Adsorption behavior of Pb(II) onto xanthated rubber (*Hevea brasiliensis*) leaf powder

Wan Khaima Azira Wan Mat Khalir¹, Megat Ahmad Kamal Megat Hanafiah^{1,*}, Siti Zaiton Mat So'ad², Wan Saime Wan Ngah³

¹ Universiti Teknologi MARA Pahang, Department of Chemistry, 26400, Bandar Jengka, Pahang, Malaysia.

² International Islamic University Malaysia, Kulliyyah of Pharmacy, 25200, Kuantan, Pahang, Malaysia

³ Universiti Sains Malaysia, School of Chemical Sciences, 11800, Minden, Penang, Malaysia

* Corresponding author: makmh@pahang.uitm.edu.my

A plant waste, rubber (*Hevea brasiliensis*) leaf powder was modified with carbon disulfide (xanthation) for the purpose of introducing sulfur groups, and the adsorbent performance in removing Pb(II) ion was evaluated. Pb(II) adsorption was confirmed by spectroscopic analysis, which involved Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). The amount of Pb(II) adsorbed increased with increasing pH, contact time and concentration but slightly decreased with increasing ionic strength. Adsorption equilibrium was achieved in less than 60 min and followed the pseudo-second order model. The isotherm data indicated that Pb(II) adsorption on xanthated rubber leaf (XRL) fitted well with Langmuir isotherm model. The maximum adsorption capacity computed from the Langmuir isotherm model was 166.7 mg/g. Pb(II) adsorption occurred via ion-exchange and complexation mechanisms.

Keywords: Adsorption, Isotherm, Kinetic, Lead, Xanthated rubber leaf powder.

INTRODUCTION

Lead is one of the most toxic heavy metals widely used in battery, paint, electronic, chemical and fertilizer^{1,2}. Lead can enter the human body through inhalation or ingestion, which may lead to various chronic diseases such as anemia, headache, diarrhea and reduction in hemoglobin formation³. Due to its toxic properties, many governments have introduced stringent acts, which are compulsory to be followed by industries. According to Malaysian Environmental Quality (Industrial Effluents) Act (1974), the permissible level of lead in the effluent (Standard B) is 0.50 mg/L⁴.

Adsorption technique can be an alternative to conventional methods such as precipitation or coagulation with advantages such as lower cost, efficient at low concentration of heavy metals, easy to handle and reducing a sludge disposal problem⁵. Adsorbents from agricultural wastes are able to remove heavy metals due to the presence of various functional groups such as hydroxyl, amino, carboxyl and ether, which function as the active sites⁶. Large quantities of matured rubber leaves from rubber plantations can pose a disposal problem and in order to overcome this problem, it can be used as an adsorbent. Therefore, the usage of this adsorbent could benefit the environment and the industries. Recently, chemical modification of adsorbent has attracted researchers since this method can enhance the adsorption capacities of heavy metal ions and improve the recyclability of adsorbent⁷. Hanafiah et al.⁸ reported a low adsorption capacity of 46 mg/g Pb(II) ion by untreated rubber leaf powder. The maximum adsorption capacity of rubber leaf powder increased to 95 mg/g after modification with KMnO4 followed by Na₂CO₃⁶. There is however, a need to discover another chemical modification which can give a much higher value of adsorption capacity than untreated rubber leaf. For instance, xanthated orange peel was reported to have an increase of 150% adsorption capacity of Pb(II) in comparison to pristine sample⁹. Xanthation

is a modification process that introduces sulfur-bearing groups on the adsorbent surface. According to Liang et al.⁹ sulfur group shows good affinity for heavy metal ions but low affinity for light metal ions.

This study highlighted the application of chemically modified rubber leaf powder via the xanthation process for removing Pb(II) from aqueous solutions. The main objective of this research was to characterize the xanthated rubber leaf powder by spectroscopic and quantitative analyses for understanding Pb(II) adsorption behavior. The effects of various physicochemical parameters on adsorption efficiency of Pb(II) particularly pH, initial Pb(II) concentration, contact time and ionic strength were investigated. The desorption study was conducted using various concentrations of HCl and EDTA.

EXPERIMENTAL

Chemical and adsorbent collection

Lead(II) nitrate stock solution (1000 mg/L) was purchased from Spectrosol (England) and desired concentrations of Pb(II) were prepared by dilution with deionized water. All chemicals used were of analytical reagent grade. Matured, brownish rubber leaves were collected from Universiti Teknologi MARA Pahang rubber plantation, Malaysia during the dry period (February – March 2010). To remove the dirt or adhering particles, the leaves were washed thoroughly with water before drying in an oven at 105°C for 24 h. They were later ground and sieved to obtain particle size of <180 μ m by using a mechanical grinder. The untreated rubber leaf powder (URLP) was stored in a container for further treatment.

Preparation of xanthated rubber leaf powder

The xanthation process was performed according to the previous method⁹ 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 $(30 \pm 0.5^{\circ}\text{C})$ and for another 3 h after the addition of 10 mL carbon disulfide. Treatment with NaOH will result in the formation of alkoxide (-CH₂O⁻) group. This alkoxide group is easier to be converted into the xanthate group¹⁰. The xanthation process can be represented by the following equations:

 $RCH_2OH + NaOH \rightarrow RCH_2ONa + H_2O$ (1)

(2)

$$\text{RCH}_2\text{ONa} + \text{CS}_2 \rightarrow \text{RCH}_2\text{OCS}_2\text{Na}$$

After allowing the mixture to settle for 30 min, the supernatant was decanted. The xanthated rubber leaf powder was extensively washed with 200 mL deionized water 20 times to remove excess base. Finally, the xanthated rubber leaf powder was dried in an oven at 50°C for 24 h. The xanthated rubber leaf powder was designated as XRL.

Characterization of XRL

Possible mechanisms involved in the adsorption process between Pb(II) ion and XRL can be predicted by performing adsorbent characterization. Functional groups present in XRL were identified using the Fourier transform infrared (FTIR) spectrometer (Perkin Elmer, spectrum RXI, USA). A scanning electron microscope (SEM; LeoSupra VP50, Carl-Zeiss SMT, Germany) coupled with energy dispersive X-ray (EDX) spectrometer were used to determine the surface morphology and elemental composition on XRL. Micromeritics ASAP 2010 gas adsorption surface analyzer was used to determine surface area and average pore diameter. The composition percentage of sulfur and other nonmetallic elements such as nitrogen, carbon, hydrogen and oxygen was determined using CHNS analyzer (Slash EA 2000, Italy). The pH of aqueous slurry (pH_{slurry}) was determined by mixing 0.50 g XRL with 50 mL deionized water and the mixture was left for 24 h before reading the final pH. Solid addition method¹¹ was used to determine the pH of zero point charge (pH_{ZPC}). The process was conducted as follows: 0.50 g XRL and 50 mL (0.01 M) KNO₃ were added into a series of Erlenmeyer flasks with initial pH in the range of 2-11. The initial pH value was adjusted by adding drops of 1.0 M NaOH or HCl solutions. After 24 h, the final pH of the solution was measured using a pH meter (Jenway 3305, UK). The ash content was determined by combusting 1.0 g XRL in a furnace (Carbolite, England) at 550°C for 2 h.

Batch adsorption experiments

All Pb(II) adsorption experiments were conducted in the batch mode and were duplicated. The results for adsorption experiments showed that the relative standard deviation (RSD) was lower than 5%. The effects of pH, initial Pb(II) concentrations and contact time were studied and all experiments were conducted at room temperature ($30 \pm 0.5^{\circ}$ C) in stoppered 100 mL Erlenmeyer flasks with XRL dosage of 0.02 g, initial Pb(II) concentration of 40 mg/L, 50 mL volume of Pb(II) solution at pH 4, and shaking speed of 120 stroke/min for 90 min (unless stated otherwise). The effect of pH on Pb(II) adsorption was studied at the pH range of 2–5. The experiment was not performed at higher pH values to avoid Pb(II) precipitation¹². The effects of initial Pb(II) concentration and contact time were carried out by shaking a known weight of XRL with different Pb(II) concentrations (20, 40, 80 mg/L) at various contact times (0-90 min). Isotherm study was conducted by mixing 0.02 g XRL with 50 mL of Pb(II) solutions at different concentrations (20-200 mg/L) and was shaken for 90 min (equilibrium time). The effect of ionic strength was investigated by using NaCl as the ionic medium. The concentration of NaCl was varied from 0.001 to 0.05 M. For desorption study, a strong acid (HCl) and a chelating agent (EDTA) were used as desorbing solutions and deionized water was used as control. After loading with 50 mL (40 mg/L) of Pb(II) solution, the metal-laden adsorbent was filtered and dried in an oven at 80°C for 1 h. Dried metal-laden adsorbent was added into 50 mL of different concentrations of HCl or EDTA. The mixture was shaken for 1 h, and separated by filtration on Whatman No. 42 filter paper. The filtrates containing Pb(II) ion were analyzed using an atomic absorption spectrophotometer (Perkin Elmer, AAnalyst 800 model, USA) at wavelength of 283.3 nm. After analysis, the amount of Pb(II) adsorbed $(q_e, mg/g)$ and percent removal were calculated by using eqs. (3) and (4), respectively:

$$q_e = \frac{C_o - C_e}{m} V \tag{3}$$

Removal (%) =
$$\frac{C_o - C_e}{C_o} x100$$
 (4)

where C_o and C_e are Pb(II) concentration before and after adsorption (mg/L), respectively; V is the Pb(II) volume (L), and m is the weight of XRL (g). The percentage of desorption (D_p) of Pb(II) was determined by using eq. (5):

$$D_{p} = \frac{C_{(des)}}{C_{(ads)}} \times 100$$
(5)

where $C(_{des})$ and $C(_{ads})$ are Pb(II) concentration (mg/L) desorbed and adsorbed, respectively.

RESULTS AND DISCUSSION

Characterization of XRL

Based on CHNOS analysis (Table 1), the major elemental compositions in XRL are carbon, oxygen and the lowest content is nitrogen. In a previous study, sulfur was not detected in the raw rubber leaf powder¹³. However, after the xanthation process, there was an increase

Table 1. Physicochemical properties of XRL

Analysis	XRL
Carbon (%)	45.55 ± 0.13
Oxygen (%)	46.49 ± 0.43
Hydrogen (%)	6.12 ± 0.05
Nitrogen (%)	0.76 ± 0.01
Sulfur (%)	0.98 ± 0.10
pH _{slurry}	9.18 ± 0.09
pH _{ZPC}	9.65 ± 0.21
$S_{\text{BET}}^{a}(\text{m}^{2}/\text{g})$	0.89
S_{L}^{b} (m ² /g)	3.57
$D_{\rm p}^{\rm c}$ (Å)	50.00
Particle size (µm)	< 180
Ash (%)	25.30 ± 0.71
3	

^aBET surface area

^bLangmuir surface area

^cAverage pore diameter (BJH)

in the content of sulfur which indicated a successful introduction of sulfur bearing group on XRL surface. As the treatment was carried out under alkaline solution, XRL is therefore slightly basic as indicated by the pH_{slurry} value. The pH_{ZPC} value was close to the pH_{slurry} value (Table 1), which indicated that at this pH, the XRL surface has net neutrality. Adsorption of cations will be more favorable at pH > pH_{ZPC} because the adsorbent surface carries more negative charge.

The high ash content in XRL is commonly associated with the presence of high metallic content such as calcium and sodium, which will form metal oxides upon combustion. The surface area of XRL was determined by using Langmuir and Brunauer-Emmett-Teller (BET) equations. BET is applicable to heterogeneous surface while Langmuir is based on monolayer adsorption and their values are shown in Table 1. The low values of BET and Langmuir surface areas indicated that XRL has low porosity. This also means that Pb(II) would be adsorbed on the external XRL surface.

Agro-waste materials have cellulose, hemicellulose and lignin as the major components. Therefore, FTIR analysis was conducted to identify possible functional groups in XRL which could serve as active sites for Pb(II) adsorption. A comparison of FTIR spectra of URLP, XRL and Pb(II) loaded XRL is shown in Fig. 1. URLP spectrum (Fig. 1a) showed a number of adsorption peaks and a previous study by Wan Ngah and Hanafiah¹³ indicated that rubber leaf powder contains hydroxyl, amino, aromatic, carboxylic acid and ether groups. These functional groups can act as adsorption sites, which are capable of binding heavy metal ions via various mechanisms such as physical adsorption, ion exchange, chelation and complexation.

The FTIR spectrum of XRL (Fig. 1b) showed some shift in wavenumbers or reduction in intensity after the xanthation process. The intensity of the shoulder at 1731 cm⁻¹ in URLP was reduced upon chemical treatment, suggesting the conversion of carboxylic acid or ester to carboxylate. The presence of -C=S group was confirmed by the peak at 1432 cm⁻¹. The FTIR spectrum of Pb(II) loaded XRL (Fig. 1c) showed some shift in wavenumbers. The peak at 3433 cm⁻¹ shifted to 3445 cm⁻¹ after Pb(II) adsorption, which could indicate the involvement of -OH (hydroxyl) and -NH₂ (amine) groups in forming complexes with Pb(II) ion. The shift in wavenumber from 1432 cm⁻¹ to 1399 cm⁻¹ would suggest the binding of Pb(II) to sulfur groups. The formation of bond between C-O-C and Pb(II) ion could be identified by the shifting of peak at 1030 cm⁻¹ to 1026 cm⁻¹. Based on the FTIR spectra, -OH, -NH₂, -COO⁻, C-O-C and -C=S were identified as the main functional groups involved in Pb(II) adsorption. According to 'Hard and Soft Acid Base' (HSAB) concept¹⁴, Pb(II) can be classified as a 'borderline' metal ion. Therefore Pb(II) can form a covalent complex with a soft base like xanthate group or ionic complexes with hydroxyl, carboxylate, ether and amino groups. As Pb(II) is able to induce a dipole or polarizable, this results in a higher affinity of xanthate group towards Pb(II).

The SEM images and EDX spectra of XRL are shown in Fig. 2. The SEM image of XRL before Pb(II) adsorption (Fig. 2a) showed uneven surface and irregular structure, which could favor the adsorption of Pb(II). The EDX spectrum indicated the presence of Na⁺ and Ca²⁺ (light metal ions) at 1.0, 3.7 and 4.0 keV, respectively. These light metal ions are nutrients in plants and treatment with NaOH would increase the content of Na⁺ in XRL. As FTIR spectrum of XRL (Fig. 1) suggested the presence of xanthate group, EDX analysis on sulfur was also carried out. The sulfur peak which was not detected in the FTIR spectrum of URLP emerged at 2.3 and 2.4 keV in the EDX spectrum of XRL (Fig. 2b). This is a confirmation of successful introduction of sulfur group after the xanthation process. The adsorption of Pb(II) on XRL surface can be proven by the appearance of Pb peaks at 2.35 and 9.1 keV. It is most likely that there are two major possible mechanisms involved in Pb(II) adsorption on XRL. Firstly, the light metal cations attached to the adsorption sites are exchanged with Pb(II). As shown in Fig. 2a, the weight percent of sodium and calcium in XRL are 1.19% and 2.60%, respectively. After Pb(II) adsorption, the values dropped to 0.67% and 0.44%; respectively, thus suggesting ion exchange process



Figure 1. FTIR spectra of (a) URLP, (b) XRL and (c) XRL after Pb(II) adsorption



Figure 2. SEM at 500X magnification and EDX spectra of XRL (a) before and (b) after Pb(II) adsorption

as a mechanism involved in Pb(II) removal. Secondly, the ligands in XRL can form bond with Pb(II) via the complexation process. This is consistent with the findings by Homagai et al.¹⁵ in the adsorption of Pb(II) on xanthated sugarcane bagasse.

Effect of pH

As shown in Fig. 3, adsorption of Pb(II) was very low at pH 2. This was due to Pb(II) ions which had to compete with a high number of hydronium ions for adsorption sites. As more H_3O^+ were attached to the XRL surface, the repulsive force between Pb(II) ion and adsorption sites became much stronger. As pH increased from 2 to 4, a drastic increase in the amount of Pb(II) adsorbed was observed. This pH region is commonly associated with the dissociation of carboxyl group and can be called 'pH adsorption edge¹⁶. Hence, Pb(II) ion could be adsorbed to the negatively charged carboxylate (-COO⁻) group. Beyond pH 4, there was no significant increase in the amount of Pb(II) adsorbed. Based on this finding, pH 4 was considered as the optimum pH for subsequent Pb(II) adsorption.



Figure 3. Effect of pH on Pb(II) adsorption by XRL (adsorbent weight: 0.02 g, volume: 50 mL, shaking speed: 120 stroke/min, equilibrium time: 90 min, initial Pb(II) concentration: 40 mg/L)

Effect of initial Pb(II) concentrations and contact time

Initial metal concentration is another important factor that affects the amount of Pb(II) adsorbed, which can also give important information on the driving force to transport adsorbate to the adsorbent surface. The driving force increases with increasing the concentration of metal solution and a higher probability of collision between the adsorbate and adsorbent surface could occur¹⁷. As shown in Fig. 4, the amount of Pb(II) adsorbed increased from 48.15 to 130.63 mg/g as the Pb(II) concentration was increased from 20 to 80 mg/L, respectively. The time required to reach equilibrium was 20 min for 20 mg/L Pb(II), but increased to 60 min for 80 mg/L. At a low Pb(II) concentration, there would be plenty of adsorption sites available. The ratio of Pb(II) ion to the number of adsorption sites, however increased as Pb(II) concentration increased. Therefore, more time was required to allow more Pb(II) ions to be adsorbed. In order to ensure the maximum removal of Pb(II), a contact time of 90 min was selected for isotherm studies.

The study on adsorption kinetic is useful for determining the rate determining steps (film diffusion, intraparticle diffusion, etc.) which control the time taken for Pb(II) to be adsorbed on XRL. The pseudo-second order kinetic model was applied and it is based on the assumption that the rate determining step is due to chemisorption^{18,19}. The pseudo-second order kinetic equation is given by: t 1 1

$$\frac{\mathbf{d}}{\mathbf{q}_{t}} = \frac{\mathbf{d}}{\mathbf{h}} + \frac{\mathbf{d}}{\mathbf{q}_{e}} \mathbf{t}$$
(6)

where $h = k_2 q_e^2$ can be regarded as the initial adsorption rate and k_2 is the rate constant of pseudo second-order adsorption. From Table 2, a high correlation coefficient (>0.99) was obtained for all Pb(II) concentrations. The calculated values of adsorption capacities ($q_{e,cal}$) and the experimental values ($q_{e,exp}$) were close to each other. This would suggest that the pseudo-second order model fitted well with the adsorption data and chemisorption could be the rate-determining step.



 Table 2. The pseudo-second order parameters at different concentrations of Pb(II)

Figure 4. Effect of initial Pb(II) concentration and contact time of Pb(II) adsorption by XRL (adsorbent weight: 0.02 g, pH: 4, volume: 50 mL, shaking speed: 120 stroke/min)

Adsorption isotherm

According to Sun et al.²⁰, the adsorption isotherm describes the relationship between the amount of the adsorbate adsorbed per unit weight of adsorbent and the concentration of the adsorbate in bulk solution at a given temperature under equilibrium conditions. Other important information that can be obtained from an isotherm study is adsorption mechanisms, surface properties and affinity of an adsorbent towards heavy metal ions²¹. The most commonly used isotherm models is the Langmuir model, developed based on the assumptions that adsorption occurs at specific homogenous sites on the adsorbent²². The Langmuir equation can be written as: $\frac{C_e}{C_e} = \frac{1}{C_e} + \frac{C_e}{C_e}$ (7)

$$\overline{q_e} = -\frac{1}{q_{max}b} + \frac{1}{q_{max}}$$
(7)

where q_{max} is the maximum adsorption capacity (mg/g) and b is a constant (L/mg). The Langmuir plot of Pb(II) ion is shown in Fig. 5. The values of q_{max} , b and correlation coefficient (R²) are 166.7 mg/g, 0.30 L/mg and 0.998, respectively. In general, the isotherm plot showed that the adsorption capacities increased with increasing initial Pb(II) concentrations until the XRL surface reached saturation. The shape of the isotherm plot obtained was "L2" type isotherm according to the Giles classification



Figure 5. Adsorption isotherm plot. Inset: Linearized Langmuir plot (adsorbent weight: 0.02 g, pH: 4, volume: 50 mL, shaking speed: 120 stroke/min, initial Pb(II) concentration: 20–200 mg/L, equilibrium time: 90 min)

system²³. It is an indication of chemical adsorption and reflects a relatively high affinity or strong interaction between Pb(II) and the adsorption sites. Since the values of q_{max} and R^2 are high, this indicated that adsorption of Pb(II) onto XRL fitted well to Langmuir isotherm model and suggested a monolayer adsorption behavior. The q_{max} recorded from this work was three times higher than untreated rubber leaf powder⁸. Therefore, it can be concluded that xanthation is an effective treatment process to improve adsorbent performance for Pb(II).

The performance of XRL was compared with other adsorbents cited in the literature based on the values of maximum adsorption capacity (q_{max}) as shown in Table 3. It was found that XRL recorded a much higher value of adsorption capacity compared to other agricultural wastes. XRL is seen as having a great potential to replace the costly activated carbon since rubber leaves are highly abundant, have high adsorption capacity to remove Pb(II) and the preparation method of XRL can be considered as relatively easy. This study also indicated that surface area is not the only factor that influences the amount of adsorbate adsorbed as XRL having a very low surface area recorded a much higher adsorption capacity than activated carbon derived from the palm shell.

Effect of ionic strength

Generally, wastewaters do not only contain heavy metal ions but also different kinds of cationic and anionic species³⁰. The composition of these species varies depending on the types of industries. The effect of ionic strength was studied in order to determine the behavior of Pb(II) adsorption in the presence of cations

Table 3. A comparison of maximum adsorption capacity of Pb(II) by different adsorbents

Adsorbent	Pretreatment	q _{max} (mg/g)	рΗ	Temperature (K)	References
Xanthated rubber leaf powder	Carbon disulfide	166.7	4.0	303	This study
Acorn waste	Formaldehyde Sulfuric Acid	164.2 124.1	5.0 5.0	298 298	24 24
Firmiana simplex leaf powder	Physical activation	136.7	4.0	298	25
Bael leaf powder	Hot deionized water	104.1	4.0	323	26
Activated carbon (palm shell)	Physical activation	95.2	5.0	300	27
Cinnamomum camphora leaf powder	Untreated	75.8	5.0	333	28
Sugarcane bagasse	Sulfuric acid Untreated	7.3 6.4	5.0 5.0	298 298	29 29



Figure 6. Effect of ionic strength on Pb(II) adsorption (adsorbent weight: 0.02 g, pH: 4, volume: 50 mL, shaking speed: 120 stroke/min, initial Pb(II) concentration: 40 mg/L, NaCl concentration: 0.001–0.05 M, equilibrium time: 90 min)

and anions. Five different concentrations of NaCl were used and the results are shown in Fig. 6. The amount of Pb(II) adsorbed was slightly reduced as more NaCl was added into Pb(II) solutions. In the absence of NaCl, XRL recorded the highest amount of adsorption (77.83 mg/g). However, this value dropped to 68.75 mg/g as the concentration of NaCl was increased to 0.05 M. This indicated that Pb(II) had to compete with Na⁺ for the adsorption sites. Another possible explanation is the formation of lead chloro-complexes such as PbCl⁺, PbCl₂, PbCl²⁻₄ and PbCl⁻₃, which resulted in low affinity of XRL for these complexes.

Desorption studies

Elucidation of adsorption behavior can be detected from desorption studies³¹ and the percentage of desorption is shown in Table 4. The fact that not all Pb(II) ions could be desorbed from the XRL surface suggests that chemical adsorption was involved during the Pb(II) adsorption process. In general, the desorption percentage increased with the increase in HCl and EDTA concentrations. Between the two desorbing solutions, EDTA recorded a higher percentage of desorption than HCl. EDTA is a chelating agent that has hexavalent ligand, and is capable of forming complexes with Pb(II) through two amines and four carboxylates. Therefore, EDTA performs better in trapping Pb(II). As Pb(II) ions were also able to be desorbed by HCl, this would suggest that ion-exchange is one of the important mechanisms involved in Pb(II) adsorption. Proton (H⁺) is a hard acid and can displace the Pb(II) ions that are attached to hard base groups. This explains the ability of protons to desorb Pb(II) through acid washing. Washing with deionized water, however did not exhibit any recovery of Pb(II). Regeneration of XRL for several cycles was not conducted as the method could lead to a reduction in the amount of Pb(II) adsorbed and would be costly since

 Table 4. Desorption of Pb(II) by HCl and EDTA as desorbing solutions at various concentrations

Concentration	Desorption (%)		
(M)	HCI	EDTA	
0.001	61.02	63.86	
0.010	61.99	81.27	
0.050	72.92	82.09	
0.100	74.11	86.14	

chemicals are used for desorption purpose. Furthermore, unlike synthetic ion-exchange resins, rubber leaves are highly abundant, can be considered as a much cheaper adsorbent and the Pb(II) laden XRL can be disposed by means of incineration.

CONCLUSIONS

The performance of XRL in removing Pb(II) has been evaluated and it was found that XRL can act as a potential adsorbent in wastewater treatment since XRL recorded a high adsorption capacity. The amount of Pb(II) adsorbed was influenced by pH, initial Pb(II) concentration, contact time and ionic strength. The kinetic data followed the pseudo-second order model, suggesting chemical adsorption as the rate-determining step. The isotherm plot agreed with the Langmuir model, an indication of monolayer adsorption of Pb(II) on XRL surface. EDTA was more effective in releasing Pb(II) from XRL surface than protons. Possible mechanisms involved in the Pb(II) adsorption onto XRL surface include ion-exchange and complexation as supported by FTIR spectra, SEM-EDX analysis and desorption studies.

Acknowledgements

The authors would like to express sincere gratitude to the Malaysian Ministry of Higher Education for financial support (Grant No. 011000100005). One of the authors (Wan Khaima Azira Wan Mat Khalir) is thankful to the Malaysian Ministry of Science, Technology and Innovation via National Science Fellowship (NSF) and Universiti Teknologi MARA for providing Postgraduate Research Scheme.

LITERATURE CITED

1. Balaria, A. & Schiewer, S. (2008). Assessment of biosorption mechanisms for Pb binding by citrus pectin. *Sep. Purif. Technol.* 63, 577–581. DOI:10.1016/j.seppur.2008.06.023.

2. Naiya, T.K., Bhattacharya, A.K., Mandal, S. & Das, S.K. (2009). The sorption of lead(II) ions on rice husk ash. J. Hazard. Mater. 163, 1254–1264. DOI:10.1016/j.jhazmat.2008.07.119.

3. Qaiser, S., Saleemi, A.R. & Umar, M. (2009). Biosorption of lead from aqueous solution by *Ficus religiosa* leaves: batch and column study. *J. Hazard. Mater.* 166, 998–1005. DOI:10.1016/j. jhazmat.2008.12.003.

4. Environmental Quality Act (1974) Act 127 & Subsidiary Legislation, (1995). Legal Research Board, International Law Book Services, Kuala Lumpur.

5. Wang, X.S., Miao, H.H., He, W. & Shen, H.L. (2011). Competitive adsorption of Pb(II), Cu(II), And Cd(II) ions on wheat-residue derived black carbon. *J. Chem. Eng Data.* 56, 444–449. DOI:10.1021/je101079w.

6. Kamal, M.H.M.A., Azira, W.M.K.W.K., Kasmawati, M., Haslizaidi, Z. & Wan Saime, W.N. (2010). Sequestration of toxic Pb(II) ions by chemically treated rubber (*Hevea brasiliensis*) leaf powder. *J. Environ. Sci.* 22, 248–256. DOI: 10.1016/S1001-0742(09)60101-7.

7. Wan Ngah, W.S. & Hanafiah, M.A.K.M. (2008). Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review. *Bioresour. Technol.* 99, 3935–3948. DOI:10.1016/j.biortech.2007.06.011.

8. Hanafiah, M.A.K.M., Wan Ngah, W.S., Ibrahim, S.C., Zakaria, H. & Ilias, W.A.H.W. (2006). Kinetics and thermodynamic study of lead adsorption from aqueous solution onto rubber (*Hevea brasiliensis*) leaf powder. *J. Appl. Sci.* 6, 2762–2767. DOI: 10.3923/jas.2006.2762.2767. 9. Liang, S., Guo, X., Feng, N. & Tian, Q. (2009). Application of orange peel xanthate for the adsorption of Pb²⁺ from aqueous solutions. *J. Hazard. Mater.* 170, 425–429. DOI:10.1016/j. jhazmat.2009.04.078.

10. Kumar, S., Rao, N.N. & Kaul, S.N. (2000). Alkalitreated straw and insoluble straw xanthate as low cost adsorbents for heavy metal removal – preparation, characterization and application, *Bioresour. Technol.* 71, 133–142. DOI:S0960-8524(99)00064-4.

11. Balistrieri, L.S. & Murray, J.W. (1981). The surface chemistry of goethite (α -FeOOH) in major ion seawater. *Am. J. Sci.*, 281, 788–806. DOI:10.2475/ajs.281.6.788.

12. Guo, S., Li, W., Zhang, L., Peng, J., Xia, H. & Zhang, S. (2009). Kinetics and equilibrium adsorption study of lead(II) onto the low cost adsorbent-*Eupatorium adenophorum* spreng. *Process Saf. Environ. Prot.* 87, 343–351. DOI:10.1016/j. psep.2009.06.003.

13. Wan Ngah, W.S. & Hanafiah, M.A.K.M. (2008). Biosorption of copper ions from dilute aqueous solution on base treated rubber (*Hevea brasiliensis*) leaves powder: kinetics, isotherm and biosorption mechanisms. *J. Environ. Sci.* 20, 1168–1176. DOI:10.1016/S1001-0742(08)62205-6.

14. Shriver, D.F., Atkins, P.W. & Langford, C.H. (1990). *Inorganic Chemistry* (pp. 173–174). United Kingdom: Oxford University Press.

15. Homagai, P.L., Ghimire, K.N. & Inoue, K. (2011). Characterization of charred xanthated sugarcane bagasse for the separation of heavy metals from aqueous solutions. *Sep. Sci. Technol.* 46, 330–339. DOI: 10.1080/01496395.2010.506903.

16. Kumar, U. & Bandyopadhyay, M. (2006). Sorption of cadmium from aqueous solution using pretreated rice husk. *Bioresour. Technol.* 97, 104–109. DOI:10.1016/j.biortech.2005.02.027.

17. Ozsoy, H.D. & Kumbur, H. (2006). Adsorption of Cu(II) ions on cotton ball. *J. Hazard. Mater.* 136, 911–916. DOI:10.1016/j.jhazmat.2006.01.035.

18. Ho, Y.S. & McKay, G. (2000). The kinetics of sorption of divalent metal ions onto sphagnum moss peat. *Water Res.* 34, 735–742. DOI:10.1016/S0043-1354(99)00232-8.

19. Senthil Kumar, P., Ramalingam, S., Sathyaselvabala, V., Kirupha, S.D. & Sivanesan, S. (2011). Removal of Copper(II) ions from aqueous solution by adsorption using cashew nut shell. *Desalination*. 266, 63–71. DOI:10.1016/j.desal.2010.08.003.

20. Sun, H., Cao, L. & Lu, L. (2010). Magnetite/reduced graphene oxide nanocomposites: one step solvothermal synthesis and use as a novel platform for removal of dye pollutants. *Nano Res.* 3, 676–684. DOI: 10.1007/s 122274-011-0111-3 CN 11-5974/04.

21. Ho, Y.S., Porter, J.S. & McKay, G. (2002). Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: copper, nickel and lead single component systems. *Water, Air, Soil Pollut.* 141, 1–33. DOI: 10.1023/A:1021304828010.

22. Langmuir I. (1916). The constitution and fundamental properties of solids and liquids. *J. Am. Chem. Soc.* 38, 2221–2295. DOI: 10.1021/ja02268a002.

23. Giles, C.H., Smith, D. & Huitson, A. (1974). A general treatment and classification of the solute adsorption isotherm. I. Theoretical. *J. Colloid Interface Sci.* 47, 755–765. DOI:10.1016/0021-9797(74)90252-5.

24. Örnek, A., Özacar, M. & Sengil, I.A. (2007). Adsorption of lead onto formaldehyde or sulphuric acid treated acorn waste: Equilibrium and kinetics studies. *Biochem. Eng. J.* 37, 192–200. DOI:10.1016/j.bej.2007.04.011.

25. Li, Z., Tang, X., Chen, Y., Wei, L. & Wang, Y. (2009). Activation of *Firmiana simplex* leaf and the enhanced Pb(II) adsorption performance: Equilibrium and kinetic studies. *J. Hazard. Mater.* 169, 386–394. DOI:10.1016/j.jhazmat.2009.03.108.

26. Chakravarty, S., Mohanty, A., Sudha, T.N., Upadhyay, A.K., Konar, J., Sircar, J.K., Madhukar, A. & Gupta, K.K. (2010). Removal of Pb(II) ions from aqueous solution by adsorption using bael leaves (*Aegle marmelos*), *J. Hazard. Mater.*

173, 502-509. DOI:10.1016/j.jhazmat.2009.08.113.

27. Issabayeva, G., Aroua, M.K. & Sulaiman, N.M.N. (2006). Removal of lead from aqueous solutions on palm shell activated carbon. *Bioresour. Technol.* 97, 2350–2355. DOI:10.1016/j. biortech.2005.10.023.

28. Chen, H., Zhao, J., Dai, G., Wu, J. & Yan, H. (2010). Adsorption characteristics of Pb(II) from aqueous solution onto a natural biosorbent, fallen *Cinnamomum camphora* leaves. *Desalination*. 262, 174–182. DOI:10.1016/j.desal.2010.06.006.

29. Martín-Lara, M.Á., Rico, I.L.R., Vicente, I.D.L.C.A, García, G.B. & Hoces, M.C.D. (2010). Modification of the sorptive characteristics of sugarcane bagasse for removing lead from aqueous solutions. *Desalination*. 256, 58–63. DOI:10.1016/j. desal.2010.02.015.

30. Tchobanoglous, G., Burton F.L. & Stensel, H.D. (2003). *Wastewater engineering: Treatment and reuse* (4th ed.) (pp. 186–187). New York: Metcalf & Eddy Inc.

31. Ahmad, R. & Kumar, R. (2011). Adsorption of amaranth dye onto alumina reinforced polystyrene. *Clean: Soil, Air, Water*. 39, 74–82. DOI: 10.1002/clen.201000125.