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Adsorption of Pb(II) Ions on Sulfuric Acid Treated *Leucaena leucocephala* Leaf Powder

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Abstract. Sulfuric acid treated Petai belalang (*Leucaena leucocephala*) leaf powder (SLLP) was used as an adsorbent for Pb(II) ions removal. The experimental adsorption parameters investigated include pH, dosage and initial Pb(II) concentration. Pb(II) removal was more favored at a higher adsorbent dosage, pH and temperature. Adsorption kinetics conformed to the pseudo-second order model while Langmuir isotherm model recorded the value of maximum adsorption capacity (q_{max}) of 222 mg/g. The major functional groups involved in the adsorption process were identified as hydroxyl, amino and ether as revealed by the FTIR analysis. The prepared adsorbent demonstrated a potential application for efficient removal of Pb(II) ions from industrial wastewater.

1 Introduction

The fast growth of human population and an increase number of industries are often associated with serious water pollution. Batteries, alloys and steels, pigments, ammunition and metal industries are responsible for the release of toxic heavy metals into the environment. Lead (Pb), in particular is considered as one of the harmful heavy metals to humans, even if it is present in a low concentration in a human body [1]. Pb can cause serious diseases such as cancer, anemia and intellectual disability [2]. The overcome the release of Pb(II) ions into water bodies, numerous conventional treatments are used such as membrane process, chemical precipitation, electrodialysis and coagulation [3]. These treatments however, are inefficient to treat low concentrations of Pb(II) ions and can generate production of secondary pollutants at the end of the treatment processes [4]. Another approach of sequestering heavy metal ions involves adsorption, which is much simple and cost effective. This study introduced a new biomaterial, *Leucaena leucocephala* leaf powder as an adsorbent for removal of Pb(II) ions. *Leucaena leucocephala* leaves were chosen because agricultural wastes contain various functional groups that are capable of binding Pb(II) ions efficiently.

2 Experimental

2.1 Adsorbent preparation and characterization

A 1000 mg/L Pb(II) standard solution was purchased from Merck (Germany). The green *Leucaena leucocephala* leaves were collected in Jengka, Malaysia, then brought to the lab and washed thoroughly with deionized water. The leaves were dried in an oven at 80 ^{0}C before being ground and sieved to obtain the particle size of 180-355 µm. Five grams of the leaf powder were mixed with 200 mL sulfuric acid (0.50 M), heated at 105 ^{0}C and washed with deionized water. The leaf powder was soaked overnight in 3 % (w/v) of sodium hydrogen carbonate ($NaHCO_3$) solution to remove residual acid. Finally, the powder was filtered and washed until the pH of the solution reached near neutral and oven dried at 105 ^{0}C for 24 h. The sulfuric acid treated *Leucaena leucocephala* leaf powder was abbreviated as SLLP. Characterization experiment involved determination of functional groups using a Fourier transform infrared spectrometer (PerkinElmer, Spectrum 100, USA).

2.2 Adsorption experiments

For pH effect, pH 2 until 5 was selected because precipitation occurred beyond pH 5. A weight of 0.02 g SLLP was mixed with 50 mL (50 mg/L) of Pb(II) solutions, shaken in a water bath shaker for about 90 min at 120 stroke/min. The initial pH of solution was adjusted by adding drops of 0.10 M HCl or NaOH solutions. In the study of effect of SLLP dosage, the SLLP weight was varied from 0.02 g to 0.10 g while the volume and concentrations of Pb(II) were fixed at 50 mL and 50 mg/L, respectively. Three different concentrations of Pb(II) solutions (50, 100 and 150 mg/L) were selected in the kinetics study while concentrations were varied from 50 to 300 mg/L in the isotherm study. The SLLP weight was fixed at 0.02 g in kinetics and isotherm studies. All experiments were conducted in duplicate and results were

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presented as average. Eqs. 1 and 2 below showed the amount of Pb(II) adsorbed, qe (mg/g) and their percentage removal (%), respectively:

$$q_e = \frac{V\,(C_0 - C_e)}{m} \quad (1)$$

$$\text{Removal}\ (\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

3 Results and discussion

3.1 FTIR spectra

The FTIR spectra of SLLP and Pb-SLLP are shown in Fig.1. For SLLP, the broad peak observed at 3374 cm^{-1} indicated the stretching of hydroxyl (-OH) group. The characteristic of carbonyl group (C=O) is shown at 1696 cm^{-1}. The broad peak observed at 1594 cm^{-1} was attributed to the amino and aromatic C=C bending. C-O stretching of alcohols, carboxylic acids, esters and ethers are represented by the peaks around 1320-1000 cm^{-1}. The peak observed at 2922 cm^{-1} was due to the C-H stretching of alkanes. After Pb(II) was adsorbed on SLLP, a shift in wavenumber from 3374 to 3360 cm^{-1} was observed. This observation suggested hydroxyl group was responsible for binding of Pb(II) ions. Another functional group that could adsorb Pb(II) ions was C-O-C as there was a shift in wavenumber from 1035 to 1030 cm^{-1}. Based on this FTIR study, it can be concluded that the large amount of hydroxyl and ether groups presence on SLLP provide active sites for Pb(II) to adsorb.

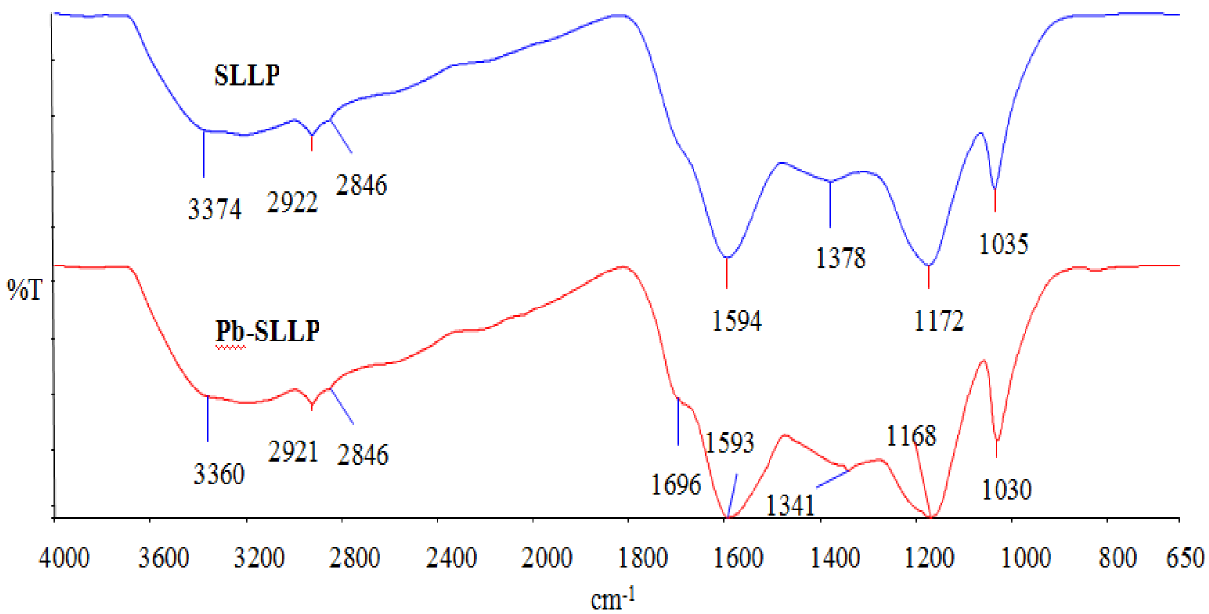
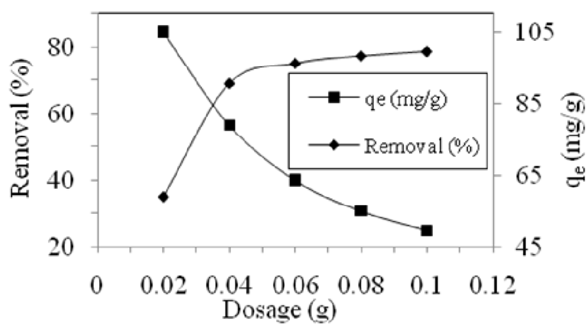


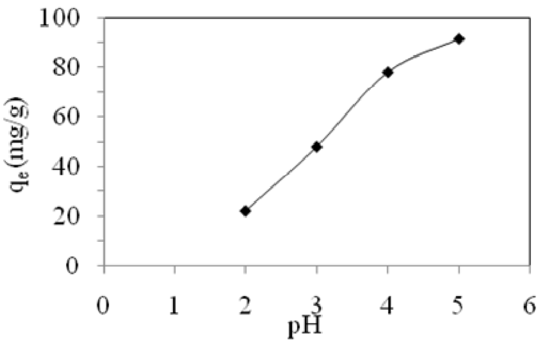
Figure 1. FTIR spectra of SLLP and Pb-SLLP.

3.2 Effects of SLLP dosage and pH

The percentage removal of Pb(II) ions increased from 58.95 to 99.53 % as the SLLP dosage increased from 0.02 g to 0.10 g (Fig. 2a). This phenomenon confirmed that more active sites as well as surface area are available for the binding of heavy metal ions with increasing the adsorbent dosage [5]. However, the amount of Pb(II) ions adsorbed (mg/g) decreased from 84.61 to 24.88 mg/g due to unsaturation of adsorption sites [6]. In the other word, aggregation occurred due to the particle interaction that led to the surface area reduction of the adsorbent. Pb(II) ions adsorption increased with the increase in the pH of solution as shown in Fig. 2b. Beyond pH 5.5, precipitation occurred to form $Pb(OH)_2$ due to the high number of OH^- ions presence in the solution [7]. Below pH 4, Pb(II) uptake decreased from 91.66 to 21.98 mg/g, primarily because of the competition between H_3O^+ ions and the metal ions.



(a)



(b)

Figure 2. Effects of SLLP dosage (a) and pH (b) on Pb(II) uptake.

3.3 Effects of initial Pb(II) concentrations and contact time

The effects of Pb(II) concentration and contact time are presented in Fig. 3. It can be seen that initial rapid adsorption process occurred in the first stage. It was due to the large number of available vacant or active sites [8]. The rapid transfer of Pb(II) ions with the external surface of adsorbent occurred and more Pb(II) ions was removed in the first 20 min. More functional groups participated in the metal ions uptake as the time increased until equilibrium was achieved in 90 min.

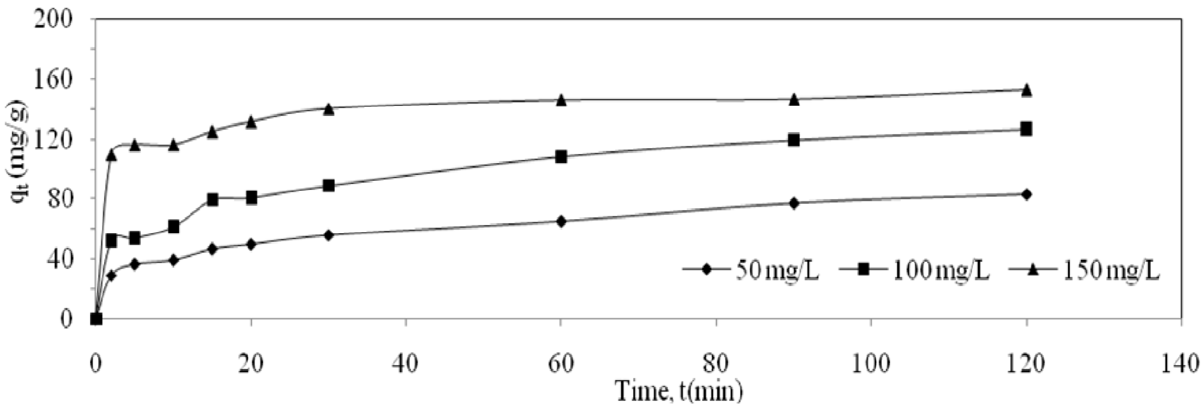


Figure 3. Effects of initial concentration and time on Pb(II) adsorption on SLLP.

3.4 Adsorption kinetic modeling

The pseudo-first order [9] and pseudo-second order [10] kinetic models were used to analyze the kinetics data:

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1}{2.303}t \quad (3)$$

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

where q_t and q_e (mg/g) indicate the amount of Pb(II) adsorbed at time, t (min) and equilibrium respectively. k_1 (1/min) and k_2 (g/mg/min)) refer to the rate constants of the pseudo-first order and pseudo-second order adsorption process, respectively. The values of k_1 and correlation coefficient (R^2) were obtained from the plot of log (q_e-q_t) against t (min) while the values of h and k_2 were obtained from an equation of $h=k_2q_e^2$. The values of correlation coefficient (R^2) for pseudo-second were close to unity (Table 1), while the value of normalized standard deviation (Δq), calculated from Eq. 5 showed a lower value compared to the pseudo-first order model. A similar observation was also reported by [11].

Table 1. Adsorption kinetics parameters of Pb(II) on SLLP

[Pb] (mg/L)		50	100	150
Pseudo-first order	$q_{e,cal}$ (mg/g)	111.230	100.000	116.550
	$q_{e,exp}$ (mg/g)	83.150	126.730	153.090
	k_1 (1/min)	0.021	0.023	0.198
	R^2	0.307	0.319	0.330
	Δq	23.88	14.91	16.88
Pseudo-second order	$q_{e,cal}$ (mg/g)	84.96	130.55	153.14
	$q_{e,exp}$ (mg/g)	83.15	126.73	153.09
	k_2 (g/mg/min))	0.001	0.095	0.003
	R^2	0.979	0.988	0.999
	Δq	1.539	2.131	0.023

$$\Delta q\ (\%) = \sqrt{\frac{\Sigma\left[\left(q_{e,exp} - q_{e,cal}\right) / q_{e,exp}\right]^2}{n-1}} \quad (5)$$

3.5 Adsorption isotherm

The monolayer adsorption of adsorbate onto homogeneous surface of adsorbent with a finite number of active sites can be described by using Langmuir isotherm model [12], expressed by Eq. 6:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} b} + \frac{C_e}{q_{max}} \quad (6)$$

where C_e is the equilibrium concentration (mg L^{-1}), q_e is the equilibrium adsorption capacity (mg g^{-1}) and b is the Langmuir constant or rate of adsorption (L mg^{-1} or L mol^{-1}). The Langmuir plots showed good linearity (Fig. 4).

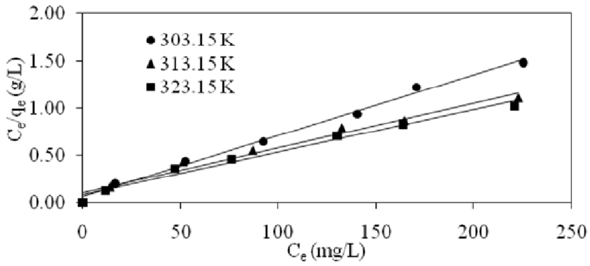


Figure 4. Langmuir isotherm plot of SLLP.

Based on Table 2, the correlation coefficients were close to unity and it proved that the Langmuir isotherm model was fitted well. The amount of Pb(II) adsorbed was found to increase with the increase in temperature. This is an indication of endothermic adsorption process.

Table 2. Adsorption isotherm parameters of SLLP.

Temperature (K)	q_{max} (mg/g)	b (L/mol)	R^2
303.15 K	153.84	0.001	0.993
313.15 K	208.33	0.048	0.973
323.15 K	222.22	0.055	0.979

4 Conclusions

This work showed that SLLP is an effective adsorbent for the removal of Pb(II) ions from aqueous solutions. The presence of hydroxyl (-OH), amino ($-NH_2$) and ether (C-O-C)) provided a large number of active sites for Pb(II) to adsorb efficiently. Pb(II) adsorption was more favored at higher temperatures, which indicated an endothermic process.

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References

1. A. Bahrami, A. Besharati-Seidani, A. Abbaspour, M. Shamsipur, Electrochimica Acta. **118**, 92-99 (2014)
2. G. Zhao, X. Ren, X. Gao, Dalton Trans. **40**, 10945-10952 (2011)
3. M. Motsa, M. Mamba, B. B. Thwala, J. M. Msagati, T.A.M, J. Colloid Interf. Sci. **359**, 210-219 (2011)
4. A. Papandreou, C. J. Stournars, D. Panias, J. Hazard. Mater. **148**, 538-547 (2007)
5. K. Jayaram, I. Y. L. N. Murthy, H. Lalhruaitluanga, M. N. V. Prasad, Colloids Surf. B. Biointerfaces **71**, 248-254 (2009)
6. L. J. Yu, S. S. Shukla, K. L. Dorris, A. Shukla, J. L. Margrave, J. Hazard. Mater. **100**, 53-63 (2003)
7. P. X. Sheng, Y. P. Ting, J. P. Chen, L. Hong, J. Colloid Interface Sci. **275**, 131-141 (2004)
8. M. Kousha, E. Daneshvar, M. S. Sohrabi, M. Jokar, A. Bhatnagar, Chem. Eng. J. **192**, 67-76 (2012)
9. Y. S. Ho, G. McKay, Process Saf. Environ. Protect **76**, 332-340 (1998)
10. Y. S. Ho, G. McKay, Water Res. **34**, 735-742 (2000)
11. N. Nasuha, B. H. Hameed, Chem. Eng. J. **166**, 783-786 (2011)
12. I. Langmuir, J. Am. Chem. Soc. **38**, 2221-2295 (1916)