

## Sorption of Cd(II) and Pb(II) ions onto *Shorea acuminata* sawdust: Isotherm, kinetics and sorption mechanism studies

*Penjerapan ion Cd(II) dan Pb(II) ke atas habuk kayu Shorea acuminata: Kajian isoterma, kinetik dan mekanisma penjerapan*

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### Abstract

The potential of *Shorea acuminata* (also known as Dark Red Meranti) sawdust as a sorbent to clean-up metal contaminated water was investigated in a batch sorption system. Its efficacy was evaluated at different pH, contact time and initial metal concentration. Equilibrium isotherm data were best described using the Langmuir isotherm model, while the kinetics followed the pseudo-second-order model. The maximum sorption capacity ( $Q$ ) of Dark Red Meranti sawdust, estimated from the Langmuir equation were 94 and 328 mg/g for Cd(II) and Pb(II), respectively. FTIR analysis confirmed that O- and N-containing functional groups are the main sorption sites in Dark Red Meranti sawdust.

**Keywords** sorption, sawdust, isotherm, kinetics, sorption mechanism

### Abstrak

Potensi habuk kayu *Shorea acuminata* (juga dikenali sebagai Meranti Merah Tua) sebagai suatu penjerap untuk merawat air yang dicemari oleh logam telah diselidik di dalam satu sistem penjerapan berkelompok. Kemujarabannya pada tahap berbeza telah dinilai pada pH, masa sentuhan dan kepekatan awal logam. Model isoterma Langmuir telah menerangkan data keseimbangan isoterma dengan baik, manakala kinetik penjerapan mematuhi model tertib-pseudo-kedua. Kapasiti penjerapan maksimum ( $Q$ ) habuk kayu Meranti Merah Tua, dianggarkan dari persamaan Langmuir ialah 94 mg/g untuk Cd(II) dan 328 mg/g untuk Pb(II). Analisis FTIR mengesahkan bahawa kumpulan berfungsi yang mengandungi atom-atom O dan N adalah tapak penjerapan utama yang terdapat pada habuk kayu Meranti Merah Tua.

**Kata kunci** penjerapan, habuk kayu, isoterma, kinetik, mekanisma penjerapan

### Introduction

Heavy metals are ubiquitous contaminants and are of great concern due to their harmful effects and long-term persistence in the environment (Kamari *et al.*, 2011a). Anthropogenic

activities such as mining, industry and agriculture have increased the level of heavy metals in the environment tremendously (Kamari *et al.*, 2011b; Demirbas, 2008). Heavy metals such as Cd, Cr, Cu, Ni, Pb and Zn are usually associated with tendency to accumulate in living organisms and can be detrimental when adsorbed to human body (WHO, 2011). For example, excessive intake of cadmium by humans (600 - 2000  $\mu\text{g}/\text{day}$ ) results in 'itai-itai' disease (osteomalacia with various grades of osteoporosis accompanied by severe renal tubular disease) (WHO, 2011).

Several techniques are available to remediate water contaminated by heavy metals. These include flocculation, coagulation, ion exchange, membrane filtration, electrodeposition and chemical precipitation. However, many of these techniques are costly and ineffective in removing metal ions at trace quantities (Ozsoy & Kumbur, 2006; Kamari & Wan Ngah, 2009). Adsorption has been reported to be an economically feasible alternative and has been regarded as one of the most important physicochemical processes that occur at the solid-phase interface (Dąbrowski, 2001; Febrianto *et al.*, 2009). This technique has been shown to be effective in removing heavy metals at low concentrations ( $< 100 \text{ mg/L}$ ) from aqueous solutions (Wan Ngah & Hanafiah, 2008; Kurniawan *et al.*, 2006).

Activated carbon is one of the most widely used sorbents for water treatment throughout the world (Kalavathy *et al.*, 2010; Wang & Chen, 2009). Despite its prolific use, commercial activated carbon remains an expensive sorbent (Gupta and Ali, 2006; Febrianto *et al.*, 2009; Mall *et al.*, 1996). In recent years, the use of waste-derived materials for water treatment has received much attention due to their low cost and ready availability in large quantities (Kamari *et al.*, 2011a; Witek-Krowiak *et al.*, 2011). Dark Red Meranti is native to Southeast Asia and an important wood species for furniture in Malaysia. The ultimate aim of this work is to evaluate the potential of Dark Red Meranti sawdust as a sorbent for the remediation of water contaminated with heavy metals.

## Materials and Methods

Dark Red Meranti sawdust was obtained from Hong Huat Sawmill, Butterworth, Pulau Pinang. Sawdust was rinsed thoroughly with distilled water and dried at  $70^\circ\text{C}$  for 10 h in an oven. After drying, the sawdust was crushed and sieved through 150-250  $\mu\text{m}$  size fraction using an American Society for Testing and Materials (ASTM) standard sieve. Surface area and average pore diameter analyses were carried out on a Micromeritics ASAP 2010 Gas Adsorption Surface Analyser. FTIR spectra of the sawdust were recorded on a Thermo Scientific Nicolet 6700 FTIR Spectrophotometer using KBr disc technique. The characteristics of the sawdust are given in Table 1.

**Table 1** Physical characteristics of *Shorea acuminata* sawdust.

Physical properties	Appearance/Value
Colour	Dark reddish-brown
BET surface area ( $\text{m}^2/\text{g}$ )	7.85
Average pore diameter ( $\text{Å}$ )	2.16
Bulk density ( $\text{g}/\text{cm}^3$ )	0.71
Moisture content (%)	14.5
Ash content (%)	5.8
Cation exchange capacity ( $\text{meq}/\text{g}$ )	12.7
Surface charge density ( $\text{meq}/\text{m}^2$ )	1.62

Stock metal solutions were prepared using analytical grade of  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{Pb}(\text{NO}_3)_2$  salts (obtained from Fluka) in deionised water. The solutions were further diluted to the required concentrations before use. Sorption isotherm studies were carried out by suspending 0.1 g of sawdust in 50 mL of each of the metal ion solutions of desired concentration (50-500 mg/L) in a 250 mL beaker. The suspension was stirred at a constant speed of 150 rpm at room temperature for 200 min. For the kinetics study, a single metal concentration (500 mg/L) was used and the suspensions were stirred for a period of time (between 15 and 300 min). To study the effect of pH, the pH of the sorption system was varied between 1.0 and 8.0 using either 0.1 mol/L HCl or 0.1 mol/L NaOH. At the end of the predetermined time interval, the sawdust was removed by filtration using Whatman No. 2 filter paper. The equilibrated metal concentration in the supernatant was measured by means of a Perkin-Elmer Analyst 400 Atomic Absorption Spectrometer (AAS).

In this study, pH of the zero point of charge ( $\text{pH}_{\text{zpc}}$ ) of sawdust was determined by the acid-base titration method outlined by Jha *et al.* (1988). The pH value was measured using a CyberScan 1500 pH meter. In each experiment, metal and sawdust free blanks were run as controls. Each sorption experiment was performed in triplicate and the mean values are presented in this work. The error obtained was  $\pm 2.5\%$ . The sorption capacity,  $q$  (mg/g) was estimated according to Equation (1) (Kamari & Wan Ngah, 2009):

$$q = \frac{(C_o - C_f) V}{W} \quad (1)$$

where,  $C_o$  and  $C_f$  (mg/L) are the initial and final metal concentrations, respectively.  $V$  (mL) is the volume of metal solution, and  $W$  (g) is the weight of sawdust.

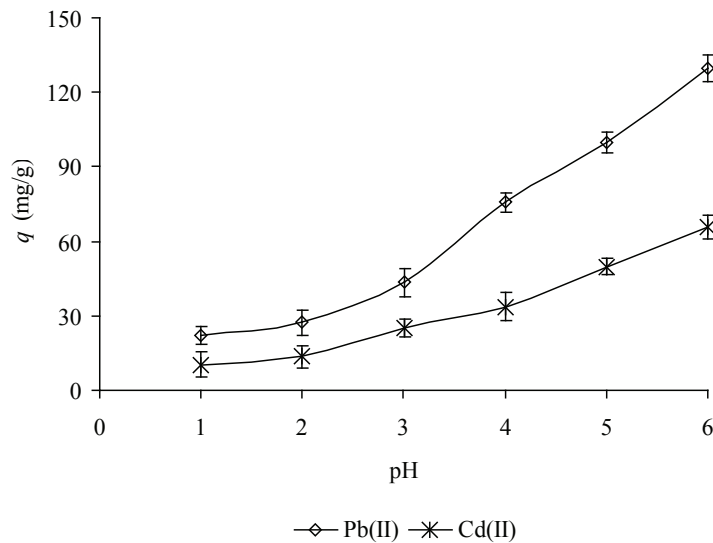
## Results and Discussion

The study of pH effect on metal ion sorption by sorbent is essential, as it affects the binding performance of the sorbent. The amount of Cd(II) and Pb(II) ions sorbed by sawdust as a function of pH is shown in Figure 1. It can be seen that the sorption of Cd(II) and Pb(II) ions increased with increasing pH of the solution. This can be explained by the fact that in low pH solution, more  $\text{H}^+$  ions are available to compete with Cd(II) and Pb(II) ions for the sorption sites of the sawdust. However, the sorption of Cd(II) and Pb(II) ions increased at higher pH values and this was due to the weak inhibitory effect of  $\text{H}^+$  ions. It was observed that Cd(II) and Pb(II) precipitation occurred simultaneously at pH values higher than 6.5 and 7.0, respectively. Therefore, pH 6.0 was chosen as the optimum pH for the sorption of Cd(II) and Pb(II) ions to avoid the formation of Cd(II) and Pb(II) hydroxides which will affect the sorption onto sawdust.

The  $\text{pH}_{\text{zpc}}$  describes the behaviour and ability of a sorbent to sorb contaminants from aqueous environment. In this study,  $\text{pH}_{\text{zpc}}$  obtained for sawdust is 3.7. As discussed by Mall *et al.* (2006), sorption of cations is favoured at  $\text{pH} > \text{pH}_{\text{zpc}}$ , while the sorption of anions is favoured at  $\text{pH} < \text{pH}_{\text{zpc}}$ . As shown in Figure 1, the maximum sorption of Cd(II) and Pb(II) onto sawdust was at pH 6.0, higher than  $\text{pH}_{\text{zpc}}$  value.

The sorption data at different contact time and initial metal concentrations are shown in Figures 2(a-b). The amount of Cd(II) and Pb(II) ions sorbed increased with contact time for all metal ion concentrations. The time profiles reveals that the kinetics of Cd(II) and Pb(II)

ions sorption mainly consists of two stages. The initial rapid stage can be related to the instantaneous external surface sorption of metal ions. The second slower stage is the gradual sorption that takes place before metal ion sorption attains equilibrium. The high sorption rate during the initial period of 30 min is due to the availability of sorption sites of the sawdust. However, as these sites are progressively occupied, the rate of sorption decreased. The sawdust attained equilibrium at 200 min. A higher initial metal concentration results in greater sorption capacity. This can be attributed to higher probability of collision between metal ions and the surface of sawdust. This effect reduces the mass transfer resistance (Ozsoy & Kumbur, 2006).



**Figure 1** Effect of pH on the sorption of Cd(II) and Pb(II) onto *Shorea acuminata* sawdust (Error bars are  $\pm$  standard deviation of 3 replicates)

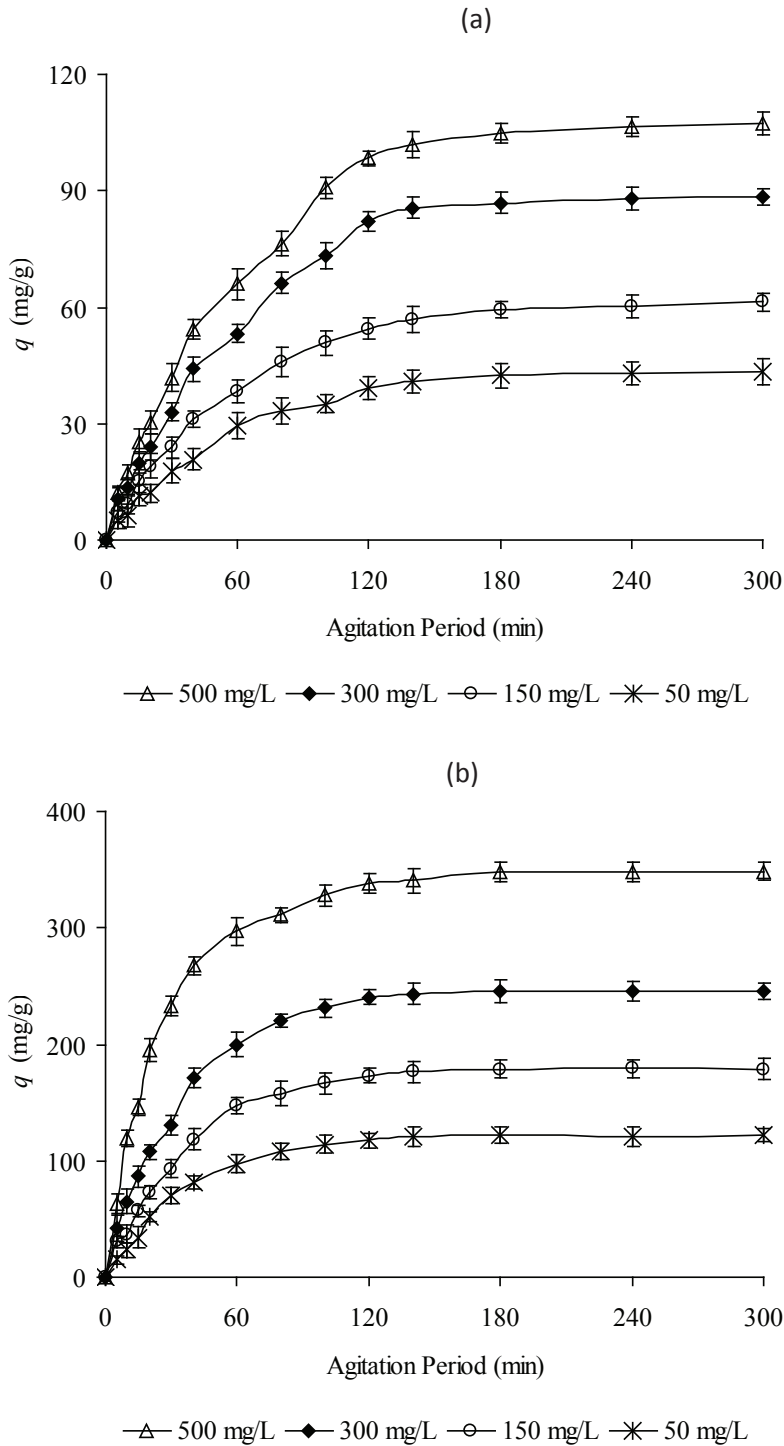
Equilibrium sorption isotherm studies are fundamental, especially when designing an ideal sorption system for industrial application. The interactive behaviour between sorbent and sorbate is generally described using Freundlich and Langmuir isotherm models. These models were applied to describe the isotherms and determine the isotherm constants of metal ion sorption by the sawdust.

The linear form of the Freundlich equation, based on sorption on a heterogeneous surface is given by Equation (2) (Freundlich, 1906):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (2)$$

where,  $C_e$  (mg/L) is the equilibrium concentration of metal ions,  $q_e$  (mg/g) is the amount of metal ions sorbed per unit weight of sawdust at equilibrium,  $K_F$  (mg/g) is the relative sorption capacity constant, and  $n$  is the Freundlich constant indicating sorption intensity.  $K_F$  and  $n$  can be determined from linear plot of  $\log q_e$  against  $\log C_e$ .

The linear form of the Langmuir equation, which is valid for monolayer sorption is expressed as Equation (3) (Langmuir, 1916):



**Figure 2** Effect of agitation period and initial metal concentrations on the sorption of (a) Cd(II) and (b) Pb(II) onto *Shorea acuminata* sawdust (Error bars are  $\pm$  standard deviation of 3 replicates)

$$\frac{C_e}{q_e} = \frac{C_e}{Q} + \frac{1}{Qb} \quad (3)$$

where,  $Q$  (mg/g) is the maximum sorption capacity, and  $b$  (L/mg) is the Langmuir constant related to the affinity of binding sites. A linearised plot of  $C_e/q_e$  against  $C_e$  gives  $Q$  and  $b$ .

The Freundlich and Langmuir constants and  $R^2$  values are given in Table 2. The Langmuir model fitted the isotherm equilibrium data very well with  $R^2$  values of  $\geq 0.9983$ . As presented in Table 2, the  $1/n$  values lie between 0 and 1 indicating the Cd(II) and Pb(II) ions are favourably bound onto sawdust. The  $1/n$  value can be used to predict binding affinity of the sorbent toward contaminant, whereby a smaller value of  $1/n$  implies stronger interaction between sorbent and contaminant (Freundlich, 1906). From Table 2, the  $1/n$  value for Pb(II) was found to be lower than for Cd(II) suggesting stronger binding interaction between Pb(II) and active sites of the sawdust. This was further evident by the greater value of  $b$  for Pb(II) obtained from the Langmuir model.

**Table 2** Freundlich and Langmuir isotherm constants for Cd(II) and Pb(II) sorption onto *Shorea acuminata* sawdust

Metal ion	Freundlich			Langmuir		
	$K_F$ (mg/g)	$1/n$	$R^2$	$Q$ (mg/g)	$b$ (L/mg)	$R^2$
Cd(II)	67	0.8691	0.7629	94	0.97	0.9983
Pb(II)	173	0.2388	0.8268	328	1.82	0.9991

The essential feature of the Langmuir isotherm can be expressed in terms of an equilibrium parameter,  $R_L$ , which was defined by Hall *et al.* (1966), and is given by Equation (4):

$$R_L = \frac{1}{1 + bC_0} \quad (4)$$

$R_L$  values indicate the shape of the isotherm (Hall *et al.*, 1966): (i) irreversible ( $R_L = 0$ ), (ii) favourable ( $0 < R_L < 1$ ), (iii) linear ( $R_L = 1$ ), and (iv) unfavourable ( $R_L > 1$ ). It was found that the  $R_L$  values are in the range of  $0 < R_L < 1$  (Table 3), which suggests that the sorption of Cd(II) and Pb(II) ions on the sawdust is favourable.

**Table 3**  $R_L$  values based on the Langmuir equation

Initial concentration, $C_0$ (mg/L)	$R_L$ value	
	Cd(II)	Pb(II)
50	0.6144	0.4803
100	0.6072	0.4951
150	0.5295	0.3978
300	0.4188	0.2645
400	0.3742	0.1174
500	0.2619	0.0945

It is necessary to compare the maximum sorption capacity value obtained from this study with values from other reported low-cost sorbents, since this will suggest the effectiveness of sawdust as a potential sorbent to remediate metal contaminated water. The sorption capacities for Cd(II) and Pb(II) using Dark Red Meranti sawdust are comparable with other low-cost sorbents as shown in Table 4.

**Table 4** Comparison of sorption capacities of Cd(II) and Pb(II) on various low-cost sorbents

Metal ion	Sorbent	$q_{\max}$ (mg/g)	Reference
Cd(II)	Coconut copra	4.99	Ho and Ofomaja (2006)
	Rice husk	8.58	Kumar and Bandyopadhyay (2006)
	Sugarcane bagasse	38.03	Mohan and Singh (2002)
	Mango peel	68.92	Iqbal <i>et al.</i> (2009)
	Grape bagasse	86.9	Farinella <i>et al.</i> (2004)
	<i>Shorea acuminata</i> sawdust	94	This study
Pb(II)	Coffee residue	63	Boudrahem <i>et al.</i> (2009)
	Wheat bran	69.0	Bulut and Baysal (2006)
	Grape bagasse	88.7	Farinella <i>et al.</i> (2004)
	Mango peel	99.05	Iqbal <i>et al.</i> (2009)
	Coir pith	263	Kadirvelu and Namasivayam (2000)
	<i>Shorea acuminata</i> sawdust	328	This study

Three kinetic models, namely pseudo-first-order (Lagergren, 1898), pseudo-second-order (Ho & McKay, 2000) and intraparticle diffusion (Weber & Morris, 1963) were applied to determine the rate constant and the controlling mechanism of metal ions sorption onto sawdust. The linear form of pseudo-first-order equation is rendered as Equation (5) (Lagergren, 1898):

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (5)$$

where,  $q_e$  and  $q_t$  (mg/g) are the amount of metal ions sorbed at equilibrium and at time  $t$  (min), respectively and  $k_1$  (1/min) is the rate constant of pseudo-first-order equation.

The linear form of pseudo-second-order equation is expressed as Equation (6) (Ho & McKay, 2000):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

where,  $k_2$  (g/mg/min) is the rate constant of pseudo-second-order equation.

The intraparticle diffusion equation is described as Equation (7) (Weber & Morris, 1963):

$$q_t = k_{id} t^{0.5} \quad (7)$$

where,  $k_{id}$  (mg/g/min<sup>0.5</sup>) is the rate constant of intraparticle diffusion equation.

The kinetic parameters obtained for the sorption along with their corresponding  $R^2$  values are given in Table 5. The experimental equilibrium sorption capacities ( $q_e$  Exp.) determined from the contact time study were in good agreement with the theoretical equilibrium sorption capacities ( $q_e$  Theor.) calculated using the pseudo-second-order kinetic model. Moreover, the  $q_e$  Exp. and  $q_e$  Theor. values were close to the  $Q$  values obtained from the Langmuir equation (Table 2). Results suggest that the sorption of Cd(II) and Pb(II) ions by sawdust was best described by the pseudo-second-order kinetic model and that the chemical binding reaction was the rate-determining step, as discussed by Ho and McKay (2000).

**Table 5** Kinetic parameters for Cd(II) and Pb(II) sorption onto *Shorea acuminata* sawdust.

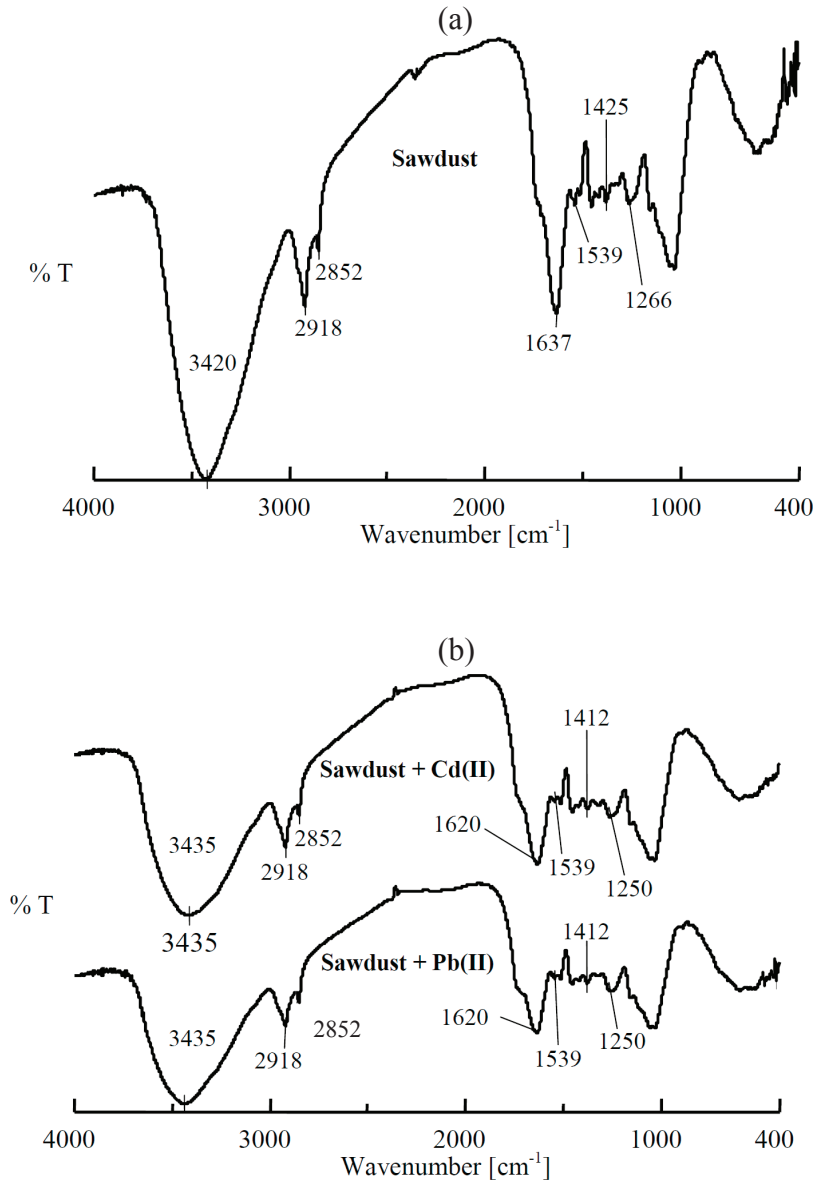
Metal ion	Pseudo-first-order		Pseudo-second-order				Intraparticle diffusion	
	$k_1$ (1/min)	$R^2$	$k_2$ (g/mg/min)	$q_e$ (mg/g)		$R^2$	$k_i$ (mg/g/min <sup>0.5</sup> )	$R^2$
				Exp.	Theor.			
Cd(II)	$2.94 \times 10^{-3}$	0.2167	$1.63 \times 10^{-3}$	92	95	0.9976	3.81	0.4899
Pb(II)	$2.68 \times 10^{-3}$	0.2484	$1.42 \times 10^{-3}$	328	326	0.9990	3.29	0.4275

The contribution of the ion exchange mechanism to metal ion sorption was investigated by measuring pH of the initial and final solutions. After the sorption process, there was a slight increase (ca. 0.4 units) in the pH value (data not shown) suggesting the ion exchange mechanism was not involved.

In order to identify functional groups present in Dark Red Meranti sawdust, as well as to elucidate the sorption mechanism, FTIR analysis was performed. As depicted in Figure 3a, a broad band appeared at 3420 cm<sup>-1</sup> corresponds to the intermolecular H-bonded O-H and the extension vibration of N-H. Two discernible bands at wavenumbers 2918 and 2852 cm<sup>-1</sup> are assigned to saturated C-H stretchings. According to Crews *et al.* (1998), the prominent band observed at 1637 cm<sup>-1</sup> can be attributed to N-H bending, while an absorption band located at 1539 cm<sup>-1</sup> is characteristic of amine deformation. O-H bending was represented by two absorption bands observed at 1425 and 1266 cm<sup>-1</sup>.

After Cd(II) and Pb(II) sorption (Figure 3b), the absorption band of intermolecular H-bonded O-H and extension vibration of N-H at 3420 cm<sup>-1</sup> was shifted to 3435 cm<sup>-1</sup>, while absorption band of N-H bending at 1637 cm<sup>-1</sup> was shifted to 1620 cm<sup>-1</sup>. The absorption intensity of the amine deformation band at 1539 cm<sup>-1</sup> decreased significantly following metal interaction. The interaction of metal ions with hydroxyl groups was proven by the shift in the wavenumbers of the O-H bending vibration. The absorption bands had shifted from 1425 cm<sup>-1</sup> to 1412 cm<sup>-1</sup> and from 1266 cm<sup>-1</sup> to 1250 cm<sup>-1</sup>, respectively. The change in the wavenumber and absorption intensity of functional groups could be owing to complexation between metal ions and binding sites of the sawdust, through electron pair sharing between electron donor atom and metal ion. The FTIR results suggest that O- and N-containing functional groups are indeed the main sorption sites in Dark Red Meranti sawdust.





**Figure 3** FTIR spectra of *Shorea acuminata* sawdust (a) before and (b) after metal sorption.

## Conclusions

This study has shown that Dark Red Meranti sawdust has great potential to be used as an alternative low-cost sorbent to remediate metal laden industrial effluents. Batch sorption however is one technique of evaluation. It is also necessary to assess the sorption capacity by using other technique such as fix bed column. In Malaysia, sawdust is a by-product of the timber industry and abundantly available at low economic value. The use of sawdust in water treatment converts the by-product into cost-effective sorbent.

## Acknowledgement

We thank Mr. Ariffin Majid and Mr. Hashim Othman (School of Chemical Sciences, USM), and, Mr. Mohd Zurin Mahmood, Mrs. Johana Jumiran and Mr. Hengkyiriawan Hairuddin (Department of Chemistry, Faculty of Science and Mathematics, UPSI) for their assistance. The financial support from Universiti Pendidikan Sultan Idris under Short Term Research Grant (Research Code: 2011-0112-102-01) is gratefully acknowledged.

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