Adsorption of Pb(II) from Solution using Peanut Shell as Biosorbent in the Presence of Amino Acid and Sodium Chloride

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Currently, marine protein byproducts are mainly hydrolyzed and prepared for applications that depend on their physiological activity. Such uses require strict removal of heavy metal ions from the material. In this work, a green approach was proposed using peanut shells as adsorbent to remove Pb(II) from solutions containing amino acid and sodium chloride. The effects of amino acids and sodium chloride on the removal of Pb(II), as well as the influence of liquid to solid ratio, pH, temperature, and contact time on the adsorption, were studied. The results showed that the content of sodium chloride and amino acid could significantly decrease the adsorption efficiency for Pb(II). The experimental data could be described with the Langmuir adsorption isotherm model and pseudo-second order kinetic model. The adsorption capacity of the sorbent for Pb(II) was calculated from the Langmuir isotherm model and found to be 7.1 mg g⁻¹ at pH 4.

Keywords: Peanut shell; Adsorption; Pb(II); Sodium chloride; Amino acid

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INTRODUCTION

The processing of sea fish can result in bulk protein byproducts (Jayathilakan et al. 2012), and these marine protein byproducts can be fully utilized by hydrolysis to prepare products having physiological activity, such that they can be used as feed ingredients and can be used to prepare antioxidative products (Rojo et al. 2007; Sathivel et al. 2003; Vieira et al. 2005). With the tremendous increase in the use of heavy metals in industry, sea water pollution has become a severe problem. Metallic substances can be ingested by fish and accumulate in vital organs at high levels (Hosseini et al. 2013; Maulvault et al. 2013; Squadrone et al. 2013). These heavy metals can easily enter the human body through the food chain, and cause severe damage to organs, exert teratogenic and carcinogenic effects, or even lead to deadly diseases (Cao et al. 2010; Zheng et al. 2013, 2007). Therefore, from a food safety point of view, it is necessary to remove heavy metal ions from marine protein hydrolyzate before utilization of the protein byproducts.

Lignocellulosic biomass is a type of biopolymer full of fibers and capillaries (Dridi-Dhauadi et al. 2011; Yang et al. 2007) and has been used as an environmentally-friendly adsorbent to remove metal ions from water and wastewaters (Chen et al. 2010b; Liu et al. 2013). Various studies using lignocelluloses for adsorption of various metal ions have been investigated (Chamarthy et al. 2001; Wafwoyo et al. 1999; Wilson et al. 2006; Witek-Krowiak et al. 2011). Peanut shells are an inexhaustible, nonedible, and renewable lignocellulosic material resource that can be used as an economical sorbent.

(Chamarthy et al. 2001; Wafwoyo et al. 1999; Witek-Krowiak et al. 2011). Therefore, these lignocellulosic sorbents are promising for the removal of heavy metal ions from aqueous solutions.

In marine protein hydrolyzates solution, there is not only possible contamination by heavy metal ions (Hosseini et al. 2013; Maulvault et al. 2013; Squadrone et al. 2013; Zeng et al. 2013), but also by high concentrations of amino acids (Chalamaiah et al. 2012) and sodium chloride (Kim et al. 2003). During the adsorption process, the competitive adsorption between heavy metal ions, sodium chloride (Wang et al. 2013), and amino acids can affect adsorption efficiency. Extensive research regarding the use of plant wastes for adsorption of Pb(II) from aqueous solutions have been reported (Amarasinghe and Williams 2007; Chen et al. 2010b; Inagaki et al. 2013; Quek et al. 1998; Rajkumar et al. 2013; Singh et al. 2006; Zhong et al. 2012). However, to the best of our knowledge, there is still no report about the effects of amino acids and sodium chloride on the absorption of Pb(II) from aqueous solution. Therefore, the potential for the use of peanut shells in the removal of Pb (II) from solution in the presence of amino acids and sodium chloride deserves study.

This paper aims to study the potential for the use of peanut shells for the removal of Pb(II) from solution in the presence of amino acids and sodium chloride. In the present work, the adsorption kinetics and isotherm under different experimental conditions (such as liquid to solid ratio, pH, temperature, and contact time) were investigated.

EXPERIMENTAL

Materials

Chemical reagents

Peanuts were purchased from a market in Zhoushan (Zhejiang province, China), and the peanut shells were collected. The peanut shells were milled to a powder and filtered in a sieve (Test Sieve Shakers, Retsch GmbH & Co. KG, Germany) to obtain particles less than 150 μm in size.

The standard solution of Pb(II) was purchased from National Analysis Center for Iron and Steel (Beijing, China). A stock solution of Pb(II) was prepared by diluting the standard solution of lead nitrate in double distilled water. All the other chemicals were of analytical grade, and all working solutions were prepared with double distilled water.

Preparation of adsorbent

The peanut shell powder was completely washed with distilled water until the supernatant was free of color and turbidity. The dried sorbent was then subjected to 0.1 M hydrochloric acid for 24 h and washed with distilled water until the washes were pH 7. The sorbent material was added to 0.1 M sodium hydroxide for 24 h, washed with distilled water until neutral, soaked with 90% (w/v) ethanol for 3 h, and then washed completely with distilled water. Finally, the sorbent was dried in an air oven at 80 °C for 48 h.

The characterization of the peanut shell was carried out by Fourier transform infrared spectroscopy (FTIR) using a Nicolet 6700 FTIR (Thermo Nicolet Corporation, USA). The spectrum was collected in the range of 4000 to 500 cm⁻¹ with a resolution of 4 cm⁻¹.
Preparation of Pb(II) solutions

Pb(II) solutions containing different concentrations of arginine (0.1 to 0.25 g mL\(^{-1}\)) and sodium chloride (5 to 45 mg mL\(^{-1}\)) were used in batch experiments.

Methods

Adsorption experiment

All absorption experiments were carried out in a batch mode. With the exception of the liquid to solid ratio studies, all experiments were conducted by mixing 20 mL of aqueous Pb(II) solution with 0.4 g of peanut shell powder. The pH values of Pb(II) solutions were adjusted with dilute nitric acid or sodium hydroxide solution with a Mettler Toledo FE20 pH meter (Mettler-Toledo International Inc., Switzerland). The mixture of the biosorbent and Pb(II) solutions were shaken in a thermostatic shaker bath (GFL 1092 shaker, GFL Ges. fur Labortechnik mbH, Germany) at 150 rpm at the desired temperature and contact time, and then the suspensions were centrifuged at 5000 rpm for 10 min. Different adsorption operating conditions, such as the liquid to solid ratio, pH, the concentration of arginine and sodium chloride, and the temperature and contact time, were taken into account. The variation of the uptake of Pb(II) with adsorption time was investigated by kinetic experiments. The Pb(II) concentration in the solution was determined with the Prodigy XP ICP (Teledyne Technologies, USA). The adsorption efficiency, \(E_a\), was defined as in the following equation,

\[
E_a = \frac{C_0 - C_e}{C_0} \times 100\%
\]

where \(C_0\) and \(C_e\) are the initial and final (equilibrium) concentrations of the Pb(II) in solution (mg L\(^{-1}\)), respectively.

In the batch experiments, a Pb(II) concentration of 70 mg L\(^{-1}\), pH 4.0, sodium chloride concentration of 5 mg mL\(^{-1}\), arginine concentration of 100 mg mL\(^{-1}\), liquid to solid ratio (mL:g) of 30:1, contact time of 100 min, and temperature of 303.2 K were selected as adsorption conditions (unless otherwise stated).

RESULTS AND DISCUSSION

Characterization of Peanut Shells

To ascertain the changes of peanut shells before and after adsorption, the infrared spectrum of the peanut shells was obtained by FTIR, and results are shown in Fig. 1. Based on the attribution of peaks in Fig. 1, adsorption at 3440 and 3410 cm\(^{-1}\) represents the stretching vibration of the hydroxyl groups (Li et al. 2009). The peaks at 1630 and 1650 cm\(^{-1}\) can be assigned to C=O stretching (Adiana and Mazura 2011; Villena et al. 2000). A strong band at 1060 and at 1050 cm\(^{-1}\) corresponds to C–O stretching (Wahab et al. 2012). The comparison of the spectrum between the peanut shells before and after adsorption show very similar infrared peaks; however, some changes have occurred in peak intensity. After adsorption, the peaks were consistent with an –OH red shift from 3410 to 3440 cm\(^{-1}\), and the peak at 1630 cm\(^{-1}\) had a red shift of 20 cm\(^{-1}\). The peaks at 3440 and 1650 cm\(^{-1}\) show a remarkable decrease in peak intensity after Pb(II) loaded. The above changes in FT-IR spectra indicated that the hydroxyl and carboxyl groups are involved in Pb(II) adsorption by surface complexation (Ngah et al. 2008).

Effect of pH

The pH of the Pb(II) solution is an important variable in the absorption of Pb(II) onto the sorbents due to the effect of sorbent on the surface charge and the degree of ionization, which affects the availability of binding sites (Bansal et al. 2009; Javaid et al. 2011; Liang et al. 2013). Therefore, the influence of the initial pH of the solution on the adsorption of Pb(II) onto peanut shell was investigated in the pH range of 2.5 to 6. The effect of pH is shown in Fig. 2.

Fig. 1. FTIR infrared spectrum of peanut shells before (a) and after (b) adsorption

Fig. 2. Effect of pH on adsorption efficiency

As can be seen, when pH was between 2.5 and 5, the adsorption efficiency exhibited no obvious differences. When the pH was higher than 5.5, the adsorption
efficiency decreased. The trends showed that the removal of metal ions increased with increasing solution pH (Lu et al. 2012), but the biosorption capacity increased gradually in the pH range from 2 to 5 and reached to a maximum value around pH 5. Adsorption efficiency remained high between pH 2.5 and 5, and then decreased as pH increased to 5.5. This can be explained by noting that the presence of sodium chloride in the solution may increase the competition between Na⁺ and Pb(II) for the binding sites of the adsorbent when pH above 5. To increase the adsorption capacity as much as possible, a pH of 4.0 was selected for the remaining batch experiments.

**Effect of Liquid to Solid Ratio**

The liquid to solid ratio is important and will have an influence on the sorption of metals (Bordas and Bourg 2001). The effect of volume of the Pb(II) solution to mass of the peanut shell ratio (mL:g) on metal ion uptake was studied, and the results are shown in Fig. 3. The adsorption efficiency decreases with an increase of the liquid to solid ratio, which can be explained by the decrease of the number of sites available for biosorption, which depends on the amount of absorbent. When the liquid to solid ratio is between 10:1 and 70:1, the adsorption has a high efficiency of 94 to 96%. As the liquid to solid ratio increases to 90:1, the efficiency decreases slightly. All the adsorption efficiencies under different liquid to solid ratios are above 87%.

![Graph showing the effect of liquid to solid ratio on adsorption efficiency.](image)

**Fig. 3.** Effect of liquid to solid ratio on adsorption efficiency

**Effect of Sodium Chloride**

Marine protein hydrolyzate commonly contains high concentrations of sodium chloride. However, ionic strength shows a significant effect on metal ion adsorption on the sorbent (Guo et al. 2008). Hence, it is necessary to study the effects of sodium chloride on the Pb(II) adsorption onto peanut shells. In the group experiments, the concentrations of sodium chloride were studied in the range from 5 to 45 mg mL⁻¹. Figure 4 shows the effect of sodium chloride on Pb(II) adsorption onto the peanut shell. When the concentration of sodium chloride is lower than 5 mg mL⁻¹, the effect of sodium chloride on adsorption efficiency is very small. A significant decrease in Pb(II)
adsorption occurred when the concentration of sodium chloride was higher than 5 mg mL\(^{-1}\), which may be explained by the formation of outer-sphere complexes due to Na\(^+\) in the background electrolyte that may compete with the metal ions for outer-sphere sorption sites.

![Graph](image1.png)

**Fig. 4.** Effect of sodium chloride on adsorption efficiency

**Effect of Amino Acids**

In marine protein hydrolyzates there are numerous amino acids. The amino acids may have an influence on heavy metal adsorption. Hence, the effects of amino acids on biosorption were investigated using arginine as a model (Fig. 5).

![Graph](image2.png)

**Fig. 5.** Effect of concentration of arginine on adsorption efficiency
The initial arginine concentrations used in this study were 0.10, 0.15, 0.20, and 0.25 g mL\(^{-1}\) for the sorbent. As can be seen in Fig. 5, the adsorption efficiency of the sorbent for Pb(II) decreased with an increasing initial concentration of arginine; the higher the concentration of arginine, the lower the adsorption efficiency. This was probably due to competitive adsorption between Pb(II) and arginine. The possibility that arginine binding with Pb(II) also should be responsible for this trend.

**Effect of Contact Time**

To investigate the effect of contact time, adsorption experiments were conducted at different times in the range of 6 to 120 min. The effect contact time on the removal of Pb(II) by peanut shells is shown in Fig. 6. The value of \(E_a\) increased as the contact time increased, until the equilibrium was reached. Adsorption of Pb(II) onto peanut shells is a very fast process, where more than 90% of the adsorption occurred within the first 30 min and equilibrium was attained within 100 min.

![Effect of contact time on adsorption efficiency](image_url)

**Effect of Temperature**

The effect of temperature on adsorption was studied at seven temperatures (293.2, 298.2, 303.2, 308.2, 313.2, 323.2, and 333.2 K). Increasing the temperature can cause a decrease in adsorption efficiency (Fig. 7). This indicates that the adsorption process is exothermic, so lower temperatures are more favorable for the adsorption of Pb(II) ions.

**Adsorption Studies**

*Sorption kinetics of Pb(II)*

To investigate the Pb(II) adsorption rate, the kinetics of Pb(II) adsorption by peanut shells was modeled using the pseudo-first order and pseudo-second order equation (Bajpai *et al.* 2012; Chen *et al.* 2011). Pseudo-first order assumes that the rate is proportional to the number of unoccupied sites. However, pseudo-second order assumes that the rate is proportional to the square of the number of unoccupied sites (McKay and Ho 1999). The linear form of pseudo-first order and pseudo-second models is expressed as equations (2) and (3), respectively,
Fig. 7. Effect of temperature on adsorption efficiency

\[
\ln(Q_e - Q_t) = \ln Q_e - k_1 t \tag{2}
\]

\[
\frac{t}{Q_t} = \frac{1}{k_2 Q_e} + \frac{t}{Q_e} \tag{3}
\]

where \(Q_t\) is the amount of the Pb(II) ion adsorbed at various times \(t\) (mg g\(^{-1}\)), \(Q_e\) is the amount of sorption at equilibrium adsorption capacity (mg g\(^{-1}\)), \(k_1\) is the pseudo-first order rate constant (min\(^{-1}\)), and \(k_2\) is the pseudo-second order rate constant for the adsorption (g mg\(^{-1}\) min\(^{-1}\)).

The values of \(\ln(q_e - q_t)\) are calculated from the data of the kinetic experiment. The models are examined by linear plot of \(\ln(q_e - q_t)\) versus \(t\) and \(t/q\) versus \(t\), respectively. The characteristic parameters of the model are listed in Table 1. By comparing the two kinetic models, the \(R^2\) value calculated by pseudo-second order model is relatively high (0.999), and the experimental values also agree with the calculated values. This suggests that the experiment data fits the pseudo-second order model better than pseudo-first order model. It can be explained that the compact structure of lignocellulosic biomass poses a hindrance for Pb(II) adsorption into the interior of adsorbent, hence, some binding sites of the adsorbent may be difficult to reach.

<table>
<thead>
<tr>
<th>Table 1. Adsorption Kinetic Model</th>
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<tbody>
<tr>
<td>(C_0) (mg/L)</td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>70</td>
</tr>
</tbody>
</table>

\(a\) Experimental

\(b\) Calculated
Isotherm study

The Langmuir and Freundlich isotherm models are commonly used to describe the adsorption process. Normally, Langmuir isotherm assumes that the adsorption process only takes place at specific homogenous sites within the adsorbent surface with uniform distribution of energy level. If the Langmuir isotherm provides a good fit to the data, then it can be concluded that the adsorption process is monolayer in nature (Weber and Chakravorti 1974). However, the Freundlich isotherm supposes that the adsorption occurs at heterogeneous sites with non-uniform distribution of energy levels. The Freundlich isotherm describes reversible adsorption and is not restricted to the formation of a monolayer (Mohd Din et al. 2009). The Langmuir and the Freundlich isotherm models are defined in Eqs. (4) and (5), respectively.

$$\frac{C_e}{Q_e} = \frac{1}{K_L Q_{\text{max}}} + \frac{C_e}{Q_{\text{max}}}$$

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e$$

In Equations 4 and 5, $C_e$ (mg L$^{-1}$) is the concentration of the Pb(II) solution at equilibrium, and $Q_e$ (mg g$^{-1}$) is the amount of sorption at equilibrium. In the Langmuir equation, $Q_{\text{max}}$ is the maximum sorption capacity and $K_L$ is the Langmuir constant. In the Freundlich equation, $K_f$ and $1/n$ are empirical constants. The values of the isotherm constants are presented in Table 2. By comparing the two models, the $R^2$ values calculated by Langmuir model is relatively high ($R^2=0.916$). This indicates that the experiment data were fit by the Langmuir model better than by the Freundlich model.

Table 2. Langmuir and Freundlich Equations, the Related Parameters, and Correlation Coefficients

<table>
<thead>
<tr>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
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<tr>
<td>$Q_{\text{max}}$ (mg/g)</td>
<td>$K_f$ (mL/mg)</td>
</tr>
<tr>
<td>7.13</td>
<td>1.48</td>
</tr>
</tbody>
</table>

CONCLUSIONS

1. This work examined the efficiency of peanut shells in the removal of trace Pb(II) from the solution containing sodium chloride and amino acid. The liquid to solid ratio, solution pH, amino acid and sodium chloride concentration, temperature, and contact time of the biosorption system played important roles in Pb(II) adsorption on peanut shells.

2. The results revealed that the presence of amino acid and sodium chloride in the solution can decrease the adsorption efficiency of Pb(II) to a large extent, depending on their concentrations. The pseudo-second order kinetic model was found to be a good fit for the sorption kinetics onto peanut shells, and equilibrium data fit the Langmuir model better than Freundlich model, with a maximum Pb(II) adsorption capacity of 7.1 mg/g.
3. Because peanut shells can be readily obtained, they can be regarded as effective economical biosorbents for the removal of toxic heavy metal ions from solutions containing sodium chloride and amino acid, such as marine protein hydrolyzate solutions.

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