



UNIVERSITI  
TEKNOLOGI  
MARA



# Globalising Knowledge and Information

## SCIENCE TECHNOLOGY

## NATIONAL SEMINAR ON

# SCIENCE TECHNOLOGY & SOCIAL SCIENCES

# 2006

30-31 May 2006

Swiss Garden Resort & Spa  
Kuantan, Pahang

## Kinetics Models for the Adsorption Process of Cd (II) Ions onto Rubber (Hevea Brasiliensis) Leaf Particles

Megat Ahmad Kamal Megat Hanafiah  
Haslizaidi Zakaria  
Suzila Shafiei

### ABSTRACT

The kinetics of  $Cd^{2+}$  adsorption onto *Hevea Brasiliensis* (HB) leaf particles were investigated at different pH using a batch adsorption technique at 30 °C. Rate coefficients obtained from pseudo-second order plots were determined to range between 3.99 to 6.21  $\times 10^1$  g/mg.min. The theoretical values of equilibrium adsorption capacities ( $q_e$ ) also agree very well with the experimental ones. The kinetic analyses suggested that the rate limiting adsorption step was chemisorption and adsorption rates were best described by the pseudo-second order model.

**Keywords:** Kinetics models, adsorption process.

### Introduction

Among many heavy metals, cadmium is one of the well-known toxic heavy metals, and is attracting wide attention of environmentalists. According to the Malaysian standard of effluent, the permissible levels for cadmium discharges in wastewater are 0.01 mg/l (Standard A) and 0.02 mg/l (Standard B) (Anon 2000). 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). With a better awareness of the problem associated with cadmium came increase in research studies related to methods of removing cadmium from wastewater. 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).

Natural materials that are available in large quantities or certain waste products from industrial or agricultural operations may have potential as inexpensive adsorbents. A previous study conducted by Hanafiah et al. (2005) revealed that HB leaf particles were capable of removing cadmium from aqueous solution at a fast reaction time and the maximum adsorption capacity determined from Langmuir plot was 3.68 mg for each gram of the adsorbent. However, a detailed study on the kinetics of adsorption of cadmium at different pH has not been conducted. The study of adsorption kinetics in wastewater treatment is vital as it provides valuable insights into the reaction pathways and into the mechanism of adsorption reactions. Furthermore, the kinetics describes the solute uptake rate which in turn controls the residence time of adsorbate uptake at the solution-solid interface. In order to develop adsorption kinetics, the knowledge on rate law is required. The rate law however cannot be inferred by the overall chemical equation, but must be determined by experimentation. This paper presents the study of adsorption kinetics of HB leaf particles for removing cadmium from aqueous solutions at different pH. The kinetics of adsorption particularly the intraparticle diffusion, Lagergen pseudo-first order and pseudo-second order models were discussed.

### Materials and Methods

#### Adsorbent

Plant biomass, which had been harvested in Jengka 8 was washed with distilled water, dried in an oven at 105°C for a period of 24 h, then ground and screened to obtain particle sizes ranging from 78 – 710  $\mu$ m. The HB leaf particles were preserved in glass bottles for use as adsorbent.

#### Batch Adsorption Experiments

Analytical grade cadmium (II) nitrate was used as the metal source and stock solutions of this metal ion were prepared in double distilled water. Adsorption tests were carried out by agitating 1 g of the adsorbent with 50 ml of

the aqueous  $\text{Cd}^{2+}$  solution in Erlenmeyer flasks (100 ml) using a water bath shaker in a constant room temperature (30 °C). The initial pH of the solutions was adjusted by adding drops of 0.1 M  $\text{HNO}_3$  or 0.1 M  $\text{NaOH}$  solution. The initial metal concentration was 2 mg/l and the agitation time ranged from 5 to 90 min. 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 spectrophotometer (Hitachi Model Z-8100 Polarized Zeeman) using air acetylene flame. Control experiments were performed to measure any adsorption of  $\text{Cd}(\text{II})$  ions onto the wall of glassware. Neither precipitation nor adsorption onto the wall of the flasks was observed. All experiments were performed in duplicates.

### Metal Uptake

The amount of  $\text{Cd}^{2+}$  adsorbed per unit weight of the adsorbent ( $q$  in mg/g) was computed by using the following expression:

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

where  $C_o$  and  $C_t$  are  $\text{Cd}^{2+}$  concentrations in mg/l before and after adsorption for time  $t$ ,  $V$  is the volume of adsorbate in liter and  $m$  (g) is the mass of the adsorbent.

## Results and Discussion

### Basic Adsorption

The adsorption data at different initial pH of the solutions is shown in Figure 1. The curves indicate that the rate of adsorption is high in the first few minutes and decreases until equilibrium is reached. It is noticed that adsorption increased with the decrease in acidity. The maximum equilibrium adsorption capacities are found to be 0.048, 0.099, 0.098, 0.099 and 0.099 mg/g at pH 2, 3, 4, 5 and 6, respectively. A rapid adsorption of cadmium is also seen at pH 3 and above. In a highly acidic solution (pH 2), lower adsorption occurred. 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 ( $\text{H}^+$ ) and metal cations for the same functional groups. At low pH, the surface of the adsorbent would be surrounded by hydronium ions, which decrease the cadmium interaction with the adsorption sites of the dried HB leaf particles by greater repulsive forces. At pH 2, most of the potential adsorption sites are protonated and prevent  $\text{Cd}(\text{II})$  ions to be adsorbed. When pH increases, adsorption capacities are improved due to lower competition between the protons and  $\text{Cd}(\text{II})$  ions.

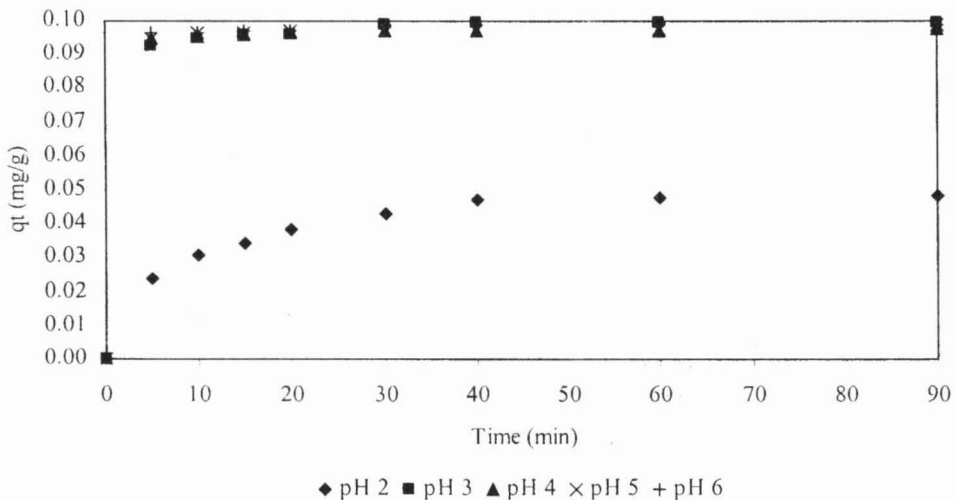


Fig. 1: Effect of Initial pH on the Adsorption of  $\text{Cd}(\text{II})$  Ions

**Kinetics of Adsorption**

If the movement of the adsorbate or solute from the bulk liquid film surrounding the adsorbent is ignored, the adsorption process for porous solids can be separated into three stages;

- i) Mass transfer (Boundary layer diffusion)
- ii) Adsorption of ions onto adsorption sites
- iii) Intraparticle diffusion

External mass transfer is characterized by the initial rate of solute adsorption. This can be obtained from the initial slope of the  $C_t/C_0$ -time curves, as shown in Fig. 2. The slopes can be derived by assuming that the relationship was linear over the first 5 – 10 min (Forster et al. 1985). This gave initial rates of 0.031, 0.095, 0.095, 0.096 and 0.097 for cadmium at pH 2, 3, 4, 5 and 6, respectively.

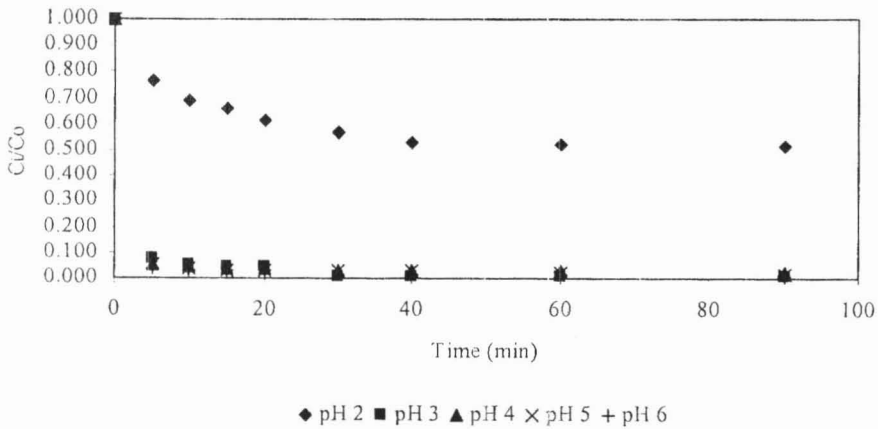


Fig. 2: The Variation of  $C_t/C_0$  with Time

In the model developed by Weber and Morris (1963), the rate of intraparticle diffusion is a function of  $t^{1/2}$  and can be defined as follows:

$$q = k_p t^{1/2} \tag{2}$$

where  $q$  (mg/g) is the amount of the metal adsorbed at time  $t$ ,  $k_p$  is the intraparticle rate constant (mg/g min<sup>1/2</sup>). If intraparticle diffusion occurs, then  $q$  versus  $t^{1/2}$  will be linear and if the plot of  $q$  versus  $t^{1/2}$  passes through origin, then the rate-limiting process is only due to the intraparticle diffusion. Otherwise, some other mechanism along with intraparticle diffusion is also involved. Figure 3 shows the relationship for the HB leaf particles and cadmium system is not linear over the entire time range, indicating more than one process is affecting the adsorption.

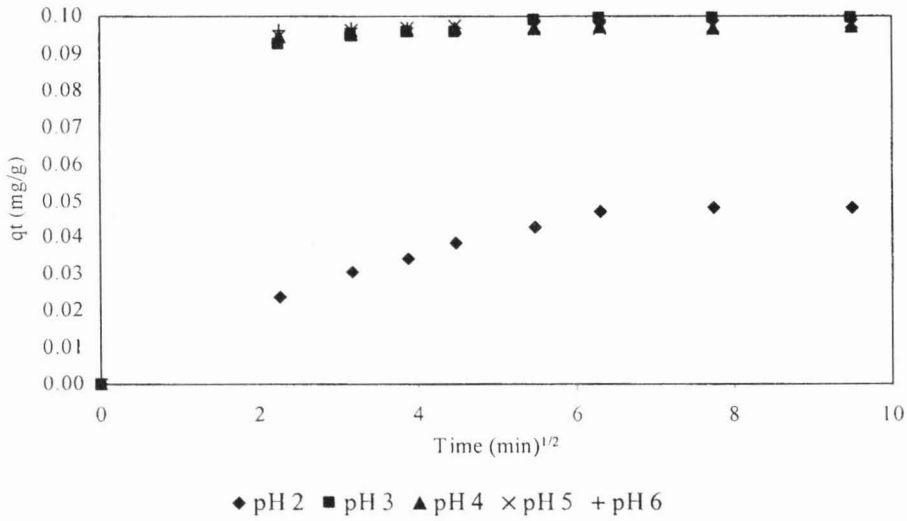


Fig.3: Intraparticle Diffusion Plots at Different pH

This type of non-linearity has been reported previously by Ho et al. (1996) and has been interpreted as showing that both boundary layer diffusion (the initial curved portion) and intraparticle diffusion (the final linear portion) are occurring. It is possible to derive an initial rate parameter,  $k_p$  by linear regression between  $t = 0$  and  $t_{lim}$  which is the first breakpoint in the relationship (Ho et al., 1996). Values of  $k_p$  at different pH are given in Table 1. These rate parameters have units of  $mg/g \text{ min}^{1/2}$  and as such are not a direct quantification of the rate. They can be interpreted in relative terms.

Table 1: Intraparticle Rate Constants at Different pH

pH	Reaction rate parameters $k_p$ ( $mg/g \text{ min}^{1/2}$ )
2	0.007
3	0.035
4	0.036
5	0.036
6	0.037

In order to further investigate the controlling mechanisms of adsorption processes, the pseudo-first-order Lagergren and pseudo-second-order rate equations were used to test the experimental data. The pseudo-first-order kinetic model is given as (Lagergren 1894):

$$\log (q_c - q_t) = \log q_c - \frac{k_{ad}}{2.303} t \quad (3)$$

where  $q_t$  and  $q_c$  are the amount adsorbed at time  $t$  and at equilibrium, and  $k_{ad}$  is the rate constant of the pseudo-first-order adsorption process ( $\text{min}^{-1}$ ). Straight line plots of  $\log (q_c - q_t)$  against  $t$  were used to determine the rate constant,  $k_{ad}$  and correlation coefficients,  $R^2$  for different cadmium concentrations. The pseudo-second-order equation (Ho and McKay 1999) is expressed as:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_c} t \quad (4)$$

where  $h = kq_e^2$  can be regarded as the initial sorption rate as  $t \rightarrow 0$ , and  $k$  is the rate constant of second-order biosorption ( $\text{g}/\text{mg}\cdot\text{min}$ ). The plot  $t/q_t$  versus  $t$  should give a straight line if second-order kinetics is applicable and  $q_e$ ,  $k$  and  $h$  can be determined from the slope and intercept of the plot, respectively. The plots of the linearized form of the pseudo-first-order and pseudo-second-order model at different pH by HB leaf particles are shown in Figs. 4 and 5, respectively.

The pseudo-first-order rate constant ( $k_{ad}$ ) and  $q_e$  determined from the model are presented in Table 2 along with the corresponding correlation coefficients. The rate constants, calculated from the slopes of the best-fit lines were in the range of  $4.60 \times 10^{-2}$  to  $1.28 \times 10^{-1} \text{ min}^{-1}$  for pseudo-first order model. The dependence of the first-order rate constant with concentration and the coefficients of correlation were lower than those found for the pseudo-second-order model. It was observed in the present work that  $q_e$  values computed from the experiment did not agree with  $q_e$  values obtained from pseudo-first-order Lagergren plots. This indicates that pseudo-first-order kinetics might not be sufficient to describe the mechanism of  $\text{Cd}^{2+}$ --HB interactions.

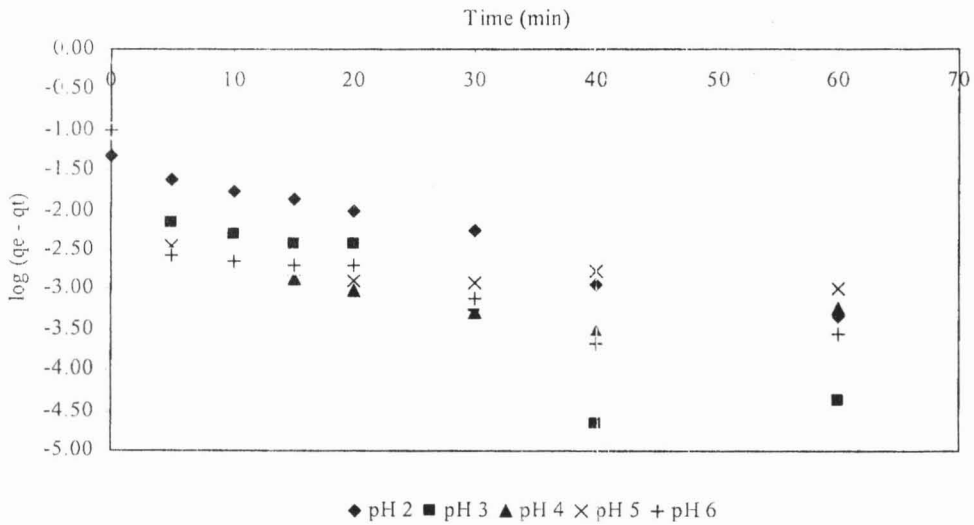


Fig. 4: Lagergren Pseudo-First-Order Kinetic Model at Different pH

The plot of  $t/q_t$  versus  $t$  for second-order model (Figure 5) yields very good straight lines (correlation coefficient,  $R^2 > 0.99$ ). The second-order rate constants were in the range of  $3.99$  to  $6.21 \times 10^1 \text{ g}/\text{mg}\cdot\text{min}$ . The theoretical values of  $q_e$  also agree very well with the experimental ones. Both facts suggest that the adsorption of  $\text{Cd}^{2+}$  ions by HB leaf particles follows the second-order kinetic model, which relies on the assumption that chemisorption may be the rate-limiting step. The values of the initial sorption rates ( $h$ ) were determined by using the values of the intercept of the straight lines plotted in Figure 5. It was found that the initial sorption rate increases with an increase in the pH of the solution.

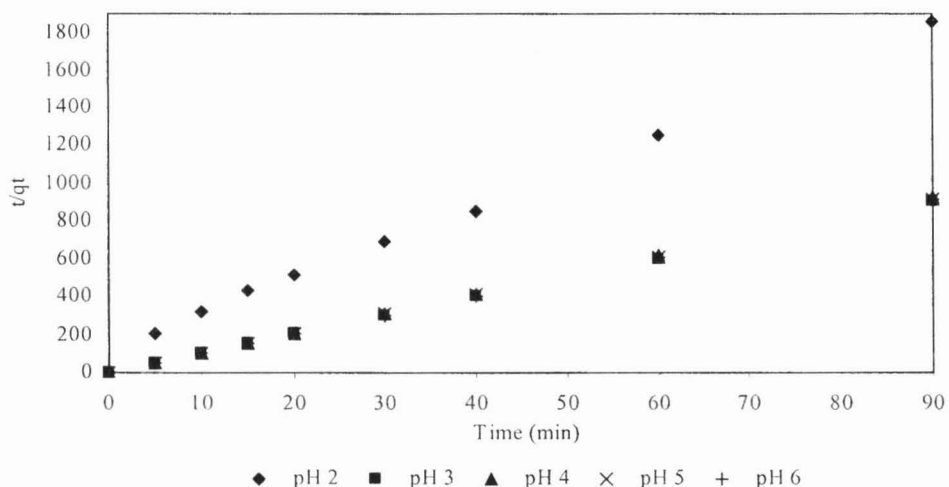


Fig. 5: Pseudo-Second-Order Kinetic Model for Cd<sup>2+</sup> ions Uptake by HB Leaf Particles at Different pH

Table 2 Comparison between Adsorption Rate Constants,  $q_e$  Estimated and Coefficients of Correlation Associated to the Lagergren Pseudo-First-Order and to the Pseudo-Second-Order Kinetic Models.

pH	Pseudo-first-order kinetic model	Pseudo-second-order kinetic model	$q_e$ (mg/g)					experiment
	$k_{ad}$ (min <sup>-1</sup> )	$q_e$ (mg/g)	$R^2$	$k$ (g/mg.min)	$q_e$ (mg/g)	$R^2$	$h$ (mg/g.min)	
2	0.078	<b>0.042</b>	0.975	3.991	<b>0.051</b>	0.994	$1.00 \times 10^{-2}$	<b>0.048</b>
3	0.128	<b>0.027</b>	0.849	23.127	<b>0.100</b>	0.999	$2.31 \times 10^{-1}$	<b>0.099</b>
4	0.064	<b>0.007</b>	0.506	62.12	<b>0.098</b>	1.000	$5.97 \times 10^{-1}$	<b>0.098</b>
5	0.046	<b>0.008</b>	0.386	39.899	<b>0.098</b>	0.999	$3.83 \times 10^{-1}$	<b>0.099</b>
6	0.077	<b>0.010</b>	0.658	44.447	<b>0.099</b>	1.000	$4.35 \times 10^{-1}$	<b>0.099</b>

### Conclusion

From the experiment, it can be concluded that the best pH range for cadmium adsorption is from 3 - 6. The order of the reaction for the adsorption of cadmium onto HB leaf particles followed a pseudo-second-order rate expression and intraparticle diffusion might not be the only rate-limiting step in the adsorption process.

### Acknowledgement

The authors thank the Institute of Research, Development and Commercialization (IRDC), UiTM for the financial support.

## References

- Anonymous. (2000). *Environmental Quality Act 1974 (Law of Malaysia)*. Kuala Lumpur: MDC Publisher Pinters Sdn Bhd.
- Forster, C.F., Mehrotra, I. & Alibhai, K.R.K. (1985). The Multiple Binding of Heavy Metals by Digested Sludge. *J Chem. Technol. Biotechnol*, 35B: pp. 15 – 20.
- Hanafiah, M.A.K.M., Jalil, M.N. & Yahya, M.Z.A. (2005). Removal of Cd(II) Ions from Wastewater by Adsorption on Rubber (*Hevea Brasiliensis*) and Lalang (*Imperata Cylindrica*) Leaves: *Proceedings of Conference on Scientific and Social Research*, Kuala Trengganu, Malaysia.
- Ho, Y.S. & McKay, G. (1999). The Sorption of Lead (II) Ions on Peat. *Water Res.*, 33: pp. 578 – 584.
- Ho, Y.S., Wase, D.A.J. & Forster, C.F. (1996). Kinetic Studies of Competitive Heavy Metals Adsorption by Sphagnum Moss Peat. *Environ Technol*, 17: pp. 71 – 77.
- Lagergren S. (1898). Zur Theorie der Sogenannten Adsorption Geloster Stoffe. Kungliga Svenska Vetenspsakademiens. *Handlingar Band*, 24 (4): pp. 1 – 39.
- Low, K.S., Lee, C.K. & Liew, S.C. (2000). Sorption of Cadmium and Lead from Aqueous Solutions by Spent Grain. *Procees Biochem*, 36: pp. 59 – 64.
- Meena, A.K., Mishra, G.K., Rai, P.K., Rajagopal, C. & Nagar, P.N. (2005). Removal of Heavy Metal Ions from Aqueous Solutions using Carbon Aerogel as an Adsorbent. *J. Hazard. Mater*, B122: pp. 161 – 170.
- Sharma, Y.C. (1995). Economic Treatment of Cadmium (II) Rich Hazardous Waste by Indigenous Material. *J. Appl. Interface Sci*, 173: pp. 66 – 70.
- Weber, W.J. & Morris, J.C. (1963). Kinetics of Adsorption on Carbon from Solutions. *J. Sanit. Eng. Div. Am. Soc.*, 89: pp. 31 – 60.

---

MEGAT AHMAD KAMAL MEGAT HANAFIAH, Faculty of Applied Sciences, Universiti Teknologi MARA Pahang.

HASLIZAIDI ZAKARIA, Faculty of Applied Sciences, Universiti Teknologi MARA Pahang.

SUZILA SHAFIEI, Faculty of Applied Sciences, Universiti Teknologi MARA Pahang.