Biosorption of \( \text{Cu}^{2+} \) and \( \text{Pb}^{2+} \) using sophora alopecuroides residue

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Abstract. Sophora alopecuroides residue (SAP), a kind of traditional Chinese herbal medicine residue, was developed in an alternative biosorbent for the removal \( \text{Cu}^{2+} \) and \( \text{Pb}^{2+} \) in simulated wastewater. The morphology and surface texture of SAP were characterized by scanning electron microscopy, which showed a loose and porous structure. The biosorption experiments of \( \text{Cu}^{2+} \) and \( \text{Pb}^{2+} \) onto SAP were investigated by using batch techniques. High biosorption percentage appeared at pH values of 4.5–6.0. The experimental data followed the second-order kinetic model well. Equilibrium fit with the Langmuir isotherm model well. The maximum biosorption capacity of an adsorbent at 25\( ^\circ \)C was respectively 60.6 mg/g \( \text{Cu}^{2+} \) and 128.1 mg/g \( \text{Pb}^{2+} \). The findings of the present study show that SAP is an attractive and effective biosorbent for \( \text{Cu}^{2+} \) and \( \text{Pb}^{2+} \).

1. Introduction
With the expansion of industrial activities, the increased emission of wastewater containing heavy metal ions has turned into a severe problem, and a threat to human health. \( \text{Cu}^{2+} \) is widely used in dyeing, papermaking, petroleum, plating plants, and in the production of some alloys [1, 2]. Wastewater containing \( \text{Pb}^{2+} \) mainly comes from battery factories, mining, mine tailings, the combustion of fossil fuels, sulphide ore smelting, and the drainage water of non-ferrous metal plants [3]. The permission limit of copper and lead in drinking water is 2 mg/L and 0.05 mg/L [4]. Various diseases can be caused as a result of excess copper and lead in drinking water. \( \text{Cu}^{2+} \) can react with protein ligands to form coordination compounds in the human body that cause the loss of normal physiological function of protein, and even lead to death [5]. \( \text{Pb}^{2+} \) has a strong neurotoxicity that may cause a variety of neurological disorders in humans, such as memory loss, learning disabilities, and behavioral anomalies [6]. The commonly used technologies for the removal of \( \text{Cu}^{2+} \) and \( \text{Pb}^{2+} \) include chemical precipitation [7], ion exchange [8] and membrane separation [9]. These conventional technologies are neither economical nor effective, and different methods have different disadvantages.
In view of this, it is significant to develop materials, or new technologies, to decrease heavy metal ions in wastewater to environmentally acceptable levels.

In numerous methods, biosorption is widely known for its efficiency, safety, low cost, and environmental protection [11]. Biosorption can utilize various different materials including microbial cells, such as bacteria, and biological materials, which contain some natural materials waste and natural material [12, 13]. Most adsorbents’ adsorption mechanism, which takes plants or waste as raw materials, can be explained in the following way: plants contain a large number of rude fibre, indicating the practicability to dislodge toxic heavy metal ions from aqueous solution, as a result of presence of various functional groups on the cellulose, such as $-\text{OH}$, $-\text{COOH}$ to be involved in metal ions binding [14]. Sophora alopecuroides L, a kind of traditional Chinese herb, contains many chemical compounds, such as: flavonoids, alkaloids, organic acid, volatile oil, protein, saccharide, amino acid, etc [15]. With sophora alopecuroides residue, active ingredients are extracted containing rude cellulose (31.42%), crude protein (17.66%) and a mass of amino acid, which provide potential for adsorption of metallic cations.

According to a report [16], more than 30 million tons of Chinese herb residues are produced yearly in China. Currently, they are buried or combust [17], which will cause not only a great waste of resources, but will have serious damage on the environment as well. Chinese herbal medicine residue can be made into biosorbent with appropriate treatment. The adsorbents have many advantages, such as being low cost, recyclable and biodegradable. The preparation of sophora alopecuroides residue adsorbent offers a new way for using the waste residue of traditional Chinese herbal medicine. In this study, the biosorption of Cu$^{2+}$ and Pb$^{2+}$ from simulated wastewater solution onto sophora alopecuroides residue at 25°C was studied.

2. Experimental

2.1. Chemicals and equipment

Stock solution (1.000 g/L) was prepared by dissolving 3.9720 g of CuSO$_4$·5H$_2$O and 1.6228 g of Pb(NO$_3$)$_2$ in 1 L of redistilled water. Diluting the stock solution provided a work solution for practical use. All reagents used in the experiment were of A.R grade. Surface morphological structure of sophora alopecuroides residue was studied using Scanning Electron Microscopy (Hitachi S-3400H). The concentrations of copper and lead were determined using atomic absorption spectrophotometer (Persee A3 series Beijing).

2.2. Preparation of biosorbent

Sophora alopecuroides residue was collected from a pharmaceutical factory in Ningxia China. Sophora alopecuroides waste was washed a few times with distilled water, and then dried inside a convection oven for 24 hours at 70°C. The sophora alopecuroides was then crushed to powder in a pulverizer, and sieved to a constant size range 0.3-0.5 mm. This treated sophora alopecuroides waste is called SAP.

2.3. Biosorption experiments
Batch adsorption tests were completed by shaking a series of conical flasks containing the desired dosage of biosorbent in a scheduled concentration of heavy metal solution with known pH. The pH of the Cu$^{2+}$ and Pb$^{2+}$ solution was adjusted to the required value by 0.1mol/L HCl and 0.1mol/L NaOH before the addition of biosorbents. 0.100 g of SAP sample was equilibrated with 25 ml of the Cu$^{2+}$ and Pb$^{2+}$ solution of known concentration in a sealed conical flask at 25°C in a thermostatic shaker bath. The effect of pH value on the biosorption of Cu$^{2+}$ and Pb$^{2+}$ was studied by mixing 0.100g of SPA with 25mL of 100mg/L Cu$^{2+}$ and 300mg/L Pb$^{2+}$ solutions of pH from 2.5 to 6.0. In kinetic experiments, the adsorption time varied from 0 to 120min using 100mg/L Cu$^{2+}$ and 300mg/L Pb$^{2+}$ solutions. 0.100g of SAP was put in 25mL of Cu$^{2+}$ (50-250mg/L) and Pb$^{2+}$ (100-500mg/L) solutions at various concentrations in order to carry out isotherm adsorption experiments. In all experiments, the glass flasks were shaken at 200 rpm on a water-bathing constant temperature vibrator for a known time. After the oscillation, supernatant was filtered and the concentration of the Cu$^{2+}$ and Pb$^{2+}$ ion remaining was determined by flame atomic absorption spectrometry. All experiments were run in triplicate.

The biosorption capacity $q$(mg/g) was determined by equation (1):

$$q = \frac{(c_e - c_i) V}{W}$$  \hspace{1cm} (1)

The adsorption percentage of heavy metal ion was determined by equation (2):

$$\text{adsorption percentage(\%)} = \frac{c_0 - c_q}{c_0}$$  \hspace{1cm} (2)

where $c_e$ and $c_i$ (mg/L) are the equilibrium and initial concentrations of copper and lead, $W$ (g) is the mass of the dry adsorbent and $V$ (L) is the volume of copper and lead solution.

3. Results and discussion

3.1. Characterization of the biosorbent

The SEM revealed the morphology and surface structure of *Sophora alopecuroides* residue (SAP) at different magnifications clearly. The SEM micrographs of SAP shown in Figure 1 indicated a loose and porous structure, which can supply a high specific surface area of SAP. It was clearly observed from the photographs that the biosorbent showed a rough structure (1000×). At 2000× magnification, the presence of asymmetric pores and irregular spiral structure in large quantity were more easily observed, which is favorable for biosorption of Cu$^{2+}$ and Pb$^{2+}$ ions.
3.2. Biosorption of copper and lead ion

3.2.1. Effect of pH on biosorption. Figure 2 shows the impact of pH on biosorption percentage of Cu$^{2+}$ and Pb$^{2+}$ by SAP. Adsorption percentage of both metal ions showed a rapid increase in pH from 2.5 to 4.5 and then stabilized at higher pH values of 4.5 to 6.0. The maximum removal percentage was 95% for Cu$^{2+}$ at pH 5.5 and 91% for Pb$^{2+}$ at pH 5.0.
Figure 3. Effect of time on biosorption.

The solution pH was selected to avoid the possible formation of metallic precipitation that restricting the true biosorption studies showed; pH value is an independent factor in the biosorption process [18]. The metal binding sites on SAP for biosorption includes −OH and −COOH functional groups [14] in which H\(^+\) ions can be exchanged for metal ions in solution. As the pH is reduced, H\(^+\) will compete with Cu\(^{2+}\) and Pb\(^{2+}\) on the active sites of SAP biosorption which results in the decrease of adsorption percentage. In contrast, with pH increasing, the surface of biosorbent is negatively charged; therefore, it is favorable for the biosorption of positively charged copper and lead ions.

3.2.2. Biosorption kinetics. Figure 3 shows the adsorption kinetics of Cu\(^{2+}\) and Pb\(^{2+}\) on SAP. The biosorption percentages of Cu\(^{2+}\) and Pb\(^{2+}\) ions on SAP increase in the initial 30 min rapidly, and then attain equilibrium at about 1 h. The ultimate adsorption percentages of two metals exceed 90%. After adsorption equilibrium, the removal rate did not obviously change with time. Compared to usual adsorbents such as adsorption resin and activated carbon, the time of equilibrium of SAP was shorter [19].

Kinetic of heavy metal ions biosorption could be modeled by the first-order equation and second-order equation shown as follows:

\[
\ln(q_e - q_t) = \ln q_e - \frac{k_1}{2.303} t 
\]

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} 
\]

where \(k_1\) and \(k_2\) are respectively the rate constant of first-order and second-order models, \(q_t\) (mg/g) and the amount of metal ion biosorbed at any given time \(t\); \(q_e\) (mg/g) the amount of metal ions adsorbed at equilibrium. The kinetic constants were given in Table 1. It was found that the coefficient of correlation \((R^2)\) for second-order model is much closer to 1 than that of the first-order kinetic model and the calculated values \((q_e)\) agree well with experimental values \((q_{e-exp})\). As a result of the second-order model reaction mechanism, the biosorption of Cu\(^{2+}\) and Pb\(^{2+}\) processes seem to be controlled by the chemical processes involving covalent forces, sharing or exchanging of electrons between the biosorbent and copper and lead ions [20].

| Adsorbent | \(q_{e-exp}\) (mg/g) | First-order equation | Second-order equation | 
|-----------|----------------------|----------------------|----------------------| 
|           | \(q_e\) (mg/g) | \(k_1\) (1/min) | \(R^2\) | \(q_e\) (mg/g) | \(k_2\) (g/mg·min) | \(R^2\) | 
| Cu(II)   | 23.31              | 5.18                | 0.057               | 0.7300 | 23.72            | 0.022               | 0.9998 | 
| Pb(II)   | 68.48              | 5.30                | 1.754               | 0.1158 | 69.40            | 0.016               | 0.9998 |
3.2.3. Adsorption isotherms. Figure 4 presents the experimental biosorption isotherms of Cu$^{2+}$ and Pb$^{2+}$ on SAP. It showed that $q_e$ increased as $c_e$ increased until the equilibrium was attained, and then $q_e$ was almost unchanged with continuing increase in $c_e$.

Freundlich and Langmuir isotherm models are used to establish the relationship between the biosorption capacity of Cu$^{2+}$ and Pb$^{2+}$ on SAP and equilibrium concentration. Langmuir isotherm model is given as equation (5):

$$\frac{c_e}{q_e} = \frac{c_e}{q_m} + \frac{1}{b q_m}$$

(5)

where $q_e$ (mg/g) is the biosorption capacity of Cu$^{2+}$ and Pb$^{2+}$ at equilibrium, $q_m$ (mg/g) is the maximum biosorption capacity of the biosorbent, $b$ (L/mg) is the Langmuir constant.

Freundlich isotherm model is given as below:

$$\log q_e = \log K_f + \frac{1}{n} \log c_e$$

(6)

where $K_f$ and $n$ are the Freundlich constant.

As shown in Table 2, the biosorption patterns of Cu$^{2+}$ and Pb$^{2+}$ on SAP are well fitted to the Langmuir model with $R^2$ of 0.985-0.999. In contrast, the Freundlich model has lower values of $R^2$, which suggests that the data follows the Langmuir model better. According to the Langmuir model, the maximum biosorption capacities ($q_m$) of SAP for Cu$^{2+}$ and Pb$^{2+}$ were respectively 60.6 mg/g and 128.1 mg/g. The constant $b$ reflects a strong affinity between SAP and Cu$^{2+}$ and Pb$^{2+}$. The $K_f$ value of the Freundlich model shows that SAP has high adsorption density in Cu$^{2+}$ and Pb$^{2+}$ solutions. Compared to some other biomass used, SAP shows better adsorption capacity (table 3).
Table 2. Isotherm models parameters for the biosorption of Cu$^{2+}$ and Pb$^{2+}$ on SAP.

|        | Langmuir equation | Freundlich equation |
|--------|-------------------|---------------------|
|        | $q_m$ (mg/g)  | $b$ (L/mg) | $R^2$ | $K_f$ | $n$ | $R^2$ | $K_f$ | $n$ |
| Cu$^{2+}$ | 60.6      | 0.147    | 0.9874 | 18.98 | 2.343 | 0.9213 | 18.98 | 2.343 |
| Pb$^{2+}$ | 128.1     | 0.040    | 0.9971 | 21.14 | 2.833 | 0.9047 | 21.14 | 2.833 |

Table 3. Maximum adsorption capacities for different biomass.

| Adsorbents                  | $q_m$ (mg/g) | References |
|-----------------------------|--------------|------------|
| Tobacco dust                | 36.0         | [21]       |
| Waste beer yeast            | 1.44         | [22]       |
| Cyclotella sp               | 26.03        | [23]       |
| S. alopecuroides residue (SAP) study | 60.1         | 96.1       | This    |

4. Conclusion

SAP, which is a traditional Chinese herbal medicine residue, was developed to remove Cu$^{2+}$ and Pb$^{2+}$ from simulated wastewater solutions. The biosorption rate was fast, and equilibrium was obtained within 60 min. The coefficient of correlation ($R^2$) of the second-order kinetic equation was greater than 0.999. The Langmuir and Freundlich adsorption models were used to express the sorption phenomenon, with a better result from the Langmuir model than the Freundlich model. The maximum adsorption capacities of SAP for Cu$^{2+}$ and Pb$^{2+}$ were 60.6 mg/g and 128.1 mg/g at pH 5.0, respectively. The results of this research indicate the feasibility and possibility that SAP can be made into an inexpensive and effective biosorbent for treatment of wastewaters containing Cu$^{2+}$ and Pb$^{2+}$.

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