant for adsorption for the present process. The plot of $\log(q_e - q)$ vs. t (Figure 2) is linear showing the proposed model to be suitable for the adsorption of Cd(II) on China clay. The values of k_{ad} at different temperatures were determined from the slopes of these plots (Table 1). At 30°C and pH 6.5, k_{ad} was found to be $5.0 \times 10^{-2} \text{ min}^{-1}$.

Intraparticle diffusion study

Most of the batch sorption processes proceed with diffusion of adsorbate into the pores of the sorbent particles and into the space available between the molecules of the adsorbate phase. Here diffusion is considered as the rate-controlling step.¹⁴ In our investigations this possibility was tested by plotting the amount of cadmium adsorbed vs. square root of time, $t_{1/2}$ (Figure 3). The plots are curved in their initial stages (30–40 min) and then became linear showing the involvement of intraparticle diffusion. The values of the rate constant of pore diffusion, k_p , were determined from the slope of the linear portions of the plots (Table 1). The value at 30°C was found to be $2.0 \times 10^{-2} \text{ mg g}^{-1} \text{ min}^{1/2}$.

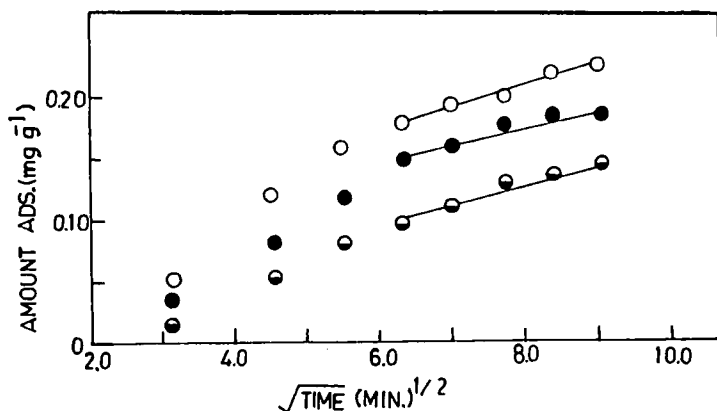


Figure 3 Intraparticle diffusion plot for the removal of Cadmium (II) by adsorption on China clay. concentration, $0.5 \times 10^{-4} \text{ M}$, temperatures: (○) 30°C, (●) 40°C and (◐) 50°C; pH 6.5; ionic strength, $1.0 \times 10^{-4} \text{ M NaClO}_4$.

Table 2 Langmuir constant and coefficient of mass transfer for Cd(II) removal

Temperature (°C)	k ($l g^{-1}$)	β_L ($cm s^{-1}$)
30	0.330	0.122
40	0.106	0.068
50	0.075	0.057

Mass transfer study

During the uptake of pollutants from aqueous solutions by sorption, the adsorbate species from the bulk solution are transferred to the solid-solution interface or the adsorbent surface. Mass transfer was studied using the McKay *et al.* model:¹³

$$\ln\left(\frac{C_t}{C_0} - \frac{1}{1 + mk}\right) = \ln\frac{mk}{1 + mk} - \frac{1 + mk}{mk} \cdot \beta_L S_s t \quad (2)$$

where C_t and C_0 (both in $mg l^{-1}$) are the concentrations of the adsorbate species at time t and at $t = 0$, respectively, m ($g l^{-1}$) is the mass of adsorbent per unit volume, k ($l mg^{-1}$) is the Langmuir constant, β_L ($cm s^{-1}$) is the mass transfer coefficient and s_s (cm^{-1}) is the outer surface of the adsorbent per unit volume. Values of the Langmuir constant for the present investigations at different temperatures are given in Table 2. The plot of $\ln(C_t/C_0 - 1/1 + mk)$ vs. t (Figure 4) is a straight line showing the

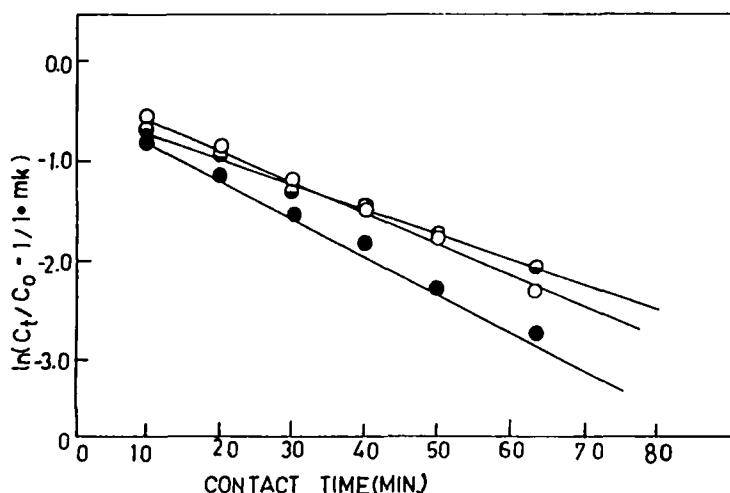


Figure 4 Mass transfer during Cd(II) uptake. Concentration, 0.5×10^{-4} M, pH 6.5; temperatures; (○) 30°C, (●) 40°C and (●) 50°C.

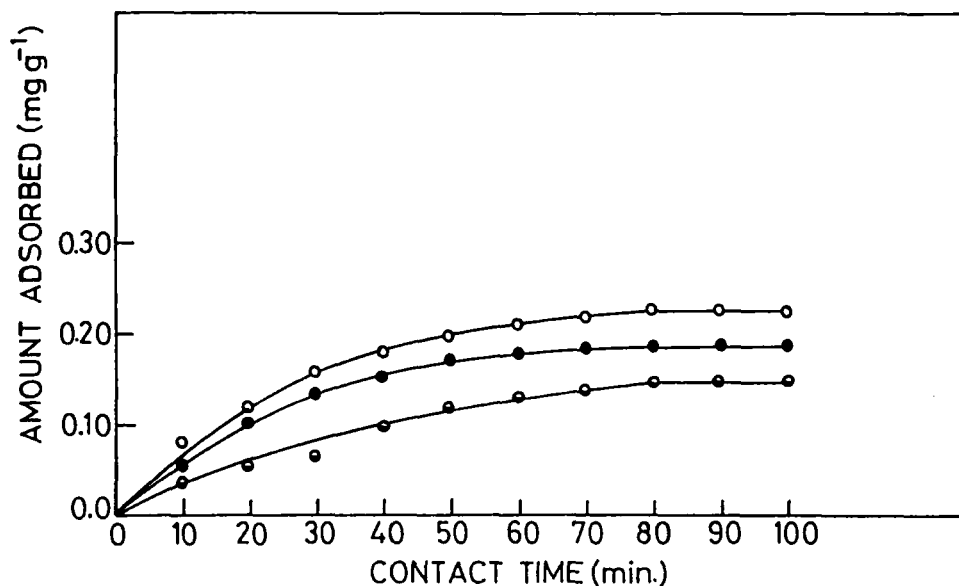


Figure 5 Effect of temperature on the removal of Cd(II) by sorption on China clay. pH 6.5; ionic strength, 10×10^{-2} M NaClO₄; temperatures; (O) 30°C, (●) 40°C and (◐) 50°C.

validity of the McKay *et al.* model for the present system. The mass transfer coefficient, β_L , at different temperatures was calculated using these plots; its values are reported in Table 2. At 30°C and pH 6.5, β_L was found to be 0.12 cm s^{-1} which indicates that the rate of transfer of Cd(II) species from the bulk to the adsorbate is rapid enough.

The values of β_L decreased from 0.12 to 0.05 cm s^{-1} when increasing the temperature from 30 to 50°C. This decrease is attributed to a decreased sorption with increasing temperatures.

Effect of temperatures

Figure 5 shows the effect of temperature on the sorption of cadmium by China clay. The uptake of Cd(II) is inversely proportional with temperature confirming the

Table 3 Results of desorption studies (all concentrations in mg l^{-1})

Initial concn. (a)	Liquid phase concentration at equilibrium (b)	Solid phase conc. at equilibrium calculated (a)-(b)	Solid phase concentration at equilibrium by desorption
5.62	4.51	1.11	0.91
11.24	7.19	4.05	3.82
16.86	8.55	8.31	8.11
22.48	9.22	13.26	13.4

Table 4 Characteristics of representative wastewater sample*

<i>Parameters</i>	<i>Values</i>
pH	6.5
Temperature (°C)	30
Total solids	1350
Suspended solids	90
Cr(VI)	2.5
Cd	5.6
Cu	1.5
Zn	2.0
Ni	9.3
Ag	0.01
CN	0.31

† All values except pH and temperature in mg l^{-1} .

exothermic nature of Cd(II) sorption on the selected adsorbent.¹⁰ It is thus clear that low temperatures will favour Cd(II) removal.

Desorption studies

The concentration of the adsorbate on the adsorbent surface was determined by desorption studies; the values so obtained are close to the calculated values although slightly lower (Table 3). Obviously, calculated values can be used without seriously affecting accuracy.

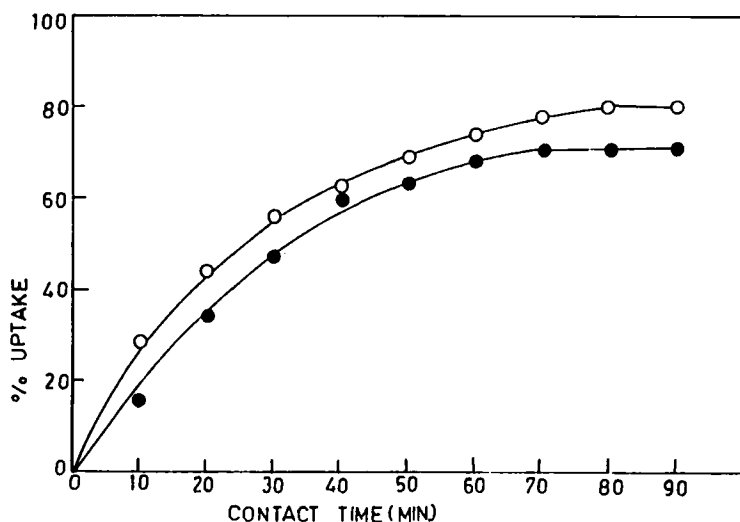


Figure 6 Percent removal of Cd(II) from wastewater sample. pH 6.5; temperature, 30°C; ionic strength, 1.0×10^{-2} M NaClO_4 . (O) Simulated sample and (●) representative wastewater sample.

Wastewater sample

Characteristic data of a representative wastewater sample are given in Table 4. From Figure 6 it can be inferred that the removal of Cd(II) from actual wastewater is less than from the simulated sample. The decreased uptake from the wastewater sample may be attributed to a competition between various cations present in the system and also due to complexation effects of organic and inorganic ligands present in the wastewater.

CONCLUSIONS

The following conclusions can be drawn:

- a) low surface coverage favours removal of Cd(II).
- b) 80% removal of Cd(II) can be achieved under optimum conditions using China clay as an adsorbent.
- c) the uptake process is exothermic, i.e. low temperature favours removal.
- d) desorption studies indicate that most of the adsorbate can be leached out under suitable conditions.
- e) the adsorption technique seems to be quite attractive for Cd(II) removal from wastewater of metal-bearing plating discharges.

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