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Batch, Column and Thermodynamic of Pb(II) Adsorption on Xanthated Rubber (*Hevea brasiliensis*) Leaf Powder

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Abstract: Rubber (*Hevea brasiliensis*) leaf powder was modified by xanthation process and its potential in removing toxic Pb(II) ion from aqueous solutions was investigated in batch and column experiments. Pb(II) adsorption efficiency was found to be affected by several physicochemical parameters such as adsorbent dosage, shaking rate and temperature. The optimum adsorbent dosage was found to be at 0.02 g with more than 80% Pb(II) removal. The amount of Pb(II) adsorbed (mg g^{-1}) increased with increasing shaking rate but decreased with increasing adsorbent dosage and temperature. Thermodynamic parameters such as enthalpy change ($\Delta H°$), free energy change ($\Delta G°$) and entropy change ($\Delta S°$) were computed and Pb(II) adsorption process was found to be exothermic. Fixed-bed column fitted well the Thomas and Yoon-Nelson models with correlation coefficients of R^2>0.96.

Key words: Adsorption, lead, rubber leaf powder, thermodynamic, xanthation

INTRODUCTION

Recovery of toxic heavy metals in the environment by adsorption process has gained the attention of many researchers since the conventional methods available nowadays are costly due to high maintenance and operation. One of the most common heavy metals found in wastewater is Pb(II) which originates from industrial wastes such as batteries, paint, metal plating and automotive (Balaria and Schiewer, 2008; Naiya *et al*., 2009). Pb(II) ions need to be recovered before reaching the water bodies to ensure that the toxic properties of Pb(II) does not pose any threat to aquatic lives and more importantly, the human health.

As the environment is faced with solid waste disposal problem, agricultural by-products have the potential to be used as adsorbents. Plant leaves for instance, have been reported to be capable of removing various heavy metal ions from wastewater (Wan Ngah and Hanafiah, 2008). Rubber trees are widely planted in Malaysia and have become one of the major plantation crops after oil palm. Rubber related industries are now expanding to meet the demands from consumers. However, the large area of rubber plantation in Malaysia generates a huge amount of 'waste' rubber leaves especially during dry season (February to March) every year. Numerous studies have been performed on the application of unmodified and chemically modified rubber leaves to sequester Cu(II), Cd(II) and Pb(II) ions (Hanafiah and Wan Ngah, 2009; Hanafiah *et al*., 2006a, b). However, the recorded adsorption capacities were found to be quite low or could hardly achieve greater than 0.3 mmol g^{-1}.

This study highlighted the introduction of sulphur groups on rubber leaf powder, a process called xanthation for removing Pb(II) from aqueous solutions. The main objective of this study was to determine the effect of physicochemical parameters particularly adsorbent dosage, shaking rate and temperature on adsorption efficiency of Pb(II). Behavior of Pb(II) adsorption in a continuous downflow packed-bed column was also studied.

MATERIALS AND METHODS

Chemicals and adsorbent preparation: All the chemicals used were of analytical reagent grade. Lead(II) nitrate stock solutions (1000 mg L^{-1}) were purchased from

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Spectrosol (England) and the desired concentrations of Pb(II) were obtained by successive dilutions with deionized water. The fresh mature (brownish color) rubber leaves were collected from Universiti Teknologi Mara Pahang rubber plantation in Pahang, Malaysia. The rubber leaves were washed thoroughly with tap water to remove dirt and particles before drying in the oven at 105°C for 24 h. The leaves were later ground using a mechanical grinder and sieved to obtain particle size of 180 μm. This Untreated Rubber Leaf Powder (URLP) was stored in a tight container for further study.

Xanthation process was performed according to the previous method by Liang *et al.* (2009) with some modification. Fifteen grams of URLP and 200 mL (4.0 M) sodium hydroxide were mixed in a 250 mL conical flask. The mixture was stirred for 3 h at room temperature (30±0.5°C) and for another 3 h after the addition of 10 mL carbon disulfide. After allowing the mixture to settle for 30 min, the supernatant was decanted. The Xanthated Rubber Leaf powder (XRL) was extensively washed with 200 mL of deionized water for 20 times to remove excess base. Finally, the leaf powder was washed with acetone followed by drying in an oven at 50°C for 24 h. Thermal stability of XRL was determined by performing thermogravimetric analysis (TGA, Perkin Elmer Pyris 1, USA). A weight of 5.90 mg of XRL was placed onto platinum crucible and the analysis was carried out under N_2 flow at the heating rate of 20°C min^{-1} with the temperature ranging from 50 to 900°C.

Batch and fixed-bed column adsorption experiments: All adsorption experiments were carried out in duplicate and the data was reported as average. Batch adsorption studies were performed in 100 mL conical flasks with 50 mL (40 mg L^{-1}) Pb(II) solutions shaken in a thermostat water bath shaker at 120 stroke min^{-1} for 90 min at room temperature, 30°C (unless state otherwise). The initial pH of Pb(II) solutions was 4. The effect of adsorption dosage on Pb(II) removal was studied by using different weight of adsorbent (0.01 to 0.10 g). The effect of shaking rate was studied by using different shaking rates from 30 to 150 stroke min^{-1}. Thermodynamic study was investigated by mixing 0.02 g of XRL with different Pb(II) concentrations (20 to 150 mg L^{-1}) at three different temperatures (303, 313 and 323 K). The mixture was shaken for 90 min at room temperature to ensure that equilibrium was achieved. After adsorption, the mixture was separated by using Whatman No. 42 filter papers and the filtrates were analyzed for remaining Pb(II) ions using atomic adsorption spectrophotometer (Perkin Elmer, AAnalyst 800 model, USA) at a wavelength of 283.3 nm.

In the fixed-bed column study, a glass column with the internal diameter of 2 cm was used. One gram of XRL was soaked in deionized water before slowly being poured into the column. This technique was done to avoid the air gaps in the column. Glass wool was placed at the bottom of the column and on the top of XRL to avoid the adsorbent from floating. The bed height of the column was 2 cm and inlet concentration of 100 mg L^{-1} of Pb(II) solution was loaded into the column at a flow rate of 12 mL min^{-1} using a peristaltic pump (Cole Parmer, USA). The column operation was stopped when XRL reached the exhaustion stage. After analysis, the amount of Pb(II) adsorbed, q_e (mg g^{-1}) and the percentage removal were calculated by using Eqs. 1 and 2, respectively:

$$q_e = \frac{C_i - C_e}{m} V \quad (1)$$

$$\text{Removal (\%)} = \frac{C_i - C_e}{C_i} \times 100 \quad (2)$$

where, C_i and C_e are Pb(II) concentration before and after adsorption (mg L^{-1}), respectively; V is the volume of Pb(II) solution (L) and m is the weight of XRL (g).

RESULTS AND DISCUSSION

Thermogravimetric (TGA) analysis: A biomass such as plant leaf consists of cellulose, hemicelluloses and lignin as the major components (Williams and Besler, 1996). TGA analysis was performed to determine the thermal degradation of XRL. The decomposition of XRL as a function of temperature under nitrogen atmosphere is shown in Fig. 1. According to Yang *et al.* (2007), hemicelluloses start to decompose at 220-315°C, while the temperature range of 315-400°C corresponds to cellulose. Lignin however, decomposes in a wider

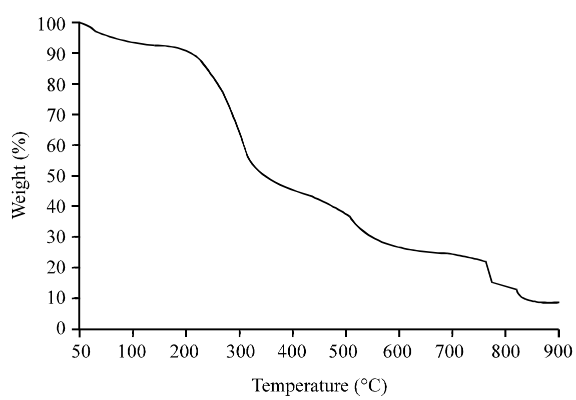

Fig. 1: TGA curve of XRL, Temperature: 50-900°C, Heating rate: 20°C min^{-1}

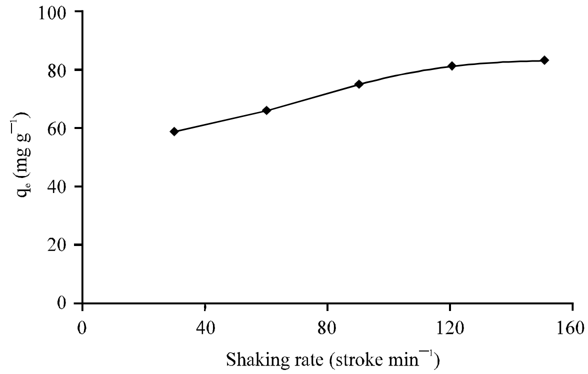

Fig. 2: Effect of shaking rate on Pb(II) adsorption by XRL, Adsorbent weight: 0.02 g, Volume: 50 mL, Shaking rates: 30-150 stroke min^{-1}, Equilibrium time: 90 min, Initial Pb(II) concentration: 40 mg L^{-1}

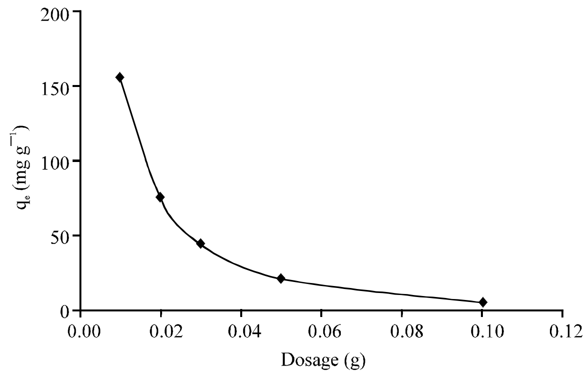

Fig. 3: Effect of adsorbent dosage on Pb(II) adsorption by XRL, Adsorbent weight: 0.01 to 0.10 g, Volume: 50 mL, Shaking rate: 120 stroke min^{-1}, Equilibrium time: 90 min, Initial Pb(II) concentration: 40 mg L^{-1}

temperature range (200-720°C) (Williams and Besler, 1996). As shown in Fig. 1, the mass loss of 7.9% in the region 50 to 188°C indicates the loss of moisture and adsorbed water. The weight loss of about 54.3% at temperature range of 188-429°C is attributed to decomposition of hemicellulose, cellulose and lignin. Higher molecular weight of lignin decomposed at a much higher temperature range (429-603°C) with 27.7% weight loss. The adsorbent still undergoing decomposition at higher temperature >700°C with 3.6% weight loss before finally produced char at 900°C.

Effect of shaking rate: The effect of shaking rate on Pb(II) adsorption onto XRL was studied at different rates (30, 60, 90, 120, 150 stroke min^{-1}). As shown in Fig. 2, the amount of Pb(II) adsorbed onto XRL increased as the shaking rate increased. The lowest amount of Pb(II) adsorbed occurred at the lowest shaking rate which was 30 stroke min^{-1} (58.28 mg g^{-1}) and the highest amount at the rate of 150 stroke min^{-1} (82.53 mg g^{-1}). At the shaking rates of 60, 90 and 120 stroke min^{-1}, the amounts of Pb(II) adsorbed were 65.18, 74.08 mg g^{-1} and 80.54 mg g^{-1}, respectively. This adsorption characteristic can be explained in term of external film diffusion. An increase in shaking rate would favor higher adsorption rate by decreasing the mass transfer resistance between the adsorbate and adsorbent surface (Ponnusami and Srivastava, 2009). However, beyond 120 stroke min^{-1}, there was no difference in the amount of Pb(II) adsorbed. Hence, shaking rate of 120 stroke min^{-1} was selected in subsequent experiments.

Effect of adsorbent dosage: The dependence of adsorbent dosage in the removal of Pb(II) ions was studied at different adsorbent dosages (0.01 to 0.10 g). The concentration of Pb(II) was fixed at 40 mg L^{-1} and the results are presented in Fig. 3. The amount of Pb(II) adsorbed decreased from 156.66 to 14.54 mg g^{-1} with increased adsorbent dosage. This was due to metal concentration shortage in solution at high dosage (Qaiser *et al*., 2007). Another possible explanation is due to the availability of more surface area and adsorption sites which is the results of plenty unadsorbed sites as dosage is increased (Gong *et al*., 2009; Kamal *et al*., 2010). In this study, the optimum dosage chosen was 0.02 g because of the high amount of Pb(II) adsorbed (81.06 mg g^{-1}) and high percentage of Pb(II) removal (81.06%). Low dosage but good percentage of metal removal means less amount of adsorbent has to be used, thus treatment process will be more economical.

Effect of temperature and adsorption thermodynamics: For all Pb(II) concentrations tested, it was found that the amount of Pb(II) adsorbed decreased as the temperature increased (figure not shown). This would suggest that the interaction between Pb(II) ions and the XRL surface is exothermic. Excess energy promotes desorption of adsorbate instead of adsorption, thus decreases the amount of adsorbate adsorbed (Gupta and Bhattacharyya, 2008). The trend also explains that with the increase in temperature, the solubility of Pb(II) ions in the aqueous phases would increase, thus decreases the Pb(II) concentration in the solid phase (Gupta and Bhattacharyya, 2008).

The thermodynamic parameters, $\Delta H°$, $\Delta S°$, $\Delta G°$ were computed from the Van't Hoff equation and Gibbs-Helmholtz equations (Eq. 3 and 4):

Table 1: Thermodynamic parameters of Pb(II) adsorption onto XRL

Pb(II) ($mg\ L^{-1}$)	ΔS° ($J\ mol^{-1}\ K^{-1}$)	ΔH° ($kJ\ mol^{-1}$)	ΔG° ($kJ\ mol^{-1}$) 303 K	313 K	323 K
20	-93.04	-38.36	-10.17	-9.24	-8.31
40	10.77	-4.081	-7.34	-7.45	-7.56
60	-52.61	-21.42	-5.48	-4.95	-4.42
80	-29.01	-12.59	-3.80	-3.51	-3.22
100	-62.60	-22.07	-3.10	-2.48	-1.85
150	-71.73	-23.09	-1.35	-0.38	0.08

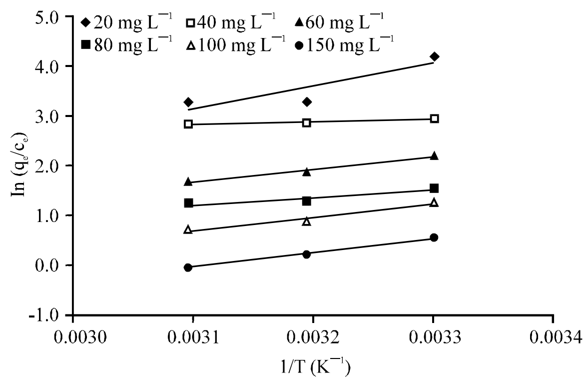

Fig. 4: Van't Hoff plot of Pb(II) adsorption onto XRL

$$\ln\left[\frac{q_e}{C_e}\right] = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{3}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{4}$$

where, q_e/C_e is the equilibrium constant ($mL\ g^{-1}$), ΔS° is standard entropy change ($J\ mol^{-1}\ K^{-1}$), ΔH° is standard enthalpy change ($kJ\ mol^{-1}$), T is absolute temperature (K) and R is the gas constant (8.314 $J\ mol^{-1}\ K^{-1}$). ΔG° is the standard free energy change ($kJ\ mol^{-1}$). ΔH° and ΔS° can be determined from the slope and intercept of linear plot of ln (q_e/C_e) versus 1/T, respectively (Fig. 4). From Table 1, the negative values of ΔH° explain the exothermic nature of interactions between Pb(II) ions and XRL surface. The adsorption of Pb(II) was spontaneous as ΔG° values were negative. The low negative values of ΔH° indicated that one of the main mechanisms of Pb(II) adsorbed on XRL was a physical adsorption.

Fixed-bed column studies: As industries generate a large quantity of wastewater, it is more practical to remove heavy metal ions by applying continuous column method. In a column operation, solution continuously enters and leaves the column until the adsorbent surface becomes fully saturated. The overall performance of the column is judged by the time the adsorbed heavy metal penetrates the column bed and is detected in the effluent (Hanafiah *et al*., 2010). A breakthrough curve can be

Table 2: Adsorption breakthrough data and Thomas and Yoon-Nelson parameters for a fixed-bed column experiment

Parameter	Value
t_b (min)	29
$t_{50\%}$ (min)	48
V_b (mL)	348
q_b ($mg\ g^{-1}$)	35
t_{exh} (min)	87
V_{eff} (mL)	1152
V_{exh} (mL)	1044
Thomas model	
k_{Th} ($mL\ min^{-1}\ mmol^{-1}$)	182.34
q_o ($mmol\ g^{-1}$)	0.30
q_o ($mg\ g^{-1}$)	62.20
R^2	0.966
Yoon-Nelson model	
k_{YN} (min^{-1})	0.088
q_{oYN} ($mg\ g^{-1}$)	62.04
τ (min)	51.72
R^2	0.966

Pb(II) concentration: 100 $mg\ L^{-1}$, pH: 4, column internal diameter: 2 cm, bed height: 2 cm, adsorbent weight: 1.0 g, flow rate: 12 $mL\ min^{-1}$

obtained by plotting effluent concentration (C_{eff}) versus treated volume (V) or service time (t). The ideal breakthrough curve is the 'S' shape, which indicates favorable adsorption process (Al-Degs *et al*., 2009). A breakthrough curve (figure not shown) can give important parameters such as breakthrough time (t_b), breakthrough volume (V_b), exhaustion volume (V_{exh}) or column exhaustion time (t_{exh}), which occurs at 95% of inlet concentration (C_i) and breakthrough capacity (q_b, $mg\ g^{-1}$). The total effluent volume and breakthrough capacity can be calculated from Eq. 5 and 6, respectively:

$$V_{eff} = Qt \tag{5}$$

$$q_b = \frac{Qt_{10\%}C_i}{m} \tag{6}$$

where, Q is the volumetric flow rate ($mL\ min^{-1}$), t is the time (min), $t_{10\%}$ is the time taken (min) to reach 10% of the inlet concentration, C_i is the initial Pb(II) concentration ($mg\ L^{-1}$) and m is the weight of XRL (g).

All the data from fixed-bed column study are presented in Table 2. The behavior of Pb(II) adsorption under column operation was further analyzed by using two column models: Thomas and Yoon-Nelson. Thomas model is based on several assumptions such as adsorption follows Langmuir isotherm, no axial dispersion and second order adsorption kinetics (Qaiser *et al*., 2009). Yoon-Nelson model is based on the assumptions that the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent (Aksu *et al*., 2007). The linear forms of the Thomas and Yoon-Nelson model are given by Eqs. 7 and 8, respectively:

$$\ln = \left[\frac{C_i}{C_t} - 1\right] = \frac{k_{Th}\, q_o m}{Q} - \frac{k_{Th}\, C_i\, V_{eff}}{Q} \quad (7)$$

$$\ln = \frac{C_t}{C_i - C_t} = k_{YN} - \tau k_{YN} \quad (8)$$

where, C_t is the Pb(II) concentration (mg L^{-1}) at time t (min), k_{Th} is the Thomas rate constant (mL min^{-1} $mmol^{-1}$), q_o is the column adsorption capacity (mmol g^{-1}), Q is the volumetric flow rate (mL min^{-1}), V_{eff} is the effluent volume (mL), m is the weight of XRL in column (g), k_{YN} is the Yoon-Nelson rate constant (min^{-1}) and is measured off the slope of the breakthrough curves. Steeper breakthrough curves will have higher values of k_{YN}. τ is the time required for 50% adsorbate breakthrough (min). A linear plot of ln $((C_i/C_t)$-1) versus V_{eff}/Q (or t) was employed to determine the values of k_{Th} and q_o, which were obtained from the slope and intercept, respectively (plot not shown). The column capacity based on the Yoon-Nelson model (q_{oYN}) can be computed from the Eq. 9:

$$q_{oYN} = \frac{C_t\, Q_\tau}{1000m} \quad (9)$$

Both column models (plots not shown) showed good correlation coefficient values with R^2>0.96. High values of correlation coefficients were obtained and the time required to achieve 50% of adsorbate breakthrough (τ) was closed to the experimental data ($t_{50\%,exp}$). As such this would strongly suggest that adsorption of Pb(II) onto XRL in column process agreed well with these models.

CONCLUSION

Based on the experimental data presented in this study, XRL could be used as an alternative adsorbent in removing Pb(II) ions from aqueous solution since the amount of Pb(II) adsorbed was high even though only a low dosage (0.02 g) was used. The effect of dosage, shaking rate and temperature has a great influence on the amount of Pb(II) adsorbed. TGA analysis showed that XRL has good chemical stability since the adsorbent decomposed at a higher temperature. Thermodynamic study proved the adsorption process of Pb(II) ions was exothermic. XRL is also suitable to be used under column operation.

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