Investigation of lead(II) biosorption onto *Hydrilla verticillata*

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Abstract. The aim of the present research is to study the applicability of using dead *Hydrilla verticillata* powder to remove lead(II) ion from aqueous solution by means of batch experiments. Influence of oscillation time, solution pH value, and initial Pb(II) level upon its biosorption was examined in some detail. The result indicated that Pb(II) adsorption is highly pH dependent. The pH range from 5.0 to 5.5 is most favorable for Pb(II) removal with ca. 90% of Pb(II) removed. The adsorption data was in agreement with pseudo-first-order kinetics with an adsorption equilibrium time of 50 min. Isotherm data can be described by the Langmuir equation with a maximum adsorption capacity of 157.23 mg/g. These findings suggest that *H. verticillata* could be a promising biosorbent for Pb(II) removal.

1. Introduction

The extensive application of lead has brought about severe environmental pollution and growing public health concern. When lead entered human or animal body by accident, it leads to serious diseases and permanent harm to the health of organisms [1]. Children and infants are extremely vulnerable to the toxic impressions of lead, especially jeopardizing the growth of the cerebrum and nervous system. Therefore, removal of Pb(II) from wastewater is of great importance to protect public health.

Up to date, biosorption is often used to remove poisonous heavy metals from effluents. In the past years, much interest has been paid to the biosorption of Pb(II) by the biomass of various aquatic plant species [2]. *H. verticillata* is a submerged fast-growing macrophyte. Since it propagates very quickly, it is regarded as one of the most undesirable aquatic weeds around the world. It has the potential to alter fishery populations, cause shifts in zooplankton communities and affect water chemistry. This species is considered as one of the most aggressive invasive species in aquatic habitats.

If the widely distributed alga is used to remove Pb(II), we can transform trash into treasure. Previous studies reported that *H. verticillata* could be used as a good adsorption material because it contains many binding sites that could sequester several heavy metals, such as copper(II), nickel(II), cadmium(II) and chromium(VI) [3-6]. But no investigation has been carried out on the Pb(II) biosorption by *H. verticillata*. The purpose of this investigation was to evaluate the possibility of using *H. verticillata* to get rid of Pb(II) from wastewater. Batch tests were performed to examine the
influence of several adsorption parameters (oscillation time, solution pH value, and initial lead concentration) on its uptake, and some kinetic and isotherm equations were utilized to characterize the uptake process.

2. Materials and methods

2.1 Chemicals and biosorbent pretreatment

The *H. verticillata* biomass was provided by Honghu Liangshui Aquatic Plant Co. Ltd, Jingzhou, China. The fresh biomass without roots was washed enough with tap water to eliminate silt, sand, diatoms, and other epiphytic organisms. The alga was first dried in the sun for 72 h and then dried in an oven at 80 °C for 24 h (higher temperatures could not be used to avoid likely degradation of organisms). The dried alga serving as the biosorbent was pestled and allowed to pass through an 80-mesh sieve (i.e., pore size=180 μm). The treated alga was put in a desiccator to be used in the following biosorption experiments. The structural features of *H. verticillata* surface were observed through SEM.

A Pb(II) stock solution (1000 mg/L) was prepared through dissolving Pb(NO₃)₂ in distilled water. The stock solution was subsequently diluted to the other required levels and their pH values could be adjusted to suitable values with 0.1 or 1.0 mol/L of sodium hydroxide or hydrochloric acid solution.

2.2 Biosorption experiments

Batch experiments were performed in a series of 250 mL flasks to examine the impact of the above-mentioned variables on the Pb(II) biosorption process. Preliminary test were also conducted to define the optimum range of all variables. Generally, approx. 100 mL of Pb(II) solution was mixed with a certain dose of *H. verticillata*. Then, these flasks were shaken at 140 rpm on a thermo controlled rotary shaker. Lastly, the equilibrated solutions were took out and the algae were extracted from them by centrifugation. The remained Pb(II) level in the solution was determined via a microtitration approach presented by Li et al. [7]. All of the adsorption experiments were repeated three times and average values were adopted for calculation.

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

\[
Ad\% = \frac{C_0 - C_t}{C_0} \times 100 \tag{1}
\]

\[
Q_t = \frac{(C_0 - C_t) \times V}{W} \tag{2}
\]

\[
Q_e = \frac{(C_0 - C_e) \times V}{W} \tag{3}
\]

where *Ad*% represents the Pb(II) removal efficiency; *Q*ₜ and *Q*ₑ represent the Pb(II) adsorption capacity at time *t* (min) and at equilibrium (mg/g), respectively; *C*₀, *C*ₜ and *C*ₑ represent the initial Pb(II) concentration, solution Pb(II) concentration at time *t*, and the Pb(II) concentration at equilibrium (mg/L), respectively; *V* represents the aqueous solution volume (L); and *W* represents the biosorbent mass (g).

2.3 Adsorption kinetic equations

Pseudo-first-order and pseudo-second-order kinetic equations are often employed to fit kinetic curves in kinetic studies. The pseudo-first-order equation is a simple kinetic model describing the kinetic process of liquid-solid phase adsorption presented by Lagergren [8]. Its nonlinear form could be written as follows:

\[
Q_t = Q_e (1 - e^{-k_f t}) \tag{4}
\]
where \( k_1 \) represents the rate constant of pseudo-first-order model \((\text{min}^{-1})\). Apparently, \( k_1 \) and \( Q_e \) could be worked out by plotting \( Q_t \) against \( t \).

The pseudo-second-order model could be written as the following linear form [9]:

\[
\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{k_2 Q_e^2}
\]

where \( k_2 \) represents the rate constant of pseudo-second-order sorption \((\text{g·mg}^{-1}·\text{min}^{-1})\). Apparently, \( Q_e \) and \( k_2 \) could be derived experimentally by plotting \( t/Q_t \) against \( t \).

2.4 Adsorption isotherm equations

Langmuir and Freundlich models are usually utilized to characterize the adsorption isotherms. The former assumes adsorption homogeneity, e.g. identically energetic sorption sites, monolayer surface coating, and no interactions between sorbate molecules on neighboring sites. The latter is suitable for nonideal sorption on heterogeneous surfaces embracing multi-layer adsorption. In this research, Langmuir and Freundlich sorption models were both utilized to fit the experimental isotherm data. The linear Langmuir equation can be written as follows [10]:

\[
\frac{C_e}{Q_e} = \frac{1}{Q_{\text{max}}} C_e + \frac{1}{b Q_{\text{max}}}
\]

where \( Q_{\text{max}} \) is the maximum monolayer adsorption capacity \((\text{mg/g})\), and \( b \) is the Langmuir adsorption constant related to the adsorption bonding energy \((\text{L/mg})\).

The linear Freundlich model could be written as follows [11]:

\[
\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e
\]

where \( K_F \) is the Freundlich constant representing the adsorbent adsorption capacity \((\text{mg·}(\text{L/mg})^{1/n})\), and \( n \) is the Freundlich exponent representing adsorption intensity. As for the Freundlich model, both monolayer and multi-layer sorptions occur during the adsorption process.

3. Results and discussion

3.1 Biosorption kinetics analysis

Influence of adsorption time on the Pb(II) biosorption was investigated. It was found that approx 75% of Pb(II) was removed within 30 min and the adsorption equilibrium was achieved after 50 min. The quick adsorption observed at the beginning could be due to the great concentration gradient between the Pb(II) cations in the solution. Besides, substantial empty sites could be easily available on the algal surface during this period. The fitting model parameters were given in Table 1. Apparently, the \( R \) value of pseudo-first-order model was much nearer to 1 when compared with that of pseudo-second-order one. Furthermore, the \( Q_e \) value calculated from the former was much nearer to the experimental one \((Q_{e, \text{exp}}=136 \text{ mg/g})\), but this was not the case for the latter. Therefore, the Pb(II) biosorption onto \( H. \) verticillata could be described very well by pseudo-first-order model.

| \( Q_{e, \text{exp}} \) (mg/g) | Pseudo-first-order | Pseudo-second-order |
|-----------------------------|-------------------|---------------------|
| \( Q_e \) (mg/g) | \( k_1 \) (min\(^{-1}\)) | \( R \) | \( k_2 \) (g·mg\(^{-1}·\text{min}^{-1}\)) | \( Q_e \) (mg/g) | \( R \) |
| 136 | 0.0428 | 148.27 | 0.9917 | 0.00017 | 200.42 | 0.9541 |

\(^a\)Experimental condition: pH=5.0; \( T=25 \text{ °C} \); initial Pb(II) level: 150 mg/L; \( H. \) verticillata dosage: 1.0 g/L; Solution volume: 100 mL.
3.2 Effect of pH
Solution pH is a main factor affecting the ionization degree of metals in solution and the adsorption properties because of its influence on the charge state of the adsorbent surface [12]. Considering the formation of lead(II) hydroxide precipitation as pH value approached 6.0, the Pb(II) biosorption was studied in the pH range of 2.0~5.5 (Figure 1). Apparently, Pb(II) removal was highly pH-dependent and the best pH range for Pb(II) adsorption was between 5.0 and 5.5 in which 89.25~91.44% of Pb(II) was eliminated. When the solution pH is low, carboxyl and hydroxyl groups on the H. verticillata surface are protonized and occurred in the positively charged form, reducing the number of active adsorption sites. What’s more, the electrostatic repulsion between the positively charged groups and Pb(II) could hinder the Pb(II) sequestration onto the algal surface. Hence, the adsorption of Pb(II) was adverse in acidic medium. When the solution pH elevated, those protonized carboxyl and hydroxyl are progressively deprotonated and more active adsorption sites are released on the algal surface, which could promote the combination of Pb(II) with the functional groups and thereby encourage the Pb(II) removal.

![Figure 1. Effect of pH on Pb(II) biosorption onto algae H. verticillata](image)

Figure 1. Effect of pH on Pb(II) biosorption onto algae H. verticillata ($T=25^\circ C$; oscillation time: 50 min; initial Pb(II) concentration: 150 mg/L; H. verticillata dosage: 1.0 g/L; Solution volume: 100 mL).

3.3 Adsorption isotherm models
The isotherm parameters ($Q_{\text{max}}$, $b$, $n$, and $K_F$) and the correlation coefficients ($R$) for the aforementioned models are shown in Table 2. Apparently, the $R$ value of Langmuir model (0.9977) is near 1.0 and much larger than that of Freundlich one (0.5241). Besides, the deduced theoretical value of $Q_{\text{max}}$ (157.23 mg/g) is very close to the experimental adsorption capacity (ca. 155 mg/g). Therefore, the equilibrium adsorption can be well characterized by Langmuir isotherm instead of Freundlich one, indicating that the Pb(II) removal could be monolayer adsorption.

The maximum adsorption capacity $Q_{\text{max}}$ is a key parameter assessing the ability of adsorbents to sequestrate Pb(II) from waste water. The $Q_{\text{max}}$ value for Pb(II) uptake by H. verticillata here was approximately 157.23 mg/g, suggesting that H. verticillata can be effectively used for Pb(II) removal from aqueous solutions. In actual fact, it showed very good adsorption performance compared with other adsorbents, such as 35.5 mg/g of peanut shell activated carbon [13], 9.912 mg/g of natural walnut shell [14] and 156.25 mg/g of polyacrylonitrile/magnetite nanofiber [15].
Table 2. Isotherm parameters for Pb(II) biosorption onto H. verticillata.

| Model        | Parameter            | Value  |
|--------------|----------------------|--------|
| Langmuir     | $Q_{\text{max}}$ (mg/g) | 157.23 |
|              | $b$ (L/mg)           | 0.3266 |
|              | $R$                  | 0.9977 |
| Freundlich   | $K_F$ ((mg⋅L/mg)$^{1/n}$) | 81.45  |
|              | $n$                  | 7.143  |
|              | $R$                  | 0.5241 |

*Experimental condition: $T=25$ °C; pH=5.0; oscillation time: 50 min; H. verticillata dosage: 1.0 g/L; Solution volume: 100 mL.

3.4 Characterization of H. verticillata surface

The structural features of H. verticillata with and without exposure to Pb(II) were observed using SEM (Figure 2). Generally, the raw algal surface displayed a special texture, where a series of stripe ribbons was juxtaposed (Fig. 2a). After the process of Pb(II) biosorption, the algal surface assumed the irregular rectangular structure and some concave grooves emerged among the adjacent rectangles (Figure 2b). Comparing Figure 2a with 2b, we believed that H. verticillata could adjust its surface structure to promote the Pb(II) adsorption. In another word, its irregular shapes and concaved surface might be favorable for a high-affinity adsorption toward Pb(II).

![Figure 2. SEM micrographs of H. verticillata.](image)

(a) before Pb(II) sorption, (b) after Pb(II) sorption, magnification ×600.

4. Conclusions

This study reported the possibility of using H. verticillata to remove Pb(II) from the aqueous solution. The biosorption process depended highly upon pH and an optimum removal with approx. 90% of Pb(II) removed was found in the pH range between 5.0 and 5.5. The Pb(II) biosorption onto H. verticillata agreed with pseudo-first-order kinetics and Langmuir isotherm model with a maximum adsorption capacity of 157.23 mg/g. In short, H. verticillata may be a promising biosorbent for the bioremediation of lead-containing wastewater.

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References

[1] Yin, X.J., Bai, J., Fan, F.L., Cheng, W.W., Tian, W., Wang, Y., Qin, Z. (2015) Amidoximed silica for uranium(VI) sorption from aqueous solution. J. Radioanal. Nucl. Chem., 303: 2135–2142.

[2] Sekabira, K., Oryem Origa, H., Basamba, T.A., Mutumba, G., Kakudidi, E. (2011) Application of algae in biomonitoring and phytoextraction of heavy metals contamination in urban stream water. Int. J. Environ. Sci. Technol., 8: 115–128.

[3] Mishra, A., Tripathi, B.D., Rai, A.K. (2016) Packed-bed column biosorption of chromium(VI) and nickel(II) onto Fenton modified *Hydrilla verticillata* dried biomass. Ecotoxicol. Environ. Saf., 132: 420–428.

[4] Li, G.X., Li, Q.S., Zhang, D.D., Wang, L. (2016) Biosorption of Cu(II) and Zn(II) ions from aqueous solution by a new sorbent prepared from *Hydrilla verticillata* and Fe3O4 nanoparticles: one-component and binary systems. Desal. Water Treat., 57: 8480–8493.

[5] Huang, L.Z., Zeng, G.M., Huang, D.L., Li, L.F., Du, C.Y., Zhang, L. (2010) Biosorption of cadmium(II) from aqueous solution onto *Hydrilla verticillata*. Environ. Earth Sci., 60: 1683–1691.

[6] Pilli, S.R., Goud, V.V., Mohanty, K. (2012) Biosorption of Cr(VI) on immobilized *Hydrilla verticillata* in a continuous up-flow packed bed: prediction of kinetic parameters and breakthrough curves. Desal. Water Treat., 50: 115–124.

[7] Li, F.W., Wei, X.X., Li, C.T., Zhang, D.J., Zhai, Y.B. (2002) Determination of the concentration of lead ions in wastewater by chelatometric titration. Ind. Water Treat., 22: 38–39.

[8] Skodras, G., Diamantopoulou, I., Pantoleontos, G., Sakellaropoulos, G.P. (2008) Kinetic studies of elemental mercury adsorption in activated carbon fixed bed reactor. J. Hazard. Mater., 158: 1–13.

[9] Wang, S.B., Li, H.T. (2005) Dye adsorption on unburned carbon: kinetics and equilibrium. J. Hazard. Mater., 126: 71–77.

[10] Zhao, G.X., Li, J.X., Ren, X.M., Chen, C.L., Wang, X.K. (2011) Few-layered graphene oxide nanosheets as superior sorbents for heavy metal ion pollution management. Environ. Sci. Technol., 45: 10454–10462.

[11] Tan, X.L., Fang, M., Chen, C.L., Yu, S.M., Wang, X.K. (2008) Counter ion effects of nickel and sodium dodecylbenzene sulfonate adsorption to multiwalled carbon nanotubes in aqueous solution. Carbon, 46: 1741–1750.

[12] Yi, Z.J., Zhu, M.J., Chen, H.L., Wang, F., Liu, X. (2017) Biosorption characteristics of *Ceratophyllum demersum* biomass for removal of uranium(VI) from an aqueous solution. J. Radioanal. Nucl. Chem., 313: 19–27.

[13] Xu, T., Liu, X.Q. (2008) Peanut shell activated carbon: characterization, surface modification and adsorption of Pb2+ from aqueous solution. Chin. J. Chem. Eng., 16: 401–406.

[14] Celebi, H., Gok, O. (2017) Evaluation of lead adsorption kinetics and isotherms from aqueous solution using natural walnut shell. Int. J. Environ. Res., 11: 83–90.

[15] Malik, H., Qureshi, U.A., Muqet, M., Mahar, R.B., Ahmed, F., Khatri, Z. (2018) Removal of lead from aqueous solution using polyacrylonitrile/magnetite nanofibers. Environ. Sci. Pollut. Res., 25: 3557–3564.