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Pb(II) Adsorption onto Urea Treated *Leucaena leucocephala* Leaf Powder: Characterization, Kinetics and Isotherm Studies

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ABSTRACT

The use of *Leucaena leucocephala* leaf powder treated with urea (treated-ULLP) as an alternative adsorbent for the adsorption of Pb(II) ions has been investigated. The adsorption studies were performed under batch mode and focused on the effects of pH, adsorbent dosage and initial Pb(II) concentrations. The pseudo-second order kinetics model fitted well the adsorption data with the values of correlation coefficient (R^2) > 0.97. Large amounts of hydroxyl, carboxyl and amine as detected by the Fourier transform infrared (FTIR) spectrophotometer suggested that these functional groups were responsible for the adsorption of Pb(II) ions. Treated-ULLP demonstrated a good potential for Pb(II) ions removal with the maximum adsorption capacity of 90.09 mg/g, calculated from the Langmuir isotherm model.

INTRODUCTION

A lot of heavy metals are released into the environment, which include copper (Cu), chromium (Cr), lead (Pb), zinc (Zn), cadmium (Cd), nickel (Ni), manganese (Mn), and mercury (Hg) (Babarinde et al., 2006). Volesky (2001) stated that lead [Pb(II)] is one of the most toxic metals that has gained major attention due to its health impact on humans. Pb(II) could be stored in human tissues such as kidney and liver and can pose health hazards even in small concentrations (Puranik & Pakniker 1997). Pb(II) may originate from different types of industrial activities such as electronic, fossil fuel, painting, mining, automobile, sewage wastewater and fertilizer (Singh et al. 2008). A few decades ago, various conventional methods such as ion exchange, filtration, chemical precipitation, reverse osmosis, and electro deposition have been applied to remove Pb(II) from industrial wastewaters (Zheng et al. 2008). However, these treatments suffered some limitation such as production of sludge at the end of the treatment process (Papandreou et al. 2007), and less effective at trace levels of Pb(II). So, adsorption is an alternative process which has several advantages such as low cost, simple, more effective and records a high adsorption capacity value (q_{max}). A variety of adsorbent materials have been applied to remove Pb(II) from aqueous solutions, which include activated carbon, zeolites, resins and plant wastes. *Leucaena leucocephala* leaves was used in this study because it contains various organic compounds such as lignin, cellulose, hemicellulose, polyphenols, protein, lipids, flavonoids, mimosine and tannins (Zarin et al. 2016), which can act as the active sites for Pb(II) adsorption. The main objectives of this work were to evaluate the parameters that could influence the uptake of Pb(II) on urea treated *L. leucocephala* leaves, to determine the rate of Pb(II) adsorption based on kinetics models, and to determine the maximum adsorption capacity based on the Langmuir isotherm model.

MATERIALS AND METHODS

Materials

Leucaena leucocephala leaves were collected in Jengka, Malaysia. The leaves were brought to the lab and washed several times with deionized water. The leaves were dried in an oven overnight at 353 K. Then, the leaves were ground and sieved to obtain the particle size of 180-355 μm. Working solutions of Pb(II) were prepared from a 1000 mg/L Pb(II) stock solution and diluted to desired concentrations using deionized water. The chemical treatment of *L. leucocephala* leaf powder was performed according to the method proposed by Kong et al. (2014). In brief, 3 g of *L. leucocephala* leaf

powder was mixed with 50% (w/v) of urea $[CO(NH_2)_2]$ solution and underwent steamed process at 398 K for 30 min by using a steam bath. The urea solution was placed in a round bottom flask with steam below it and this process was carried out for 30 min. During the treatment, the mixture was stirred by using a glass rod, cooled and washed several times with deionized water until the solution reached near neutral. The sample was dried in an oven at the temperature of 378 K for 24 h. The adsorbent sample was designated as Treated-ULLP.

Characterization of Treated-ULLP

The pH_{slurry} was determined by mixing 0.10 g of Treated-ULLP with 100 mL deionized water in a stoppered flask. The mixture was shaken at 100 strokes/min for 24 h at room temperature (298 K) in a water bath shaker. The mixture was filtered, and the final pH of this solution was determined by a pH meter. The zero-point charge of Treated-ULLP at a particular pH or pH_{zpc} was also determined. Firstly, 25 mL of 0.01 M KNO_3 was placed in a series of 100 mL conical flasks. The initial pH of the solution (pH_i) was adjusted from 2 to 9 by adding drops of 0.05 M HCl or NaOH solution. Then, 0.10 g of Treated-ULLP was added to each flask and shaken in a water bath shaker for 24 h at 100 strokes/min. Finally, the mixture was filtered and the final pH (pH_f) of each solution in the flasks was measured by using a pH meter. The pH_{zpc} value was determined from the curve that intercepts the x-axis of the plot pH ($pH_i - pH_f$) versus pH_i. The functional groups responsible for uptake of Pb(II) were

analysed by a Fourier transform infrared spectrophotometer (PerkinElmer, Spectrum 100, USA). The total content of carbon, hydrogen, nitrogen, oxygen and sulphur in Treated-ULLP was determined by a CHNS analyser (vario MACRO cube CHNS, Germany). The scanning electron microscope (SEM, Carl Zeiss SMT, Germany) coupled with energy dispersive x-ray (EDX, Oxford Instrument, UK) spectrometer was used to analyse the surface morphology and the elemental composition of Treated-ULLP. Prior to this analysis, Treated-ULLP was coated with a thin layer of gold to improve conductivity, signal to noise ratio, and to reduce charging of the adsorbent material. The SEM image was scanned at 500 X magnification.

Adsorption Experiments

The pH ranging from 2 to 5 was selected and the adsorbent dosage was varied from 0.02 to 0.10 g for the effects of pH and adsorbent dosage, respectively. Drops of 0.05 M NaOH or HCl solution were added to adjust the pH. Three different concentrations of Pb(II) (50, 100, 150 mg/L) were used in the kinetics study and the concentrations were varied from 50 to 250 mg/L in the isotherm study. The dosage of Treated-ULLP was maintained at 0.02 g while the volume of Pb(II) solution was fixed at 50 mL. All Pb(II) solutions were shaken in a water bath shaker at 100 strokes/min. After adsorption, the adsorbent was filtered and the filtrates were analysed for unadsorbed Pb(II) by an Atomic Absorption Spectrometer (AAS, Perkin Elmer, PinAAcle 900T, USA). The linear range for Pb(II) in the calibration curve was from 0
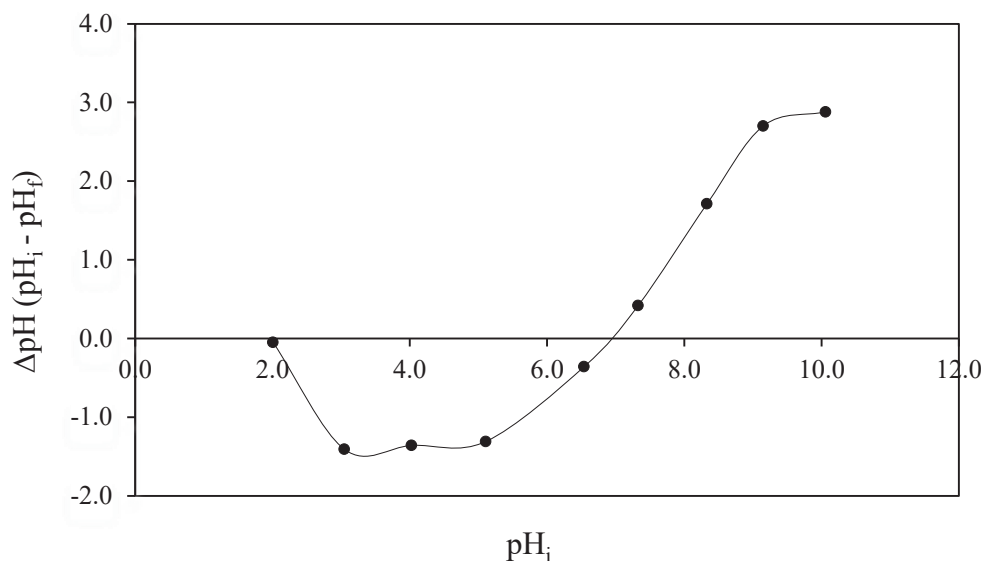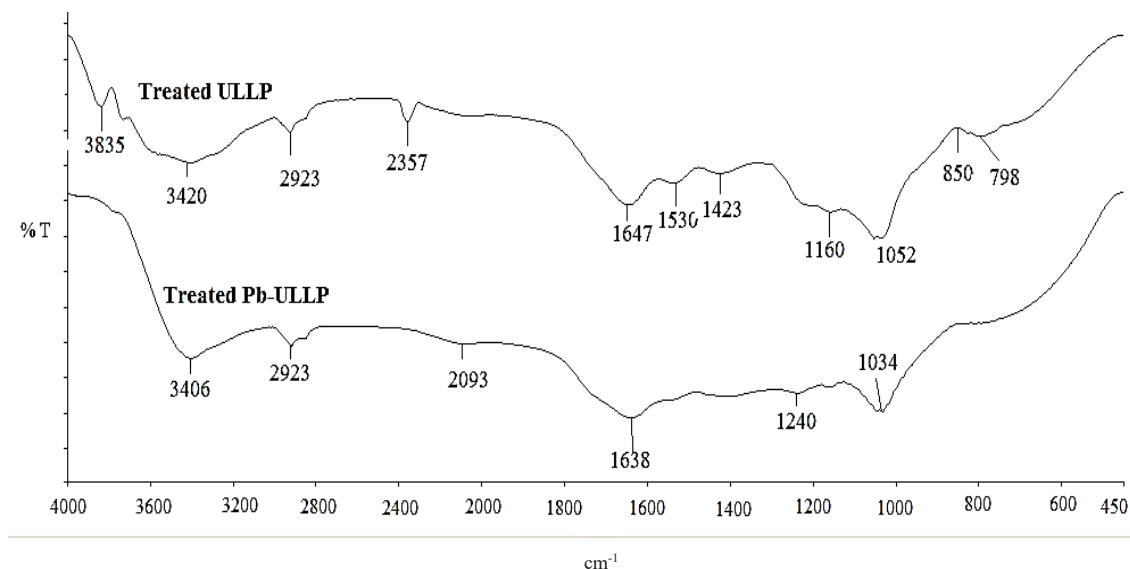

Fig. 1: The pH_{zpc} plot of Treated-ULLP.

Fig. 2: FTIR spectra of Treated-ULLP before and after adsorption of Pb(II) ions.

Table 1: CHNOS content of treated-ULLP.

Elemental composition (%)				
C	H	N	S	O*
47.67	7.19	7.58	0.29	37.27

*by difference

to 20 mg/L. All the experiments were conducted in duplicate and the results were presented as the average. The relative standard deviation was < 3%. The amount of Pb(II) adsorbed at equilibrium (q_e) and the percentage removal (%) were calculated by using the following equations:

$$q_e = \frac{V(C_0 - C_e)}{m} \qquad \ldots(1)$$

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

Where, C_0 and C_e represent the Pb(II) concentration before and after adsorption (mg/L), respectively. V is the volume of adsorbate (L), q_e is the amount of Pb(II) adsorbed (mg/g) at equilibrium and *m* is the weight of Treated-ULLP (g).

RESULTS AND DISCUSSION

Characterization of Treated-ULLP

The pH_{slurry} of Treated-ULLP was found to be 6.74, which is slightly acidic, possibly due to the presence of carboxylic acid group (Zayed & Samling 2016). The pH_{zpc} plot is shown in Fig. 1 and the value was found to be 6.90. At pH < pH_{zpc}, the surface of Treated-ULLP would carry more positive charge than the negative charge. More negative charge, however, would appear at pH > pH_{zpc}.

Fig. 2 shows the FTIR spectra for Treated-ULLP before and after Pb(II) adsorption. The strong and broad peak from 2600 to 3600 cm^{-1} confirmed the presence of carboxylic acid group (-COOH) (Kong et al. 2013), which overlapped with -OH and -NH groups. The peak observed at 2923 cm^{-1} was assigned to the stretching C-H of alkyl group. The peak at 1647 cm^{-1} was attributed to the stretching of C=O or C=C groups. The peaks appeared at 1160 and 1052 cm^{-1} indicated the stretching of C-N and C-O-C groups, respectively (Chen et al. 2010, Saygideger et al. 2005). The presence of -CH group of aromatics was represented by the peak at 850 cm^{-1}.

The wave number at 3420 cm^{-1} had shifted to 3406 cm^{-1}, indicating that Pb(II) was adsorbed to the hydroxyl, -COOH and amine groups. The wave number at 1647 cm^{-1} shifted to 1638 cm^{-1}, suggesting the involvement of C=O and C=C groups in the removal of Pb(II). Other functional groups possible for attracting Pb(II) ions would be the C-N and
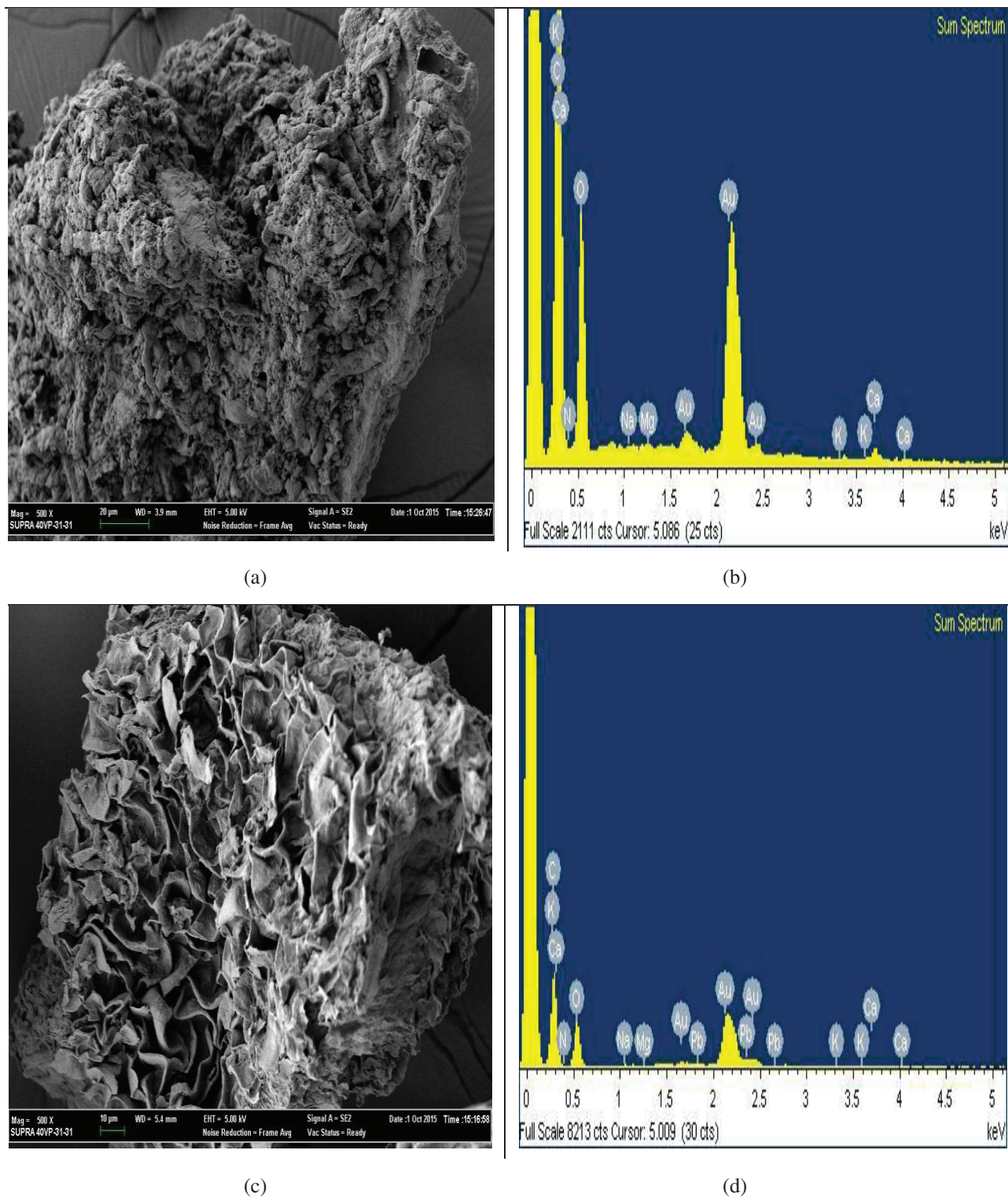
(a)

(b)

(c)

(d)

Fig. 3: SEM (500 X magnification) and EDX images of treated-ULLP before (a and b) and after Pb(II) adsorption (c and d).
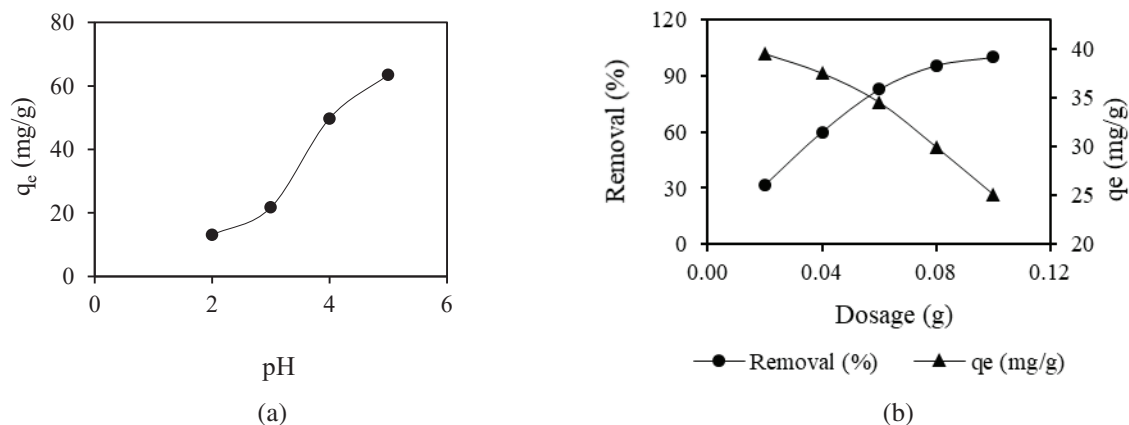
(a)

(b)

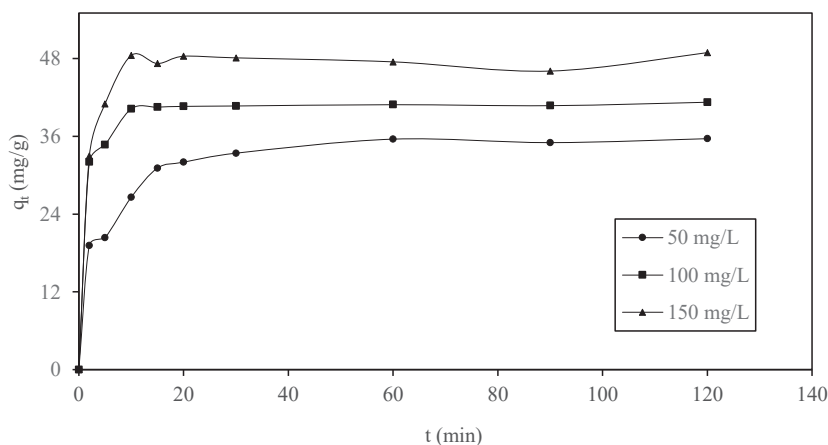Fig. 4: Effects of pH (a) and dosage (b) on the Pb(II) adsorption on treated-ULLP.

Fig. 5: Effects of concentration and contact time on the Pb(II) adsorption.

C-O-C as there was a decrease in the intensity of the peak at 1160 cm^{-1} and the shift in wave number from 1052 to 1034 cm^{-1}, respectively. The presence of hydroxyl, amino, ether, aromatics and carbonyl functional groups acted as the active sites for adsorption process to occur. Meanwhile, the elemental composition of the Treated-ULLP is given in Table 1. The percentage of N contained in the Treated-ULLP was much higher than pristine *L. leucocephala* leaf (4.2 %), reported by Meena Devi et al. (2013). This finding concludes that after chemical modification, the urea was successfully introduced in the Treated-ULLP.

The SEM and EDX images of Treated-ULLP before and after Pb(II) adsorption are shown in Fig. 3. Treated-ULLP (Fig. 3a) possesses rough, irregular and nonporous surface morphology. Important minerals for plants such as Na, Mg, K and Ca were clearly detected EDX as shown in Fig. 3b. Pb(II) however, was not present. After adsorption (Figs. 3c and 3d), Pb(II) was clearly detected on the surface of Treated-ULLP

at 1.8, 2.3 and 2.7 keV (Fig. 3d). This finding concludes the success of removal of Pb(II) from the aqueous solution onto the adsorbent surface.

Effects of pH and Dosage

The effects of pH and adsorbent dosage on Pb(II) adsorption are shown in Fig. 4. Pb(II) adsorption increased with increasing pH of the solution, started from pH 2 to 5 for initial Pb(II) concentration of 50 mg/L [Fig. 4(a)]. The amount of Pb(II) adsorbed was very low at pH 2 due to the stiff competition between protons (H$^+$) in the solutions and the Pb(II) for the adsorption sites. Furthermore, it was also due to the stronger electrostatic repulsion between Pb(II) and the positively charged adsorbent surface. At pH 3, the amount of Pb(II) adsorbed started to increase because the -COOH started to dissociate to liberate more -COO$^-$ groups, which could easily adsorb the positively charged Pb(II) (Lalhruaitluanga et al. 2010). The amount of Pb(II) adsorbed

Table 2: Adsorption kinetics parameters at different Pb(II) concentrations.

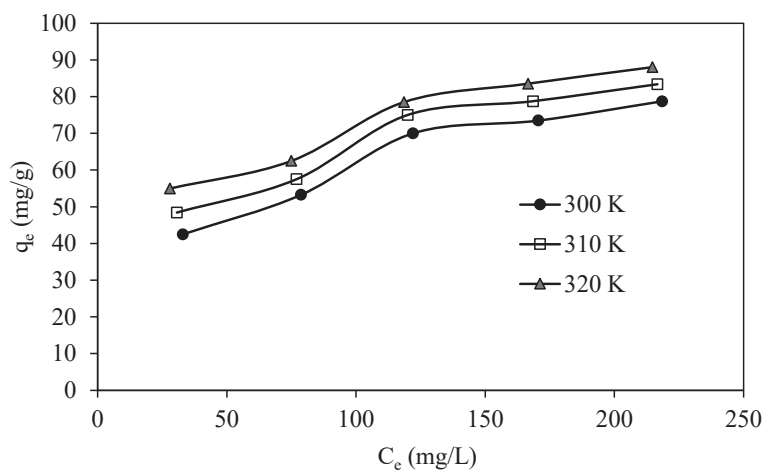| Kinetics models	Parameters	Pb(II) concentrations		
		50 mg/L	100 mg/L	150 mg/L
Pseudo-first-order	$q_{e,cal}$ (mg/g)	46.71	91.41	276.24
	$q_{e,exp}$ (mg/g)	35.63	41.27	48.90
	k_1 (1/min)	0.049	0.025	0.008
	R^2	0.673	0.413	0.050
Pseudo-second-order	$q_{e,cal}$ (mg/g)	36.54	41.28	48.12
	$q_{e,exp}$ (mg/g)	35.63	41.27	48.90
	k_2 (g/mg.min))	0.008	0.046	0.039
	R^2	0.999	1.000	0.999

Fig. 6: Pb(II) adsorption isotherm plots at different temperatures.

continued to increase at pH 4 and 5 due to a much lower concentration of H^+ in the solution, hence less competition between H^+ and the metal ions (Wu et al. 2011). Therefore, more Pb(II) could easily be adsorbed to the adsorption sites. The subsequent adsorption experiments were conducted at pH 4 only to avoid the formation of precipitate ($Pb(OH)_2$) or $Pb(OH)^-$ due to the high number of OH^- ions present in the solution at pH > 5 (Sheng et al. 2004). Adsorbent dosage experiment was conducted to give an idea on the effectiveness of the amount of adsorbent used. The percentage removal of Pb(II) increased as the adsorbent dosage increased from 0.02 to 0.10 g [Fig. 4(b)].

This phenomenon confirmed that more active sites as well as surface area were available for the binding of Pb(II) with increasing the adsorbent dosage. However, the amount of Pb(II) adsorbed showed the opposite trend and it was associated to the increased number of unadsorbed sites when the dosage was increased (Yu et al. 2002). Aggregation also occurred due to the particles interaction that led to the surface area reduction of Treated-ULLP.

Effects of Initial Pb(II) Concentrations and Contact Time

The effect of initial concentration and contact time of Pb(II) on Treated-ULLP is shown in Fig. 5. The plots showed that three main phases were involved during the adsorption process. The first phase was called the initial rapid adsorption process followed by slow adsorption process and the last phase was dynamic equilibrium time. The initial rapid adsorption process occurred in the first 3 min. It was possibly due to high number of available adsorption sites (Kousha et al. 2012), causing the rapid transfer of Pb(II) to the external surface of Treated-ULLP. The slow adsorption rate was observed in the range of 5 to 10 min due to the less availability
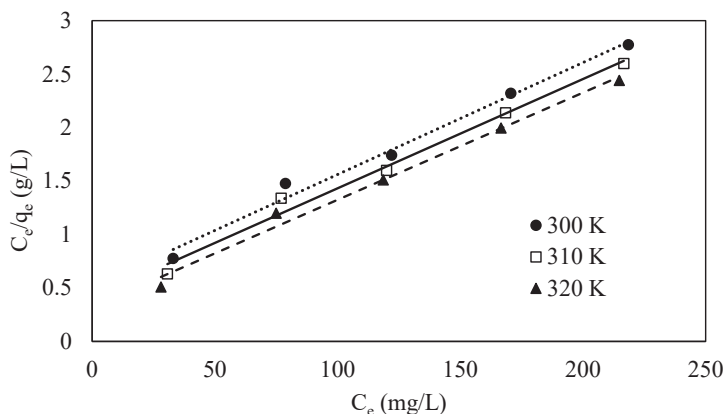
Fig. 7: Langmuir isotherm plots at different temperatures.

Table 3: Langmuir adsorption isotherm parameters at different temperatures.

Isotherm model	Parameters	Temperatures (K)		
		300	310	320
Langmuir	q_{max} (mg/g)	82.65	86.21	90.09
	$q_{e,exp}$ (mg/g)	78.00	83.65	87.90
	K_L (L/mol)	0.046	0.050	0.063
	R^2	0.965	0.966	0.978

of active sites or stiff competition among the Pb(II) ions for the active sites. After 30 min, there was only a small change in the amount of Pb(II) adsorbed, which the process was considered to have achieved the equilibrium time.

Adsorption Kinetics Models

Adsorption kinetics models were applied to further investigate the rate of Pb(II) adsorption process. The pseudo-first-order (Ho & McKay 1999) and pseudo-second-order models (Ho & McKay 2000) were expressed in Equations 3 and 4, respectively.

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

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

Where the symbols q_e and q_t indicate the amount of Pb(II) adsorbed (mg/g) at equilibrium and at time t (min), respectively. k_1 (1/min) is the rate constant of adsorption process for the pseudo-first-order model. The initial adsorption rate (mg/g.min) is represented by the symbol of h while the k_2 [g/(mg.min)] is the rate constant for the pseudo-second-order model. The values of k_2 and h were obtained by using an equation of $h = k_2 q_e^2$.

Both the plots have not shown, but the values of correlation coefficient (R^2) were close to unity (0.999-1.000) as in the case of the pseudo-second-order kinetics model. In addition, the values of calculated adsorption capacities ($q_{e,cal}$) were almost match to the values of experimental ($q_{e,exp}$). Based on these two observations, it can be concluded that the adsorption kinetics fitted well the pseudo-second-order kinetics model (Table 2).

Adsorption Isotherms

The adsorption isotherm plots at three different temperatures are presented in Fig. 6. In general, the adsorption capacities were found to increase with increasing temperatures, an indication of an endothermic reaction. The plots were further analyzed using the most widely used isotherm model, which is the Langmuir model (Langmuir 1918), developed based on the assumption that all the adsorption sites have the same energy and is given by Equation 5:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{q_{max}K_L} \qquad …(5)$$

Where, q_{max} is the maximum adsorption capacity and K_L represents the Langmuir constant. The Langmuir plots showed good linearity ($R^2 > 0.96$) and the predicted

maximum adsorption capacity values were close to the experimental values (Table 3 & Fig. 7). The increase in the maximum adsorption capacity values with increasing temperatures suggested the endothermic type of adsorption. The adsorption mechanism of Pb(II) onto Treated-ULLP could be understood in terms of hard-soft acid base principle (HSAB). Table 3 shows that Treated-ULLP contains N (a borderline ligand), S (a soft-base ligand) and O (a hard-base ligand). These three types of atoms could act as metal-binding donor atoms for Pb(II). As Pb(II) is classified as a borderline metal ion (Nieboer & Richardson 1980), it would be attracted to all categories of ligands to form stable complexes.

CONCLUSION

Treated-ULLP showed a satisfactory removal of Pb(II) from aqueous solutions under batch mode sorption techniques. Based on the FTIR spectrum of Treated-ULLP, the detected functional groups such as carbonyl (C=O), hydroxyl (-OH) carboxylic acid (-COOH), amino ($-NH_2$) and ether (C-O-C) acted as the active sites for Pb(II). The attachment of Pb(II) on Treated-ULLP was confirmed by the EDX images. The rate of Pb(II) removal was considered quite rapid as the time to reach equilibrium was less than 30 min. Pb(II) adsorption was more favoured at a higher temperature, an indication of endothermic adsorption process.

ACKNOWLEDGEMENT

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