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Kinetics and Thermodynamic Study of Lead Adsorption from Aqueous Solution onto Rubber (*Hevea brasiliensis*) Leaf Powder

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Abstract: The ability of rubber or *Hevea Brasiliensis* (HB) leaf powder to adsorb Pb²⁺ from aqueous solution has been investigated through batch experiments. The Pb²⁺ adsorption was found to be dependent on contact time, initial Pb²⁺ concentration and temperature. The kinetic processes of Pb²⁺ adsorption onto HB leaf powder were described by applying pseudo-first-order and pseudo-second-order rate equations. The kinetics data for the adsorption process obeyed pseudo-second-order equation. The equilibrium data were described well by the Langmuir and Freundlich isotherms. The maximum adsorption capacity determined from the Langmuir isotherm was found to be 46.73 mg g⁻¹ at 303 K. Thermodynamic parameters such as ΔG° , ΔH° and ΔS° were also calculated. The adsorption process was found to be exothermic and spontaneous in nature. The studies showed that HB leaf powder could be used as a good adsorbent material for Pb²⁺ removal from aqueous solution.

Key words: Rubber leaf powder, adsorption, lead, kinetics, thermodynamic, isotherm

INTRODUCTION

Industrialization is one of the major sources of the release of heavy metals in the atmosphere. Industries discharge different types of heavy metals into the environment at an unprecedented and constantly increasing rate. Lead is one of the heavy metals, which is highly toxic to humans, plant and animals. The metal is of special concern because it is non-degradable and therefore persistent. The major sources of lead release into the environment by waste streams are metallurgical industry, electroplating and metal finishing industries, paint manufacture, storage battery manufacture, munitions manufacture, petroleum refining and drainage from ore mines. The environmental impact due to lead toxicity has led to the enforcement of stringent standards for the maximum allowable limits of lead discharge into open landscapes and water bodies. According to the Malaysian standard of effluent, the permissible levels for lead discharges in wastewater are 0.10 mg L⁻¹ (Standard A) and 0.50 mg L⁻¹ (Standard B) (Anonymous, 2000). Among many methods available to reduce heavy metal concentrations from wastewater, the most common are chemical precipitation, filtration, ion exchange, reverse osmosis, ultrafiltration, electrochemical deposition and

adsorption on activated carbon. However, the aforementioned methods are not economically feasible for small and medium industries. It is therefore necessary to search for low-cost techniques that may be effective, less environmentally degrading and economical. Adsorption processes using agricultural and industrial waste products are becoming the new alternative for wastewater treatment because they are cheap, simple, sludge free and involve small initial cost and land investment. Some of the agricultural and industrial wastes, which have been used as adsorbent materials for removal of heavy metals from aqueous solution, include tree fern (Ho, 2003), sawdust (Yu *et al.*, 2003), fly ash (Gupta *et al.*, 2003), chitosan (Ngah and Fatinathan, 2006; Ngah *et al.*, 2002, 2004), aquatic plant (Keskinan *et al.*, 2004) and slag (Dimitrova, 2002; Dimitrova and Mehandgiev, 1998). A previous study has been conducted on the potential of HB leaf powder for removal of cadmium from wastewater (Hanafiah *et al.*, 2006). The study found that HB leaf powder was able to remove cadmium at a fast reaction time and the maximum adsorption capacity was reported 3.68 mg g⁻¹. Plant waste particularly HB leaf powder was selected as the adsorbent in this study as it is inexpensive and very common in Malaysia due to its relative abundance. The objective of

this study was to investigate the adsorption characteristics of Pb²⁺ ions onto HB leaf powder. The adsorption process is studied from kinetic, thermodynamic and isotherm standpoints.

MATERIALS AND METHODS

HB leaves were collected from a rubber plantation in Jengka 8, Pahang. The leaves were washed several times with double distilled water to remove dust and soluble impurities. The leaves were dried in an oven at 100°C for a period of 24 h until the leaves became crisp. The dried leaves were then converted into fine powder by grinding in a mechanical grinder and screened through a sieve to get geometrical size of <125 µm. The sieved materials were then stored in an airtight plastic container for further experiments. Atomic absorption spectroscopy grade metal solution of Pb(II), concentration 1000 mg L⁻¹ (Merck) was used as the source of Pb²⁺ and diluted with double distilled water to desired concentrations. The kinetics study was carried out by agitating 100 mL flasks containing 1.0 g of HB leaf powder and 50 mL Pb²⁺ solutions in a water bath shaker (Memmert, Germany). The mixture was agitated at 150 rpm at room temperature (30°C). The agitation time was varied from 1 to 120 min. At predetermined time, the flasks were withdrawn from the shaker and the reaction mixtures were filtered through Whatman filter paper (No. 40). For thermodynamic study, the experiment was performed using 0.05 g HB leaf powder added to 50 mL of lead solution in 100 mL flasks. The flasks were shaken at 150 rpm for 90 min at pH 5. The initial lead concentration used in this study was 50 mg L⁻¹. The isotherm study was performed using various concentrations of lead solutions (10-200 mg L⁻¹). A 0.5 g HB leaf powder with 50 mL lead solution of various concentrations was shaken at 150 rpm for 90 min at room temperature. The initial pH of the solutions was adjusted to 5. All experiments were performed in duplicates. The concentrations of lead in the solutions before and after equilibrium were determined by atomic absorption spectrometer (Hitachi Model Z-8100 Polarized Zeeman). Adsorption capacity of lead ion (mg g⁻¹) at any time (q_t) was calculated using the mass balance equation:

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

where V is the solution volume (mL), m is the mass of adsorbent (g) and C₀ and C_t are the initial and lead concentrations at any time (mg L⁻¹), respectively.

RESULTS AND DISCUSSION

Adsorption kinetics: Adsorption kinetics, which describes the solute adsorption rate, is an important characteristic in evaluating the efficiency of adsorption. The adsorption data at different initial Pb²⁺ concentration is shown in Fig. 1. These plots show that for both initial concentrations of lead, the amount of lead adsorbed increased rapidly with time at the beginning and became slow towards the end of the process. For the first 10 min, the adsorption rate was found to be increased for an increase in initial lead concentration from 20 to 50 mg L⁻¹. After 20 min of adsorption, the adsorption rates of lead slowed significantly probably due to saturation on the surface of HB leaf powder. It is clear from the results that the agitation time required to attain equilibrium is dependent on the initial concentration of lead. According to Meena *et al.* (2005), at lower metal ion concentrations, sufficient adsorption sites are available for adsorption of metal ions. The 20 mg L⁻¹ lead solution is able to attain equilibrium quickly because the lead ions can easily adsorb onto abundantly unhindered or unoccupied sites first. However, at higher concentrations, the number of lead ions is relatively higher compared to availability of adsorption sites. This is the main reason the 50 mg L⁻¹ lead solution took longer time to reach equilibrium due to the proportionally higher number of lead ions present.

The equilibrium adsorption capacity of HB leaf powder was found to increase with increasing initial lead concentration. This indicates that there are plenty adsorption sites in HB leaf powder available for the adsorption of lead. The enhanced adsorption of lead 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. By increasing the agitation time, the boundary layer resistance will be reduced and there will be an increase in the mobility of ions in the solution (Horsfall and Abia, 2003). In order to investigate the controlling mechanisms of adsorption processes, the pseudo-first-order and pseudo-second-order rate equations were used to test the experimental data. The pseudo-first-order rate equation is given as (Lagergren, 1898):

$$\log (q_e - q_t) = \log q_e - \frac{k_{ad}}{2.303} t \quad (2)$$

where q_t and q_e are the amount adsorbed (mg g⁻¹) at time t and at equilibrium and k_{ad} is the rate constant of the pseudo-first-order adsorption process (min⁻¹). Straight line plots of log (q_e-q_t) against t were used to determine the rate constant, k_{ad} and correlation coefficients, R² for different lead concentrations, as shown in Fig. 2.

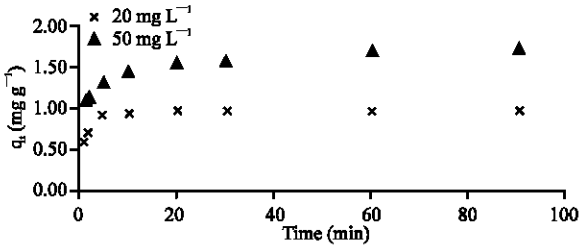


Fig. 1: Effect of initial lead concentration on agitation time

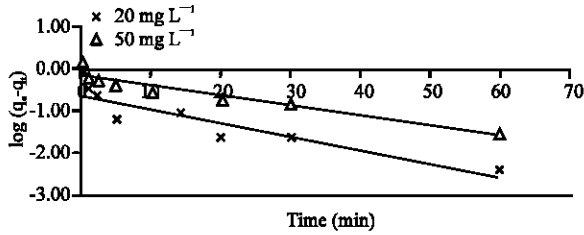


Fig. 2: Pseudo-first-order reaction for Pb²⁺ ions adsorbed onto HB leaf powder at different concentrations

The pseudo-second-order equation is expressed as (Ho and McKay, 1999):

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad (3)$$

where $h = kq_e^2$ ($\text{mg g}^{-1} \text{min}^{-1}$) can be regarded as the initial adsorption rate as $t \rightarrow 0$ and k is the rate constant of pseudo-second-order biosorption ($\text{g mg}^{-1} \text{min}^{-1}$). The plot t/q_t versus t should give a straight line if pseudo-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-second-order reaction at different Pb²⁺ concentrations by HB leaf powder are shown in Fig. 3. The pseudo-first-order and pseudo-second-order rate constants determined from Fig. 2 and 3 are presented in Table 1 along with the corresponding correlation coefficients.

The plot of t/q_t versus t for pseudo-second-order model (Fig. 3) yields very good straight lines (correlation coefficient, $R^2 > 0.99$) as compared to the plot of pseudo-first order. The pseudo-second-order rate constants were in the range of 0.380 to 2.093 $\text{g mg}^{-1} \text{min}^{-1}$. The theoretical values of q_e also agree very well with the experimental ones. Both facts suggest that the adsorption of Pb²⁺ ions by HB leaf powder follows the pseudo-second-order kinetic model, which relies on the assumption that chemisorption may be the rate-limiting step. According to Atkins (1995), in chemisorption (chemical adsorption), the metal ions stick to the adsorbent surface by forming

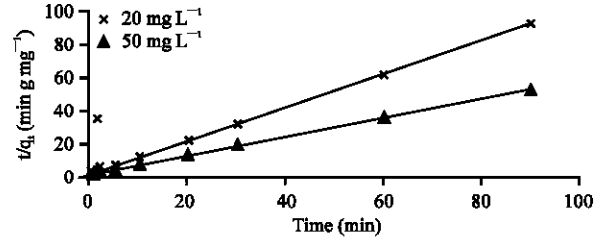


Fig. 3: Pseudo-second-order reaction for Pb²⁺ ions adsorbed onto HB leaf powder at different concentrations

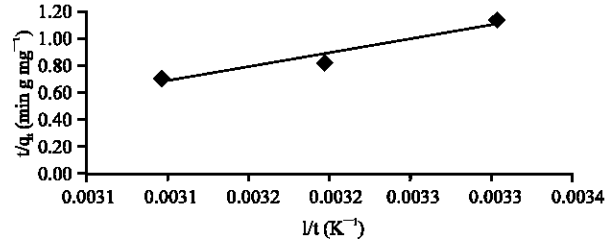


Fig. 4: Influence of temperature on the thermodynamic behavior of adsorption of Pb²⁺ ions on HB leaf powder

a chemical (usually covalent) bond and tend to find sites that maximize their coordination number with the surface.

A detail analysis on the pseudo-second-order reveals that the values of the initial adsorption rates (h) increases with decrease in the initial lead concentration. According to Wong *et al.* (2003), the lower the concentration of metal ions in the solution, the lower the probability of collisions between these species is and hence the faster lead ions could be bonded to the active sites on the surface of the adsorbent. The equilibrium adsorption capacity (q_e) however increased with increase in initial lead concentration due to large number of lead ions are adsorbed at the available adsorption sites. Based on the values of R^2 obtained from the plots of pseudo-first-order and pseudo-second-order rate equations, it is obvious that with increasing initial concentration of the adsorbate, the correlation of experimental data to the pseudo-second order kinetics model decreases while that to the pseudo-first order model increases. The finding from this study is in complete agreement with the kinetics model developed by Azizian (2004).

Thermodynamics of adsorption: For the calculation of thermodynamic parameters, the following equations were used:

$$K_c = \frac{C_{Ae}}{C_e} \quad (4)$$

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

[Pb] (mg L ⁻¹)	Pseudo-first-order equation			Pseudo-second-order equation				
	k_{ad} (min ⁻¹)	q_e (mg g ⁻¹)	R ²	k (g mg ⁻¹ min ⁻¹)	q_e (mg g ⁻¹)	R ²	h (mg g ⁻¹ min ⁻¹)	q_e , exp (mg g ⁻¹)
20	0.081	0.248	0.809	2.093	0.973	0.999	1.982	0.968
50	0.055	0.746	0.899	0.380	1.745	0.998	1.157	1.733

Table 2: Thermodynamic parameters for adsorption of Pb²⁺ ions on HB leaf powder

[Pb] (mg L ⁻¹)	- ΔH° (kJ mol ⁻¹)	- ΔS° (J mol ⁻¹ K ⁻¹)	- ΔG° (kJ mol ⁻¹) at temperature		
			303 K	313 K	323 K
50	40.44	112.18	6.63	4.90	4.41

Table 3: Langmuir and Freundlich adsorption isotherms constants and correlation coefficients for removal of Pb²⁺ ions on HB leaf powder

Langmuir constants			Freundlich constants		
Q° (mg g ⁻¹)	b (l mg ⁻¹)	R ²	1/n	K _F (mg g ⁻¹)	R ²
46.73	0.081	0.986	0.858	3.37	0.996

Table 4: The adsorptive capacities of various adsorbents for Pb²⁺

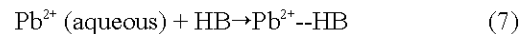
Adsorbent	Q° (mg g ⁻¹)	Reference
Hevea Brasiliensis leaf powder	46.73	This study
Sago waste	46.64	Quek <i>et al.</i> (1998)
Phosphatic clay	37.20	Singh <i>et al.</i> (2001)
Live biomass	35.69	Yan and Viraraghavan (2003)
NaOH-treated spent grain	35.50	Low <i>et al.</i> (2000)
Moroccan stevensite	34.16	Benhammou <i>et al.</i> (2005)
Sawdust <i>Pinus sylvestris</i>	22.22	Taty-Costodes <i>et al.</i> (2003)
Activated carbon (coconut shell)	26.51	Sekar <i>et al.</i> (2004)
Activated carbon (apricot stone)	22.85	Kobyia <i>et al.</i> (2005)
Granular activated carbon	21.50	Rivera-Utrilla <i>et al.</i> (2003)
Carbon nanotubes	16.14	Li <i>et al.</i> (2005)

$$\Delta G^\circ = -RT \ln K_c \quad (5)$$

$$\log K_c = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \quad (6)$$

where K_c is the equilibrium constant (unitless), C_e is the equilibrium concentration in solution (mg L⁻¹) and C_{Ac} is the solid-phase concentration at equilibrium (mg L⁻¹). ΔG° , ΔH° and ΔS° are changes in Gibbs free energy (kJ mol⁻¹), enthalpy (kJ mol⁻¹) and entropy (J mol⁻¹ K⁻¹), respectively. R is the gas constant (8.314 J mol⁻¹ K⁻¹), T is the temperature (K). 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. 5. Adsorption of Pb²⁺ on HB leaf powder decreased when the temperature was increased from 303 to 323 K, as shown in Fig. 4. The process was thus exothermic in nature. The plots were used to compute the values of the thermodynamic parameters (Table 2). The values of enthalpy change (ΔH°) and entropy change (ΔS°) recorded from this work were -40.44 kJ mol⁻¹ and -112.18 J mol⁻¹ K⁻¹, respectively for Pb²⁺ concentration of 50 mg L⁻¹. The negative value of ΔS° indicates the distribution of Pb²⁺ ions in solution was more chaotic compared to Pb²⁺ ions bound to HB surface, resulted in a net decrease in entropy.

Spontaneity of the adsorption process was demonstrated by the increase in Gibbs free energy, ΔG° (values varied from -6.63 to -4.41 kJ mol⁻¹ in the temperature range 303-323 K). The negative values of ΔG° indicate that the equilibrium:



shifts to the right in a spontaneous manner leading to binding of Pb²⁺ ions on to surface constituents of HB leaf powder. ΔG° values were found to be less negative with increasing temperature, which indicated that the adsorption of Pb²⁺ ions on HB leaf powder became less favorable at higher temperature.

Adsorption isotherms: Adsorption data for wide range of adsorbate concentrations are most conveniently described by Langmuir and Freundlich isotherms, which relate adsorption density q_e (amount of lead adsorbed in mg g⁻¹) to equilibrium adsorbate concentration in the bulk fluid phase, C_e (Fig. 5 and 6). To measure the isotherm, initial lead concentrations were varied while the adsorbent weight was kept constant. The linearized Langmuir isotherm is presented as (Langmuir, 1918):

$$\frac{C_e}{q_e} = \frac{1}{Q^\circ b} + \frac{C_e}{Q^\circ} \quad (8)$$

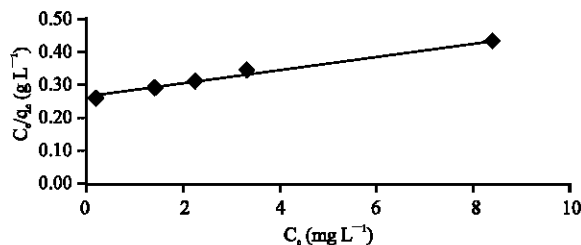


Fig. 5: Langmuir isotherm plot

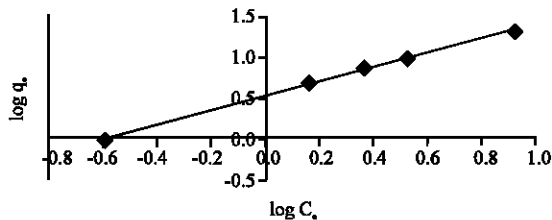


Fig. 6: Freundlich isotherm plot

where C_e is the concentration of the adsorbate at equilibrium (mg L⁻¹), q_e the amount of lead adsorbed at equilibrium (mg g⁻¹), Q° the maximum adsorption capacity (mg g⁻¹) and b is constant related to the binding energy of the adsorption system (l g⁻¹). The values of Q° and b were obtained from the slope and intercept of the plot, respectively. The Freundlich equation can be described by the linearized form (Freundlich, 1906):

$$\log q_e = \log K_f + (1/n) \log C_e \quad (9)$$

where K_f (mg g⁻¹) and n are the Freundlich constants of the system, indicating the adsorption capacity and adsorption intensity, respectively. The values of n and K_f can be calculated from the slope and intercept of the plot, respectively. The Freundlich equation assumes a logarithmic decrease in the enthalpy of adsorption with the increase in the fraction of occupied sites. Figure 5 and 6 show the Langmuir and Freundlich adsorption isotherms obtained by plotting C_e/q_e versus C_e and $\log q_e$ versus $\log C_e$, respectively.

The values of maximum adsorption capacity (Q°) and binding energy (b) obtained from the Langmuir plot were determined as 46.73 mg g⁻¹ and 0.081 L mg⁻¹. The values of K_f and n obtained from the Freundlich plot are 3.37 mg g⁻¹ and 1.166, respectively. The value of n is above unity, which indicates favorable adsorption of lead by HB powder. High regression correlation coefficients for both Freundlich and Langmuir plots suggest that monolayer adsorption as well as heterogeneous surface conditions may co-exist under the applied experimental conditions. The summary of data obtained from both isotherm plots is presented in Table 3.

It is important to compare the value of maximum adsorption capacity obtained from this study with values from other reported adsorbents, since this will suggest the effectiveness of HB leaf powder as a potential adsorbent for use in the treatment of water containing lead. The adsorption capacity for lead using HB leaf powder is of the same order or higher than other reported adsorbents, as shown in Table 4.

CONCLUSIONS

The adsorption process is exothermic and pseudo-second-order kinetic equation is better obeyed than the pseudo-first-order. Langmuir and Freundlich isotherm models govern the adsorption. This work indicates that HB leaf powder has rapid adsorption rate and high adsorption capacity for lead. HB leaf powder is a non-useful plant waste and could be used as a low-cost adsorbent for small and medium-scale industry in developing countries, hence may enhance the economies of local farmers.

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