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Mistletoe leaves as a biosorbent for removal of Pb(II) and Cd(II) from aqueous solution

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ABSTRACT

The adsorption of Pb(II) and Cd(II) ions onto the biosorbent from leaves of *Ramus Loranthi, Scurrula Parasitica L.*, family *Loranthaceae*, commonly known as mistletoe or Tam gui in Vietnam, (henceforth to be referred as mistletoe leaves) was studied. The results showed that adsorption equilibrium was established in 150 min of contact time. The maximum adsorption for both metals obtained was at pH 5.5. The time-dependent experimental data of Pb(II) and Cd(II) adsorption process well fitted the pseudo-second-order model. The Redlich-Peterson, Toth, and Langmuir models were appropriate to describe the adsorption process, indicating the chemisorption process onto mistletoe leaves. The maximum adsorbent capacity was increased with an increase in temperature. It was found to be 44.8, 47.85, 49.1, and 50.07 mg/g for Cd(II) and 59.76, 63.25, 66.3, and 68.53 mg/g for Pb(II) at 303, 308, 313, and 318 K, respectively. The positive value of ΔH indicated the endothermic adsorption process. The high adsorption capacity for Pb (II) and Cd(II) obtained in this study shown that mistletoe leaves are a potential biosorbent for removal of these metals from wastewater and contaminated water.

Keywords: Lead; Cadmium; Mistletoe leaves; Biosorbent; Adsorption isotherms; Adsorption kinetics

1. Introduction

Lead and cadmium have been known to be very toxic metals whose acute exposure even at low levels can be extremely harmful to human health [1–5]. Lead and cadmium mostly enter human bodies through the digesting system due to contaminated foods or drinking water. Contaminated water is a more difficult challenge because of the wide distribution of sources and affected areas. Similar to other types of heavy metal, lead and cadmium found in surface and groundwater systems often from, to name a few, sources such as runoff from solid waste disposal sites and agriculture fields or directly through effluent from industrial manufacturing sites, for example, mines, acid battery, and electroplating [6–9]. While efforts have been made at both ends to stemmed this problem, that is, preventing water from contamination with lead and cadmium, and cleaning contaminated water, it is often found that the latter is a more practical approach.

A variety of research studies have been made to find suitable treatment technologies for effective removing of these heavy metal-contaminated waters.

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Technologies such as precipitation, ion exchange, and adsorption have been widely employed, depending on specific scenarios [10–16].

More recently, the biosorption technology based on metal binding capacity of various biological materials has been explored as a potential alternative for removal of these metal ions from industrial waste streams and contaminated water [17–19]. This is because of it relies on relatively inexpensive, readily available, and abundant local biomass which is already biodegradable. Further, the attractive point of this biosorption technology is its efficiency in removing pollutants at very low concentrations of metal ions [20–22].

A variety of biosorbents from local plant leaves have been studied to identify their ability in absorbing heavy metals. For example, materials from bael leaves have been employed in lead(II) and cadmium(II) ions adsorption [23]. Similarly, other biosorbents from sesame leaves [24], *Azadirachta indica* (neem) leaf powder [25], lalang (*Imperata cylindrica*) leaf powder [26], *Ficus Hispida* leaves powder [27], *Ficus carcia* leaves [28], and *Ulmus carpinifolia* and *Fraxinus excelsior* tree leaves [29] have been studied. Their results have indicated the potential of using those local biomass resources in removing Pb(II) and Cd(II) from metal-polluted water.

Climbing mistletoe, *Ramus loranthi, Scurrula parasitica L.*, family *Loranthaceae*, commonly known as Tam gui in Vietnam, (hereafter to be referred as mistletoe) is a plant living on host trees and is common in tropical regions. This plant is often found on star apple trees, *Chrysophyllum cainito*, family *Sapotaceae*, commonly known as milk fruit tree or Vu Sua in Vietnam. Mistletoe is considered as an epidemic for star apple trees because it reduces the development and yield of the host tree. Annually, farmers have to systematically remove mistletoe from star apple trees, resulting in a large amount of mistletoe biomass which currently has not been utilized.

The aim of this study was to evaluate the adsorption ability for Pb(II) and Cd(II) of mistletoe leaves collected from star apple trees in the south of Vietnam. The focus is on affecting parameters such as pH, contact time, biosorbent dose, and temperature to identify optimal adsorption conditions. The adsorption kinetics and isotherms were also investigated to clarify the adsorption process of these metals on mistletoe leaves.

2. Materials and methods

2.1. Preparation of biosorbent

Mistletoe leaves, collected from local star apple tree gardens in Thu duc district, Ho Chi Minh City, Vietnam, were used for procedure absorbent material in this study. The fresh leaves were washed thoroughly with water and dried in oven at 80°C for three hours. The dried leaves were ground and sieved to obtain the desired particle size at 0.25–0.40 mm and stored in a polythene bag. The biosorbent obtained was characterized by FTIR spectra using a FTIR system 8400 Model, Shimadzu. Surface morphology of the adsorbent was identified using a scanning electron microscopy (SEM) S-3000N model, Hitachi, and pH_{zpc} of the adsorbent was determined by acid titration method [28].

2.2. Adsorption procedure

Batch adsorption experiments were conducted by agitating 0.1 g powder of mistletoe leaves with 50 ml solution containing 10, 20, and 30 mg/l concentration of each metal ion in flasks at 250 rpm using a water-batch shaker at 303 K. The effect of pH on the adsorption of metal ions on mistletoe leaves was studied by changing pH of the adsorption solution from 1 to 6. The effect of contact time on the removal of Pb(II) and Cd(II), at the optimum pH, was investigated by changing shaking time of the adsorption solutions from 10 to 200 min. The effect of biosorbent dose on the removal of 30 mg/l of Pb(II) and Cd(II) was determined by varying the dosage from 2.0 to 16.0 g/l. Cadmium and lead sorption isotherms at optimum pH were studied at 303, 308, 313, and 318 K by varying the concentrations of both Pb(II) and Cd(II) in range of 10–210 mg/l. Liquid samples of the adsorption solutions were collected at regular intervals. The liquid phase was separated from adsorption mixtures by filtering through the filter paper. Concentrations of Pb(II) and Cd(II) in liquid phase were determined using a voltammetry method [29].

The adsorption capacity, q_t (mg/g), defined as an amount of Cd(II) and Pb(II) ions per unit mass of adsorbent, is calculated using the following formula:

$$q_t = \frac{C_i - C_t}{C_i} \times \frac{V}{m} \quad (1)$$

where C_i is the initial concentration of metal ions (mg/l), C_t is the concentration of metal ions at time t (mg/l), V is the volume of adsorbate (l), and m is the mass of adsorbent (g).

2.3. Data analysis

2.3.1. Kinetic models

In order to evaluate the controlling mechanism of adsorption process of Pb(II) and Cd(II) on mistletoe leaves such as mass transfer and chemical reaction, the pseudo-first-order model, the pseudo-second-order model, and the intraparticle diffusing model [30–34] were used to fit the experimental data.

The pseudo-first-order equation is represented as:

$$q_t = q_e(1 - e^{-k_1 t}) \tag{2}$$

where q_e is the amount of metal ions absorbed at equilibrium (mg/g), q_t is the amount of metal ions absorbed at time t (mg/g), and k_1 is the rate constant of pseudo-first-order sorption (l/min).

The pseudo-second-order model is given by equation:

$$q_t = \frac{q_e^2\, k_2 t}{1 + t k_2 q_e} \tag{3}$$

where q_e is the amount of metal ions absorbed at equilibrium (mg/g), q_t is the amount of metal ions absorbed at time t (mg/g), and k_2 is the rate constant of pseudo-second-order model (g/mg min).

The intraparticle diffusing model proposed by Weber and Morris [35] was used to describe the process of the mass transfer characterized by either external mass transfer or intraparticle diffusion or both. The relation between the amount of adsorbate on the adsorbent surface and retention time is given as:

$$q_t = k_i t^{1/2} + C \tag{4}$$

where q_t is the amount of metal ions absorbed at time t (mg/g), k_i is the rate constant of intraparticle diffusion (mg/g min), and C is a constant.

2.3.2. Adsorption isotherm models

The adsorption process of Pb(II) and Cd(II) from solution to adsorbent surface leads to a thermodynamically defined distribution whose equilibrium at a fixed temperature and pH can be described by an isotherm equation whose parameters express the surface properties and affinity of the adsorbent. Therefore, the adsorption isotherm should be described mathematically based on the experimental data of the adsorption system. In this study, four isotherm models, such as Langmuir, Freundlich, Toth, Redlich-Peterson, and Temkin, were used to analyze the appropriate adsorption isotherm [36–41].

Langmuir model assumes a monolayer adsorption on a surface with a finite number of identical sites, which all sites are energetically equivalent and there is no interaction between adsorbate molecules. The general Langmuir sorption model is expressed by:

$$q_e = \frac{Q_{\max} K_L C_e}{(1 + K_L C_e)} \tag{5}$$

where C_e is the metal ion concentration in solution at equilibrium (mg/l), q_e is the amount of adsorbed metal ions per unit of adsorbent (mg/g), K_L is Langmuir isotherm constant (l/mg) related to the theoretical maximum adsorption capacity, $Q_{\max}$ (mg/g), and energy of adsorption.

Freundlich model is an empirical equation based on adsorption on a heterogeneous surface and is expressed by:

$$q_e = K_F\, C_e^{1/n} \tag{6}$$

where C_e is the metal ion concentration in solution at equilibrium (mg/l), q_e is the amount of adsorbed metal ions per unit of adsorbent (mg/g), n is the constant that related to adsorption intensity, and K_F is the Freundlich isotherm constant (mg/g) related to adsorption capacity. The larger the value of K_F indicates the greater adsorption process.

Toth model is a modified Langmuir equation to reduce the error between experimental data and predicted values of equilibrium adsorption data. The model can be represented by the following equation:

$$q_e = \frac{a C_e}{(b + C_e^d)^{1/d}} \tag{7}$$

where a is the Toth maximum adsorption capacity (mg/g), b is the Toth equilibrium constant, and d is the Toth model exponent.

Redlich-Peterson isotherm is the first three-parameter isotherm model that incorporates the features of both the Langmuir and Freundlich isotherm models. The model may be used to represent adsorption equilibrium over a wide concentration range, and it can be described as following:

$$q_e = \frac{K_R C_e}{(1 + a_R C_e^{\beta})} \tag{8}$$

where K_R (l/g), a_R (l/mg), and β (between 0 and 1) are empirical parameters without physical meaning.

Temkin isotherm model assumes that the heat of adsorption of all the molecules in layer decreases linearly with coverage due to adsorbent–adsorbate interactions. The model can be expressed as:

$$q_e = \frac{RT}{b_T} \ln (K_T C_e) \tag{9}$$

where R is the universal gas constant (8.314 J/mol K), K_T is the equilibrium binding constant (l/mg), and b_T is the variation of adsorption energy (kJ/mol).

In order to evaluate thermodynamic parameters of the adsorption process such as Gibbs free energy ΔG (kJ/mol), change of enthalpy ΔH (kJ/mol), and change of entropy ΔS (J/mol K), the equations [42] were used:

$$\Delta G = -RT \ln K_0 \tag{10}$$

$$K_0 = \frac{C_s}{C_e} \tag{11}$$

where K_0 is the equilibrium constant, C_e is concentration of metal ions in solution at equilibrium (mg/l), C_s is concentration of metal ions on the adsorbent surface at equilibrium (mg/g), T is solution temperature (K), and R is the gas constant (8.314 J/mol K).

The change of enthalpy ΔH and change of entropy ΔS of adsorption were calculated from the slope and intercept from the plot of ln (K_0) vs. $1/T$ according to the van't Hoff equation at different adsorption temperatures:

$$\ln (K_0) = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{12}$$

Parameters of isotherm models were determined by nonlinear optimization technique to generate the residual root mean square error (RMSE), whose value indicate the match between the experimental data and model prediction. In general, the smaller the RMSE value, the better the curve fitting [43,44].

$$\text{RMSE} = \sqrt{\frac{1}{n-1} \sum\nolimits_{n-1}^{n} (q_{e,\text{exp}} - q_{e,\text{cal}})^2} \tag{13}$$

where $q_{e,\text{exp}}$ is the equilibrium adsorption capacity found from the batch experiment, $q_{e,\text{cal}}$ is calculated from the isotherm model for corresponding to C_e, and n is the number of observation.

3. Results and discussion

3.1. Characteristics of adsorbent

The FTIR spectra of mistletoe leaves before and after Pb(II) and Cd(II) adsorption are showed in Fig. 1(a)–(c), respectively. In FTIR spectra of mistletoe leaves (Fig. 1(a)), a broad absorption band at 3,363 cm^{-1} is due to O–H stretching vibrations of cellulose and hemicelluloses. The band at 2,921 cm^{-1} corresponds to CH_2 and CH_3 stretching vibrations. The band at 1,735 cm^{-1} is due to carbonyl groups (C=O) stretching and vibration of acetyl groups of hemicelluloses. The absorption peak at 1,619 cm^{-1} suggests the presence of oxygen-containing compounds. The broad peak at 1,059 cm^{-1} is due to C–OH stretching vibration of cellulose backbone [45–47]. The FTIR spectra of mistletoe leaves after the adsorption of either Pb(II) (Fig. 1(b)) or Cd(II) (Fig. 1(c)) show the intensity of the peaks at 3,363, 1,619, and 1,059 cm^{-1} is significantly reduced. The peaks at 1,619 cm^{-1} shift to lower wavenumber at 1,634 cm^{-1}. The FTIR spectrum of mistletoe leaves after the adsorption of Pb(II) or Cd (II) is similar to each other, indicating that these metal ions were adsorbed on mistletoe leaves in the same mechanism involving mainly protonated –OH groups.

SEM images of virgin and exhausted biosorbents are shown in Fig. 2(a)–(c), respectively. It is clear from the SEM images that the external surfaces of the virgin biosorbent (Fig. 2(a)) were rough and revealed porous structures, while the exhausted biosorbent (Fig. 2(b) and (c)) shows metal layer on its surface. This leads to significant change on the surface of biosorbent before and after the adsorption of Pb(II) and Cd(II).

3.2. Effect of pH

The effect of pH on the adsorption of Cd(II) and Pb(II) ions onto the mistletoe leaves is illustrated in Fig. 3. As shown, the adsorption capacity of Cd(II) and Pb(II) increases with increasing pH of the solution and reaches the maximum value at pH 5.5. The change of the adsorption capacity at different pH values can be explained as the competition of hydrogen ion for adsorption sites on the adsorbent surface. Similar trend has also been reported in study of Cd(II) adsorption on lalang leaf powder and adsorption of Pb(II) on bael tree leaves powder [23,26]. Also, the pH_{zpc} of mistletoe leaves shown in Fig. 4 provides a favorable condition for the adsorption process of metals on its surface. The pH_{zpc} value of mistletoe leaves was found to be at 7.8. At pH less than pH_{zpc}, the absorbent surface becomes positively charge due to the adsorption of cations

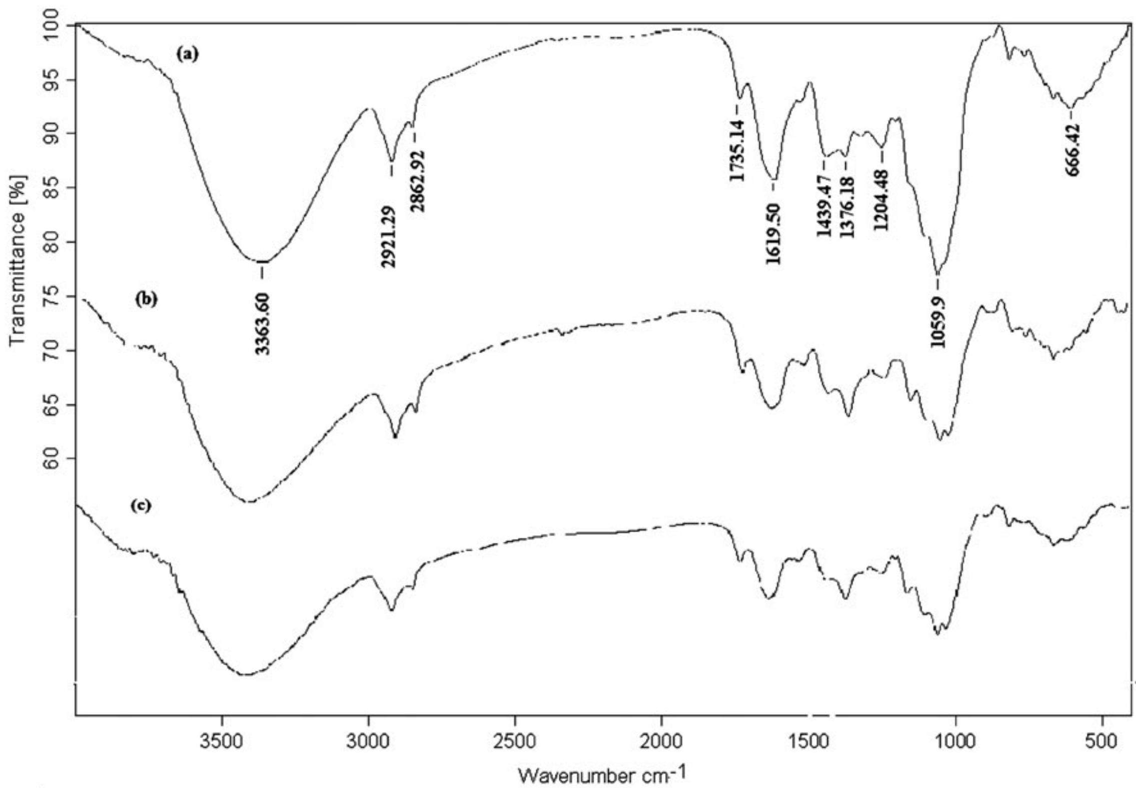

Fig. 1. FTIR spectra of (a) mistletoe leaves, (b) after adsorption of Pb(II), and (c) after adsorption of Cd(II).

such as H^+, Pb^{2+}, and Cd^{2+}. In contrast, at pH greater than pH_{zpc}, the concentration of anion OH^- increases, leading to the surface of mistletoe leaves becomes negatively charged. Further, because both Pb(II) and Cd(II) ions are mainly in the simple cation species as Pb^{2+} and Cd^{2+} at $pH \leq 6$ [48], they are strongly attracted by available active sites on the adsorbent surface. Thus, pH and metal species in the solution hold important roles in the adsorption process. At pH greater than or equal to 7, Pb(II) and Cd(II) ions begin to precipitate in the form of $Pb(OH)_2$ and $Cd(OH)_2$, respectively. This leads to an increase in the removal efficiency by the combination of precipitation–adsorption on the adsorbent surface. To avoid the precipitate lead and cadmium hydroxyl forms in further experiments, pH 5.5 was selected. As can be seen in FTIR spectra shown in Fig. 1(b) and (c), the binding Cd(II) and Pb(II) ions with active sites mainly involves in the –OH groups of cellulose backbone of mistletoe leaves. In addition, carboxyl groups may be also responsible for the metal binding since carboxyl groups have pKa values between 3 and 4. This trend in pH suggests that by reducing the pH, the bound metal ions can be desorbed [49].

3.3. Effect of contact time

The results of study of contact time effect on the adsorption of Pb(II) and Cd(II) by mistletoe leaves are shown in Fig. 5. As shown in the results, the adsorption rate of Cd(II) and Pb(II) ions occurred quickly in the initial stage, then slowed down, and reached the plateau after 150 min for both Pb(II) and Cd(II). This adsorption behavior of these metal ions could be explained using the number of available active sites on the surface of adsorbent. During the early stage of the adsorption reaction, all active sites are available, facilitating the quickly reduction of the metal ion concentration in the liquid phase. The reaction rate later decreases as the number of adsorbent active sites is reduced, leading to the equilibrium adsorption of metal ions between the liquid and solid phases. From results obtained, 150 min of adsorption time was sufficient to achieve the equilibrium condition for the Pb (II) and Cd(II) ions adsorption onto the biosorbent.

3.4. Effect of adsorbent dose

The effect of adsorbent dose on adsorption capacities of Pb(II) and Cd(II) is presented in Fig. 6. As

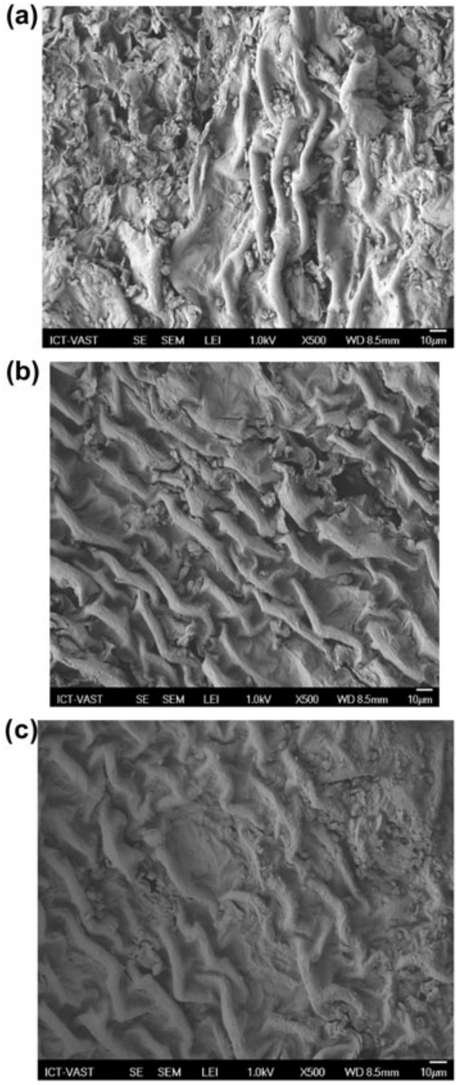

Fig. 2. SEM images of (a) mistletoe leaves, (b) after adsorption of Pb(II), and (c) after adsorption of Cd(II).

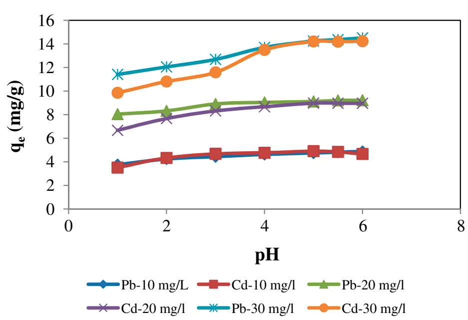

Fig. 3. Effect of pH on the adsorption of mistletoe leaves for Pb(II) and Cd(II) at 303 K, 150 min contact time, and adsorbent dose 2 g/l.

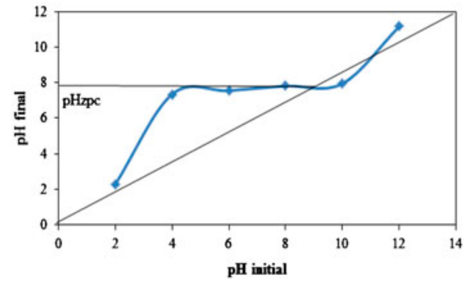

Fig. 4. pH_{zpc} of mistletoe leaves.

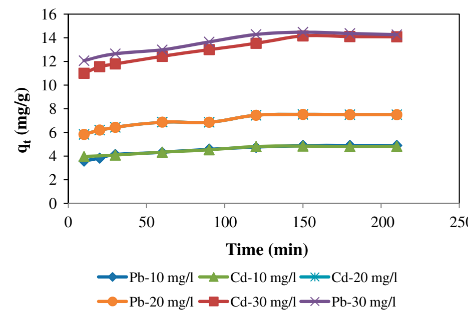

Fig. 5. Effect of contact time on the adsorption of mistletoe leaves for Pb(II) and Cd(II) at 303 K, pH 5.5, and adsorbent dose 2 g/l.

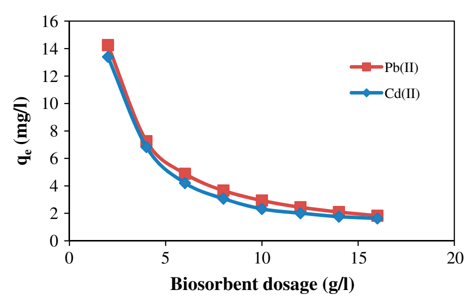

Fig. 6. Effect of adsorbent dose on the adsorption of mistletoe leaves for Pb(II) and Cd(II) at 303 K, pH 5.5, and 150 min of contact time.

shown in the results, the adsorption capacity reached 14.3 mg/g for Pb(II) and 13.7 mg/g for Cd(II) at 2.0 g/l of mistletoe leaves and then decreased to 1.83 and 1.63 mg/g at 20 g/l of mistletoe leaves for Pb(II) and Cd(II), respectively. Such adsorption behavior is related to the specific surface adsorption of mistletoe leaves. The increase of adsorbent dose leads to surplus of adsorption sites on the adsorbent surface so that no further Pb(II) and Cd(II) ions adsorption occur.

3.5. Adsorption kinetic

The nonlinear plots for the pseudo-first-order model and the pseudo-second-order model from Eqs. (2) and (3) for Pb(II) and Cd(II) are showed in Figs. 7 and 8, respectively. The parameters obtained for models are showed in Table 1. From results, it is seen that the experimental data fitted the models, especially the pseudo-second-order model for both Pb (II) and Cd(II). However, the RMSE value calculated from Eq. (13) for the pseudo-first-order model was very high, 14.6 at initial Pb(II) concentration of 30 mg/l. This indicates that the adsorption process of Pb(II) onto mistletoe leaves followed only the pseudo-first-order model at initial concentration smaller than 30 mg/l. As can be seen also in Table 1, the adsorption rate constants, k_2 of the pseudo-second-order model, decrease with increasing initial concentration of both Pb(II) and Cd(II). This is consequence of high initial concentration of metals leading to reduced diffusion rate of metal ions in the boundary layer and to enhance diffusion rate in the solid. The adsorption process strongly followed toward the pseudo-second-order model, indicating the chemisorption may be rate limiting in the adsorption of mistletoe leaves for Pb(II) and Cd(II). Similar trend has been also observed in the studies of the adsorption of Cd(II) on *Terminalia catappa* linn leaf powder [50], adsorption of cadmium (II) and lead(II) ions onto *Ficus cassia* leaves [28], adsorption of copper(II) on dry fruit product [51], and adsorption of Cu(II) on peat [32]. Their data have

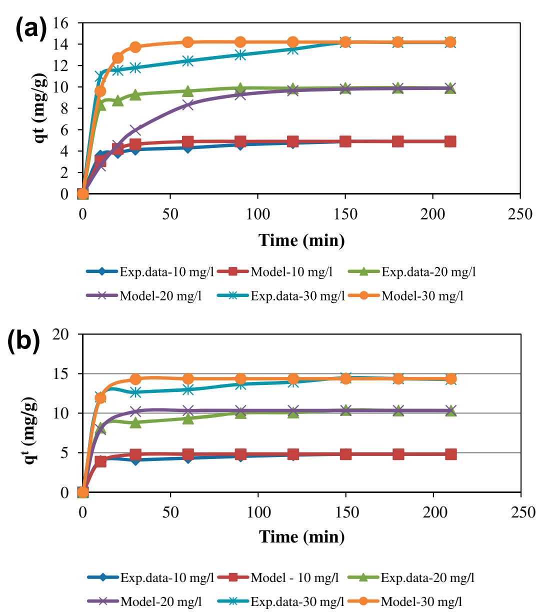

Fig. 7. Plot of the pseudo-first-order model, (a) for Pb(II) and (b) for Cd(II) at 303 K.

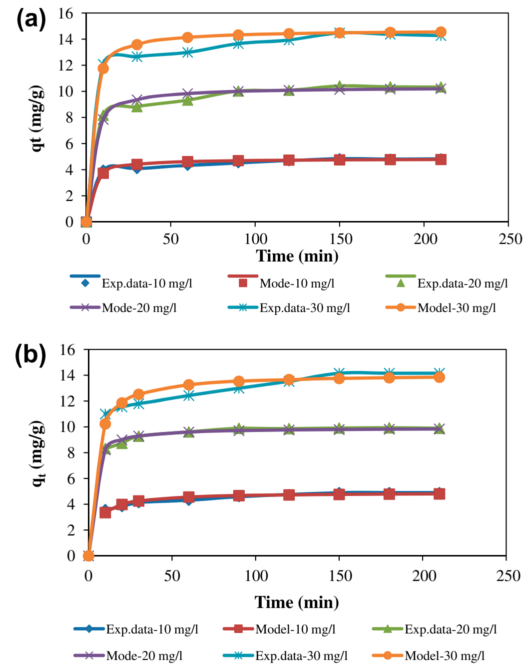

Fig. 8. Plot of the pseudo-second-order model, (a) for Pb (II) and (b) for Cd(II) at 303 K.

suggested that the pseudo-second-order model provides the best correlation data for the rate-limiting step that may be sorption or chemical sorption involving valence forces through sharing or exchange of electron between sorbent and sorbate.

Parameters of the intraparticle diffusion model obtained from Eq. (4) for different concentrations of Pb(II) and Cd(II) are also included in Table 1. According to the Weber and Morris Equation, a plot of q_t against $t^{1/2}$ yields a straight line which should pass through the origin if intraparticle diffusion is involved in rate-limiting step of the adsorption process. However, the plots shown in Fig. 9 did not pass through the origin, indicating the rate of adsorption processes was also contributed by the mass transport mechanism of Pb(II) and Cd(II) from the solution through liquid film to the biosorbent exterior surface [31,52].

3.6. Adsorption isotherm and thermodynamic

The plots of the nonlinear isotherm models from Eqs. (5)–(9) for Pb(II) and Cd(II) adsorption process at different temperatures are presented in Figs. 10 and 11, respectively. Calculated parameters of Langmuir, Freundlich, Toth, Redlich-Peterson, and Temkin models for Pb(II) and Cd(II) adsorption on mistletoe leaves are summarized in Tables 2 and 3, respectively. As shown in results, the RMSE values obtained from all isotherm models suggest that the experimental data

Table 1
Parameters of kinetic models for lead(II) and Cd(II) adsorption processes

Initial conc. (mg/l)		Pseudo-first-order model		Pseudo-second- order model		Intraparticle diffusion model		
		k_1 (l/min)	RSM	k_2 (g/mg min)	RSM	k_i (mg/g min)	C	RSM
Pb(II)	10	0.018	0.40	0.048	0.168	0.118	3.361	0.122
	20	0.310	3.00	0.030	0.148	0.017	8.890	0.397
	30	0.112	14.60	0.018	0.609	0.298	10.170	0.188
Cd(II)	10	0.165	0.338	0.068	0.200	0.086	3.682	0.068
	20	0.146	0.673	0.0300	0.329	0.202	7.745	0.225
	30	0.177	0.872	0.027	0.661	0.218	11.44	0.207

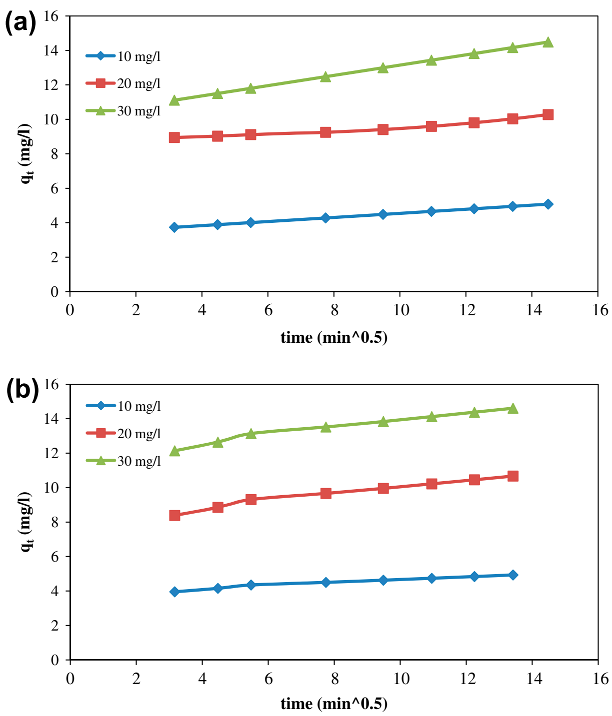

Fig. 9. Intraparticle diffusing model, (a) for Pb(II) and (b) for Cd(II).

fitted isotherm models, but the best fit is obtained with Redlich-Peterson and Toth models, followed by Langmuir, Temkin, and Freundlich models. The values β in Redlich-Peterson and values of parameter d in Toth model are close to unit for both metals, especially for of Pb(II), meaning that the isotherms are approaching the Langmuir isotherm [32]. The Freundlich and Temkin models do not well fit the experimental data obtained for both Pb(II) and Cd(II), indicating that the homogenous surface of adsorbent and monolayer adsorption [52].

The effect of temperature on the Pb(II) and Cd(II) adsorption process on mistletoe leaves has been studied at 303, 308, 313, and 318 K. It was observed that the adsorption capacity for both metals increases with increasing in temperature. This can be explained that the increase in maximum capacity with temperature is due to increase in the number of available active sites on the adsorbent and the decrease in boundary layer thickness surrounding the adsorbent leading to reduction in the mass transfer resistance of adsorbate in the boundary layer. According to Langmuir model, the maximum capacity, Q_{max}, for Cd(II) was found to be 44.8, 47.1, 49.1, and 50.07 mg/g at 303, 308, 313, and 318 K, respectively. Meanwhile, the maximum adsorption capacities of Pb(II) are higher than those of Cd(II) at to the same temperatures (59.76, 63.25, 66.30, and 68.53 mg/g, respectively). Comparison of the maximum adsorption capacity (Q_{max}) of mistletoe leaves with those of some other plant leaves reported in the literatures is presented in Table 4. It shows that mistletoe leaves are among the adsorbents that have high maximum capacity for Pb (II) and Cd(II) ions. The difference in adsorption capacity for Pb(II) or Cd(II) observed in Table 4 can be explained by differences in the concentrations of metal binding compounds that are available in plant leaves.

The thermodynamic parameters for Pb(II) and Cd (II) adsorption on mistletoe leaves including ΔG, ΔH, and ΔS are calculated from Eqs. (10)–(12). The results obtained are given in Table 5. The negative values of Gibbs energy (ΔG) confirm the spontaneous nature and feasibility of the adsorption process. The ΔG values decreasing from −2.184 to −2.383 kJ/mol for Cd (II) and from −1.975 to −2.335 kJ/mol for Pb(II) at 303–318 K indicate that the favorable Cd(II) and Pb(II) adsorption processes take place with increasing temperature. The enthalpy change ΔH is positive indicating the endothermic nature of the adsorption process. The positive value of entropy ΔS reflects the affinity of the biosorption for Cd(II) and Pb(II) ions and suggests increased randomness at the adsorbent/solution surface during the adsorption [31]. The values of ΔG

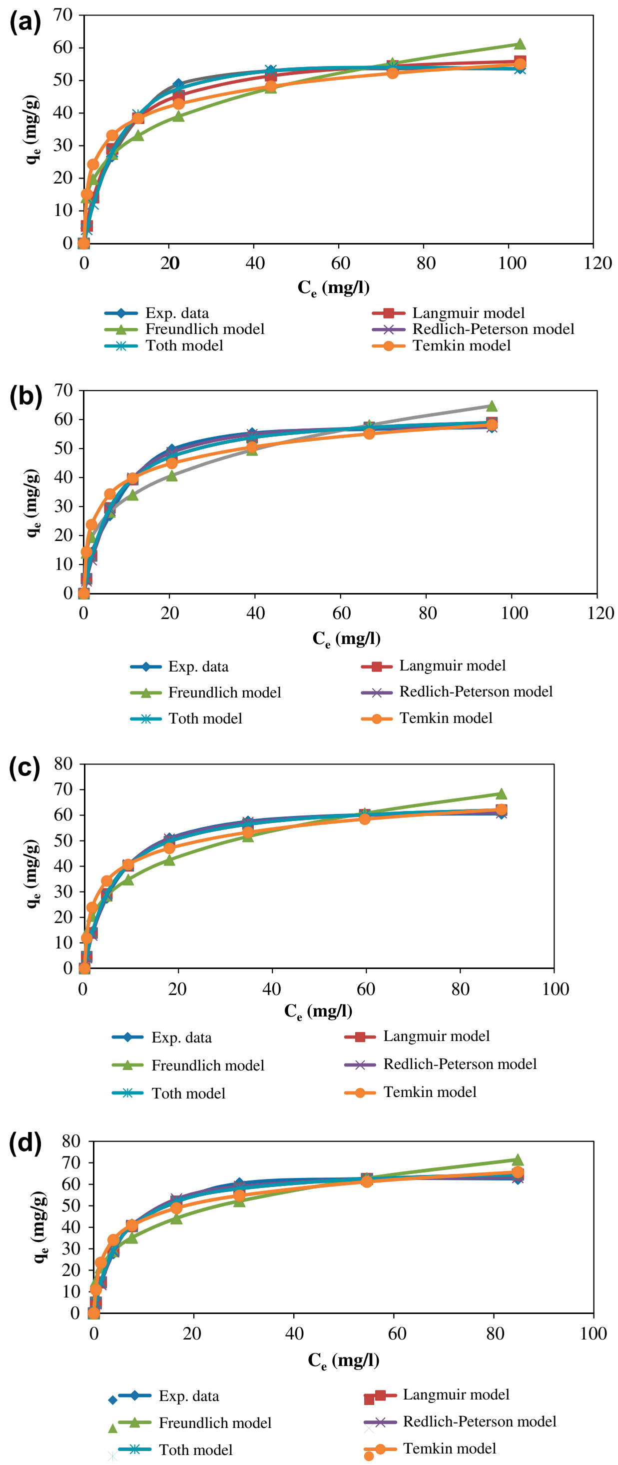

Fig. 10. Nonlinear plots of isotherm models for the adsorption of Pb(II) on mistletoe leaves at (a) 303 K, (b) 308 K, (c) 313 K, and (d) 318 K.

calculated for the Cd(II) and Pb(II) do not differ significantly from each other. However, the ΔS value for Pb (II) is more positive than that of Cd(II), suggesting that

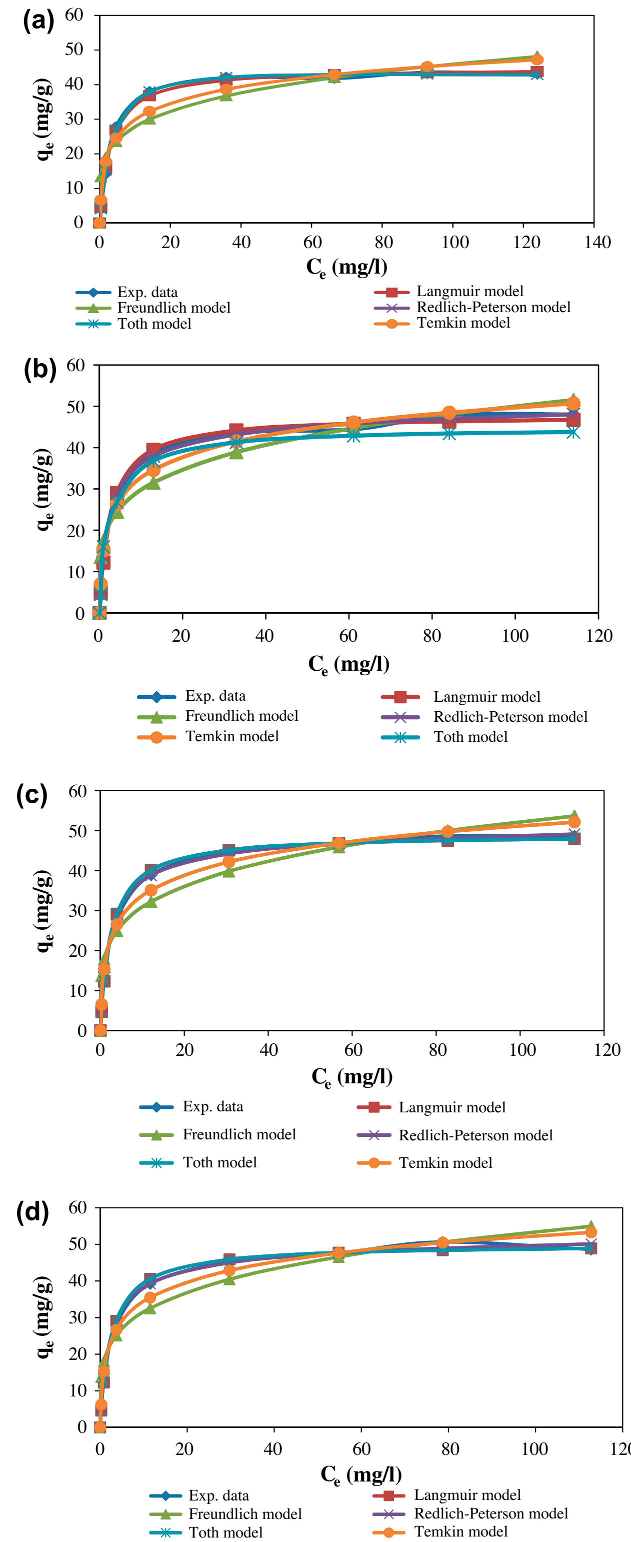

Fig. 11. Nonlinear plots of isotherm models for adsorption of Cd(II) on mistletoe leaves at (a) 303 K, (b) 308 K, (c) 313 K, and (d) 318 K.

Table 2
Isotherm parameters for Pb(II) adsorption on mistletoe leaves at different temperatures

Adsorption isotherm	Parameter	Temperature (K)			
		303	308	313	318
Langmuir	K_L (l/mg)	0.140	0.144	0.166	0.190
	$Q_{\max}$ (mg/g)	59.76	63.25	66.30	68.53
	RMSE	1.945	1.669	1.029	1.282
Freundlich	K_F (mg/g)	15.60	16.30	17.85	19.38
	n	3.389	3.300	3.340	3.401
	RMSE	6.936	6.732	6.833	7.491
Redlich-Peterson	K_R (l/g)	6.224	7.412	9.654	11.35
	β	1.138	1.091	1.052	1.060
	a_R (l/mg)	0.056	0.082	0.114	0.131
	RMSE	1.089	1.291	0.692	0.918
Toth	a (mg/g)	125.7	101.6	88.12	91.51
	b	17.73	12.58	8.661	7.634
	d	1.137	1.088	1.052	1.063
	RMSE	1.089	1.291	0.931	0.918
Temkin	b_T (l/mg)	0.315	0.295	0.272	0.257
	K_T (kJ/mol)	0.009	0.009	0.008	0.007
	RMSE	6.780	6.453	5.691	5.512

Table 3
Isotherm parameters for Cd(II) adsorption on mistletoe leaves at different temperatures

Adsorption isotherm	Parameter	Temperature (K)			
		303	308	313	318
Langmuir	K_L (l/mg)	0.323	0.365	0.372	0.372
	$Q_{\max}$ (mg/g)	44.81	47.85	49.10	50.07
	RMSE	1.071	1.425	1.151	1.402
Freundlich	K_F (mg/g)	16.85	17.65	18.23	18.58
	n	4.593	4.424	4.280	4.361
	RMSE	5.778	5.052	5.297	5.458
Redlich-Peterson	K_R (l/g)	12.53	22.29	22.44	22.94
	a_R (l/mg)	1.003	0.947	0.955	0.955
	β	0.232	0.584	0.553	0.554
	RMSE	0.781	0.715	0.683	1.033
Toth	a (mg/g)	56.21	36.13	38.73	39.42
	b	4.302	1.710	1.806	1.801
	d	1.042	0.947	0.955	0.955
	RMSE	0.782	0.915	0.682	1.033
Temkin	b_T (kJ/mol)	0.036	0.345	0.341	0.338
	K_T (l/mg)	0.008	0.008	0.008	0.008
	RMSE	3.620	2.305	2.428	2.562

the affinity adsorption for Pb(II) ions much stronger than that for Cd(II).

3.7. Desorption/sorption study

In order to check the reusable of mistletoe leaves, this biosorbent was subjected to several loading and elution experiments with Pb(II) and Cd(II) ions from acid–lead battery wastewater that contains 12 mg/l Pb(II) and 0.56 mg/l Cd(II). The solution of 0.05 M EDTA was used as a elution solution for removal of both Pb(II) and Cd(II) from the exhausted biosorbent. For adsorption, the wastewater sample (0.5 l) with pH 2.5 was filtered through filter paper to

Table 4
Comparison of maximum adsorption capacities of mistletoe leaves with other plant leaves as biosorption for Pb(II) and Cd(II)

Biosorbent	Metal	Q_{max} (mg/g)	Reference
Pine cone	Cd	14.706	[9]
Tectona grandis L.F. (teak leaves powder)	Cd	29.94	[18]
Prunus avium leaves	Cd	45.45	[19]
Carica papaya leaf powder	Pb	11.13	[22]
Bael leaves	Pb	104	[23]
(Neem) leaf	Pb	300	[25]
Ficus Hispida leaves powder	Pb	32.42	[27]
Ficus carcia leaves	Cd	30.30	[28]
	Pb	34.36	
Ulmus carpinifolia tree leaves	Cd	80.0	[29]
	Pb	201.1	
Terminalia catappa Linn leaf	Cd	35.84	[50]
Xanthated rubber (Hevea brasiliensis) leaf powder	Pb	166,7	[51]
Mistletoe leaves	Cd	44.81 at 30°C	Our work
		47.10 at 35°C	
		49.11 at 40°C	
		50.07 at 45°C	
	Pb	59.76 at 30°C	
		63.25 at 35°C	
		66.30 at 40°C	
		68.53 at 45°C	

Table 5
Thermodynamic parameters for Pb(II) and Cd(II) adsorption on mistletoe leaves

	Cd(II)			Pb(II)		
Temperature (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)
303	−2.184	2.076	14.06	−1.975	5.293	23.99
308	−2.420			−2.090		
313	−2.325			−2.214		
318	−2.383			−2.335		

remove any suspended solid. pH of the sample was adjusted to 5.5, and 1.0 g of the mistletoe leaf powder then was added. The mixture in a glass beaker was agitated for 200 min. After equilibrium, the liquid phase was separated and taken for analysis of Pb(II) and Cd(II). For desorption, the exhausted biosorbent was mixed with 50 ml of 0.05 M EDTA solution in a glass beaker. The mixture was mixed by a mechanical mixer for 100 min. The solid phase was then separated by filter through the filter paper and washed several times with distilled water at pH 5.5. The resulting biosorbent was dried at 80°C. This step was considered

Table 6
Removal percentage of lead(II) and Cd(II) from acid–lead battery wastewater using mistletoe leaves as biosorbent

		Removal percentage of Pb(II) and Cd(II)		
Composition	Initial concentration (mg/l)	Cycle 1	Cycle 2	Cycle 3
Pb	12.1	99.81	99.58	96.47
Cd	0.56	99.74	98.82	96.21

as a first cycle. In the next cycle, the resulting biosorbent obtained in the first cycle was added in a flask containing 0.5 l of the wastewater. Similar experiments of sorption/desorption were performed as in the first cycle. The results obtained shown in Table 6 indicate that the removal percentage of the mistletoe leaves for Pb(II) and Cd(II) in acid–lead battery wastewater was unchanged after two cycles and slightly reduced only at third cycle. From the results, it could be concluded that mistletoe leaves can be multi-time used for removal of Pb(II) and Cd(II) from aqueous solution.

4. Conclusions

This study shows that absorbent material produced from underutilized biomass mistletoe leaves is an effectively biosorbent for Pb(II) and Cd(II) ions in aqueous solutions. The maximum adsorption capacity for Pb(II) and Cd(II) reached at pH 5.5 and 150 min of contact time. The adsorption kinetic for both metal ions is found to follow the pseudo-second-order model. Among the two-parameter isotherm models, the Langmuir model is found to well describe the experimental data for both Pb(II) and Cd(II). The three parameter models, Redlich-Peterson and Toth models, well fit with the experimental data, suggesting that these two models can be used to describe the adsorption of these metal ions on mistletoe leaves. The adsorption process of Pb(II) and Cd(II) is temperature dependent. The maximum adsorption capacities of both metal ions increase with increasing in temperature, and the thermodynamic parameters such as ΔG and ΔS are favorable for Pb(II) and Cd(II) adsorption on this biosorbent. In desorption/sorption study, three cycles sorption/desorption were used to remove Pb(II) and Cd(II) from acid–lead battery wastewater. It was found that the removal percentage of mistletoe leaves for both metal ions was virtually unchanged after three cycles using 0.05 M EDTA solution as an elution solution.

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