Evaluation of lead(II) biosorption kinetics and isotherms from aqueous solution with dry *Myriophyllum spicatum* powder

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Abstract. Lead as an important element used by mankind for years is highly toxic in water and regarded as a long-standing environmental contaminant. In our research, biouptake of lead(II) from simulated wastewater by *Myriophyllum spicatum* was examined via batch tests. Impacts of pH, adsorption time and initial Pb(II) level on its biosorption process were examined. The best pH favorable to Pb(II) adsorption was equal to 6. The Pb(II) biosorption reached equilibrium after 50 min. Langmuir and Freundlich adsorption isotherm models were used to analyze the adsorption data, indicating that the former could describe the Pb(II) biosorption with the maximum biosorption capacity of 34.13 mg/g. The Pb(II) biosorption kinetics was analyzed by pseudo-second-order and pseudo-first-order equations. It was found that Pb(II) biosorption may be described by pseudo-second-order kinetic equation. The results suggested that *M. spicatum* powder may be utilized as an efficient biosorbent to eliminate Pb(II) from aqueous effluent.

1. Introduction

The discharge of metals into ecological environment is increasing unceasingly owing to our industrial activities. Heavy metals are major contaminants in the environment because of their toxicity and threats to humankind. Lead as a common heavy metal in natural environment has a variety of industrial applications, including lead-acid batteries production, print pigments, ceramic, photographic materials, glass, fuels, wood production, phosphate fertilizer, and explosive manufacturing, and other industries [1]. Lead can be easily ingested into human body through food chain and accumulate in the body tissues due to its nonbiodegradability. Long-term drinking water containing high amount of lead could give rise to serious diseases and disorders, such as anemia, mental retardation, encephalopathy, hepatitis and nephritic syndrome [2].

Various approaches of lead removal from wastewater have been developed, such as coagulation or flocculation, chemical precipitation, ultra-filtration, reverse osmosis and ion exchange. The high cost of above methods as well as the severe standard on the drinking water quality encouraged a growing effort on looking for new high efficient adsorbents. So far, biosorption has often been employed to remove deleterious metals from wastewater. In the past decades, more attention was focused on the uptake of lead onto a variety of freshwater plant species. *Myriophyllum spicatum* is a perennial...
submerged aquatic alga, which prefers freshwater environment and but can extend into brackish marshes. Once entering a new region it spreads downstream quickly, mainly by vegetative regeneration from stem fragment or sexual propagation. *M. spicatum* has long-term deleterious effects on streams, rivers and lakes, and leads to a series of environmental problems. These include interference with irrigation water flow, boat transport, recreation activities and fisheries. Therefore, it is considered as a prohibited weed in many provinces of China.

If this widespread macrophyte was reaped and further utilized to remove Pb(II) pollution, we could change waste into valuable. Other studies have reported that *M. spicatum* could be utilized as a good biosorbent binding a variety of heavy metals, such as cadmium(II), copper(II) and nickel(II) [3, 4]. Here we reported on the Pb(II) removal by *M. spicatum*. Batch tests were performed to explore the impacts of several adsorption parameters (adsorption time, solution pH value & initial lead level). Meanwhile, several kinetic/isotherm models and fit constants corresponding to these models were applied to describe the adsorption process.

2. Materials and methods

2.1 Biosorbent preparation and characterization

The biosorbent (*M. spicatum* biomass) was bought from Honghu Liangshui Aquatic Plant Company, Hubei, China. The fresh alga was rinsed completely with tap water to get rid of silt, sand, and diatoms. The alga was first bathed in sunlight for three days and then dried in a drying stove at 60 °C for 24 h (higher temperatures was not utilized to avoid possible decomposition of the alga). The dried biomass which was used as the biosorbent was pound into powder and allowed to pass through an 80-mesh sieve (i.e., pore size=180 μm). The treated biomass was put in a desiccator to be applied in the following sorption tests. The surface morphology of *M. spicatum* was characterized via SEM.

2.2 Preparation of stock solution

The standard Pb(II) stock solution was prepared by dissolving a certain amount of Pb(NO₃)₂ in distilled water. This stock solution could be then diluted to other needed concentrations and their pH values could be adjusted to required values using 0.1 or 1.0 mol/L of NaOH or HCl solution with the help of PHS-25 type pH meter (Shanghai Leici Equipment Factory, China). All the chemicals (lead nitrate, sodium hydroxide and hydrochloric acid) were bought from Merck Company and employed without further treatment.

2.3 Pb(II) biosorption experiments

Batch tests were carried out in a series of 250 mL flasks to examine the effects of the aforementioned variables on the Pb(II) sorption. Some preliminary experiments were also performed to make certain of the best range of all variables. Generally, 100 mL of Pb(II) solution was mixed with a certain amount of *M. spicatum*. Subsequently, these flasks were shaken at 140 rpm on a thermo controlled rotary shaker. Finally, the equilibrated solutions were withdrawn and the biomass could be separated from them by centrifugation. The remained Pb(II) level in the supernatant was measured by a microtitration method given by Li et al. [5]. All of the biosorption experiments were repeated thrice and the average values could be used for further computations.

The metal removal efficiency and metal adsorption capacity were calculated out using the following formulas:

\[ R(\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \]  \hspace{1cm} (1)

\[ q_t = \frac{(C_0 - C_t)V}{m} \]  \hspace{1cm} (2)

\[ q_e = \frac{(C_0 - C_e)V}{m} \]  \hspace{1cm} (3)
where \( R% \) 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 \( m \) is the mass of biosorbent (g).

2.4 Biosorption kinetics simulation

Two basic kinetic models (pseudo-second-order and pseudo-first-order models) were employed to study the biosorption kinetics. Pseudo-first-order equation was utilized to correlate the experimental data [7], which could be described as Equation (4):

\[
\ln(q_e - q_t) = \ln q_e - k_1 t
\]

where \( k_1 \) represents the rate constant of pseudo-first-order model. Pseudo-second-order model was employed to describe the process and gain insights into the possible adsorption mechanisms [6], which could be expressed as Equation (5):

\[
t / q_t = 1/(k_2 q_e^2) + t / q_e
\]

where \( k_2 \) represents the rate constant of pseudo-second-order equation.

2.5 Biosorption isotherm simulation

Two common adsorption isotherms, Freundlich as well as Langmuir equations were utilized in order to clarify the proper isotherm for Pb(II) biosorption on the biomass [7]. Langmuir & Freundlich equations could be expressed as Equations (6) and (7), respectively.

\[
q_e = q_m K_L C_e / (1 + K_L C_e)
\]

(6)

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

(7)

where \( q_m \) represents the maximum Pb(II) biosorption uptake (mg/g), \( K_L \) represents the Langmuir constant related to adsorption energy (L/mg), and \( n \) (dimensionless) and \( K_F \) ((mg (L/mg)^1/n)) represent intensity factors and Freundlich constants, respectively.

3. Results and discussion

3.1 Biosorption kinetics analysis

The biosorption of Pb(II) as a function of contact time was investigated. The Pb(II) removal efficiency increased fast in the beginning. Subsequently, it dropped progressively with time elapsed till it achieved an equilibrium state beyond which no significant change in the Pb(II) removal was observed. An equilibrium state was achieved within 50 min and therefore 50 min was selected as an equilibrium time in this study. The fast biosorption process in the beginning may be interpreted that many active adsorption sites were available on the biosorbent surface. The adsorption took place rapidly and was generally regulated by the diffusion process from the solution toward the surface. However, the biosorption was probably an adherence-controlled process at a later stage owing to the scarcity of available adsorption sites, which could result in the gradual slow adsorption until equilibrium was reached. The applicability of the two commonly used kinetic models was examined using the biosorption data. The model parameters (rate constant ‘\( k \)’ and theoretical ‘\( q_e \)’ ) and the correlation coefficients (\( R \)) were calculated out and given in Table 1.

As seen from Table 1, the \( R \) value derived from the pseudo-second-order kinetic model was greater than 0.99, and the theoretical \( q_{e,2} \) value was nearer to that derived from the experiment (\( q_{e,exp} \)). By contrast, the \( R \) value for the pseudo-first-order model was less than that of the pseudo-second-order
one. And the theoretical $q_{e,1}$ value was not in agreement with $q_{e,exp}$. The result indicates that lead biosorption process could follow pseudo-second-order kinetic equation.

Table 1. Kinetics parameters for the lead biosorption onto $M. spicatum$ ($T$=298 K, pH=6.0).

| $q_{e,exp}$ (mg/g) | Pseudo-first-order |        | Pseudo-second-order |        |
|-------------------|-------------------|---------|---------------------|---------|
|                   | $k_1$ (min$^{-1}$) | $q_{e1}$ (mg/g) | $R$       | $k_2$ (g·mg$^{-1}$·min$^{-1}$) | $q_{e2}$ (mg/g) | $R$       |
| 43.55             | 0.018             | 117.19  | 0.9766              | 0.11    | 41.67   | 0.9997   |

3.2 Influence of pH
The initial solution pH is a critical parameter influencing the biosorption of heavy metals. In order to examine the influence of pH on the Pb(II) biosorption process, batch experiments was investigated over the pH range from 2 to 7 (Figure 1). The percentage Pb(II) removal increased with the increase of pH between pH 2.0 and 6.0 and reached a maximum at pH 6.0. Subsequently, the Pb(II) removal decreased a little at higher pH. The pH effect on the biosorption was mainly associated with surface functional groups on the biosorbents as well as Pb(II) species in the aqueous solution. Generally speaking, the $H^+$ concentration is much more than that of the metals at low pH values. Therefore, $H^+$ competes with Pb(II) for the biosorbent surface, which could prevent the Pb(II) cations from reaching the adsorption sites of the biosorbent and cause lower adsorption of Pb(II). The decrease of Pb(II) removal when pH is greater than 6.0 could be explained that lead hydroxide complexes formed at higher pH values retarding the Pb(II) biosorption.

![Figure 1. Effect of pH on Pb(II) biosorption onto the alga $M. spicatum$ ($T$=298 K).](image)

3.3 Adsorption isotherm models
The Langmuir and Freundlich adsorption parameters with the correlation coefficients ($R$) for the biosorption of Pb(II) onto $M. spicatum$ are presented in Table 2. Due to the lower value of $R$ for Freundlich isotherm model, this model did not accurately characterize the correlation between the amounts of adsorbed Pb(II) and the equilibrium levels in the solution. By contrast, high regression correlation coefficient for the Langmuir model (>0.9994) show that the adsorption process of Pb(II) by algae $M. spicatum$ can be well described by this model. The result of good Langmuir fitting implied that this biosorbent surface took on the characteristics of homogeneous monolayer adsorption.
The maximum adsorption capacity \( q_m \) derived from the Langmuir isotherm is a critical parameter describing the uptake capability of biosorbents. The \( q_m \) value for lead binding by \textit{M. spicatum} in our investigation was 34.13 mg/g. \textit{M. spicatum} showed much better adsorption performance when compared with \( q_m \) values of other biosorbents, such as 13.87 mg/g of pomegranate peel [8], 7.79 mg/g of walnut shell [9], 2.0 mg/g of tea waste [10], 9.33 mg/g of oxalic acid modified maize husk [11], 17.3 mg/g of \textit{otostegia persica} biomass [12], 17.24 mg/g of dried \textit{Portulaca} plant material [13], 27.39 mg/g of wheat straw [14].

Table 2. Isotherm parameters for Pb(II) biosorption onto \textit{M. spicatum} \( (T=298 \text{ K}, \text{pH}=6.0) \).

| Model   | Parameter          | Value  |
|---------|--------------------|--------|
| Langmuir| \( q_m \) (mg/g)   | 34.13  |
|         | \( K_L \) (L/mg)   | 0.057  |
|         | \( R \)            | 0.9994 |
| Freundlich | \( K_F ((\text{mg} \cdot (L/mg)^{1/n})) \) | 7.15  |
|         | \( n \)           | 3.31  |
|         | \( R \)           | 0.9575 |

3.4 SEM characterization of algal surface

The structural morphology of \textit{M. spicatum} surface before and after contact Pb(II) were observed with SEM (Figure 2). Obviously, the raw algal surface before exposure to Pb(II) displayed a planar net structure, in which a series of rectangles were well arranged as a huge crisscrossed network and some shallow concave grooves exist among the neighboring rectangles (Fig. 2a). After exposure to Pb(II), the algal surface takes on a relatively smooth structure (Figure 2b). It is speculated that the crisscrossed network surface of \textit{M. spicatum} could be beneficial to the high-affinity adsorption of Pb(II) and the depressed groove could be stuffed with Pb(II).

![Figure 2. SEM micrographs of \textit{M. spicatum}.](image)

(a) Before Pb(II) biosorption, (b) After Pb(II) biosorption, magnification \( \times 600 \).

4. Conclusions

The biosorption of Pb(II) by \textit{M. spicatum} was investigated as a function of pH, contact time and initial Pb(II) concentration. The biosorption is highly dependent on pH and the maximum adsorption occurs at pH 6.0. Kinetic study suggested that the adsorption process was very fast and achieved equilibrium within 50 min and kinetic data agreed with pseudo-second-order equation. The biosorption isotherms were assessed with Langmuir and Freundlich isotherms. The biosorption followed the Langmuir adsorption isotherm and the maximum adsorption capacity derived from Langmuir model was 34.13
mg/g. In summary, M. spicatum could be used effectively for Pb(II) removal from lead-containing wastewater. Regeneration of the biosorbent requires further research.

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References
[1] Huang, H.Y., Cheng, G.L., Chen, L., Zhu, X.Q., Xu, H. (2009) Lead(II) removal from aqueous solution by spent Agaricus bisporus: Determination of optimum process condition using taguchi method. Water Air Soil Pollut., 203: 53–63.
[2] Chen, Z., Pan, X.H., Chen, H., Lin, Z., Guan, X. (2015) Investigation of lead(II) uptake by Bacillus thuringiensis 016. World J. Microbiol. Biotechnol., 31: 1729–1736.
[3] Sivaci, E.R., Sivaci, A., Skmen, M. (2004) Biosorption of cadmium by Myriophyllum spicatum L. and Myriophyllum triphyllum orchard. Chemosphere, 56: 1043–1048.
[4] Li, G.X., Xue, P.Y., Yan, C.Z., Li, Q.Z. (2010) Copper biosorption by Myriophyllum spicatum: Effects of temperature and pH. Korean J. Chem. Eng., 27: 1239–1245.
[5] 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.
[6] Ding, H.L., Zhang, X.N., Yang, H., Zhang, Y., Luo, X.G. (2019) Biosorption of U(VI) by active and inactive Aspergillus niger: equilibrium, kinetic, thermodynamic and mechanistic analyses. J. Radioan. Nucl. Chem., 319: 1261–1275.
[7] Das, B., Mondal, N.K., Bhaumik, R., Roy, P. (2014) Insight into adsorption equilibrium, kinetics and thermodynamics of lead onto alluvial soil. Int. J. Environ. Sci. Technol., 11: 1101–1114.
[8] El-Ashtoukhy, E.S.Z., Amin, N.K., Abdelwahab, O. (2008) Removal of lead(II) and copper(II) from aqueous solution using pomegranate peel as a new adsorbent. Desalination, 223: 162–173.
[9] Wolfova, R., Pertile, E., Fecko, P. (2013) Removal of lead from aqueous solution by walnut shell. J. Environ. Chem. Ecotoxicol., 5: 159–167.
[10] Ahluwalia, S.S., Goyal, D. (2005) Removal of heavy metals by waste tea leaves from aqueous solution. Eng. Life Sci., 5: 158–162.
[11] Adeogun, A., Idowu, M., Ofude, A., Kareem, S., Ahmed, S. (2013) Comparative biosorption of Mn(II) and Pb(II) ions on raw and oxalic acid modified maize husk: kinetic, thermodynamic and isothermal studies. Appl. Water Sci., 3: 167–179.
[12] Alavi, S.A., Zilouei, H., Asadinezhad, A. (2015) Otostegia persica biomass as a new biosorbent for the removal of lead from aqueous solutions. Int. J. Environ. Sci. Technol., 12: 489–498.
[13] Dubey, A., Shiwani, S. (2012) Adsorption of lead using a new green material obtained from Portulaca plant. Int. J. Environ. Sci. Technol., 9: 15–20.
[14] Farooq, F., Farooq, U., Batool, M., Athar, M., Salman, M., Ahmed, Q., and Ashraf, A. (2015) Use of wheat straw for effective binding of metal ions via a novel modification. Korean J. Chem. Eng., 32: 1818–1826.