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Adsorption of Cd(II) Ions from Aqueous Solutions by Lalang (*Imperata cylindrica*) Leaf Powder: Effect of Physicochemical Environment

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Abstract: The adsorption of cadmium from aqueous solution with a plant waste particularly Lalang or *Imperata cylindrica* (IC) leaf powder was investigated. The effect of various operating variables mainly adsorbate concentration, adsorbent dose, adsorbent size, temperature and pH was studied. The adsorption of Cd²⁺ ions increased with increase in pH, temperature, adsorbent dose and decrease in adsorbent size. Adsorption was rapid and occurred within 15 min for cadmium concentration of 1 mg L⁻¹ and 30 min for cadmium concentrations of 2 and 5 mg L⁻¹. The kinetic process of Cd²⁺ adsorption onto IC leaf powder was found to fit the pseudo-second-order rate equation.

Key words: *Imperata cylindrica*, cadmium, adsorption, thermodynamic, kinetic

INTRODUCTION

Among many heavy metals, cadmium is one of the well-known toxic heavy metals and is attracting wide attention of environmentalists. Adverse health effects due to cadmium are well documented and it has been reported to cause renal disturbances, lung insufficiency, bone lesions, cancer and hypertension in humans (Sharma, 1995). Considerable research has been carried out in developing cadmium removal techniques. Conventional methods, such as chemical precipitation, chemical oxidation or reduction, filtration, electrochemical treatment, application of membrane technology, evaporation recovery, solvent extraction and ion exchange processes, have been traditionally employed for heavy metal removal from industrial wastewater. However, these methods have significant disadvantages, which include incomplete metal removal, requirements for expensive equipment and monitoring systems, high-energy requirement and generation of toxic sludge or other waste products that require disposal. This has initiated research in new, low-cost materials for possible use as adsorbents. In general, an adsorbent can be assumed as low cost if it requires little processing, is abundant in nature, or is a byproduct or waste materials from another industry (Low *et al.*, 2000). A plant waste particularly IC leaves was selected as the adsorbent as it is inexpensive and very common in Malaysia due to its high availability. IC is considered as one of the world's 10 worst weeds (Holm *et al.*, 1977). It is widely distributed in

Africa, Asia, Australia and America. This species is considered a pernicious pest plant due its ability to successfully displace desirable vegetation and disrupt ecosystems. In this present research, the effectiveness of adsorption of cadmium ion by IC leaf powder was studied by determining the parameters that influence adsorption such as temperature, initial cadmium concentration, adsorbent dose, adsorbent size and pH.

MATERIALS AND METHODS

IC leaves were collected from the surrounding area of University Teknologi MARA, Pahang campus, Malaysia. The leaves were washed with distilled water, dried in an oven at 80°C for a period of 24 h, then ground and screened to obtain particle sizes ranging from 78-1000 µm. The powder was preserved in glass bottles for use as adsorbent. All the chemicals used in the experiments were of analytical grade. Cd(NO₃)₂·4H₂O (Merck) was used as the source of Cd(II) and all of the solutions were made in distilled water. The solutions of Cd(II) were prepared from a stock solution containing 1000 mg L⁻¹ of Cd(II). Batch adsorption experiments were carried out in a series of Erlenmeyer flasks of 100 mL capacity by agitating 1 g of the adsorbent (unless otherwise stated) with 50 mL of the aqueous Cd(II) solution in a constant temperature, water bath shaker (Mettler, Germany) for a pre-determined time interval at a constant speed of 150 rpm. The adsorbent size of 78-250 µm (unless otherwise stated) was used in all experiments. The study on the effect of

adsorbent size was performed by using the initial cadmium concentration of 2 mg L⁻¹. For the study on effects of initial metal concentration, temperature and adsorbent size, no adjustment of pH of the solutions were carried out. However, the study on effect of adsorbent dose was performed at pH 5. The acidity of Cd(II) solutions was adjusted by addition of drops of 0.1 M HNO₃ or 0.1 M NaOH solutions. The pH of cadmium solutions was measured using a glass electrode (Jenway, model 3010). All experiments were duplicated. After adsorption, the mixture was filtered through Whatman filter paper (No. 40). The concentrations of cadmium in the solutions before and after equilibrium were determined by atomic absorption spectrometer (Hitachi Model Z-8100 Polarized Zeeman) using air acetylene flame. The amount of Cd(II) adsorbed (*q* in mg g⁻¹) was computed by using the following expression:

$$q = \frac{C_0 - C_t}{m} V \quad (1)$$

where *C*₀ and *C*_{*t*} are Cd(II) concentrations in mg L⁻¹ before and after adsorption for time *t*, *V* is the volume of adsorbate in liter and *m* (g) is the weight of the adsorbent. For the calculation of thermodynamic parameters, the following equations were used (Namasivayam and Ranganathan, 1995):

$$K_c = \frac{C_{Ae}}{C_e} \quad (2)$$

$$\Delta G = -RT \ln K_c \quad (3)$$

$$\log K_c = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \quad (4)$$

where *K*_{*c*} is the equilibrium constant, *C*_{*e*} is the equilibrium concentration in solution (mg L⁻¹), *C*_{*Ae*} is the solid-phase concentration at equilibrium (mg L⁻¹) and *R* is gas constant (8.314 × 10⁻³ kJ mol⁻¹ K⁻¹). ΔG (kJ mol⁻¹), ΔH (kJ mol⁻¹) and ΔS (J mol⁻¹ K⁻¹) are changes in free energy, enthalpy and entropy, respectively. The values of ΔH and ΔS are determined from the slope and the intercept of the plots of log *K*_{*c*} versus 1/*T*. The ΔG values were calculated using Eq. 3.

RESULTS AND DISCUSSION

Adsorption kinetic: The adsorption of cadmium ions on IC leaf powder was studied for agitation times varying from 0 to 120 min. The experimental results for the rate of adsorption of cadmium at different concentration are presented in Fig. 1 as plots of *C*_{*t*}/*C*₀ versus time. It is

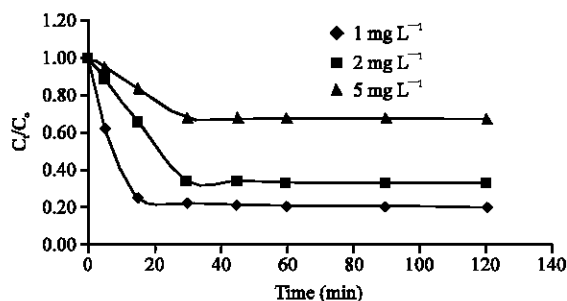


Fig. 1: Adsorption of cadmium by IC leaf powder at different initial cadmium concentrations

found that the adsorption of cadmium increased with increased agitation time at room temperature (30 °C). The plots also showed that at lower cadmium concentration (1 mg L⁻¹) the equilibrium is reached faster, within 15 min, whereas increase in concentration from 2 to 5 mg L⁻¹ slowed down the adsorption rate and consequently more time was required for attaining equilibrium. After 30 min of adsorption, the adsorption rates of cadmium slowed significantly probably due to saturation on the biomass surface. It is evident from the results that the agitation time required to attain equilibrium is dependent on the initial concentration of cadmium.

In the case of low concentration, the ratio of the initial number of moles of metal ions to the available surface area is larger. The adsorption sites took up the available metal ions more quickly at low concentration. At higher cadmium concentrations, there would be greater competition to occupy the available adsorption sites. Hence, for a dilute solution equilibrium was reached faster than that of concentrated solutions. Therefore, this method is suitable for the removal of relatively low concentration of cadmium. Based on the results, the equilibrium time was fixed at 90 min for the rest of the batch experiments to make sure that equilibrium is achieved. According to Horsfall and Abia (2003), the enhanced adsorption of metal ion with increase in agitation time may be due to the decrease in boundary layer resistance to mass transfer in the bulk solution and an increase in the kinetic energy of hydrated ions.

The kinetic of adsorption was also studied by applying the pseudo-second-order equation proposed by Ho (1995), which is expressed as:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_c} t \quad (5)$$

where *h* = *k*₂*q*_{*e*}² can be regarded as the initial adsorption rate as *t*→0. The plot *t*/*q* versus *t* should give a straight line if pseudo second-order kinetics is

Table 1: Comparison between adsorption rate constants, q_e estimated and coefficients of correlation associated to the pseudo-second-order kinetic model

[Cd ²⁺]	Pseudo-second-order kinetic model				q_e (mg g ⁻¹) experiment
	k_2 (g mg ⁻¹ min ⁻¹)	q_e (mg g ⁻¹)	h (mg g ⁻¹ min ⁻¹)	R^2	
1	12.800	0.041	2.15×10^{-2}	0.998	0.040
2	1.164	0.076	6.72×10^{-3}	0.959	0.067
5	0.923	0.093	7.98×10^{-3}	0.954	0.082

applicable and q_e , k_2 and h can be determined from the slope and intercept of the plot, respectively. The second-order rate constants were in the range of 0.923 to 12.8 g mg⁻¹ min⁻¹. The pseudo-second-order equation yields very good straight lines ($R^2 > 0.95$), as shown in Fig. 2. The theoretical values of q_e also agree with the experimental ones as shown in Table 1. Both facts suggest that the adsorption of Cd²⁺ ions by IC leaf powder follows the pseudo-second-order kinetic model. This finding was similar to other studies on the adsorption of cadmium by low-cost adsorbents. For instance, pseudo-second-order kinetic was also observed in the adsorption of cadmium and lead by spent grain (Low *et al.*, 2000) and adsorption of cadmium onto *Hevea brasiliensis* leaf powder (Hanafiah *et al.*, 2006). It was found that the initial sorption rate increased with a decrease in the initial metal concentration. According to Wong *et al.* (2003), the lower the concentration of metal ions in the solution, the lower the probability of collisions between metal species is and hence the faster the metal ions could be bonded to the adsorption sites on the surface of the adsorbent.

Effect of pH: pH is an important parameter for adsorption process due to its influence on the ionization state of the functional groups on the surface of adsorbent and different ionic forms of cadmium. According to Namasivayam and Ranganathan (1995), precipitation of cadmium starts at pH 8.2. Therefore, in this study the effect of pH on cadmium adsorption was performed at pH range 2-7. As can be seen in Fig. 3, the adsorption of Cd²⁺ ion from aqueous solution is mainly influenced by solution pH. It is noticed that adsorption increased continuously with the decrease in acidity until it reached maximum adsorption capacities between pH 6 and 7. The maximum adsorption capacities for cadmium concentration of 1 mg L⁻¹ are found to be 0.013, 0.041, 0.043, 0.044, 0.045 and 0.045 mg g⁻¹ at pH 2, 3, 4, 5, 6 and 7 respectively. For cadmium concentration of 5 mg L⁻¹, the adsorption capacities are 0.059, 0.194, 0.205, 0.210, 0.219 and 0.225 mg g⁻¹ at pH 2, 3, 4, 5, 6 and 7, respectively. In a highly acidic solution (pH 2), lower adsorption of cadmium occurred due to the competition between Cd²⁺ and H⁺ ions for adsorption sites on the adsorbent surface. According to Meena *et al.* (2005), the increase in metal removal as pH increases can be explained on the basis of a decrease in competition between proton (H⁺) and metal

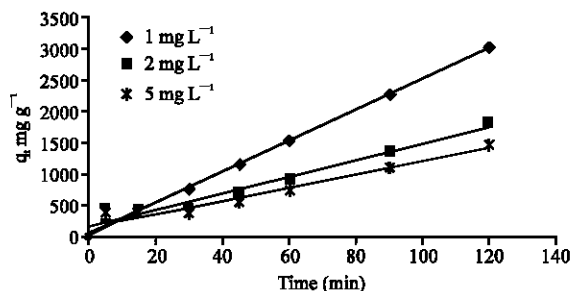


Fig. 2: Pseudo-second-order plots for the adsorption of cadmium by IC leaf powder

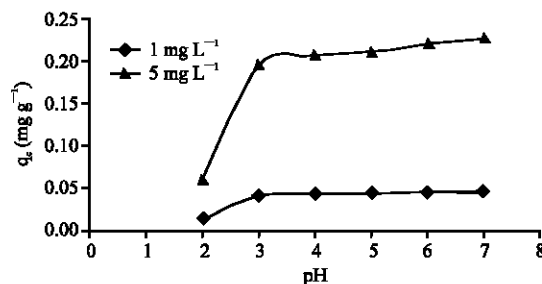


Fig. 3: Effect of pH on cadmium adsorption by IC leaf powder

cations for the same functional groups. The decrease in positive charge surface as pH increases would result in lower electrostatic repulsion between the surface of adsorbent and metal ions.

Effect of adsorbent dose: The dependence of adsorption of cadmium on the amount of IC leaf powder was studied at room temperature (30°C) at pH 5 by varying the adsorbent doses from 0.20 to 2.5 g while keeping the volume (50 mL) and concentrations of the cadmium solution (5 and 10 mg L⁻¹) constant. The results are shown in Fig. 4 and Table 2. Different [Cd²⁺]/adsorbent ratios were obtained by increasing the quantity of IC leaf powder while the cadmium ion concentration was kept constant. A decrease in [Cd²⁺]/adsorbent ratio was linked with the increase in the adsorption of cadmium due to the increase in surface area of IC leaf powder. However, as the weight of IC leaf powder was increased, the unoccupied adsorption sites became surplus, thus the values of metal adsorbed (q_e) decreased (Shukla *et al.*, 2002).

Table 2: Effect of change in [Cd²⁺]/adsorbent ratio on adsorption of cadmium

Adsorbent concentration (g L ⁻¹)	[Cd ²⁺]/adsorbent ratio		Metal adsorbed, q _e (mg g ⁻¹)	
	5 mg L ⁻¹ Cd	10 mg L ⁻¹ Cd	5 mg L ⁻¹ Cd	10 mg L ⁻¹ Cd
4	1.25	2.50	1.172	2.359
10	0.50	1.00	0.479	0.955
20	0.25	0.50	0.241	0.475
30	0.167	0.33	0.160	0.319
40	0.125	0.25	0.120	0.240
50	0.100	0.20	0.096	0.192

Table 3: Thermodynamic parameters for the adsorption of cadmium, [Cd]: 5 mg L⁻¹

Temperature (K)	Equilibrium constant (K _e)	ΔG (kJ mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)
303	0.487	-1.81	8.73	22.91
313	0.557	-1.52		
323	0.604	-1.35		

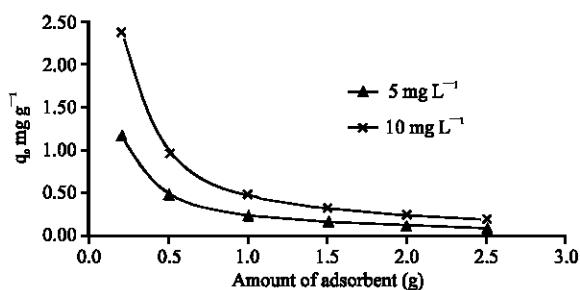


Fig. 4: Effect of amount of adsorbent on cadmium adsorption by IC leaf powder

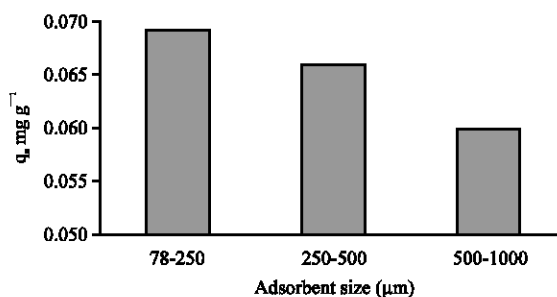


Fig. 6: Effect of adsorbent size on Cd(II) adsorption by IC leaf powder

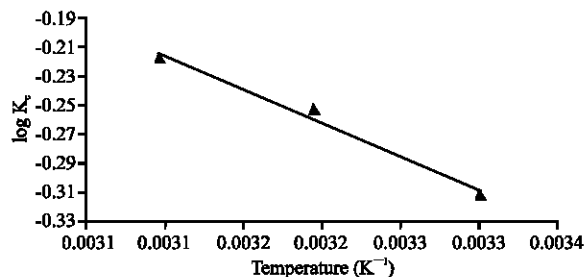
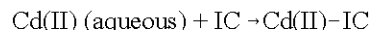


Fig. 5: Van't Hoff plot for the adsorption of Cd(II) by IC leaf powder

Thermodynamic studies: A van't Hoff plot of log K_e versus 1/T was found to be linear (Fig. 5). ΔH and ΔS were obtained from the slope and intercept of the van't Hoff plot. The positive value of ΔH confirmed the endothermic adsorption of cadmium. The positive value of ΔS was characteristics of increased randomness at the solid-solution interface during the adsorption of cadmium on IC leaves. In the adsorption of cadmium, the adsorbate species displaces adsorbed solvent molecules to gain more translational entropy than was lost by the adsorbate ions, thus allowing randomness in the system. The values of ΔH, ΔS and ΔG are shown in Table 3. The increase in the uptake of Cd(II) with temperature may be due to the dissolution of the adsorbing species, the changes in the

size of the pores and the enhanced rate of intraparticle diffusion of adsorbate, as diffusion is an endothermic process (Sekar *et al.*, 2004). Spontaneity of the adsorption process was demonstrated by the increase in Gibbs energy, ΔG (values varied from -1.81 to -1.35 kJ mol⁻¹ in the temperature range 303-323 K). The negative values of ΔG indicate that the equilibrium:



shifts to the forward direction in a spontaneous manner leading to adsorption of Cd(II) ions on to surface constituents of IC leaf powder.

Effect of adsorbent size: The surface of contact between any adsorbent and the liquid phase plays an important role in the phenomena of adsorption. The effect of particle size of adsorbent was studied using three particle groups: 78-250, 250-500 and 500-1000 μm. Figure 6 shows that adsorption capacities of Cd(II) by IC leaf powder increases from 0.060 to 0.068 mg g⁻¹ as the particle size decreases from 1000 to 78 μm. The specific surface available for adsorption will be greater for smaller particles. Hence, adsorption of cadmium increases as particle size decreases. According to Evans *et al.* (2002), the slower rate of uptake of cadmium by larger sized

particles was due to the adsorption to the outer surface in the initial stage. This suggests the adsorption to be primarily a surface phenomenon, since the surface area available for adsorption increases with decreasing particle size. For larger particles, the diffusional resistance to mass transport is higher and most of internal surface of the particle may not be utilized for adsorption. Consequently, the amount of Cd(II) adsorbed is small.

CONCLUSIONS

Significant data were obtained through this study for the removal of cadmium by adsorption on IC leaf powder. IC leaf powder appears to be a promising adsorbent for the removal of cadmium, due to its rapid rate of adsorption. The adsorption of cadmium is found to be dependent on amount of adsorbent, temperature, particle size, pH and concentration. Since IC leaves are highly abundant and shows a good adsorption capacity for Cd(II) ions, it can be evaluated as an alternative adsorbent to treat wastewater containing cadmium ions.

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