

KINETICS STUDY OF Pb (II) ADSORPTION ON XANTHATED *Leucaena leucocephala* LEAF POWDER

Mardhiah Ismail^{1*}, and Liyana Ainun Yamin³

^{1,2}Faculty of Applied Science
Universiti Teknologi MARA (UiTM) Pahang, 26400 Bandar Jengka

*Corresponding author: marismael@uitm.edu.my

Abstract

Leucaena leucocephala (LL) is abundant and has the potential to be a cheap and readily available biosorbent. This species is among the fast-growing trees, which is widely used in Malaysia including in the furniture industry for its wood. In this study, LL leaf powder was treated with xanthate and evaluated for its act in the removal of low concentration Pb (II) ion from aqueous solution. The functional groups of xanthates-treated *L. leucocephala* leaf powder (XLL) was investigated using the ATR-Fourier Transform Infrared (ATR-FTIR) analysis. The study also covered the influence of several parameters on the adsorption of Pb (II) onto XLL, such as pH, adsorbent dosage, and kinetics. The optimum pH range for Pb (II) adsorption was at pH 4. Two kinetic models; pseudo-first-order model and pseudo-second-order model, were used to analyze the Pb (II) adsorption process, and the results showed that the pseudo-second-order model close-fitting well with a correlation coefficient, R_2 , of 0.99. The maximum adsorption capacity of Pb (II) was 76.34 mg g⁻¹. This study hopes to increase the value of this fast-growing tree species.

Keyword: Adsorption, lead, *Leucaena leucocephala*, xanthate.

Introduction

Lead has been used for a really long time. It can be described as purely toxic, but still widely used and important to our economy. The major uses of lead come from various industrial activities, such as the manufacturing of batteries, printing, pigments, fuels, photographic materials, and explosives (Yuvaraja et al., 2014). Heavy metals tend to accumulate in the environment, especially in lakes, estuarine, and marine sediments; threatening the environment for future generations. The toxicological effects of Pb (II) in humans include an inhibition of hemoglobin formation which is known as anemia, sterility, hypertension, learning disabilities problem, abortion, kidney damage, and mental retardation issues. Hence, the removal of lead from water is vital to protect social health and the environment (Abdelhafez & Li, 2016).

Therefore, in order to remove heavy metal from aqueous solutions, many methods of treatment have been reported. Activated carbon is the most used adsorbent, but it is relatively high cost. Agricultural wastes, industrial by-products and wastes, and natural substances have been introduced as adsorbents for heavy metal treatment as they are inexpensive and easily available (Fu & Wang, 2011). The previous study used biosorbents for its high effectiveness in reducing the heavy metal ions and was considered a low cost-adsorbent. *Leucaena leucocephala* (LL) could potentially be a cheap and readily available biosorbent since this species is widely found in Malaysia. Based on the previous study, no research was performed on the adsorption of lead using carbon disulphide, CS₂. (xanthate) treated with *L. leucocephala* (LL) leaf powder.

Materials and Methods

Adsorbent Preparation

L. leucocephala (LL) leaves were collected in Jengka, Malaysia. The fresh leaves were separated from the stem; then washed with tap water several times to remove dust and soluble impurities, before being rinsed with deionized water. The clean leaves were dried at 60 °C in the oven overnight before being ground and sieved using a grinder to obtain an average particle size of 75-355 µm. 15.0 g of ground leaves and 200 mL (4 M) NaOH was mixed in a 250 mL conical flask. The mixture was stirred for three hours at room temperature (30 ± 0.5 °C). Then 10 mL carbon disulfide was added into the reaction mixture and stirred continuously for another three hours. The formation of the alkoxide (CH₂O-) group was formed after treated with NaOH. The supernatant was decanted after the mixture was settle down for 30 minutes. The xanthate LL (XLL) leaf powder was washed successively with 4 L deionized water to remove the excess base. Finally, the XLL leaf powder was dried in an oven at 60 °C for 24 hours (Liang et al., 2010).

Adsorbent Characterization

The types of functional groups present in XLL surface were determined by Fourier Transform Infrared spectrometer (ATR-FTIR) (Spectrum 100, Perkin Elmer, USA).

Adsorption Experiment

Lead nitrate (Pb(NO₃)₂, MW = 331.2 g mol⁻¹) was bought from MERCK, Malaysia. The stock solution of 1000 mg L⁻¹ Pb (II) was prepared and diluted to the required concentrations with deionized water. The effect of dosages toward adsorption system was achieved by separately mixing 0.02, 0.04, 0.06, 0.08, and 0.1 g XLL with 50 mL (10 mg L⁻¹) Pb (II); and stirred at 120 strokes per minute at 298 ± 1 K for 90 min to attain equilibrium. The effect of pH was studied in the pH range of between 2 to 5. A kinetic study of adsorption was conducted using three different Pb (II) concentrations (10, 20, and 30 mg L⁻¹) at various contact times (0-90 min). After adsorption, the XLL was filtered and the final concentration of Pb (II) was determined using Atomic Absorption Spectrometer (PinAAcle 900T, Perkin Elmer, USA). All the experiments were piloted in duplicate and the RSD values of the analyses were less than 5%. The amount of Pb (II) ion adsorbed (q_e, mg g⁻¹) and percentage removal (%) was calculated using equations (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 is the initial concentration and C_e is the and final concentrations (mg L⁻¹) of Pb (II) and m is the weight of XLL (g).

Results and Discussion

Adsorbent Characteristic

ATR-FTIR analysis was used to identify functional groups on the XLL surface before and after chemical modification of LL, which are responsible for adsorption of Pb (II). ATR-FTIR spectra in the range of 4000-400 cm⁻¹ are shown in Figure 1. Based on the spectrum, LL has broad absorption peak at 3282 cm⁻¹, which suggests the presence of hydroxyl (-OH) and overlapping with weak amine (-NH₂) absorption band. The peaks at 2917 cm⁻¹ and 2849 cm⁻¹

were responsible for sp^2 hybridized $-CH$. The FTIR spectrum of XLL showed some shift in wavenumbers after the xanthation process. The intensity at 1729 cm^{-1} in LL was reduced upon the chemical treatment, indicating the carboxylic acid or ester were converted to carboxylate. The presence of $-C=S$ group was confirmed by the peak at 1158 cm^{-1} (Chand et al., 2015). In the spectra of XLL, C-S near 569 cm^{-1} was identified as a weak broad stretching peak (Torres-Blancas et al., 2013). The peak, 1016 cm^{-1} shifting to 1018 cm^{-1} for XLL and XLL-Pb after adsorption, showed that it could be the formation of a bond between C-O-C and Pb (II) ion (Chand et al., 2015).

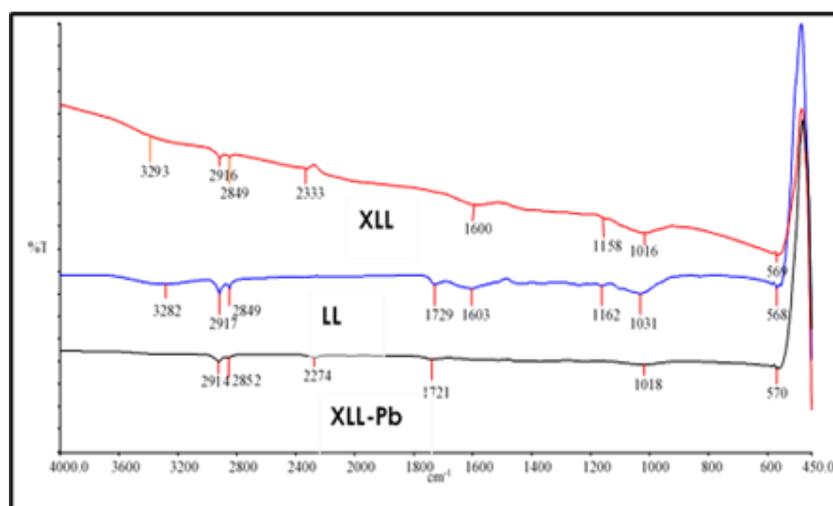


Figure 1 FTIR spectra of XLL, LL, and XLL-Pb after Pb(II) adsorption

Effect of pH

The pH of a solution is one important factor that affects the adsorption of metal ions (Anwar et al., 2010). The effect of pH was studied in the range of 2-5. Figure 2 shows the effect of pH on the adsorption of Pb (II) by XLL. The optimum pH for removal of Pb (II) ion on XLL was selected at pH 4 although maximum removal of Pb (II) was around pH 5. This is due to the formation of $Pb(OH)_2$ precipitation when the solution exceeds pH 5 (Torres-Blancas et al., 2013). The lowest amount of Pb (II) ions adsorbed occurred at pH 2 (6.80 mg g^{-1}), and the highest at pH 5 (12.43 mg g^{-1}). It can be observed from this figure the amount of Pb (II) adsorbed increases with increasing pH values. When the pH increases, competition with H_3O^+ decreases and Pb^{2+} could easily adsorb on the available adsorption sites (Soliman et al., 2016). Besides that, there was more exposed adsorbent surfaces, which carried negative charges and caused less repulsion of Pb (II). Deprotonation of XLL surface can attract more positively charged Pb (II) ion (Nassar, 2010). The amount of Pb (II) adsorbed was lower in acidic conditions at pH 2 (6.80 mg g^{-1}). This condition occurs because of the lack of binding sites for Pb (II) to bind on, due to competition between hydrogen ion and Pb (II) for the active binding site on the surface of XLL. Moreover, the concentration of hydrogen ion is higher than Pb (II), which causes the hydrogen ion to occupy the binding sites on the XLL, leaving Pb (II) free in the solution (Taty-Costodes et al., 2003a).

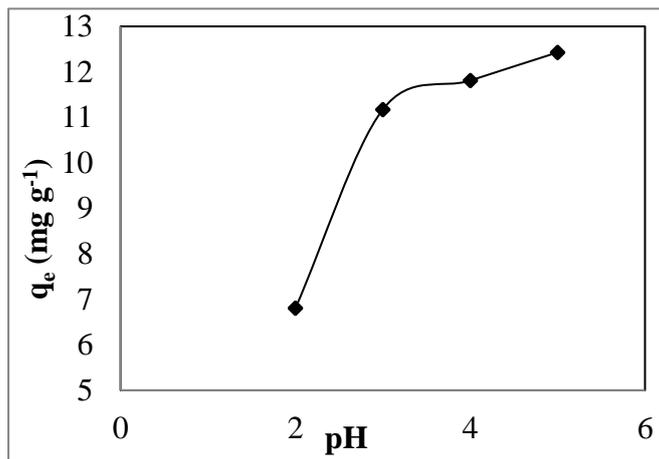


Figure 2 Effect of pH on Pb (II) adsorption XLL

Effect of Dosages

Adsorbent dosage plays an important role in the adsorption process as it determines the potential of the adsorbent through several binding sites accessible to remove metal ions at a specified initial concentration (Yuvaraja et al., 2014). The effect of XLL dosages on Pb (II) removal was carried out in the range of 0.02-1.0 g. Results presented in Figure 3 show that the adsorption of Pb (II) ions as a function of XLL dosage. Based on the graph, it is observed that despite the increased dosage of XLL, the Pb (II) ions percentage removal did not change much. The adsorption capacity of Pb (II) decreased from 24.41 mg g⁻¹ to 6.15 mg g⁻¹ with increased adsorbent dosage. This was due to petite metal concentration in solution at high dosage (Qaiser et al., 2007). Another reason was that many unadsorbed sites were formed from the availability of more surface area and adsorption sites as the dosage was increased (Gong et al., 2009). In this study, the optimum dosage chosen was 0.04 g because of the high amount of Pb (II) adsorbed (12.26 mg g⁻¹), and a high percentage of Pb (II) removal (98.24%). Low dosage with good percentage of metal removal means less amount of biosorbent is needed, thus treatment process will be preferable.

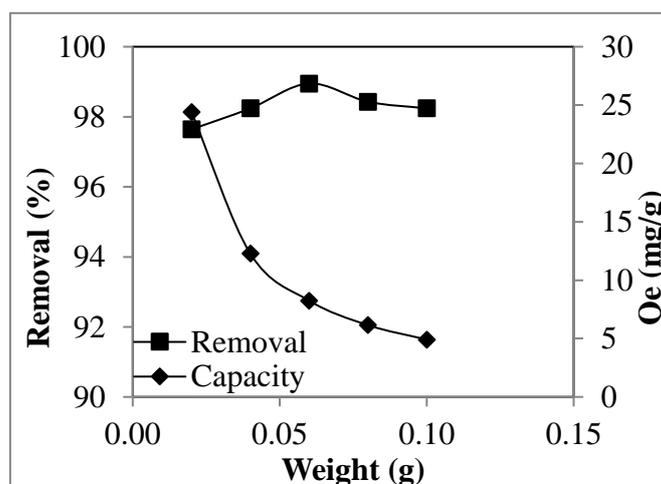


Figure 3 Effect of adsorbent dosage on Pb (II) adsorption by XLL

Effect of Initial Concentration and Contact Time

One of the most important factors of the adsorbent is how fast the Pb (II) ion transfers from the Pb (II) solution onto the XLL surface. The initial concentration of Pb (II) ion also affected the efficiency of Pb (II) ion removal. The initial concentrations used in this experiment was 10, 20, and 30 mg L⁻¹, respectively with a constant pH of pH 4 and varying contact times (1-120 min). Figure 4 shows the contact time profile of XLL on Pb (II) adsorption. The adsorption rate of Pb (II) ions was rapid in the beginning but it slowed down in the later stages. The rapid adsorption in the beginning was caused by the increased active site surfaces for Pb (II), which allowed the Pb (II) ion to bind at the vacant surface sites. As the contact time increased, the number of active sites on the XLL surface available for Pb (II) ion reduced, which led to a slower adsorption rate (Azouaou et al., 2010). The maximum adsorption capacity obtained at 10, 20, and 30 mg L⁻¹ was 24.84, 49.94, and 74.80 mg g⁻¹, respectively. The adsorption capacity increases with the increasing concentration of metal ions due to a high driving force for mass transfer (Taty-Costodes, et al., 2003b). The availability of the Pb (II) ions without steric hindrance is also one of the kinetic characteristics besides the presence of the active binding sites (Athar et al., 2013).

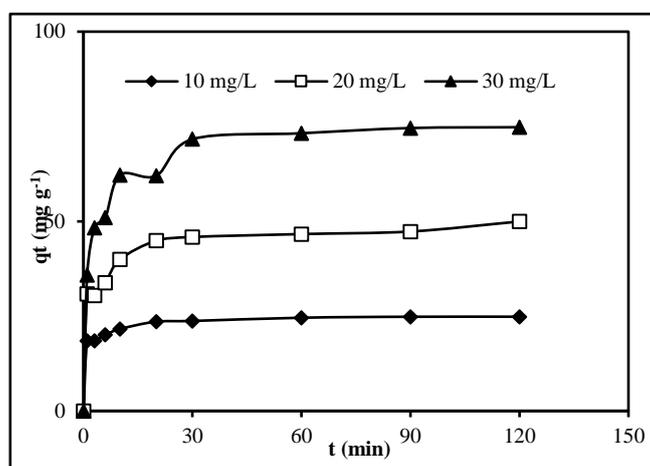


Figure 4 Effect of initial Pb (II) ions concentration and contact time of Pb (II) ions adsorption by XLL

Kinetic Study

Pseudo-first-order and pseudo-second-order were tested to assess the kinetic mechanism that controls the adsorption process. The data for the adsorption of Pb (II) onto XLL were plotted according to the equation (3) and (4) below:

$$\log (q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

Where q_e and q_t are the amount of adsorbed Pb (II) ions on XLL adsorbent at the equilibrium, and at time t , respectively. K_1 is the rate constant of the first-order adsorption. $\log (q_e - q_t)$ versus t gives a straight line (plot not shown) and all data were reported in Table 1. Adsorption rate constant K_1 and adsorption capacity q_e for the adsorption of Pb (II) ions of 10, 20, and 30 mg L⁻¹ concentration of adsorbate, were calculated from the slope and intercept of the plotted

$\log(q_e - q_t)$ against t . The experimental values of q_e were 24.83, 47.30, and 74.59 mg g^{-1} and different from the calculated values 7.19, 14.09, and 30.28 mg g^{-1} for 10, 20, and 30 mg L^{-1} , respectively. Therefore, it is observed that the pseudo-first-order kinetic model was inaccurate for this experiment data as it failed to provide a real estimation of q_e onto XLL.

Table 1 The pseudo-first-order, pseudo-second-order at different concentration of Pb (II)

[Pb] mg/L	q_e, exp (mg g^{-1})	Pseudo-first-order			Pseudo-second-order			
		q_e, cal (mg g^{-1})	K_1 (min^{-1})	R^2	h ($\text{mg}/(\text{g}\cdot\text{min})$)	K_2 (min^{-1})	q_e, cal (mg g^{-1})	R^2
10	24.83	7.19	0.03	0.97	20.41	0.03	25.06	0.999
20	47.30	14.09	0.02	0.76	21.32	0.01	50.00	0.999
30	74.59	30.28	0.04	0.97	31.85	0.01	76.34	0.999

The pseudo-second-order was also applied in the kinetic adsorption process. The pseudo-second-order uses chemisorption as a rate control and predicts the behaviour of the whole range of studies supporting the validity. Pseudo-second-order model can be expressed by the equation (5) below:

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

The initial sorption rate constant, h (mg/g min), at $t = 0$ can be defined as

$$h = K_2 q_e^2 \quad (6)$$

The initial sorption rate, h , equilibrium adsorption capacity q_e , and pseudo rate constant; can be obtained from the y-intercept and slope of the second-order plot t/q_t versus t (Fig. 5) and presented in Table 1. The results show that the correlation coefficient of XLL for the pseudo-second-order kinetic model was close to 1.0. The higher the value of R^2 and the calculated value of equilibrium sorption capacity, $q_{e,\text{cal}}$, which was very close with experimental $q_{e,\text{exp}}$ values; implied that the adsorption system of XLL follows the pseudo-second-order kinetic model at all time intervals (Bhattacharyya & Sharma, 2004). The plot t/q_t versus t gives a linear relationship as observed in Fig. 5, showing the effectiveness of the pseudo-second-order kinetic model. The increase in initial Pb (II) concentrations reduced the rate of constant (K_2), which led to the competition for adsorption sites. So, the Pb (II) uptakes onto XLL surface was governed by the pseudo-second-order model; where adsorption occurs on localized sites and does not involve interaction between the adsorbed lead ions (Largitte & Pasquier, 2016).

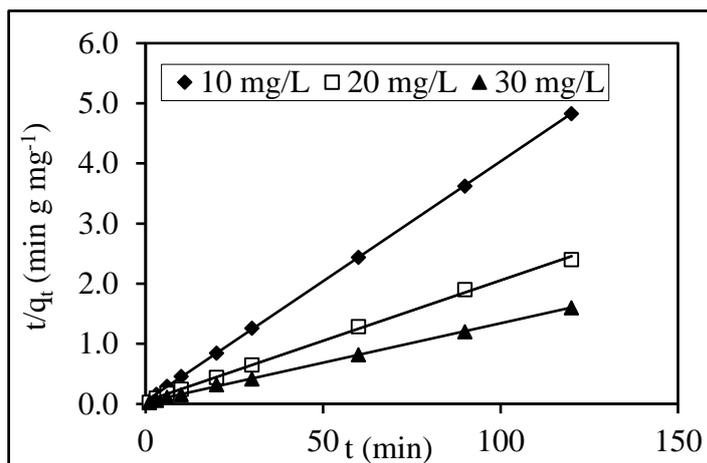


Figure 5 Pseudo-second-order plot on Pb (II) ions adsorption by XLL

Conclusion

L. leucocephala leaf powder treated with xanthate showed lower adsorption capacity of Pb (II) ions. Therefore, not all chemically modified adsorbents will return high adsorption capacity of Pb (II) ions. Each chemical adsorbent will give different physical and chemical characteristics to the treated adsorbent surface. Other than the type of adsorbent used, the type of chemical modifications also plays an important role in returning optimum capacity. The maximum adsorption of Pb (II) using XLL is 76.34 mg g^{-1} . The adsorption capacity of Pb (II) onto XLL increased with increasing adsorbent dosage and the maximum pH was pH 4. ATR-FTIR analysis indicated that xanthate-treated *L. leucocephala* introduced some functional groups of active site surface, such as $-\text{OH}$, $-\text{NH}_2$, $-\text{COO}^-$, and $-\text{C}=\text{S}$. The adsorption kinetics of Pb (II) adsorption on XLL obeyed pseudo-second-order model, which suggests that there is chemisorption on the overall rate reaction involved between the adsorbent and adsorbate.

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Conflict of interest

The author declare that there is no conflict of interest.

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