Biosorptive removal of divalent lead ions in wastewater by *Elodea canadensis*

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Abstract. The purpose of this investigation was to explore the feasibility of utilizing heat inactivated (killed) *Elodea canadensis* to eliminate divalent lead ions from water solution via batch tests. The Pb(II) biosorption features of *E. canadensis* biomass were examined with regard to adsorption time, solution pH value and Pb(II) concentration. Our experimental result suggested that the lead biosorption depended highly on medium pH. A pH of 5.0 is most beneficial to lead removal. The biosorption data agreed with pseudo-second-order kinetic model with an adsorption equilibrium time of 60 minutes. Isotherm data agreed with Langmuir isotherm equation with 21.36 mg/g of maximum biosorption capacity. The results suggested that *E. canadensis* is an inexpensive and efficient sorbent for the elimination of Pb(II) from wastewater.

1. Introduction

Along with the fast developing of industries such as mining and milling, textile, paper and pulp, fertilizer and pesticides, batteries, a lot of wastewater containing various toxic metals were released into water bodies unceasingly. The metal contamination is a key environmental problem concerning water and has great influence on humankind and water ecosystem. Lead (Pb) is a very dangerous heavy metal to living organisms due to its neurotoxicity to the nervous system. It is unbiodegradable and capable of entering food chain easily via different ways, which leads to gradual toxic effects with progressive accumulation in living organisms over a long period [1]. Although acute toxicity is unlikely, but long-term chronic poisoning of low-level Pb was unavoidable, which could result in the degeneration of bone and the harm of liver and lung [2]. Besides, the metal Pb could adhere to cell membranes and result in the destruction to transport processes through cell wall. In consideration of the undegradable and poisonous characteristics of Pb, an urgent attempt is made to the elimination of heavy metals from effluents. It is very important to the protection of public health.

So far, biosorption is the most common employed technology for the elimination of poisonous metals from wastewater. During the past decades, great concern focused on the binding of metals using various freshwater algae. *Elodea canadensis* as one submerged macrophyte which may play a big part in the ecology of some littoral areas. As well known, it is invasive and capable of propagating via nonsexual reproduction. *E. canadensis* can function as a sink for poisonous chemicals and remove them before they can influence the biomass. This alga could be utilized to bioremediate metal-polluted zones. Earlier investigations reported that *E. canadensis* can be employed as a promising biosorption
material in that its surface contained adsorption sites which could grasp some metals, such as U(VI), Cr(VI), Cd(II) and Ni(II) [3-5]. The aim of the present study was to assess the likelihood of utilizing \textit{E. canadensis} to eliminate Pb(II) from water solution. Batch tests were performed in order to examine the influence of several adsorption parameters on the Pb(II) uptake, and several common kinetic and isotherm equations were employed to characterize the biosorption procedure.

2. Materials and methods

2.1 Source of biosorbent and preparation of Pb(II) stock solution

The \textit{E. canadensis} biomass was provided by Honghu Liangshui Aquatic Plant Company, China. This fresh alga could be washed enough using tap water to get rid of silt, sand, diatoms. This alga was sunbathed for 72 h and then subsequently dried at 80 $^{\circ}$C for 24 h. The dried alga was ground and permitted to pass through an eighty-mesh sieve. The pretreated sample was placed in a dryer to be utilized in the subsequent adsorption tests. The surface morphology of \textit{E. canadensis} was observed through scanning electronic microscopy (SEM).

The stock solution of Pb(II) (1.0 g/L) was prepared by the dissolution of Pb(NO$_3$)$_2$ in pure distilled water. The stock solution was then diluted to other needed levels and the pH values could be adjusted to required values with sodium hydroxide or hydrochloric acid solution. The chemicals in this study were analytical pure grade and could be directly employed without further treatment.

2.2 Pb(II) biosorption tests

Batch tests were performed in many Erlenmeyer flasks (volume = 250 mL) to explore the influence of several variables on the removal of Pb(II). Preliminary tests were performed to make certain the maximum and minimum values of all variables. Generally, approx 100 mL of Pb(II) solution was mixed with a certain amount of \textit{E. canadensis} powder. Then, the flasks were agitated at 140 rpm on a rotary shaker. Lastly, the equilibrium solutions were extracted and the adsorbents were separated from them through centrifugation. The remained Pb(II) concentration in the solution was measured through a standard microtitration method presented by Li et al. [6]. The experiments were all repeated twice or thrice and the average values were adopted.

The Pb(II) removal efficiency and Pb(II) adsorption capacity could be figured out with the help of the following formulas:

\[
Ad\% = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)
\]

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

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

where \(Ad\%\) represents the Pb(II) removal efficiency; \(Q_e\) and \(Q_t\) the Pb(II) adsorption capacity (mg/g) at equilibrium state and at time \(t\) (min), respectively; \(C_0\), \(C_e\) and \(C_t\) the initial Pb(II) concentration, equilibrium Pb(II) concentration and liquid-phase Pb(II) concentration at time \(t\) (mg/L), respectively; \(V\) the aqueous solution volume (L); \(W\) the biosorbent mass (g).

2.3 Adsorption kinetic equations

Pseudo-second-order and pseudo-first-order kinetic equations are often adopted to study the meal adsorption kinetics. The latter equation is a simple kinetic model characterizing the kinetic process of liquid-solid phase adsorption which was put forward by Lagergren [7]. The nonlinear form of the latter can be written in the following formula:

\[
Q_t = Q_e (1 - e^{-kt}) \quad (4)
\]
where \( k_1 \) represents the rate constant of pseudo-first-order adsorption (min\(^{-1}\)). Apparently, \( Q_e \) and \( k_1 \) could be calculated out via the plot of \( Q_t \) against \( t \) and via subsequent nonlinear regression treatment.

The pseudo-second-order equation on the basis of the adsorption equilibrium capacity could be written as the following linear formula [8]:

\[
\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{k_2Q_e^2}
\]

where \( k_2 \) represents the rate constant of pseudo-second-order adsorption [g/(mg \cdot \text{min})]. Obviously, \( Q_e \) and \( k_2 \) can be determined experimentally by plotting \( t/Q_t \) versus \( t \).

### 2.4 Adsorption isotherm equations

Langmuir and Freundlich models are utilized to delineate the adsorption isotherms. The former assumes homogeneous adsorption, such as homogeneous energetic binding sites, monolayer surface coating, and no interaction between sorbate molecules on neighbouring sites. The latter is suitable for nonideal adsorption onto nonuniform surfaces embracing multilayer adsorption. The linear Langmuir equation can be expressed as the following form [9]:

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

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

The linear Freundlich model could be delineated in the following form [10]:

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

where \( K_F \) represents the Freundlich constant indicating the adsorption capacity of the adsorbent (mg \cdot (L/mg)^{1/n})", and \( n \) represents the Freundlich exponent indicative of the adsorption intensity.

### 3. Results and discussion

#### 3.1 Adsorption kinetics

Effect of contact time on the Pb(II) binding was examined. Most of Pb(II) was removed in 35 min and biosorption equilibrium was reached within 60 min. The fast biosorption rate at early stage might be owing to the vast concentration gradient between the algal surface and the solution Pb(II). In addition, many free sites might be readily obtainable on the algal surface during the adsorption process. The derived equation parameters were presented in Table 1. The correlation coefficient \( R \) obtained from the pseudo-first-order modelling suggested that this model is reasonable to fit the biosorption process. However, the calculated \( Q_e \) value does not match the experimental value \( Q_{e,\text{exp}} \) (18.36 mg/g) for the adsorption process. Therefore, the pseudo-first-order model should be excluded. By contrast, the \( R \) value of the pseudo-second-order kinetic model was higher than 0.99 and the values of \( Q_e \) from the experimental data approached the calculated \( Q_e \) value. Therefore, the biosorption of Pb(II) onto the alga followed pseudo-second-order kinetic equation.

| \( Q_{e,\text{exp}} \) (mg/g) | **Pseudo-first-order** | **Pseudo-second-order** |
|--------------------------|-----------------------|------------------------|
| \( k_1 \) (min\(^{-1}\)) | \( Q_e \) (mg/g) | \( R \) | \( k_2 \) (g \cdot mg\(^{-1}\) \cdot min\(^{-1}\)) | \( Q_e \) (mg/g) | \( R \) |
| 18.36 | 0.0074 | 4.22 | 0.984 | 0.0182 | 16.73 | 0.998 |

* Sorption condition: Temperature: 25 °C; pH=5.0; Pb(II) level: 46 mg/L; *E. canadensis* dosage: 0.4 g.
3.2 Influence of the pH
The medium pH is an important factor influencing the ionization state of heavy metals in solution and the adsorption features because of its impact on the charge state of the biosorbent surface [11]. In the range of pH 2.0~8.0, the adsorption of Pb(II) by *E. canadensis* tended to increase first, then decreased and eventually increased (Figure 1). This is because the redox potential of lead was lower and the pKₐ of the carboxyl group was equal to 5.0. When the pH was lower, there were many hydrions in aqueous solution, and carboxyl groups existed in the form of $\text{COOH}$. Hence, the activated sites that can be bound by metal ions were reduced. Accompanied with the pH increase, the hydrions of carboxyl groups were neutralized by hydroxide ions and the dominant groups were $\text{COO}^-$ and the adsorption capacity increased. Similar changes also took place in other groups such as amino and phosphoric acid groups, which promote the rapid adsorption of metal cations. However, when pH was greater than 7.0, a large number of hydroxide ions combined with hydrions and Pb(II) precipitation occurred in the solution, resulting in a significant increase in the Pb(II) adsorption capacity. In a word, the Pb(II) biosorption onto *E. canadensis* was affected by pH. It was known that the optimum pH for binding of Pb(II) could be 5.0, and the Pb(II) biosorption capacity could reach 12.53 mg/g.

![Figure 1. Influence of pH value on Pb(II) binding by *E. canadensis* (Temperature: 25 °C; Contact time: 60 min; Metal concentration: 46 mg/L; *E. canadensis* amount: 0.4 g).](image)

3.3 Biosorption isotherm study
The biosorption data were simulated with two above-mentioned isotherms to make certain of the adsorption feature between active sites on the adsorbent and aqueous Pb(II) in the solution. The correlation coefficients ($R$) as well as isotherm parameters ($Q_{\text{max}}$, $b$, $n$, and $K_F$) for two isotherm models are reported in Table 2. It was found that biosorption data might be reasonably characterized by Langmuir equation ($R=0.996$) compared with Freundlich equation ($R=0.966$), indicating that the Pb(II) biosorption onto *E. canadensis* was monolayer adsorption. As listed in Table 2, the $Q_{\text{max}}$ of the alga was evaluated to be 21.36 mg/g at room temperature.

The $Q_{\text{max}}$ is a key parameter describing the potential of this biosorbent to sequestrate Pb(II) from wastewater. The $Q_{\text{max}}$ value for Pb(II) binding onto *E. canadensis* in this study was approximately 21.36 mg/g, suggesting that *E. canadensis* could be effectively utilized for Pb(II) removal from wastewater. Actually, it exhibited good adsorption ability compared with other sorbents, such as 13.87 mg/g of pomegranate peel [12], 9.912 mg/g of natural walnut shell [13] and 15.47 mg/g of molding Ti-pillared bentonite [14], 13.05 mg/g of activated carbon made from a new precursor hazelnut shell [15]. It should be noted that *E. canadensis* could be utilized as a promising material for the cost-effective purification of Pb(II)-containing wastewater due to its low permeability, low cost, natural availability, regeneratability and environmental friendliness.
Table 2. Isotherm parameters for Pb(II) biosorption onto E. canadensis.

| Fitting equation | Parameter | Value |
|------------------|-----------|-------|
| Langmuir         | $Q_{\text{max}}$ (mg/g) | 21.36 |
|                  | $b$ (L/mg)  | 0.084 |
|                  | $R$        | 0.996 |
| Freundlich       | $K_F$ ((mg·(L/mg)$^{1/n}$)) | 2.26 |
|                  | $n$        | 2.23  |
|                  | $R$        | 0.966 |

* Sorption condition: Temperature: 25 °C; pH=5.0; Sorption time: 60 min; E. canadensis amount: 0.4 g.

3.4 Characterization of E. canadensis surface

The structure of raw E. canadensis surface was described using FTIR and SEM (Figure 2). As to the FTIR spectrum of E. canadensis, the wide bands observed at 3275 cm$^{-1}$ might be assigned to N–H and O–H stretching vibrations (Figure 2a). The peak at 1608 could be attributed to symmetrical stretch vibrations of carboxyl. The peak at 1007 cm$^{-1}$ might be assigned to C–OH stretching vibration, a characteristic peak of polysaccharose. These hydroxyl, amino and carboxyl groups might play a critical part in Pb(II) biosorption. As to SEM picture of E. canadensis, there were many depressions on the uneven surface and the algal surface exhibited the texture of juxtaposed stripe ribbons with the width of 0.02 mm (Figure 2b). Actually, these depressed grooves could hold many Pb(II) cations since the size of Pb(II) ion was only approx 175 pm of diameter. Therefore, its depressed surface might be beneficial to the great affinity toward Pb(II).

4. Conclusions

Biosorption of heavy metals could be an attractive technology involved in the removal of poisonous metals from wastewater. The submerged aquatic plant, E. canadensis, was used as a biosorbent for Pb(II) removal from wastewater. The biosorption of Pb(II) onto E. canadensis was highly dependent on contact time, pH value and initial Pb(II) level. The best biosorption conditions were found to be 5.0 of pH and 60 min of contact time. The Pb(II) adsorption by E. canadensis can be well characterized using pseudo-second-order kinetic equation and Langmuir isotherm. The maximum Pb(II) adsorption capacity was 21.36 mg/g. In summary, E. canadensis could be an efficient sorbent for the treatment of Pb(II)-bearing effluent.
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