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Removal of Pb(II) from aqueous solutions by *Phytolacca americana* L. biomass as a low cost biosorbent

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Abstract Screening a new biosorbent with low cost and high efficiency from a native plant material is a key to the adsorption of heavy metal ions from wastewater. In this study, the potential of *Phytolacca americana* L. as a biosorbent for Pb(II) removal from aqueous solutions was investigated. Experiments were performed to evaluate the effect of biosorbent dosage, pH, initial Pb(II) concentration and contact time on the Pb(II) removal. The results indicated that the hydroxyl, carboxyl and amine groups may take part in Pb(II) binding. HNO₃-modified *P. americana* (HPAL) showed a significant higher uptake capacity compared to original *P. americana* (PAL) ($p < 0.05$). A dose of 20 g L⁻¹ of biosorbents in solutions with an initial pH of 6.0, an initial Pb(II) concentration of 30 mg L⁻¹ and a contact time of 120 min resulted in the maximum Pb(II) removal efficiency. The Freundlich isotherm gave a better fit than the Langmuir isotherm revealed that the biosorption was potentially multilayer. Further, the adsorption kinetics followed a pseudo second-order model, which implied that the biosorption was mainly a chemisorption process. The thermodynamic properties showed that the Pb(II) adsorption onto the *P. americana* biomass was feasible, spontaneous and exothermic in nature. Both physisorption and chemisorption were involved in the biosorption of Pb(II) onto the surface of *P. americana* biomass through electrostatic interaction and ion exchange. Additionally, desorption studies revealed promising regeneration potential of these biosorbents. The present study showed that *P. americana* biomass could be used

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as a low-cost, eco-friendly and effective biosorbent for the Pb(II) removal from wastewater.

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1. Introduction

The wastewater contaminated with heavy metal ions has become a serious environmental issue in recent years (Farooq et al., 2010; Fomina and Gadd, 2014). Many industrial activities such as mining, electroplating and smelting resulted in the release of heavy metal ions into water (Cerino-Cordova et al., 2013; Sarada et al., 2014). Lead (Pb) has been recently gained an increasing attention owing to its high toxicity to human body (Gundogdu et al., 2009). It can cause reproductive system and central nervous system damage (Reddy et al., 2010). Therefore, there is an imperative need for the removal of Pb(II) from wastewater. Some conventional methods such as chemical precipitation, ion exchange and membrane separation have been widely used for removing Pb(II) from wastewater (Kurniawan et al., 2006a; Fu and Wang, 2011). These practices can remove Pb(II) from wastewater, but have several disadvantages such as high cost, high energy input and secondary pollution (Guo et al., 2009; Tasar et al., 2014). Hence, it is essential to develop cost-effective and eco-friendly approach to remove Pb(II) from wastewater.

Compared with the conventional methods, biosorption, as an emerging and attractive method, has gained an increasing attention on the removal of heavy metal ions from wastewater owing to its high efficiency, low cost and non-secondary pollution (dos Santos et al., 2011; Kelly-Vargas et al., 2012; Tasar et al., 2014; Liu et al., 2014). The focus of the adsorption process was to obtain an abundant and inexpensive adsorbent with high adsorption capacity. A variety of traditional adsorbents, for example activated carbon (Monser and Adhoum, 2009; Rao et al., 2009), mineral materials (Mhamdi et al., 2013; Figueiredo and Quintelas, 2014) and inorganic materials (Luo et al., 2014) have been utilized to remove Pb(II) from wastewater. However, the high cost and limited reusability hinder the widespread application of these adsorbents (Kurniawan et al., 2006b). Recently the use of agricultural, industrial and forest wastes and by-products as biosorbents to remove heavy metal ions from wastewater has become increasingly popular, because they are abundant, inexpensive and efficient (Sud et al., 2008; Saka et al., 2012; Ghasemi et al., 2014). A large number of waste materials, such as fruit cortex (Kelly-Vargas et al., 2012), peanut shell (Tasar et al., 2014), garlic peel (Liu et al., 2014), *Lemna perpusilla* Torr. (Tang et al., 2013), olive tree (Ronda et al., 2013), and *Eupatorium adenophorum* (Guo et al., 2009) have been reported for the removal of Pb(II) from aqueous solutions. When these waste materials were used as adsorbents, their chemical modification may increase the efficiency of heavy metal ions adsorption. Pretreating with acid or alkali was the common modification methods (Lasheen et al., 2012; Calero et al., 2013). However, screening new economical, easily available and highly effective adsorbents are still needed.

Phytolacca americana L. is a perennial herbaceous plant of about 1–2 m in height. Due to its fast growth and enormous

biomass, the plant is now widely distributed in South China (Liu et al., 2010), which may break the balance of native habitats. It is rich in lignin, hemicellulose and cellulose, which may contain abundant functional groups bonded with metal ions. As a type of available biomaterial, *P. americana* may be a potential biosorbent for the Pb(II) removal from wastewater.

In the present study, the potential of *P. americana* biomass as a biosorbent for the Pb(II) removal from aqueous solutions was investigated. As per literature review, there are no reference to the work involving the use of *P. americana* biomass as a biosorbent to remove Pb(II) ion from aqueous solution. The objectives of this study are: (1) to compare the efficiencies between the raw and HNO₃-modified *P. americana* as biosorbents for removing Pb(II); (2) to assess the effects of various factors including biosorbent dosage, pH, initial Pb(II) concentration, and contact time on the Pb(II) removal efficiencies; and (3) to deal with the industrial wastewater to better simulate possible application of heavy metal ions removal in an industrial process.

2. Materials and methods

2.1. Preparation of stock solution

All the chemicals and reagents used in the present study were of analytical grade. In order to avoid interference with other elements in the wastewater, the tests were carried out with aqueous solutions of Pb(II). The stock solution of Pb(II) (1000 mg L⁻¹) was prepared by dissolving the weighed amount of Pb(NO₃)₂ in double distilled water. Concentrated HNO₃ (2–3 drops) were added in the stock solution to avoid precipitation. The working solutions of different concentration were prepared by progressive dilution of the stock solution using deionized water.

2.2. Preparation of the biosorbent

P. americana (PAL) was collected from Wenjiang, Sichuan Province. The raw materials were rinsed thoroughly with deionized water and dried in an oven at 60 °C for 72 h. The dried materials were crushed and passed through 60-mesh sieve, and placed in a desiccator for further study.

HNO₃-modified *P. americana* (HPAL) was obtained by Lasheen et al. (2012), Calero et al. (2013). Treatments were conducted by soaking and shaking the PAL (10 g) in 0.1 mol L⁻¹ HNO₃ solution (1.0 L) in a rotary shaker for 6 h at constant temperature (25 ± 0.5 °C). After that, the materials were washed thoroughly with distilled water for several times until the pH became neutral. Then the treated materials were dried overnight at 60 °C. The same treatment was carried out by using deionized water instead of 0.1 mol L⁻¹ HNO₃. There was no significant weight loss during the modification process.

2.3. Characterization of the biosorbent

Proximate analysis (i.e. moisture, ash, volatile matter and fixed carbon) of PAL and HPAL was carried out according to the referred methods (Calero et al., 2013). Elemental analysis was performed with a CHNS analyzer (EA112, Thermo Finnigan, USA) to obtain the percentage of C, H, N and S. The O content was estimated by difference to 100%.

In order to identify the possible functional groups involved in the Pb(II) biosorption process, the untreated, protonated and Pb-loaded biosorbents were analyzed using a FT-IR spectrophotometer (Spectrum Two, PerkinElmer Inc., USA). The dried biosorbents were grinded sufficiently with KBr at a ratio of 1:200 in an agate mortar before pressed into a disk under high pressure. The spectra were recorded from 400 to 4000 cm^{-1} at a resolution of 4 cm^{-1} .

Scanning electron microscopy (JSM-7500F, Japan) was used to survey the surface morphology of the raw and HNO_3 -modified *P. americana* biomass before and after Pb(II) biosorption.

The solid addition method was used to measure the pH at point zero charge (pH_{PZC}) of PAL and HPAL (Mondal, 2010; Chen et al., 2010). A pH meter (pHS-3C, Shanghai INESA Scientific Instrument Co., Ltd., China) was used for the measurement of pH.

2.4. Batch adsorption experiments

Unless otherwise stated, the adsorption experiments were carried out with 50 mL solution in a series of stoppered conical flasks shaken at 200 rpm in a mechanical shaker at 25 ± 0.5 °C for a desired contact time. The pH values of solutions were adjusted with 0.1 mol L^{-1} HNO_3 and/or NaOH. Then, samples were centrifuged immediately at 4000 rpm for 15 min and filtered through 0.45- μm filter membrane. The Pb(II) concentration in the initial and filtrate solution was measured by an atomic absorption spectrophotometer (AAS) (WFX-110, Beijing Beifen-Ruili Analytical Instrument (Group) Co., Ltd., China). The Pb removal efficiency (E) and adsorption capacity of biosorbents (Q_e) were calculated through the following equation, respectively:

$$E(\%) = (C_0 - C_e) \times 100 / C_0 \quad (1)$$

$$Q_e = (C_0 - C_e) \times V / m \quad (2)$$

where Q_e represents the adsorption capacity of Pb(II) on biosorbent (mg g^{-1}), C_0 and C_e are the initial and equilibrium concentration of Pb(II) in solution (mg L^{-1}), respectively. V is the volume of Pb(II) solution (L) and m is the weight of biosorbent (g).

2.4.1. Effect of biosorbent dosage on Pb(II) removal

Biomass doses of 0.1–3.0 g were added to the Pb(II) solution (30 mg L^{-1}) at pH 5.0. Samples were agitated for 120 min. Then the samples were centrifuged and filtered. The Pb(II) concentration in the filtrate was determined.

2.4.2. Effect of solution pH on Pb(II) removal

The effect of solution pH on the Pb(II) removal was conducted over the pH ranged from 2.0 to 8.0, thereby avoiding hydrolysis and precipitation of Pb(II) ions at higher pH value. The

pH values of solutions were adjusted with 0.1 mol L^{-1} HNO_3 and/or NaOH. A biosorbent dose of 1.0 g was added to each flask containing 30 mg L^{-1} of Pb(II) ions, which was then agitated for 120 min, and then centrifuging and filtering the supernatants, and determining the Pb(II) concentration as mentioned above.

2.4.3. Effect of initial concentration on Pb(II) removal

Equilibrium experiments were performed in flasks containing 50 mL of Pb(II) ion solutions at different concentrations (5–300 mg L^{-1}). The pH values of the initial solutions were adjusted to 6.0 by using 0.1 mol L^{-1} HNO_3 and/or NaOH before biosorbent (1.0 g) was added. The samples were shaken for 120 min. Then the mixtures were centrifuged and filtered, and analyzed Pb(II) concentration as mentioned above.

2.4.4. Effect of contact time on Pb(II) removal

Batch kinetic experiments were performed at different contact times (5–480 min) at 30 mg L^{-1} initial Pb(II) ion concentration at pH 6.0. A biomass dose of 1.0 g was added in the flasks. The samples were then shaken for a preset time. Afterward, the suspension was centrifuged and filtered. The Pb(II) concentration in the filtrate was measured as mentioned above.

2.5. Desorption experiment

To investigate the reusability of biosorbent, desorption experiment was conducted. Each adsorbent (1.0 g) was saturated with 30 mg L^{-1} Pb(II) in 150 mL stoppered conical flasks for 120 min, at temperature 25 ± 0.5 °C and pH 6.0. Then the Pb-loaded biosorbents were filtered, collected and washed with deionized water for several times to remove any unabsorbed Pb(II) ions and dried in an oven at 60 °C. Following, the adsorbent sample loaded with Pb(II) ions was treated with 50 mL of 0.1 mol L^{-1} HCl solution and shaken for 120 min to desorb Pb(II) at 200 rpm in a shaker incubator. Then the samples were filtered through 0.45- μm filter membrane and the filtrates were analyzed for Pb(II) desorbed by AAS.

2.6. Disposal of industrial wastewater

To examine the applicability of *P. americana* biomass employed in industrial effluents, the experiments were carried out with 50 mL wastewater solution in a series of stoppered conical flasks shaken at 200 rpm in a mechanical shaker at 25 ± 0.5 °C. The wastewater solution was treated with the raw and HNO_3 -modified *P. americana* biomass under the optimized conditions. The real wastewater sample was collected from a metal manufactory in the outskirts of Chengdu, Sichuan Province, and filtrated for further experiment. The concentration of heavy metal ions was measured by AAS.

2.7. Biosorption isotherm models

In this study, Langmuir [Eq. (3)] and Freundlich [Eq. (4)] adsorption isotherms were applied to fit the Pb(II) equilibrium data (Meitei and Prasad, 2014).

$$C_e / Q_e = C_e / Q_{\text{max}} + 1 / (bQ_{\text{max}}) \quad (3)$$

$$\ln Q_e = \ln K_F + (1/n) \ln C_e \quad (4)$$

where C_e is the equilibrium metal concentration (mg L^{-1}), Q_e is the amount of metal ions adsorbed biosorbent (mg g^{-1}), Q_{\max} is the maximum adsorption capacity calculated from the equation (mg g^{-1}) and b is the equilibrium constant (L mg^{-1}). K_F is the Freundlich constant related to the multi-layer adsorption capacity of the biosorbent (mg g^{-1}) (L mg^{-1})^{1/n}, and n represents the sorption intensity of the biosorbent.

2.8. Biosorption kinetic models

Pseudo first-order [Eq. (5)], pseudo second-order [Eq. (6)], Elovich [Eq. (7)] and intraparticle diffusion [Eq. (8)] kinetic models were used to describe the dynamic adsorption process (Ronda et al., 2013; Ghasemi et al., 2014).

$$\ln(Q_e - Q_t) = \ln Q_e - K_1 t \quad (5)$$

$$t/Q_t = 1/K_2 Q_e^2 + t/Q_e \quad (6)$$

$$Q_t = (1/\beta) \ln(\alpha\beta) + (1/\beta) \ln t \quad (7)$$

$$Q_t = K_i t^{1/2} + C \quad (8)$$

where Q_e and Q_t are the amount of Pb(II) absorbed (mg g^{-1}) onto the biomass at equilibrium and at any time t , K_1 , K_2 and K_i are the rate constants of pseudo first-order model (min^{-1}), second-order adsorption ($\text{g mg}^{-1} \text{min}^{-1}$) and the intraparticle diffusion ($\text{mg g}^{-1} \text{min}^{-0.5}$), respectively. α and β stand for the initial adsorption rate ($\text{mg g}^{-1} \text{min}^{-1}$) and the desorption constant (g mg^{-1}), respectively. t is the time (min) and C is the intercept.

2.9. Biosorption thermodynamic studies

The thermodynamic studies were performed at temperatures 288.2 K, 298.2 K and 308.2 K, respectively. The change of Gibbs free energy could indicate the spontaneity of a chemical reaction. Thermodynamic parameters including the change of Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) can be calculated from the following equations (Bazargan-Lari et al., 2014; Meitei and Prasad, 2014; Yargıç et al., 2015).

$$\Delta G^\circ = -RT \ln K_d \quad (9)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (10)$$

$$\ln K_d = (\Delta S^\circ/R) - (\Delta H^\circ/RT) \quad (11)$$

where R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the Kelvin temperature (K) and K_d represents the equilibrium contact.

2.10. Statistical analysis

All tests were conducted in triplicate and the results were reported as the mean value. Data of statistical analysis were

performed by using SPSS Version 19.0. Variance analysis and regression analysis were performed on experimental data. For mean separations, Fisher's least significant difference (LSD) was used at $p \leq 0.05$ levels. The correlation coefficient (R^2) and the root mean square error (RMSE) were performed to measure the appropriateness of the kinetic and isotherm models.

3. Results and discussion

3.1. Characterization of the biosorbent

3.1.1. Proximate analysis

The proximate analysis was performed for the raw and HNO_3 -modified *P. americana* biomass and the results appeared in Table 1. The moisture content was 6.16% for the raw material. The proportion of volatile matter for PAL and HPAL was similar (approximately 76%), however, the fixed carbon content increased more than one times after chemical modification. These results were in agreement with olive tree pruning after HNO_3 treated (Calero et al., 2013). The ash content decreased by 35.24% after HNO_3 modification.

3.1.2. Elemental analysis

For the determination of the major chemical composition of PAL and HPAL, elemental analysis was performed, and the results were illustrated in Table 1. It could be seen that raw PAL content was 36.56% C, 4.67% H, 2.76% N, 0.63% S and 45.23% O similar to other agricultural waste (Reddy et al., 2010). After HNO_3 treated, the C and S content in HPAL decreased to 12.53% and 57.14%, respectively compared to the raw PAL. However, the other components content increased with respect to untreated PAL, being more significant for N content, which increased nearly one times.

3.1.3. FT-IR analysis

Fourier transform infrared spectroscopy (FT-IR) is often used to identify the surface groups of the adsorbents and to determine those groups in binding of metal ions (Lasheen et al., 2012; Kostić et al., 2014). The identification of the obtained spectra had the typical peaks for -OH group at $3421\text{--}3431 \text{ cm}^{-1}$ and $1053\text{--}1062 \text{ cm}^{-1}$, alkyl -CH at $2922\text{--}2925 \text{ cm}^{-1}$, the C=O bond of non-ionic carboxylic acids at $1735\text{--}1738 \text{ cm}^{-1}$ and $1244\text{--}1248 \text{ cm}^{-1}$, antisymmetrical and symmetrical C=O vibration of ionic carboxylate groups at $1618\text{--}1645 \text{ cm}^{-1}$ and $1375\text{--}1385 \text{ cm}^{-1}$, and -NH group at variable wave numbers around 1318 cm^{-1} (Fig. 1, Table 2).

Due to the interaction of the functional groups on the biosorbent with Pb(II), the FT-IR peaks might shift to lower or higher wave numbers after Pb(II) loaded. Shifting of bands to higher frequencies indicated an increase in bond strength,

Table 1 The physicochemical properties of PAL and HPAL. PAL, the raw *P. americana*; HPAL, the HNO_3 -modified *P. americana*.

Biosorbent	pH _{PZC}	Proximate analysis (%)				Elemental analysis (%)				
		Moisture	Ash	Volatile matter	Fixed carbon	C	H	N	S	O ^a
PAL	3.30	6.16	9.76	75.85	8.23	36.56	4.67	2.76	0.63	45.62
HPAL	3.90	–	6.32	76.37	17.31	31.98	6.12	4.89	0.27	50.42

^a Estimated by difference.

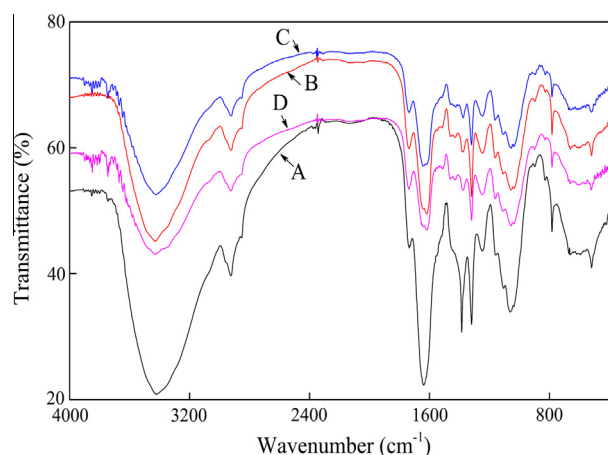


Figure 1 FT-IR spectra of PAL (A), HPAL (B), Pb-loaded PAL (C) and Pb-loaded HPAL (D). PAL, the raw *P. americana*; HPAL, the HNO₃-modified *P. americana*.

while a shift to lower frequencies showed bond weakening (Gutha et al., 2014). The broad and intense band obtained in PAL at 3421 cm⁻¹ shifted to 3428, 3422 and 3431 cm⁻¹ in the HPAL, Pb-loaded PAL and Pb-loaded HPAL, respectively. These results implied that the hydroxyl group may involve in the biosorption process. The minor shift of the peaks at 1740, 1320 and 1060 cm⁻¹ suggested that carboxyl and amine groups may participate in the biosorption process.

Similar peaks were observed in *Cinnamomum camphora* leaves for Pb(II) ion biosorption, where the peaks around 1318, 1735, 3415 cm⁻¹ were attributed to metal chelates of amine, carboxyl and hydroxyl groups, respectively (Chen et al., 2010). The results of FT-IR analysis demonstrated that the Pb(II) biosorption onto *P. americana* biomass may occur through chemical interaction, involving the functional groups such as hydroxyl, carboxyl and amine.

3.1.4. SEM analysis

Scanning electron microscope is an extremely useful tool to observe the changes in surface texture and morphology of the biosorbent (Yuvaraja et al., 2014; Nembr et al., 2015). The SEM images of raw, modified and Pb-loaded biosorbents are given in Fig. 2. The pure PAL shows a relatively smooth

surface with small pores (Fig. 2A). After HNO₃ modification, the presence of amounts of pores and cracks made the surface of PAL more uneven and irregular (Fig. 2B), which may be more helpful for adsorption. A distinct changes in the surface morphology of PAL and HPAL were observed after Pb(II) loading. The binding sites on the PAL and HPAL surface would be activated through H⁺, and then some granular metal complexes were formed in the surface (Fig. 2C and D). Additionally, the results could also owing to the irregular structure in the morphology.

3.2. Effect of biosorbent dosage on Pb(II) removal

As shown in Fig. 3A, the biosorption capacity of Pb(II) by PAL and HPAL dropped significantly with the increase in biosorbent dosage and the maximum sorption capacity of Pb(II) ion occurred at the biosorbent dosage of 2 g L⁻¹. The ratio of metal to biosorbent decreased as the biosorbent dosage increased, and then led to a reduction of biosorption capacity (Bhatti et al., 2009). However, the Pb(II) removal efficiency significantly increased as the dosage of biosorbent was increased over the range 2–20 g L⁻¹ ($p < 0.05$). It could be explained as increasing biosorbents dosages, the amount of “active sites” available for biosorption of Pb(II) increased and consequently more biosorption occurred (Yuvaraja et al., 2014). A further increase in biosorbents dosages over 20 g L⁻¹ did not lead to an appreciable increase of removal efficiencies ($p > 0.05$). This result could be explained that the overlapping or aggregation of active sites at higher dosage and decreasing in total sorbent surface area (Ghasemi et al., 2014; Kostić et al., 2014). Therefore, the optimum biosorbent dosage was 20 g L⁻¹. In addition, the protonated treatment significantly increased the Pb(II) removal efficiencies from an approximate value of 82% for untreated PAL to a value close to 98% for PAL treated with HNO₃. HNO₃-modified biosorbent may increase the surface space and pore size (Fig. 2B) and remove of the certain undesirable portions of the biomass, and thus resulting in leaving a highly active skeletal structure behind.

3.3. Effect of pH on Pb(II) removal

Because the pH of the solution could affect the valence and amount of heavy metal ions in aqueous solutions, the quantity

Table 2 Wave number of infrared adsorption peaks of different *P. americana* samples. PAL, the raw *P. americana*; HPAL, the HNO₃-modified *P. americana*.

Groups	Wavenumber (cm ⁻¹)			
	PAL	HPAL	Pb-loaded PAL	Pb-loaded HPAL
O—H groups of alcohol, phenolic and carboxylic acids (Calero et al., 2013)	3421.10	3428.58	3421.53	3430.87
C—H bonds of aliphatic acids, symmetric and asymmetric (Chen et al., 2010)	2924.93	2924.32	2922.30	2923.17
C=O bond of non-ionic carboxylic acids and esters (—COOH, —COOCH ₃) (Lasheen et al., 2012)	1735.73	1737.33	1736.36	1737.24
Ionic carboxylic groups (—COO—), antisymmetrical (Lasheen et al., 2012)	1638.24	1618.74	1644.94	1618.88
Ionic carboxylic groups (—COO—), symmetric (Barka et al., 2013)	1384.60	1376.49	1375.31	1376.04
N—H group (Lasheen et al., 2012)	1318.84	1318.74	1319.36	1318.56
C=O bond of non-ionic carboxylic acids (—COOH) (Farooq et al., 2010)	1247.12	1247.73	1245.86	1244.67
O—H of alcoholic groups (Chakravarty et al., 2010)	1061.33	1055.01	1054.13	1053.30

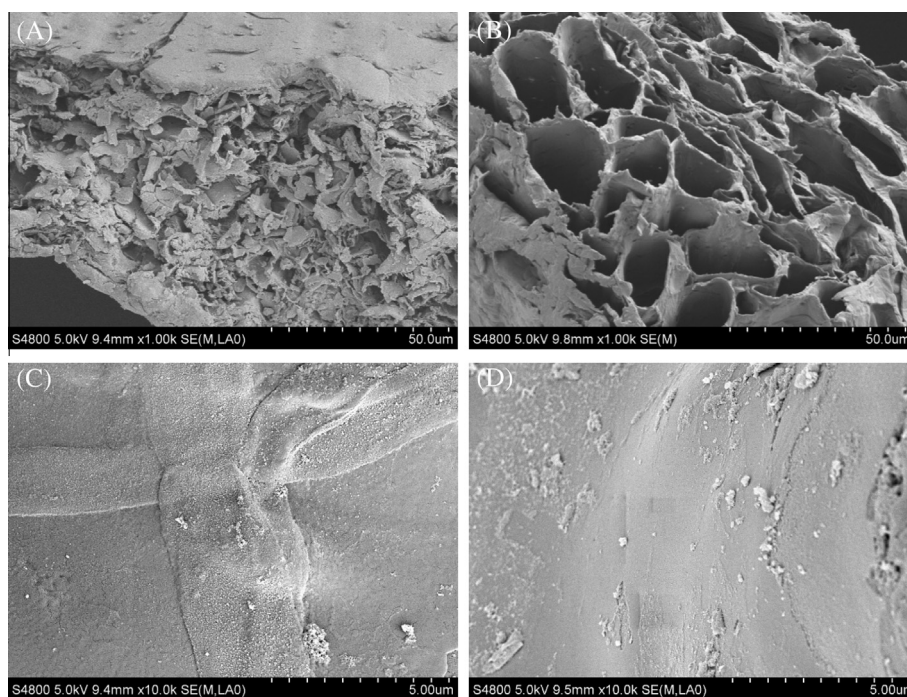


Figure 2 SEM micrographs of the PAL (A) and HPAL (B) at 1000×magnification, Pb-loaded PAL (C) and Pb-loaded HPAL (D) at 10,000×magnification. PAL, the raw *P. americana*; HPAL, the HNO₃-modified *P. americana*.

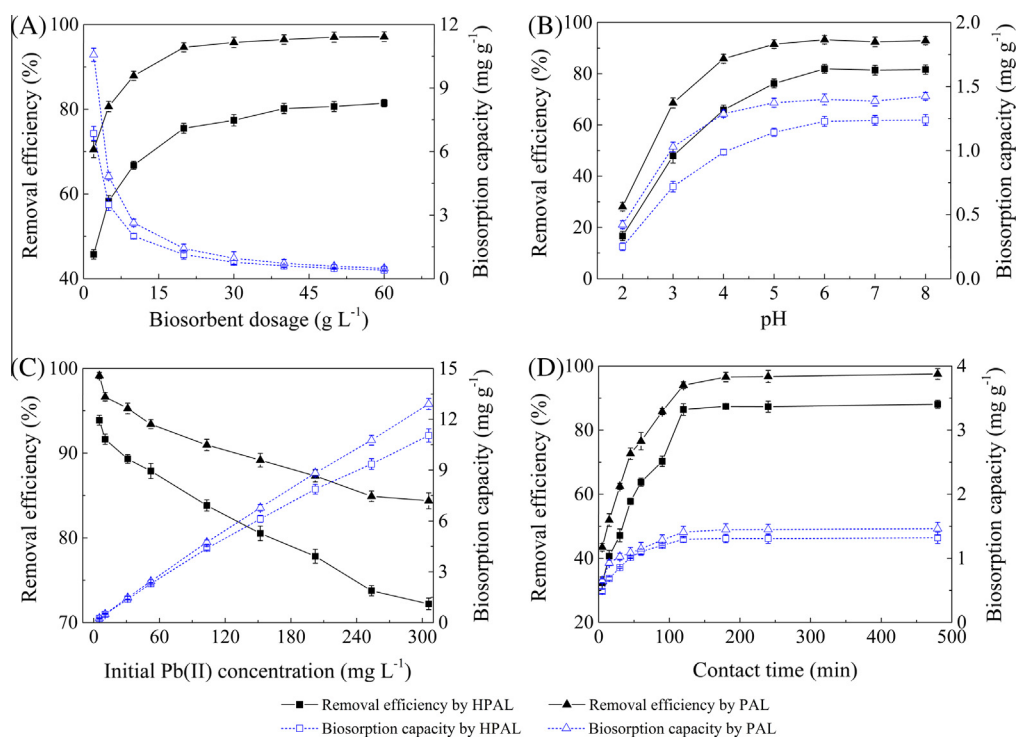


Figure 3 Effects of biosorbent dosage (A), pH (B), initial Pb(II) concentration (C) and contact time (D) on the removal of Pb(II) from aqueous solutions by PAL and HPAL. PAL, the raw *P. americana*; HPAL, the HNO₃-modified *P. americana*.

of the functional groups on the biosorbent surface sites, and the interaction between biosorbent and heavy metal ions (Gundogdu et al., 2009; Chen et al., 2010; Tasar et al., 2014), it is one of the controlling factors influencing the heavy

metal ions removal (Reddy et al., 2010; Yuvaraja et al., 2014). It is observed that a gradual rise in the removal efficiency and adsorption capacity of Pb(II) took place with an increase in pH from 2.0 to 6.0 ($p < 0.05$) and decreased slightly at the

pH > 6.0 (Fig. 3B). The maximum removal efficiencies of PAL and HPAL occurred at pH 6.0 and reached 81.97% and 93.29%, respectively. It was well known that a lower pH resulted in high concentration of H^+ in the solution, thus the functional groups of the biosorbent surface were protonated (Reddy et al., 2010; Meitei and Prasad, 2014). Hence, Pb(II) ion adsorption was hindered owing to the competition between H^+ and Pb^{2+} for the active sites on the surface of the biosorbent. In contrast, at higher pH, the H^+ concentrations decreased and the functional groups of biosorbent surface were deprotonated (Athar et al., 2013). Thus, more Pb(II) ions were adsorbed due to less competition between H^+ and Pb^{2+} . The significant influence of pH on the biosorption of Pb(II) by the raw and HNO_3 -modified *P. americana* biomass confirmed that both physisorption and chemisorption were involved in the Pb(II) ion biosorption process through the electrostatic interaction and ion exchange.

Additionally, the effect of pH on the Pb removal could be also explained according to the pH at point zero charge (pH_{PZC}) of the biosorbent (Chen et al., 2010; Yuvaraja et al., 2014). While $pH < pH_{PZC}$, the surface charges of the adsorbent are positive which lead to an electrostatic repulsion with Pb(II) (Reddy et al., 2010). In contrast, while $pH > pH_{PZC}$, the surface charges of the adsorbent become negative and the Pb(II) ions in the solutions are attracted to their surface to a greater extent (Reddy et al., 2010). The values of pH_{PZC} of PAL and HPAL are found to be 3.30 and 3.90, respectively (Table 1).

3.4. Effect of initial concentration on Pb(II) removal

The initial heavy metal ions concentrations in aqueous solutions play a vital role as a favorable driving force in conquering mass transfer resistance of metal ions between the aqueous and solid biosorbents (Liu et al., 2014). As illustrated in Fig. 3C, the biosorption capacity of the biomass increased with increasing Pb(II) concentration, however, the percentage removal of Pb(II) decreased from 93.88 to 72.21 for PAL and 99.16 to 84.37 for HPAL biosorbent as the Pb(II) ion concentrations were increased from 5.19 to 305.79 $mg L^{-1}$. The higher removal of Pb(II) at low concentration might be attributed to the availability of more “active sites” on the surface of the biosorbents (Amarasinghe and Williams, 2007; Chakravarty et al., 2010), while the lower removal of Pb(II) at high concentration may be due to the lack of available

“active sites” on the surface of biosorbents (Meitei and Prasad, 2014; Tasar et al., 2014). Further, the results obtained showed that *P. americana* biomass can be efficiently used for the removal of Pb^{2+} from wastewater with low concentration. These results were in agreement with Pb(II) and Cd(II) ions adsorbed onto *Chlorella vulgaris* biomass (Edris et al., 2014).

3.5. Effect of contact time on Pb(II) removal

As shown in Fig. 3D, the Pb(II) removal efficiencies of PAL and HPAL increased rapidly with increasing the contact time. The biosorption of Pb(II) by both PAL and HPAL biosorbents was very fast and 32.36% and 43.47% of Pb(II) ions were adsorbed within 5 min, respectively. The equilibrium adsorption was established after 120 min where the Pb(II) removal efficiencies increased up to 86.44% and 94.00% for PAL and HPAL, respectively. It showed no significant enhancement of removal efficiency with a further increasing contact time (> 120 min) ($p > 0.05$). The rapid uptake of Pb(II) ion at the initial period may be due to the availability of vacant active sites on the surface of biosorbent (Chakravarty et al., 2010). Later, owing to the decrease available adsorption sites of biosorbents, the removal became slow (Ghasemi et al., 2014). Other studies also reported similar results (two-stage sorption kinetics) for the biosorption of Pb(II) ion using *E. adenophorum* (Guo et al., 2009) or olive tree (Ronda et al., 2013).

3.6. Biosorption isotherms

Adsorption isotherm describes the equilibrium relationship between the quantities of metal ions adsorbed onto the biosorbent (Q_e) and the concentration of metal ions in solution (C_e) at a given experimental condition (Chen et al., 2010; Malamisa and Katsou, 2013). In this study, the equilibrium data were predicted by the Langmuir and Freundlich isotherms are shown in Fig. 4. The parameters of the models are listed in Table 3. The most suitable prediction of Pb(II) biosorption onto PAL and HPAL was provided by the Freundlich model, as it yielded a higher R^2 and lower RMSE values than the Langmuir model. Better fitting of Freundlich model implied that the multilayer sorption of Pb(II) mainly occurred on heterogeneous surfaces of *P. americana*. Similar result was obtained by Guo et al. (2009), where the Freundlich isotherm

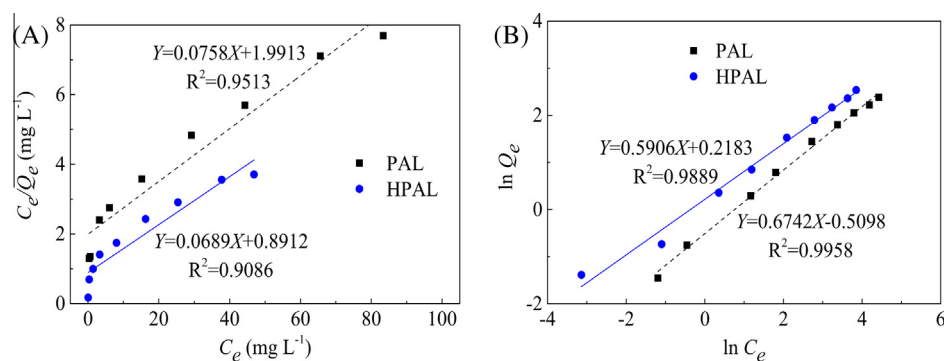


Figure 4 Linearized of Langmuir isotherm (A) and Freundlich isotherm (B) plots for Pb(II) adsorption onto PAL and HPAL. PAL, the raw *P. americana*; HPAL, the HNO_3 -modified *P. americana* (biosorbent dosage: 20 $g L^{-1}$; contact time: 120 min; pH: 6.0; temperature: 25 ± 0.5 $^{\circ}C$).

Table 3 Parameters of the Langmuir and Freundlich isotherm models for Pb(II) biosorption onto PAL and HPAL. PAL, the raw *P. americana*; HPAL, the HNO₃-modified *P. americana* (biosorbent dosage: 20 g L⁻¹; contact time: 120 min; pH: 6.0; temperature: 25 ± 0.5 °C).

Biosorbents	Langmuir					Freundlich				
	Q_{\max} (mg g ⁻¹)	b (L mg ⁻¹)	R^2	p	RMSE	K_F (mg g ⁻¹) (L mg ⁻¹) ^{1/n}	1/n	p	R^2	RMSE
PAL	13.19	0.5022	0.9513	<0.001	2.2120	0.6006	0.6742	<0.001	0.9958	0.0947
HPAL	14.51	1.1221	0.9086	<0.001	0.4088	1.2440	0.5906	<0.001	0.9889	0.1582

fitted with the equilibrium data of Pb(II) sorption onto *E. adenophorum* better than the Langmuir isotherm.

A further analysis of the Freundlich parameter supported favorable biosorption of the Pb(II) onto the *P. americana*. 1/n is a constant reflecting the adsorption intensity of biosorbent. According to the study by Bazargan-Lari et al. (2014), if the value of 1/n lay between 0.1 and 1.0, the adsorption is favorable. It can be observed that the 1/n values of PAL and HPAL were both less than 1.0 (Table 3), showing the favorability of biosorption of Pb(II) onto *P. americana* biomass.

Table 4 summarizes a comparison of the maximum Pb(II) biosorption capacity of PAL and HPAL with those reported in the literature for different biosorbents. The maximum biosorption capacity of Pb(II) onto PAL and HPAL was 10.83 and 12.66 mg g⁻¹, respectively, so their biosorption capacities of Pb(II) were higher than those of most other biosorbents reported in the literatures. Thus, *P. americana* could act as a potential biosorbent for sorption of Pb(II) from wastewater.

3.7. Biosorption kinetics

Kinetic studies of metal ions adsorption by biosorbent could determine the reasonable length of time to attain the sorption equilibrium and explain the process mechanism of metal ions adsorption onto the biosorbent (Tunali et al., 2006). As shown in Fig. 5 and Table 5, the pseudo first-order model showed a lower R^2 values in comparison with the pseudo second-order model. Furthermore, the equilibrium biosorption capacities

($Q_{e,cal}$) inferred from the pseudo first-order model were likewise not in good agreement with the experimentally determined values ($Q_{e,exp}$, Table 5). These results indicated that the biosorption of Pb(II) onto PAL and HPAL did not well fit the pseudo first-order model.

In contrast, the R^2 value for the linearized form of pseudo second-order equation was close to 1.0 (Table 5), showing a highly affinity of experimental data to this model. Moreover, the $Q_{e,cal}$ values calculated from the pseudo second-order model matched the $Q_{e,exp}$ values closely. According to these results, the Pb(II) biosorption using PAL and HPAL followed the pseudo second-order kinetic model, which indicated that the rate-limiting step of adsorption process might be the chemical sorption (Feng et al., 2011), involving valence forces through the exchange or sharing of electrons between *P. americana* biomass and Pb(II) ions. The pseudo second-order model also described the biosorption kinetics of Pb(II) onto tea waste (Amarasinghe and Williams, 2007), pine bark (Gundogdu et al., 2009), modified *Moringa oleifera* tree leaves (Reddy et al., 2010), orange peel (Lasheen et al., 2012), *T. resupinatum* (Athar et al., 2013), and peanut shells (Tasar et al., 2014).

The Elovich model was commonly used to describe chemisorption kinetics (Ronda et al., 2013). As shown in Fig. 5C and Table 5, the R^2 values for the Elovich model were 0.93 and 0.95 for PAL and HPAL, respectively, and taking into account of α and β values, we could draw a conclusion that the process of Pb(II) adsorption onto *P. americana* was involved in chemisorption.

Table 4 Comparison of the maximum biosorption capacity of *P. americana* for Pb(II) with other low cost biosorbents. PAL, the raw *P. americana*; HPAL, the HNO₃-modified *P. americana*.

Biosorbents	Q_{\max} (mg g ⁻¹)	Pb ²⁺ concentration (mg L ⁻¹)	pH	Biosorbent dosage (g L ⁻¹)	Contact time (min)	Temperature (°C)	References
<i>L. vulgaris</i> shell	33.21	10–400	5.0	4.0	–	25.0 ± 0.5	Kostić et al. (2014)
<i>Eichhornia crassipes</i>	26.32	10–60	4.84	2.0	180	30.0	Mahamadi and Nharingo (2010)
HNO ₃ -treated olive tree	14.15	150	5.0	10.0	–	25.0	Ronda et al. (2013)
Untreated olive tree	12.97	150	5.0	10.0	–	25.0	Ronda et al. (2013)
HPAL	12.66	5–300	6.0	20.0	120	25.0 ± 0.5	Present study
<i>Cladonia furcata</i>	12.30	10–400	5.0	8.0	60	20.0	Sari et al. (2007)
PAL	10.83	5–300	6.0	20.0	120	25.0 ± 0.5	Present study
Almond shell	8.08	0.1–1.0 (mM)	6.0	10.0	90	25.0 ± 2.0	Sari et al. (2007)
<i>Oryza sativa</i> L. husk	5.69	10–200	–	20.0	120	30.0	Zulkali et al. (2006)
Tobacco stems	5.54	10–50	5.0	16.0	120	299 (K)	Li et al. (2008)
Okra waste	5.00	240	5.0	–	90	25.0	Hashem (2007)
<i>E. adenophorum</i>	3.46	10–50	5.0	–	120	313 (K)	Guo et al. (2009)
Tea waste	1.35	5–20	5.8	15.0	45	303 (K)	Mondal (2010)
<i>Agave sisalana</i>	1.34	–	7.0	3.0	10	296 (K)	dos Santosa et al. (2011)
Coir	0.127	200	4.0	1.0 (g)	–	25.0 ± 2.0	Shukla and Roshan (2005)

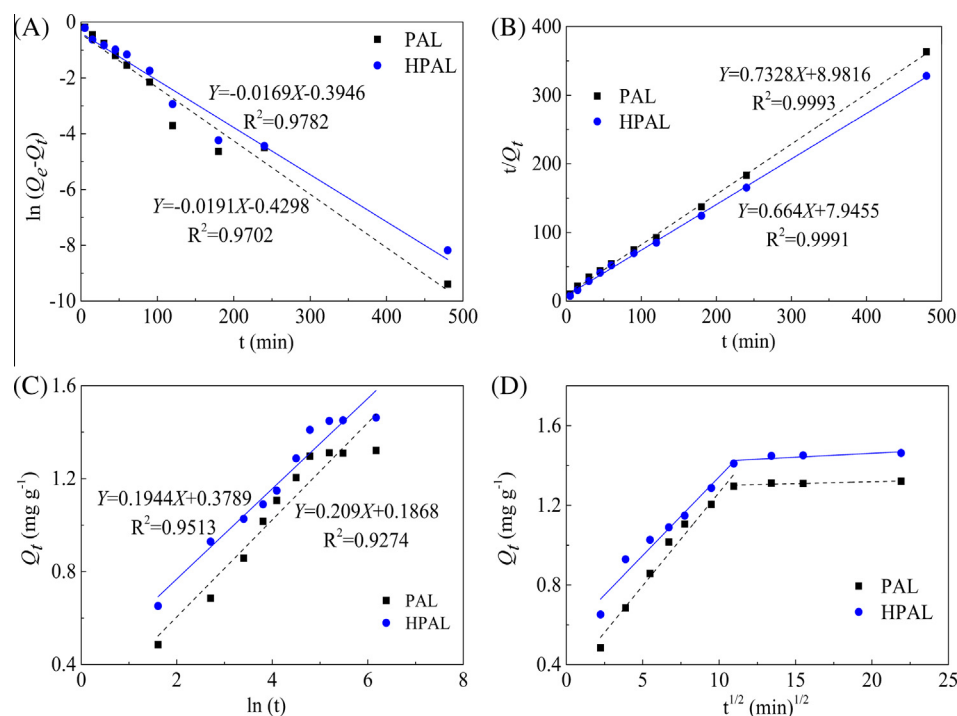


Figure 5 Plots of pseudo first-order kinetic model (A), pseudo second-order model (B), Elovich kinetic model (C), and intraparticle diffusion model (D) for Pb(II) biosorption onto PAL and HPAL. PAL, the raw *P. americana*; HPAL, the HNO₃-modified *P. americana*.

However, the well fit of pseudo second-order model did not entirely display the true nature of the sorption mechanism that

Table 5 Kinetic parameters of the pseudo first-order model, pseudo second-order model and Elovich model for Pb(II) biosorption onto PAL and HPAL. PAL, the raw *P. americana*; HPAL, the HNO₃-modified *P. americana*; $Q_{e,exp}$ was the data determined in the experiment and $Q_{e,cal}$ was the theoretical data inferred from models (Pb(II) concentration: 30 mg L⁻¹; biosorbent dosage: 20 g L⁻¹; pH: 6.0; temperature: 25 ± 0.5 °C).

Kinetic model	Biosorbents	
	PAL	HPAL
$Q_{e,exp}$ (mg g ⁻¹)	1.31	1.45
<i>Pseudo first-order model</i>		
$Q_{e,cal}$ (mg g ⁻¹)	0.6506	0.6740
K_1 (min ⁻¹)	0.0191	0.0169
R^2	0.9702	0.9782
p	< 0.001	< 0.001
RMSE	0.6534	0.4913
<i>Pseudo second-order model</i>		
$Q_{e,cal}$ (mg g ⁻¹)	1.3646	1.5060
K_2 (g mg ⁻¹ min ⁻¹)	0.0598	0.0555
R^2	0.9993	0.9991
p	< 0.001	< 0.001
RMSE	3.8528	3.9283
<i>Elovich model</i>		
α (mg g ⁻¹ min ⁻¹)	0.5109	1.3650
β (g mg ⁻¹)	4.7847	5.1440
R^2	0.9274	0.9513
p	< 0.001	< 0.001
RMSE	0.1069	0.0804

occurred on the surface of adsorbent (Schiewer and Patil, 2008). More than one kind of sorption mechanisms took place in the process of reaction kinetic equation (Malamisa and Katsou, 2013). The heavy metal ions adsorption on adsorbent is considered as a diffusion process and the intraparticle diffusion model could be used to describe this process. The linear relations of Q_t versus $t^{1/2}$ are presented Fig. 5D. It could be obviously observed that, for each biosorbent, not a straight line was obtained. Therefore, it cannot be considered that the intraparticle diffusion was the controlling step for the biosorption Pb(II) onto *P. americana*. However, there were two differential linear zones: (a) a higher slope at the initial stage which could imply the adsorption occurred on the external surface and (b) a substantially horizontal second region which would be attained the equilibrium uptake that was related to the diffusion of metal inside the particle. Thus, one might consider that the biosorption of Pb(II) with *P. americana* biosorbent occurred in more than one stage that can occur simultaneously. Similar results were reported by Ronda et al. (2013) studying the biosorption of lead onto native and chemically treated olive tree or Blázquez et al. (2014) in their study of the removal of Pb(II) from aqueous solutions using olive stone modified with H₂SO₄, HNO₃ and NaOH or Mohanty et al. (2006) showed that the relationships for *E. crassipes* and Cr(VI) at different initial concentrations were non-linearity in the entire time range, implied that more than one process was affecting the biosorption.

3.8. Thermodynamic parameters

In order to confirm whether the adsorption process of Pb(II) onto *P. americana* is spontaneous or not, thermodynamic parameters were determined. As shown in Table 6, the negative

values of Gibbs free energy change (ΔG°) imply the spontaneous and feasible nature of the adsorption of Pb(II) onto the raw and HNO₃-modified *P. americana*. Further, the decrease in the values of ΔG° with an increase in temperature reflects the adsorption process is more spontaneous at higher temperature (Chen et al., 2010). The values of enthalpy change (ΔH°) were 21.68 kJ mol⁻¹ for PAL and 9.27 kJ mol⁻¹ for HPAL, respectively. The positive values of ΔH° indicate that the adsorption process was endothermic nature (Bazargan-Lari et al., 2014; González et al., 2015). Additionally, the positive values of entropy change suggest the process is entropy driven and the increased randomness at the solid-solute interface (Chen et al., 2010; Hamza et al., 2013) during the adsorption of Pb(II) onto *P. americana*.

3.9. Desorption studies

In order to make the biosorption process more economical and prevent the secondary environmental issue (Ghasemi et al., 2014), the reusability of biosorbent is considered to be of crucial importance. Additionally, the desorption process is also important for judging the adsorption mechanism. If the desorption of the sorbate from the adsorbent surface could be easily obtained using strong desorbent like acid or alkali solutions, the adsorption mechanism is ion-exchange or chemical bonding. On the contrary, if it is a physical bonding, the sorbate could be desorbed by deionized water (Meitei and Prasad, 2014). In this study, desorption experiment was performed using 0.1 mol L⁻¹ HCl and deionized water as desorbent. During the Pb(II) ion desorption from the raw and HNO₃-modified *P. americana* biomass using 0.1 mol L⁻¹ HCl, 81.67% and 89.81% recovery were achieved for the metal compared to 9.21% and 10.93% using deionized water (Fig. 6), respectively. The results indicate that the chemical or ion-exchange mechanism is the main mechanism of the *P. americana* biomass adsorption of Pb(II) ion.

3.10. Applicability

A kind of efficient adsorbent not only could adsorb various heavy metal ions from synthetic wastewater, but also own to the ability of real wastewater treatment. Therefore, our attention was turned toward the sorption capability of PAL and HPAL on the removal of heavy metal ions from real wastewater solution. The concentrations of heavy metal ions in real wastewater before and after sorption using PAL and HPAL are presented in Fig. 7. The heavy metal ions concentrations were obviously decreased after sorption. Approximately

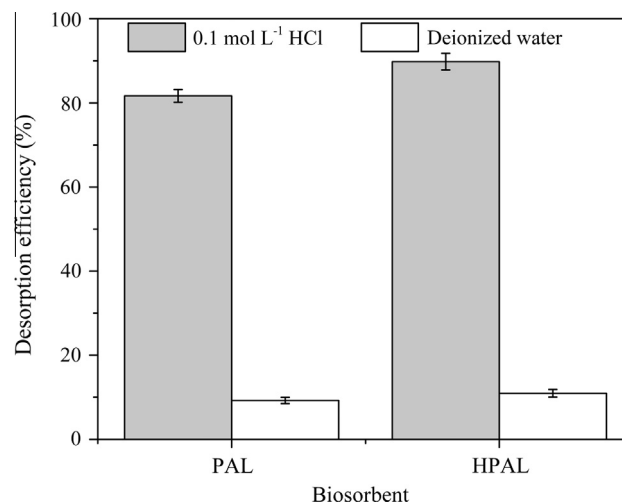


Figure 6 Desorption efficiency of Pb(II) ion from PAL and HPAL biomass using 0.1 mol L⁻¹ HCl and deionized water. PAL, the raw *P. americana*; HPAL, the HNO₃-modified *P. americana*.

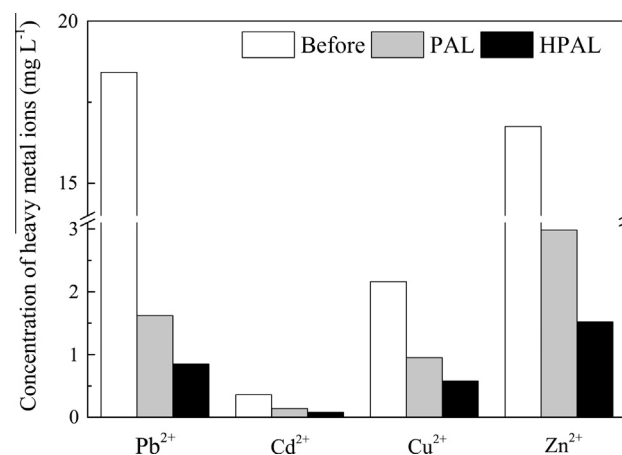


Figure 7 The removal efficiency of heavy metal ions from the real wastewater using the raw (PAL) and HNO₃-modified *P. americana* (HPAL) (biosorbent dosage 20 g L⁻¹, pH 6.0, contact time 120 min, temperature 25 ± 0.5 °C).

91.21% Pb²⁺, 61.11% Cd²⁺, 56.02% Cu²⁺ and 82.21% Zn²⁺ were removal by PAL, while 95.38% Pb²⁺, 77.78% Cd²⁺, 73.15% Cu²⁺ and 90.93% Zn²⁺ were removal by HPAL. The heavy metal ions concentrations in the industrial wastewater were lower than the maximum permissible concentration of the National Standards of PRC (GB 21900-2008) using HPAL biosorption. These results indicate that *P. americana* biomass is a applicable material for removing metal ions from wastewater.

4. Conclusions

The results indicate that *P. americana* biomass could act as an effective and potentially low-cost adsorbent for lead removal from aqueous solution. The FTIR spectra of biosorbents before and after Pb-loaded indicated that the hydroxyl, carboxyl and amine groups may take part in Pb(II) binding.

Table 6 Thermodynamic parameters for the adsorption of Pb(II) onto the raw and HNO₃-modified *P. americana*.

Biosorbents	T (K)	ΔG (kJ mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔS (kJ mol ⁻¹ K ⁻¹)
PAL	298.2	-3.073	21.68	0.0687
	308.2	-3.898		
	318.2	-4.371		
HPAL	298.2	-3.502	9.27	0.0505
	308.2	-4.450		
	318.2	-5.395		

HNO₃-modified *P. americana* (HPAL) showed a significant higher Pb(II) removal efficiencies compared with original *P. americana* (PAL) ($p < 0.05$). The Pb(II) removal efficiencies of PAL and HPAL were found to be greatly dependent on solution pH and the maximum removal of 81.97% and 93.29% occurred at pH 6.0. Kinetic experiments proved that the Pb(II) biosorption process from aqueous solutions was rapid and equilibrium was achieved within 120 min. The maximum adsorption capacities of PAL and HPAL were found to be 10.83 and 12.66 mg g⁻¹, respectively. The Freundlich isotherm and the pseudo second-order kinetic model gave a better fit the experimental data. The multilayer sorption of Pb(II) occurs on the homogeneous surface of *P. americana* biomass and this biosorption process is feasible, spontaneous and exothermic. The biosorption of Pb(II) ion onto the external surface of *P. americana* biomass was dominated by the physisorption and chemisorption through electrostatic interaction and ion exchange. *P. americana* biomass showed good reusability and capacity for treating the industrial wastewater. The results confirmed that *P. americana* biomass is a potential biosorbent for Pb removal from wastewater.

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