Removal of lead(II) ion in water by adsorbents from

Pithecellobium dulce

Vanida Chairgulprasert¹*  Nuchtima Madlah¹  Rukaiyah Pohmueya²
and Nurheedayah Madmanang³

¹Department of Science, Faculty of Science and Technology, Prince of Songkla University, Pattani Campus, Mueang, Pattani 94000, Thailand.
²Faculty of Education, Prince of Songkla University, Pattani Campus, Mueang, Pattani 94000, Thailand.

Corresponding Author, E-mail: vanida.c@psu.ac.th

ABSTRACT

The removal of lead(II) ion in water by the adsorbents from the fruit peels and leaves of Pithecellobium dulce has been studied using a batch method. Four parameters, contact time, pH, initial lead concentration and adsorbent dose were optimised to maximise adsorption. The maximum adsorption efficiency for the fruit peels was 90%, compared with 87% for the leaves. In both cases, the adsorption data followed second-order kinetics and fit the Freundlich isotherm. For the peels, the data were more effectively modelled using a simple Langmuir isotherm.
1. INTRODUCTION

Heavy metal pollution arises when untreated wastewater effluents are released into the environment from the textiles, mining, fertiliser and electronics industries. Heavy metals represent a significant hazard to animals and higher plants and have been detected in ground water, rivers, lakes and marine environments. Lead is one of the most harmful heavy metals, affecting the human central nervous system and kidneys by disrupting haeme synthesis and other biochemical pathways (Tong and Schirnding, 2000). Heavy metals may also accumulate in biological systems, raising levels of exposure and so removal of metallic pollutants from the environment is a pressing concern.

Numerous metal removal processes have been developed, including ion exchange, electro-flotation, reverse osmosis, membrane filtration, electro-chemical treatment, chemical precipitation, and adsorption. Among these techniques, adsorption is the most versatile because a wide variety of synthetic and natural adsorbents can be used to remove toxic metals (Barakat, 2011; Fenglian and Wang, 2011). Notable phytosorbents include sunflower stalks (Sun and Shi 1998), rice bran (Montanher and Oliveira, 2005), sugarcane bagasse (Garg et al., 2007) and galangal (Chairgulprasert et al, 2013). Natural agricultural waste products containing lignin and cellulose are also capable of binding to metal ions in wastewater. Phytosorbsents derived from agricultural waste also present significant benefits in terms of their low cost, abundance, effectiveness and ecological acceptability.

Pithecellobium dulce Benth. is a member of the pea family, Leguminosae, native to tropical America, but now cultivated worldwide in tropical regions. The plant has many different local names, such as Manila tamarind (UK, USA), guamuchil (Mexico, Spain), Madras thorn (India), kamatsile (Philippines) and in Thailand, “makham-thet” (Orwa, 2009). This easily cultivated and fast-growing tree affords high yields of edible pulp and seeds and is resistant to drought. The pods are reddish brown when ripe, and are surrounded by a pink or red pulp with a sweet and sour taste. In Thailand, after the fruits of P. dulce Benth have been consumed, the pod peels are discarded as waste. Similarly, while the leaves are occasionally used as an animal feed, they are usually discarded. Both the fruit peels and leaves are rich in antioxidant phenols and so represent an unexploited
phytochemical resource. Additionally, a preliminary phytochemical analysis of the leaves has uncovered the presence of alkaloids, anthraquinones, flavonoids, proteins, tannins, cardiac glycosides and terpenoids (Kumar, 2013). The carboxylic acid, ketone, amide, amine, alcohol and phenol groups present in these phytochemicals are especially effective in promoting metal adsorption (Demirbas, 2008). In order to raise the value of makham-thet, this paper discloses a method by which *Pithecellobium dulce* pod peels and leaves may be used to remove lead(II) ions from aqueous solution. The efficiency of adsorption depends on pH, exposure time, initial metal ion concentration and the dose of adsorbent. In this study, each of these parameters was optimised in order to maximise adsorption efficiency.

2. MATERIALS AND METHODS

2.1 Preparation of adsorbents

*P. dulce* fruit peels and leaves were collected from Petchaburi province, Thailand. Each material was washed with distilled water and dried in the shade, then oven dried at 70 °C for 72 h. The dried materials were ground and sieved through a 300 µm filter. The powders were stored in air tight plastic containers prior to the experiments. The FTIR spectroscopy (Bruker, Tensor 27) was applied to detect the chemical structure of adsorbents using a KBr window.

2.2 Preparation of aqueous lead waste

Stock solutions of lead nitrate (1000 mg/L) were used as the adsorbate. These were prepared by diluting lead nitrate with deionised water until the desired concentration was reached. The acidity of the solution was adjusted to between pH 2 and pH 7 by dropwise addition of either 0.1 M hydrochloric acid or 0.1 M sodium hydroxide.

2.3 Batch adsorption

A typical batch experiment was carried out using 40 mL of metal ion solution (10-60 mg/L) in a 100 mL conical flask and with the pH 2-7 adjusted as required. Powders of *P. dulce* fruit peels or leaves (0.5-2.0 g) were then added and the mixture was shaken at 125 rpm using a mechanical shaker at a controlled temperature over a desired period of time (10-80 min). After the experiment, the suspension was filtered. The initial and residual Pb(II) ion concentrations were measured using atomic absorption spectroscopy (AAS, Perkin Elmer Analyst 100). All experiments were performed in triplicate. Only average values were reported, as the maximum error did not exceed 5%. The data obtained were used to calculate the adsorption capacity, \( q_t \), and sorption efficiency, \( E \% \) for *P. dulce* using equations 1 and 2, respectively.

\[
q_t = \frac{(C_i - C_t)V}{W} \quad (1)
\]

\[
E \% = \left( \frac{(C_i - C_t)}{C_i} \right) \times 100 \quad (2)
\]
In the equations, \( q_t \) (mg/g) represents the metal ion uptake per unit mass of adsorbent at time \( t \). \( C_i \) and \( C_f \) (mg/mL) are the initial and final concentrations, respectively, of the metal ion in solution. \( V \) (mL) is the volume of the solution and \( W \) (g) is the mass of adsorbent powder.

3. RESULTS AND DISCUSSION

3.1 Characterisation of adsorbents

The FTIR spectra of \( P. \) dulce fruit peels and leaves (Figure 1) indicated the presence of several functional groups that are able to bind with lead(II) ions. The broad bands visible between 3000-3700 cm\(^{-1}\) in both spectra corresponded to OH or NH stretches. A strong absorption near 1650 cm\(^{-1}\) in the spectra of both peels and leaves is typical of the stretching frequency for a carbonyl. Fingerprint bands at around 1100-1200 and 1300-1400 cm\(^{-1}\) were also present in both spectra and indicate C-O single bonds in either a carboxylic acid or ester. An additional absorption at 1450-1500 cm\(^{-1}\) was observed and was consistent with the bending frequency for an NH bond.

3.2 Effect of contact time

The results (Figure 2) showed that over the first 10 min, phytosorption of Pb(II) ions onto peel powders occurred rapidly, after which the rate gradually decreased until equilibrium was attained at 80 min (\( E = 89.23\% \), \( q_t = 8.11 \) mg/g). Using leaf powders as the Pb(II) adsorbent, equilibrium was reached in just 50 minutes (\( E = 65.24\% \), \( q_t = 2.39 \) mg/g). The time required for equilibration is known to depend on the nature of the adsorbent surface, the functional groups present in its chemical constituents, the pH, initial metal concentration and adsorbent dose (Nurchi and Villaescusa, 2011). A variety of equilibrium exposure times for Pb(II) adsorption have been reported, including 180 min for sago waste (Karthika et al., 2010), 120 min for sesame husks (Surchi, 2011), 60 min for \( P. \) chrysosporium (Iqbal et al., 2014) and 20 min for \( C. \) demersum (Keskinkan et al., 2004).

3.3 Adsorption kinetics

The kinetics of phytosorption for Pb(II) removal by \( P. \) dulce was examined using the two most common models for pseudo-first-order, Equation 3 (Lagergren, 1898) and pseudo-second-order kinetics, Equation 4 (Ho and McKay, 1998).

\[
\log (q_e - q_t) = \log q_e - K_1 t / 2.303 \tag{3}
\]

\[
t/q_t = 1/K_2q_e^2 + t/q_e \tag{4}
\]

In Equations (3) and (4), \( q_t \) and \( q_e \) correspond to the masses of metal ions adsorbed onto the powders at time \( t \) (min) and at equilibrium, respectively, while \( K_1 \) and \( K_2 \) are the first and second-order rate constants. The plots of \( \log (q_e - q_t) \) versus \( t \) for both adsorption studies exhibited low regression coefficients,
(R²) indicating that the data could not be satisfactorily modelled by pseudo-first-order equation.

Much higher regression coefficients (R² = 0.9890 for peels and 0.9950 for leaves) were calculated for the pseudo-second-order plots of t/qe against t for both adsorptions, as shown in Figure 3. Furthermore, the derived qe values closely matched experimental qe data as depicted in Table 1. These results are consistent with Schiewer and Patil’s finding (2008) that one Pb(II) ion is bound by two monovalent active sites on P. dulce. Similar models for Pb(II) adsorption kinetics have been described for other agricultural adsorbents, including wheat bran (Bulut and Baysal, 2006), tea waste (Amarasinghe and Williams, 2007), bael leaves (Chakravarty et al., 2010), and galangal waste (Chairgulprasert et al., 2013).

Figure 1 Fourier Transform Infrared (FTIR) of P. dulce (a) fruit peels (b) leaves.
Effect of contact time on lead removal by *P. dulce* fruit peels and leaves [Dose = 0.2 g, Pb(II) conc. = 18.34 mg/L at pH 5].

Pseudo-second-order kinetic plots of lead removal by *P. dulce* fruit peels and leaves [Dose = 0.2 g, Pb(II) conc. = 18.34 mg/L at pH 5].

Table 1  Pseudo-second-order model parameters for removal of Pb(II) by *P. dulce* fruit peels and leaves

<table>
<thead>
<tr>
<th>Parts of <em>P. dulce</em></th>
<th>$q_e$ (exp) (mg/g)</th>
<th>Pseudo-second-order parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peels</td>
<td>8.11</td>
<td>$K_2$ (g/mg min) $q_e$ (cal) (mg/g) $R^2$</td>
</tr>
<tr>
<td>Leaves</td>
<td>2.34</td>
<td>0.045 8.33 0.9989</td>
</tr>
</tbody>
</table>

3.4 Effect of pH

The pH required for maximum Pb(II) ion uptake varies with different adsorbents; for example, pH 6 is the optimum acidity for metal adsorption by sporopollenin (Unlü and Ersoz, 2006), pH 5 for okra waste (Hashem, 2007) and pH 4 for bael leaves (Chakravarty et al., 2010). The pH for Pb(II) adsorption by *P. dulce* was optimised for both peels and leaves. At pH 2, the *P. dulce* fruit peels performed with low adsorption efficiency (37%) (Figure 4). However, as the pH was raised from 2 to 3, the percentage adsorption increased from 37 to a maximum of 90%,
indicating a rapid removal of lead(II) from solution. Between pH 3 and pH 6, the percentage lead adsorption remained around 90%, indicating that saturation had occurred. At pH 7, a slight precipitation was observed, so any practical adsorption process must be carried out under mildly acidic conditions. At pH <3 the adsorbent surface is largely protonated, so few negatively charged ligands would be present to effectively bind Pb(II) ions. However, under mildly acidic conditions (pH 3-6), acidic functional groups on the surface are capable of dissociation to negatively charged ligands, which efficiently bind metal ions (Li et al., 2007). Adsorption by the leaves was less sensitive to acidity, and increased steadily from 73% at pH 2 to 87% as the pH approached 6. In common with the peels, effective adsorption was no longer possible at pH ≥7 because of Pb(II) precipitation.

![Figure 4](image_url)  
**Figure 4** Effect of variation in pH on lead removal by *P. dulce* [Dose = 0.2 g, Pb(II) conc. = 15.56 mg/L, exposure time 80 min for peels and 50 min for leaves].

### 3.5 Effect of initial concentration of lead(II)

As can be seen from Figure 5, the mass of lead adsorbed increased with initial metal concentration. This effect can be explained from the high driving force for mass transfer under condition of high initial concentration (Ünlü and Ersoz, 2006), which also promote binding interactions between Pb(II) ions and the adsorbent surface.

Conversely, the percentage removal of lead decreased with initial metal concentration. However, during all experiments, the metal solutions contained the same amount of adsorbent in the presence of a limited number of binding sites, which gave rise to the observed decline in percentage removal.
Effect of initial concentration of lead removal on adsorption capacity \( (q_e) \) and adsorption efficiency \( (\%) \) \( \text{[Dose} = 0.2 \text{ g at pH 3, 80 min for peels and pH 5, 50 min for leaves]} \).

### 3.6 Adsorption isotherms

The sorption data obtained were evaluated using the Langmuir and Freundlich isotherm models. The Langmuir isotherm is based on the assumption that metal ions are adsorbed onto a homogeneous surface at specific active sites. In the Langmuir model (Equation 5), each adsorption site is regarded as identical, and adsorption only occurs with monolayer coverage, without transmigration of adsorbate over the surface (Langmuir, 1981).

\[
\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (5)
\]

Where \( q_e \) (mg/g) is the mass of metal ion adsorbed per unit mass of adsorbent, \( C_e \) (mg/L) is the equilibrium concentration in solution, \( q_m \) (mg/g) is the monolayer adsorption capacity and \( K_L \) is the Langmuir equilibrium constant. It is apparent that the data for Pb adsorption by peels were well-described by this mode \( (R^2=0.9813) \) (Figure 6a). However, adsorption by the leaves could not be satisfactorily described by this model due to the low value of \( R^2 \).

The Freundlich isotherm model (Equation 6) is based on the assumption that adsorption is a multilayer process, and that the adsorbent surface is heterogeneous (Freundlich, 1906).

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (6)
\]

Where \( K_F \) (L/g) is the Freundlich constant associated with the adsorption capacity and \( n \) is an empirical parameter related to the adsorption intensity and/or surface heterogeneity.
Figure 6 Isotherm plots for lead removal by *P. dulce* fruit peels and leaves (a) Langmuir isotherm (b) Freundlich isotherm

Table 2 Langmuir and Freundlich parameters for lead removal by *P. dulce*

<table>
<thead>
<tr>
<th>Isotherm Parameters</th>
<th>Peels</th>
<th>Leaves</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9813</td>
<td>0.7124</td>
</tr>
<tr>
<td>$K_L$</td>
<td>0.15</td>
<td>-</td>
</tr>
<tr>
<td>$q_m$ (mg/g)</td>
<td>11.36</td>
<td>-</td>
</tr>
<tr>
<td>Freundlich</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9430</td>
<td>0.9674</td>
</tr>
<tr>
<td>$K_F$</td>
<td>1.59</td>
<td>0.77</td>
</tr>
<tr>
<td>$n$</td>
<td>1.61</td>
<td>1.10</td>
</tr>
</tbody>
</table>

As can be seen in Figure 6b and Table 2, both sets of adsorption data correlated well with this model. However, for Pb-peel adsorption, the Langmuir isotherm (higher value of $R^2$) modelled the data better than the Freundlich isotherm. For both peels and leaves, $n$ was > 1, indicating that adsorption of lead(II) ions was a favourable process. The $K_F$ value for lead adsorption was greater for peels than for the leaves, confirming that the pod peels removed lead(II) ions more efficiently than the leaves.

3.7 Effect of variation in dose

As can be seen from Figure 7, increasing the mass of adsorbent improved percentage lead removal, but with a corresponding decrease in adsorption capacity, an effect previously reported. The evidence indicated that for both peels and leaves, increasing the mass of adsorbent provided more active sites and a greater surface area, which in turn improved metal ion separation.
Conversely, as the adsorbent dose was increased, the adsorption capacity decreased, indicating a less efficient exploitation of active sites in the adsorbent.

4. CONCLUSION

The waste peels and leaves of *P. dulce* can be used as an economical adsorbent for Pb(II) ions. The adsorption was found to be dependent on pH, contact time, loading lead concentration and sorbent dose. The optimum pH for peel adsorbent was ranged between 3 to 6 and for leave part was around 6. Adsorption reached equilibrium at 80 min for peels and at 50 min for leaves. The greater the initial lead concentration, the higher was the adsorption capacity for *P. dulce*, but the lower was the percentage removal from solution. Conversely, at higher doses of adsorbent, adsorption capacity was reduced, but with increased percentage removal. Equilibrium sorption data for the peels were well described by the Langmuir model, while the Freundlich was the better-fitting isotherm for leaves. Both adsorptions followed pseudo-second-order kinetics.

5. ACKNOWLEDGEMENTS

We would like to thank Division of Chemistry, Department of Science, Faculty of Science and Technology, Prince of Songkla University, Pattani Campus, Thailand, for support with chemicals and equipment. We are also grateful to Dr. Ian Beadham, lecturer in organic chemistry at Kingston University, UK., for his kind proof-reading of this manuscript.

6. REFERENCES


