Lead(II) removal from wastewater by water hyacinth

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Abstract. Lead(II) contamination is a serious environmental problem. The purpose of this research is to discuss the feasibility of utilizing dead water hyacinth granule to eliminate lead(II) cations from aqueous solution through batch tests. Effects of contact time, medium acidity-alkalinity, and solution lead concentration on this biosorption process were detailly studied. The experimental result suggested that the lead(II) biosorption depended highly on the medium pH. A pH of 5.0 was most helpful to lead(II) removal. The biosorption data conformed to pseudo-second-order kinetics and the biosorption equilibrium time was equal to 45 minutes. The biosorption isotherm data could be characterized using Langmuir model accompanied with the maximum biosorption capacity of 75.44 mg/g. Our findings revealed that water hyacinth could be an efficient adsorbent for lead(II) elimination.

1. Introduction
Much wastewater bearing lots of poisonous metals produced annually with the development of modern industry, which led to serious environmental pollution as well as health problems. Amongst these heavy metals, Pb is regarded as one of the most poisonous metals in water environment. The heavy metal ‘Pb’ generating from the manufacture of alloys, plastics, solders, batteries, pipes and pigments [1], could unavoidably bring about harmful effects on ecosystems and accumulate in human body through food chains [2]. Because lead is recalcitrant and persistent in water environment, much attention has been paid to its removal from wastewater. Many remediation approaches, such as ion exchange, ultra-filtration, electrochemical deposition, adsorption or biosorption, were used to remove toxic lead(II) ions.

So far biosorption has been employed to eliminate toxic metals from wastewater. Metal binding could involve several likely mechanisms: physico-chemical uptake, ion exchange, complex/coordination, and microprecipitation. Various dead and living biomasses as well as their cellular products (i.e. polysaccharides) could be utilized to bind heavy metals. In comparison with those living organisms, dead ones have many virtues because they are not only inexpensive in dropping toxic heavy metals to low levels but also require less operation cost and regenerate readily.

In particular, some freshwater plants, such as Salvinia herzogoi, Potamogeton lucens, Cratophyllum demersum and Myriophyllum brasiliensis were used for biosorptive removal of toxic metals from a variety of sources [3]. Water hyacinth remarkably affects the flow of water body,
prevents sunbeam from shining indigenous aquatic organisms, consumes much dissolved oxygen in water, and also serves as a good habitat for mosquitoes. It is commonly used to construct wetlands because its grows fast and uptake considerable nutrients and pollutants.

In this investigation, we reported the process of lead(II) biosorption onto water hyacinth. The aim of the study was to assess the likelihood of employing water hyacinth to eliminate lead(II) pollution from industrial effluent. Batch experiments were carried out to explore the effects of several adsorption factors (contact time, medium pH, and initial Pb concentration). In addition, several kinetic and isotherm models were also employed to describe the process of lead(II) biosorption.

2. Materials and methods

2.1. Preparation of biosorbent and stock solution
The water hyacinth biomass was obtained from Honghu Liangshui Aquatic Plant Company, Jingzhou, China. The fresh biomass was completely washed with running water to get rid of sand, silt and diatoms. The biomass was bathed under sunlight for seventy two hours and then dried in an oven at 60 °C for twenty four hours. The dried hyacinth as the sorbent was pestled and permitted to pass through an 80-mesh sieve. The treated biomass was put in a desiccator for the following use in biosorption tests. The surface morphology of water hyacinth was detected using scanning electronic microscope (SEM).

The lead(II) stock solution (1.0 g/L) was obtained through the dissolution of Pb(NO₃)₂ in demineralized water. It was further diluted to the other needed concentrations and their pHs were adjusted to proper values using NaOH or HCl solution.

2.2. Metal sorption experiments
Batch experiments were carried out in a series of 250 mL flasks to study the effect of the aforementioned variables on the lead(II) biosorption. Preliminary tests were also performed to make certain the best range of all variables. Generally, approximately 100 mL of lead(II) solution was mixed with a certain dose of water hyacinth. Then, these flasks were shaken at 140 rpm on a thermo controlled rotary shaker. Lastly, the equilibrated solutions were took out and the biomass were extracted from them by centrifugation. The remained lead(II) level in the solution was determined via a microtitration approach presented by Li et al. [4]. All of the adsorption experiments were repeated three times and average values were adopted for further calculations.

The lead(II) removal efficiency and lead(II) adsorption capacity were calculated out using the following formulas:

\[ R(\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \]  
\[ q_t = \frac{(C_0 - C_t)V}{m} \]  
\[ q_e = \frac{(C_0 - C_e)V}{m} \]

where \( R\% \) represents the lead(II) removal efficiency; \( q_t \) and \( q_e \) represent the lead(II) adsorption capacity at time \( t \) (min) and at equilibrium (mg/g), respectively; \( C_0, C_t, \) and \( C_e \) represent the initial lead(II) concentration, solution lead(II) concentration at time \( t \), and the lead(II) concentration at equilibrium (mg/L), respectively; \( V \) represents the aqueous solution volume (L); and \( m \) represents the biosorbent mass (g).

2.3. Biosorption kinetics simulation
Two common kinetic models, i.e., pseudo-first-order as well as pseudo-second-order equations, were used to investigate the biosorption kinetics. Pseudo-first-order model was adopted to the experimental data fitting [5], which could be expressed as Equation (4):

\[ \ln(q_e - q_t) = \ln q_e - k_1t \]

\( k_1 \) represents the pseudo first-order rate constant (min⁻¹).
Where \( k_1 \) represents the rate constant regarding the pseudo-first-order kinetic model. The pseudo-second-order equation was employed to describe the biosorption process and gain an insight into the likely binding mechanisms [6], which could be expressed as Equation (5).

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

(5)

Where \( k_2 \) represents the rate constant regarding the pseudo-second-order kinetic model.

2.4. Adsorption isotherm simulation

Two adsorption isotherms, i.e. Langmuir and Freundlich equations were employed to clarify the suitable one for lead(II) biosorption onto this biomass [7, 8]. They could be expressed as Equations (6) and (7), respectively.

\[
q_e = \frac{q_m K_L C_e}{1 + K_L C_e}
\]

(6)

\[
q_e = K_F C_e^{1/n}
\]

(7)

Where \( q_m \) represents the maximum adsorption capacity (mg/g), \( K_L \) represents Langmuir constant regarding adsorption energy (L/mg), \( K_F \) (mg (L/mg)^1/n) and \( n \) (dimensionless) represent the Freundlich constants and intensity factors, respectively.

3. Results and discussion

3.1. Contact time dependence of lead(II) biosorption

The adsorption time of liquid and solid phase is a critical factor in the treatment of practical wastewater because this parameter can represent the kinetics of interactions between an adsorbent and an adsorbate. Just for this reason, we studied the impact of adsorption time on lead(II) adsorption onto water hyacinth at room temperature. About 65% of lead(II) was eliminated after 20 minutes and an uptake equilibrium state was reached within 45 minutes. The fast biosorption at early stage might be explained that considerable vacant binding sites could be readily available on the surface of water hyacinth. The kinetic model parameters were calculated out and exhibited in Table 1. Although the \( q_e \) values derived from both models were close to the experimental data (\( q_{e,\text{exp}}=53 \) mg/g), the \( R \) value regarding pseudo-second-order model approached 1.0 compared with pseudo-first-order one. According to above analysis, lead(II) biosorption onto water hyacinth agreed with pseudo-second-order kinetics, in which the rate-limiting step for this process could belong to chemical adsorption.

| \( q_{e,\text{exp}} \) (mg/g) | Pseudo-first-order kinetics | Pseudo-second-order kinetics |
|-----------------------------|-----------------------------|-----------------------------|
| \( k_1 \) (min\(^{-1}\))  | \( q_e \) (mg/g) | \( R \) | \( k_2 \) (g mg\(^{-1}\) min\(^{-1}\)) | \( q_e \) (mg/g) | \( R \) |
| 53                          | 0.2307                      | 52.61                       | 0.9212 | 0.0072 | 54.37 | 0.9936 |

* Testing condition: pH=5.0; Temp= 25 °C; initial lead(II) level: 100 mg/L; water hyacinth dosage: 0.1 g; solution volume: 100 mL.

3.2. Influence of solution acidity-alkalinity

Other investigations on metal biosorption suggest that medium pH is one important factor controlling the uptake of metal ions on adsorbents because medium pH may influence the adsorption capacity. Given that the formation of lead hydroxide precipitate when the solution pH value was greater than 6.0, the lead(II) biosorption process was investigated over the pH range from 2.0 to 6.0. It was found that the biosorption of lead(II) onto water hyacinth depended highly on the pH value and the best pH for maximum metal removal was 5.0 (Figure 1). So the medium pH was adjusted to 5.0 in all of the following experiments intending to attain the best lead(II) removal. The dominant form of lead-
containing cations at lower pH is lead(II) and the increase of pH would convert lead(II) to the other speciations, i.e. Pb(OH)_2, Pb(OH)^+ and Pb(OH)_3^- [9]. The poor lead(II) adsorption at lower pHs might be ascribed to the increased level of hydron or hydroxonium cations competing for lead(II) adsorption locations on the water hyacinth. But for higher pH values, lead(II) ligands have less opportunity to be adsorbed onto the binding sites because of their large size since they are prone to form metal complexes in aqueous solution. Therefore the best pH value is considered to be 5.0 in the pH range investigated.

![Figure 1. Influence of pH on lead(II) adsorption by water hyacinth.](image)

| Initial pH value | q_e (mg/g) |
|------------------|------------|
| 2                | 10         |
| 3                | 20         |
| 4                | 30         |
| 5                | 40         |
| 6                | 50         |

Figure 1. Influence of pH on lead(II) adsorption by water hyacinth. (Temp=25 °C; contact time: 60 min; initial lead(II) level: 100 mg/L; water hyacinth amount: 0.1 g; solution volume: 100 mL).

3.3. Biosorption isotherm fittings

Investigating adsorption isotherm is very critical to assess the lead(II) adsorption capacity of water hyacinth as well as to gain an insight into the adsorption behavior. Equilibrium simulation for lead(II) biosorption process was conducted through Langmuir as well as Freundlich adsorption isotherm equations. The derived parameters (q_m, K_L, n, and K_F) as well as the correlation coefficients of above two simulations were exhibited in Table 2. Obviously, the R value regarding Langmuir equation (0.9887) approached 1.0 and was greater than that of Freundlich model (0.6355). Additionally, the derived q_m value for Langmuir model (75.44 mg/g) was near the experimental q_m value (ca. 72 mg/g). According to our above discussion, Langmuir model is more suitable than Freundlich model in explaining lead(II) adsorption on water hyacinth. The fitting result of Langmuir equation indicates that the biosorbent surface showed the characteristics of homogeneous monolayer adsorption.

Table 2. Isotherm parameters for lead(II) uptake onto water hyacinth.

| Fitting equation | Parameter | Derived value |
|------------------|-----------|---------------|
| Langmuir         | q_m (mg/g)| 75.44         |
|                  | K_L (L/mg)| 0.0476        |
|                  | R         | 0.9887        |
| Freundlich       | K_F ((mg-(L/mg)^n)) | 28.24 |
|                  | n         | 6.252         |
|                  | R         | 0.6355        |

b Testing condition: Temp=25 °C; pH=5.0; contact time: 60 minutes; water hyacinth amount: 1.0 g; solution volume: 100 mL.
The $q_m$ value is a key parameter evaluating the adsorption capability of biosorbents to remove lead(II) from wastewater. The $q_m$ value for water hyacinth was equal to 75.44 mg/g, indicating that water hyacinth could be efficiently employed for lead(II) removal from wastewater. Actually, water hyacinth showed much better biosorption capability in comparison with the other biosorbents, e. g., 0.654 mg/g of *Typha domingensis* leaf powder [10], 34.36 mg/g of *Ficus carcia* leaves [11], 13.87 mg/g of pomegranate peel [12], 32 mg/g of walnut shell [13], 0.62 mg/g of rice husk, 33.39 mg/g of olive tree pruning waste [14], 13.51 mg/g of neem leaf [15], 2.198 mg/g of heartwood charcoal of *Areca catechu* [16]. In addition, Langmuir adsorption isotherm could be characterized utilizing an equilibrium parameter ($R_L$) as follows:

$$R_L = 1/(1 + K_L C_0)$$

In this study, as $C_0$ rose from 50 to 200 mg/L, all $R_L$ values apparently lay between 0 to 1.0, revealing favorable biosorption of lead(II) onto water hyacinth [17].

### 3.4. Surface morphology of water hyacinth

The surface morphology of water hyacinth before as well as after contact with lead(II) was characterized via SEM observation (Figure 2). It can be seen that the raw water hyacinth surface took on a strange structure, in which some stripes with different width were ranked one by one (Figure 2a). By contrast, the water hyacinth surface took on the uneven structure and some depressions appeared after exposure to lead(II) (Figure 2b). It was found that water hyacinth could regulate its own surface texture in order to encourage the lead(II) biosorption from the comparison of two figures. In other words, the irregular depressed surface could be helpful to lead(II) adsorption and accommodate considerable lead(II) ions.

![Figure 2. Surface morphology of water hyacinth by SEM observation.](image)

(a) before lead(II) biosorption, (b) after lead(II) biosorption, magnification ×500.

### 4. Conclusions

In our research, water hyacinth was employed as a sorbent to eliminate lead(II) contamination from wastewater. The biosorption process was investigated by batch tests. The uptake process relied highly on the solution acidity-alkalinity and a maximum lead(II) removal occurred at pH 5.0. Kinetic and isotherm investigations were also performed. The lead(II) biosorption onto water hyacinth conformed to pseudo-second-order kinetics and Langmuir model accompanied with 75.44 mg/g of $q_m$. On the basis of experimental data, we believed that the water hyacinth could be a promising biosorbent for removing lead(II) from wastewater.
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