



Studies on the Cd(II) removal from water by adsorption

D.B. Singh^{a,*}, D.C. Rupainwar^b, G. Prasad^b, K.C. Jayaprakas^a

^a Central Mining Research Institute, Barwa Road, Dhanbad-826001, India

^b Pollution Research Laboratory, Department of Applied Chemistry, Institute of Technology,
Banaras Hindu University, Varanasi-221005, India

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Abstract

The feasibility of using hematite for the removal of Cd(II) from aqueous solutions was investigated employing an adsorption technique. The adsorption was found to depend on Cd(II) concentration, pH, particle size of hematite, agitation rate and temperature of the system. The maximum removal was found to be 98% for the cadmium concentration of $44.88 \mu\text{mol l}^{-1}$ at a temperature of 20°C and pH 9.2 with 40 g l^{-1} of hematite of particle size $< 200 \mu\text{m}$ with agitation 125 rpm rate after 2 h. The applicability of the Langmuir isotherm was tested for the Cd(II)-hematite system at optimum conditions. The process follows first order kinetics. The mass transfer coefficient, diffusion coefficient and thermodynamic parameters have been determined to elucidate the mechanism of uptake. The uptake of cadmium is partially diffusion controlled and partially due to an electrostatic effect along with specific adsorption involving Cd^{++} and CdOH^+ which seem to play an effective role. The data has been subjected to multiple regression analysis and a computer model has been developed to predict the removal of Cd(II) from water under certain boundary conditions. The present technique has been found to be cost-effective. © 1998 Elsevier Science B.V.

Keywords: Adsorption; Hematite; Cadmium; Diffusion; Electrostatic attraction; Multiple regression analysis

1. Introduction

Cadmium, which is a non-essential metal for human consumption has various applications in a variety of industrial processes and operations [1,2]. Cadmium directly meets the water bodies through the effluent of the industries causing a marked increase

* Corresponding author. Fax: +91-326-202429.

in its concentration. It has toxic effects when its concentration exceeds the threshold limit value (TLV) of 0.005 mg l^{-1} [3] in drinking water. It causes various types of acute and chronic disorders [4,5]. The conventional means for treating wastewaters containing cadmium follow alkaline precipitation and ion exchange [6,7]. But, due to high maintenance costs, these methods do not suit the needs of a developing country such as India. An attempt has been made to develop an inexpensive method which is simple, easy to operate and maintain. Out of all the methods available [6,7] an adsorption method was selected because of its sludge free clean operation. A number of adsorbents such as activated carbon [6,8,9] discarded automotive tyres, agricultural products and by-products [6], and starch Xanthate [10] have been used for cadmium removal. Removal by adsorption can be cost effective using recovery and reuse of conventional adsorbents like activated carbon or using low cost adsorbent materials with a single use followed by their destruction or retention. In the present study, the authors have selected an abundantly available and cheap adsorbent, hematite, for cadmium removal.

2. Materials and methods

The adsorbent (hematite) was obtained as an iron ore from Noamundi mine, Bihar, India. It was passed through the sieve of 200 mesh size after crushing and used as such without any pretreatment. Indian standard methods were used for the chemical analysis of the adsorbent [11]. The characterization of hematite is given in Table 1.

The adsorption experiments were carried out using a completely mixed batch reactor (CMBR) technique. Hematite solids (40 g l^{-1}) were taken from a stock suspension, prepared one week before all experiments to ensure complete hydration in polythene bottles containing a known amount of cadmium. The contents, at the desired concentration and pH, were agitated in a rotary thermostat at different temperatures with various sizes of hematite particles at different agitation rates. The pH of the solution was

Table 1
Characterizations of hematite

Constituents	% W/W ($\pm 0.5\%$)
Fe ₂ O ₃	80.80
SiO ₂	4.00
CaO	4.80
FeO	1.49
Al ₂ O ₃	2.10
P	0.05
MnO ₂	0.08
TiO ₂ , MgO, P ₂ O ₅ , etc.	6.78
Mean particle diameter	200 μm
Porosity	0.41
Surface area (BET)	4.40 $\text{m}^2 \text{g}^{-1}$
Density	5.10 g cm^{-3}
pH _{zpc}	7.10

adjusted by NaOH/HCl solutions. At the end of predetermined time intervals, the contents were centrifuged at 10^4 rpm and the supernatant liquors were analyzed by using atomic absorption spectrophotometric method [12].

3. Results and discussion

3.1. Effect of retention time and initial solute concentration

It is evident from the Fig. 1 that the uptake of cadmium increases with the lapse of time and attains equilibrium in 120 min at a agitation speed of 125 rpm for each concentration showing the independent nature of equilibrium period for the solute concentration. Such observations were also noted at various pH and temperatures of the system with adsorbent particles of different sizes. However, the uptake of cadmium from water by hematite increases with the initial concentration of cadmium. The maximum removal of saturation was found to be 98% at a temperature of 20°C and pH 9.2 for an initial concentration of $44.88 \mu\text{mol l}^{-1}$ and hematite 40 g l^{-1} .

3.2. Effect of agitation rate

Fig. 2 shows the experimental results obtained from a series of contact time studies for cadmium removal (at $71.17 \mu\text{mol l}^{-1}$ concentration, 9.2 pH and 20°C temperature with adsorbent particle size of $200 \mu\text{m}$) in which the rate of agitation was varied from 50 to 125 rpm. These results indicate that the uptake increases from 1.36 to $1.68 \mu\text{mol g}^{-1}$ with the increase in the rotational speed from 50 to 125 rpm. This may be explained by the fact that the increasing agitation rate decreases the boundary layer resistance to mass transfer in the bulk and increases the driving force of Cd ions. It may be, therefore,

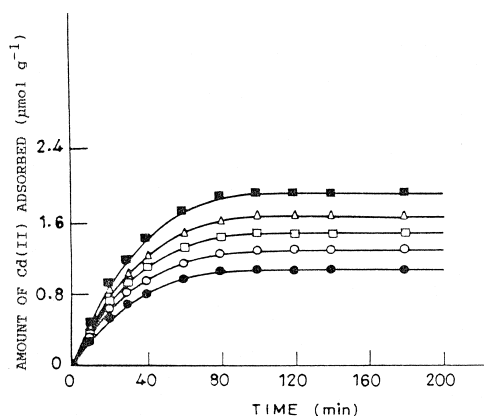


Fig. 1. Removal of Cd(II) by hematite at initial concentration of $44.48 \mu\text{mol l}^{-1}$ (●), $53.38 \mu\text{mol l}^{-1}$ (○), $62.27 \mu\text{mol l}^{-1}$ (□), $71.17 \mu\text{mol l}^{-1}$ (△) and $88.96 \mu\text{mol l}^{-1}$ (■). Conditions: Particle size: $< 200 \mu\text{m}$, Temperature: $20 \pm 0.5^\circ\text{C}$, Agitation rate: 125 rpm and pH: 9.2.

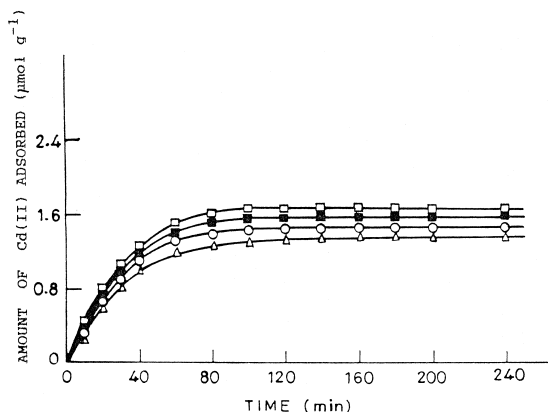


Fig. 2. Removal of Cd(II) on hematite at different agitation rates, i.e., 50 rpm (Δ), 75 rpm (\circ), 100 rpm (\blacksquare) and 125 rpm (\square). Conditions: Cd(II) concentration $71.17 \mu\text{mol l}^{-1}$, Temperature: $20 \pm 0.5^\circ\text{C}$, Particle size: $< 200 \mu\text{m}$ and pH: 9.2.

assumed that the film diffusion does not dominantly control the overall adsorption process. Similar observations were also obtained by Weber [13] and McKay et al. [14] in their experiments. It was further noted that there was no increase in uptake above 125 rpm.

3.3. Effect of temperature

The removal of Cd from the solution of $71.17 \mu\text{mol l}^{-1}$ initial concentration decreases from 1.68 to $1.54 \mu\text{mol g}^{-1}$ on increasing the temperature from 20 to 40°C (Fig. 3) at a pH of 9.2 and agitation rate of 125 rpm with an adsorbent particle size of $200 \mu\text{m}$. This indicates the exothermic nature of the process. This may be attributed to a

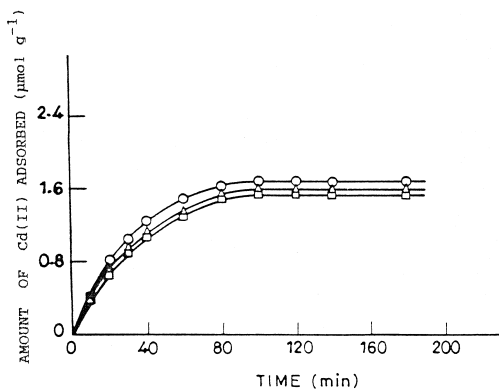


Fig. 3. Removal of Cd(II) by hematite at 20 (\circ), 30 (Δ) and $40 \pm 0.5^\circ\text{C}$ (\square). Conditions: $71.17 \mu\text{mol l}^{-1}$, Particle size: $< 200 \mu\text{m}$, pH: 9.2 and Agitation rate: 125 rpm.

Table 2
Thermodynamic parameters and Langmuir constants at different temperatures

Temperature (°C)	Thermodynamic parameters			Langmuir constants			
	$-\Delta G$ (Kcal mol ⁻¹)	$-\Delta H$ (Kcal mol ⁻¹)	$-\Delta S$ (Kcal mol ⁻¹)	Q° (mg g ⁻¹)		b (l g ⁻¹)	
				Graphical	Regression	Graphical	Regression
20	2.5902	13.8086	38.2881	0.2440	0.2339	8.9271	9.1433
30	2.2073	9.4281	23.8310	0.2336	0.2267	3.7710	4.3119
40	1.9690	–	–	0.2241	0.2241	2.4811	2.6448

relative increase in the escaping tendency of the solute from the solid phase to the bulk phase with the rise in temperature of the solution [15].

This is again confirmed by the thermodynamic parameters like free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) changes during the removal process. These parameters (Table 2) were calculated by the method described by Singh et al. [11] at 20, 30 and 40°C temperatures. The negative values of ΔG and ΔH are indicative of spontaneous and exothermic nature of the process respectively. The negative values of ΔS suggest the probability of favorable adsorption.

3.4. Adsorption dynamics study

The rate constant, K_{ad} , for Cd adsorption was determined by using the first order rate kinetic equation [8]:

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

where q and q_e (both in $\mu\text{mol g}^{-1}$) are the amount of Cd^{+2} adsorbed at any time t and at equilibrium, respectively. The plot of $\log(q_e - q)$ vs. t (Fig. 4) yielded a straight line at temperature 20°C indicating the applicability of the above equation. The value of the adsorption rate constant ($K_{ad} = 4.67 \times 10^{-2} \text{ min}^{-1}$) was calculated from the slope of the plot.

The data was also, tested for pore diffusion using the following equation [8]:

$$q = K' t^{1/2}, \quad (2)$$

where K' is rate constant for intraparticle diffusion.

It is evident from Fig. 5 that the plot q_e vs. $t^{1/2}$ is linear within a certain extent but does not pass through the origin. It appears that the pore diffusion is not the only rate

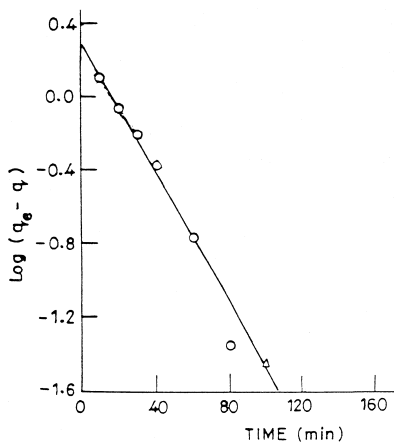


Fig. 4. Rate constant plot for adsorption of Cd(II) on hematite. Conditions: Cd(II) Concentration: 71.17 $\mu\text{mol l}^{-1}$, pH: 9.2, Temperature: 20 \pm 0.5°C, Particle size: < 200 μm and Agitation rate: 125 rpm.

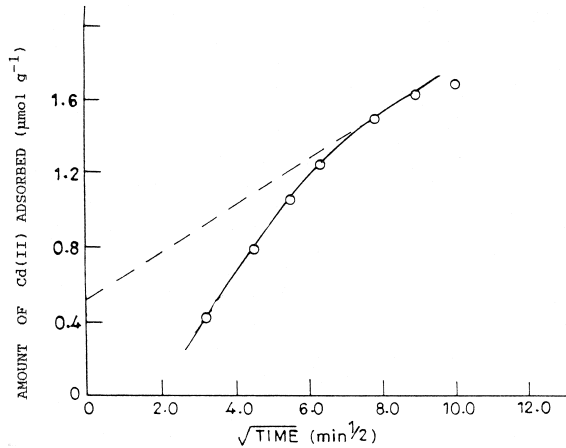


Fig. 5. Plot of q_e vs. $t^{1/2}$ for the intraparticle transport of Cd(II) on hematite at Cd(II) concentration $71.17 \mu\text{mol l}^{-1}$, pH: 9.2, Temperature: $20 \pm 0.5^\circ\text{C}$, Particle size: $< 200 \mu\text{m}$ and Agitation rate: 125 rpm.

controlling step [16,17] in the removal of cadmium. This possibility was further tested by determining the pore diffusion coefficient, \bar{D} , from the following equation [6]:

$$\bar{D} = \frac{0.03}{t_{1/2}} r_o^2, \quad (3)$$

where $t_{1/2}$ (s) is time for half adsorption and r_o (cm) is the radius of the adsorbent particles. According to Michelsen et al. [18], a \bar{D} value of the order of $10^{-11} \text{cm}^2 \text{s}^{-1}$ is indicative of intraparticle diffusion as the rate determining step. In this investigation, the value of \bar{D} ($2.17 \times 10^{-9} \text{cm}^2 \text{s}^{-1}$) is more than two order of magnitude higher which indicates that the intraparticle diffusion is not the only rate controlling step [18]. As a result, it may be concluded that both, film and pore diffusion are involved in the removal process.

3.5. Mass transfer study

The mass transfer study was carried out using the following equation [14]:

$$\ln \left(\frac{C_t}{C_0} - \frac{1}{1 + mk_L} \right) = \ln \frac{mk_L}{1 + mk_L} - \frac{1 + mk_L}{mk_L} \beta_1 S_s t, \quad (4)$$

where C_t and C_0 (both are expressed in terms of $\mu\text{mol l}^{-1}$) are the cadmium concentrations at time t and zero, respectively, k_L ($Q^\circ \cdot b, \text{l g}^{-1}$) is a constant, and m (g l^{-1}) and S_s (cm^{-2}) are the mass and outer surface of the adsorbent particle per unit volume of particle free slurry, respectively, and β_1 (cm s^{-1}) is the mass transfer coefficient. The value of β_1 ($14.58 \times 10^{-5} \text{cm s}^{-1}$) calculated from the slope and the plot of $\ln \left(\frac{C_t}{C_0} - \frac{1}{1 + mk_L} \right)$ vs. t (Fig. 6) suggests that the velocity of mass transfer of Cd onto hematite is rapid enough [11] to use this adsorbent for the treatment of wastewater rich in cadmium.

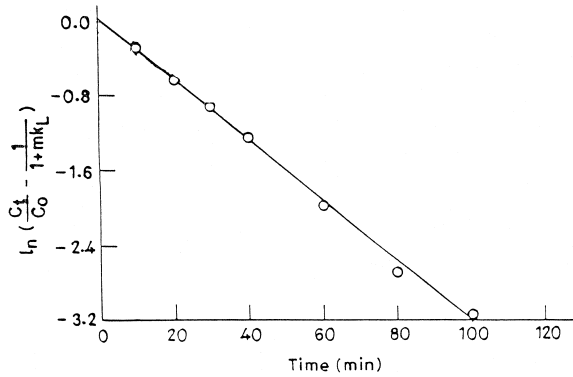


Fig. 6. Mass transfer plot for adsorption of Cd(II) on hematite. Conditions: 71.17 $\mu\text{mol l}^{-1}$, pH: 9.2, Temperature: $20 \pm 0.5^\circ\text{C}$, Particle size: $< 200 \mu\text{m}$ and Agitation rate: 125 rpm.

3.6. Adsorption isotherm

The equilibrium data for the adsorption of Cd onto hematite at 20, 30 and 40°C were fitted in the linearized Langmuir isotherm [8]:

$$\frac{1}{q_e} = \frac{1}{Q^\circ} + \frac{1}{bQ^\circ} \frac{1}{C_e}, \tag{5}$$

where C_e ($\mu\text{mol l}^{-1}$) and q_e ($\mu\text{mol g}^{-1}$) are concentration and amount of Cd adsorbed at equilibrium. The linearity of the plots $1/q_e$ vs. $1/C_e$ (Fig. 7) shows the applicability of the model, consequently suggesting the formation of monolayer coverage of the adsorbate particles on adsorbent surface. The Langmuir constants Q° and b related to the capacity and energy of adsorption, respectively, were determined at different

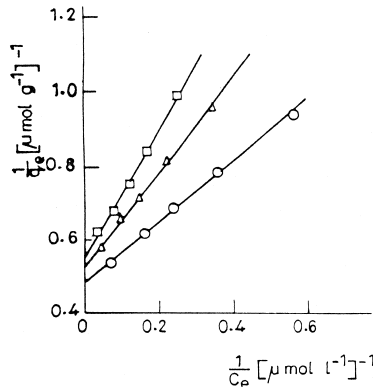


Fig. 7. Langmuir plot for the adsorption of Cd(II) on hematite at Cd(II) concentration of 71.17 $\mu\text{mol l}^{-1}$, pH: 9.2, Temperature: $20 \pm 0.5^\circ\text{C}$, Particle size: $< 200 \mu\text{m}$ and Agitation rate: 125 rpm.

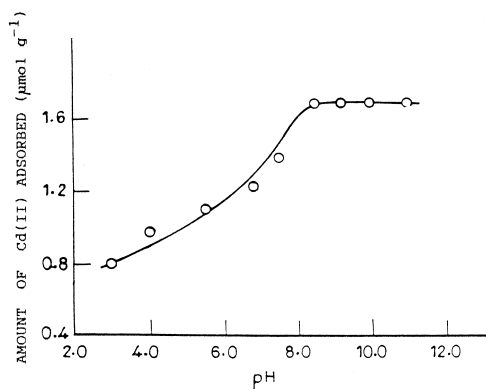


Fig. 8. Effect of pH on the removal of Cd(II) by adsorption on hematite. Conditions: $71.17 \mu\text{mol l}^{-1}$, Particle size: $< 200 \mu\text{m}$, Temperature: $20 \pm 0.5^\circ\text{C}$ and Agitation rate: 125 rpm.

temperatures from the slopes and intercepts of the respective plots. The decrease in their values (Table 2) with rise of temperature also support the present findings.

3.7. Effect of pH

It is clear from Fig. 8 that the adsorption of cadmium is higher in alkaline pH range (7.5–11.0). However, the removal is small in acidic range and reaches a maximum at around pH 9.2 and, thereafter, it remains almost unaltered. Huang et al. [8], Yadav et al. [5] and Huang et al. [17] have also observed the same trend of pH dependence in the removal of cadmium by different adsorbents. In the highly acidic medium (pH \approx 3.0), there is a chance of dissolution of the adsorbent [19] and a consequent decrease in the active sites. In addition to this effect, the adsorbent surface is highly protonated in acidic medium which is not favorable for cadmium uptake because in this medium, Cd^{++} is the dominant ion [8]. As a result, the adsorption of cadmium is hindered due to electrical repulsion. As pH increases, the degree of protonation of the surface reduces gradually and approaches to zero at pH 7.0 resulting in a gradual increase in adsorption. Above pH 7.0, where Cd^{++} and CdOH^+ species are present in solution [8], the adsorbent surface starts acquiring a net negative charge making the situation electrostatically favorable for a higher uptake of cadmium. This explanation is in tune with the surface behavior of the solid–solution interface which is schematically given below [15]:

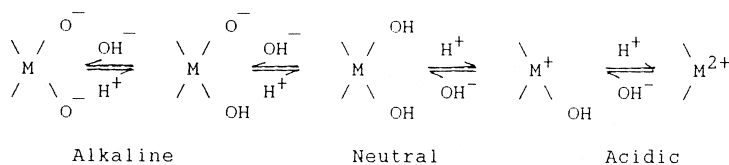


Table 3

Multiple regression analysis of percentage removal (dependent variable) vs. retention time, concentration of solute, agitation rate and temperature (independent variables) for Cd–hematite system

Square of multiple correlation coefficient (R^2)	Regression coefficients				Intercept (A)
	Time	Concentration	Agitation rate	Temperature	
0.663 ^b	0.331 ^a	−0.192 ^b	0.219 ^b	−0.394 ^a	52.228

^aDenotes significance at 5% level.

^bDenotes significance at 1% level.

Table 4

Percentage removal of cadmium at different conditions (experimental and predicted values at equilibrium time)

Initial cadmium concentration ($\mu\text{mol l}^{-1}$)	Percentage removal		Agitation rate (rpm)	Percentage removal		Temperature ($\pm 0.5^\circ\text{C}$)	% Removal	
	Exp. value	Pred. value		Exp. value	Pred. value		Exp. value	Pred. value
44.48	97.57	96.28	50	76.44	74.73	20	94.42	91.16
53.38	97.12	94.57	75	83.18	80.21	30	89.64	87.22
62.27	95.84	92.87	100	89.48	85.68	40	86.38	83.28
71.17	94.42	91.16	125	94.42	91.16	—	—	—
88.96	86.47	87.74	—	—	—	—	—	—

The calculation has been done at optimum conditions and the predicted values are upto 66.3% confidence limit.

4. Multiple regression analysis

The cumulative effect of several independent variables, such as retention time, initial solute concentration, agitation rate and temperature of the system, on a dependent variable (percentage Cd removal), has been studied using multiple regression analysis (MRA). The results are given in Table 3. From these results, it is concluded that the independent variable has a significant cumulative effect on the percentage removal. With the help of these data, the following model equation has been suggested to predict the uptake of Cd under given boundary conditions:

$$y = 52.228 + 0.331 \overset{**}{\times} x_1 - 0.192 \overset{**}{\times} x_2 + 0.219 \overset{**}{\times} x_3 - 0.394 \times x_4, \quad (6)$$

where (double asterisk denotes significance at 1% level) y is predicted value of percentage removal of Cd; x_1 , retention time; x_2 , concentration of solute; x_3 , agitation rate; and x_4 , temperature of the system (only the significant variables are used to predict the value of y). Table 4 enlists the model values calculated with the help of Eq. (6) and the experimental values. It may be seen that the predicted values are pretty close to the live situation. Higher variability of the data or cross effects or other variables are responsible for the deviation.

5. Conclusions

The removal of Cd from aqueous solutions seems feasible by adsorption onto hematite using CMBR technique. The different parameters studied have a cumulative effect on the extent of uptake, and the maximum removal (98%) has been achieved at optimum conditions (cadmium concentration $44.88 \mu\text{mol l}^{-1}$ of pH 9.2, retention time 2 h at 125 rpm agitation rate with 40 g l^{-1} of hematite). The removal of Cd follows first-order kinetics and only the intraparticle diffusion does not seem to control the mass transfer. A monolayer coverage of adsorbate is involved in the adsorption process. Electrostatic attraction and surface complexation are the major removal mechanisms involved. Reusability of the adsorbent and sludge minimization are expected to cut down operating costs and render the process attractive. The data thus obtained would prove useful in designing an efficient treatment plant for Cd rich effluents.

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