Biosorption of Uranium(VI) from Aqueous Solution by Potamogeton pectinatus L.

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Abstract: Uranium pollution poses a serious threat to the ecological environment. This study investigated the feasibility of Potamogeton pectinatus L. powder as a novel type of biosorbent for U(VI) removal from wastewater. Batch experiments were carried out to examine the effect of pH, sorption time and initial U(VI) concentration on U(VI) biosorption onto Potamogeton pectinatus L. powder. The results suggest that the biosorption process was highly pH dependent over the pH range from 3.0 to 6.5. The pH of 5.5 was most favorable for removal. The U(VI) uptake equilibrium was reached within 60 min. The Potamogeton pectinatus L. had an observed U(VI) adsorption capacity of 268.82 mg/g. In a word, the present results indicate that Potamogeton pectinatus L. could be used as a promising biosorbent for effective removal of U(VI) from wastewater.

Introduction

Although nuclear power emerged as one of the alternatives to ease the energy scarcity, nuclear weapons production as well as uranium mining and milling brought serious uranium contamination. In actual fact, lots of uranium-bearing wastewater was annually produced. Uranium as one of the most serious radionclides had great effect on environment, natural water resources and human health because of its long half-life, biological toxicity and high radioactivity [1]. Besides, uranium commonly existing as uranyl (UO$_2^{2+}$) under oxidizing conditions, is extremely soluble which can not be easily eliminated. Hence, the removal and recovery of uranium are very significant. So far, some treatment approaches, such as evaporation concentration, chemical precipitation, ion-exchange and biosorption have been widely adopted to remove uranium from waste water. Among these methods, biosorption seems to be the most effective choice due to its cheap and easy-operation characteristics for removing trace levels of uranium ions.

Over the past few decades, the use of non-living biomass of freshwater macrophytes or aquatic plant species for uranium removal is gaining increasing concern [2-5]. But little research has been done to date about the application of Potamogeton pectinatus L. (sago pondweed) in the removal of uranyl. Potamogeton pectinatus L. is a submersed plant growing in fresh, brackish, and saline waters. It is found in stagnant ponds, spring-fed rivers, and slow-flowing marshes. It can proliferate ubiquitously under optimum temperature and nutrient conditions. If Potamogeton pectinatus L. could be obtained and used to eliminate radionuclide contamination, we would make waste profitable.

In summary, the purpose of this study was to examine the biosorption ability of Potamogeton pectinatus L. to sequestrate uranyl cations. The uranium biosorption characteristics of Potamogeton pectinatus L. were studied in terms of contact time, pH, and initial U(VI) concentration via batch tests. Meanwhile, the adsorption kinetics and isotherms were also investigated.
Materials and methods

Chemical reagents and U(VI) stock solutions. *Potamogeton pectinatus L.* biomass used in this study was bought from Honghu Liangshui Aquatic Plant Co. Ltd., Jingzhou, China. The fresh biomass was washed enough with tap water to remove silt, sand, diatoms, and other epiphytic organisms. Then the biomass was dried in the sun for 3 d and subsequently dewatered at 80 °C for 24 h in a drying oven. The dried biomass was pulverized into fine powder and allowed to pass through an 80 mesh opening size sieve. The treated biomass was put in a desiccator for following use in the biosorption experiments.

The stock solution of U(VI) (1 mg/mL) was prepared by dissolving U$_3$O$_8$ in a mixture of HCl, H$_2$O$_2$ and HNO$_3$ [6]. The other concentrations were obtained from the stock solutions by proper dilution. The U$_3$O$_8$ was supplied by Nuclear Resources Engineering College, University of South China. The other chemical reagents were purchased from Sinopharm Chemical Reagent Company, Shanghai, China. All of the chemical reagents used in this research were of analytical pure grade. All experimental solutions were prepared with distilled water.

Biosorption experiments. For all biosorption experiments, 100 mL U(VI) solution was mixed with a known amount of dry *Potamogeton pectinatus* L. powder in a series of 250 ml conical flasks. The pH of the U(VI) solution was adjusted as required using 1.0 M NaOH and 1.0 M HNO$_3$ before mixing with the *Potamogeton pectinatus* L. powder. Then the experiments continued on a rotary shaker (140 r/min). A sample of solution was withdrawn at suitable time intervals, centrifuged at 10000 ×g for 15 min and U(VI) was determined in the supernatant. The U(VI) removal efficiency and equilibrium adsorption capacity of U(VI) onto the biomass (mg U/g dry *Potamogeton pectinatus* L. weight) were obtained by using the following equations:

\[
U(VI) \text{ uptake (\%)} = \left(\frac{C_0 - C}{C_0}\right) \times 100
\]

\[
Q = \left(\frac{C_0 - C}{C_0}\right) \frac{V}{M}
\]

where $Q$ (mg/g) is the amount of U(VI) adsorbed onto the unit amount of the adsorbent, $C_0$ and $C$ (mg/L) are the concentrations of the U(VI) in the solution before and after adsorption, respectively. $V$ (L) is the volume of the aqueous solution and $M$ (g) is the dry weight of the adsorbent. The U(VI) concentrations in samples were determined using a standard method given by Xie et al [7].

Results and Discussion

Effect of adsorption time and adsorption kinetics. The contact time between the adsorbate and adsorbent is a key parameter for a designed adsorption process. As shown in Fig. 1, the U(VI) percentage removal increased with time elapsed at early stage. A great amount of U(VI) was removed rapidly within the first 30 min during which about 70% of the total U(VI) was removed. Then the U(VI) sorption rate became slowly. The adsorption process reached equilibrium within 60 min after which no more metal was further adsorbed onto *Potamogeton pectinatus* L.. Therefore, 60 min was selected as uniform adsorption time in this investigation.

To examine the kinetics of U(VI) uptake onto *Potamogeton pectinatus* L. powder, the pseudo first-order kinetic model was used for analysis of adsorption kinetics [8]. The nonlinear form of pseudo first-order equation is generally expressed as follows:

\[
Q_t = Q_e \left(1 - e^{-k_1 t}\right)
\]

where $Q_e$ and $Q_t$ represents the adsorption capacity (mg/g) at equilibrium and at time $t$ (min), respectively; $k_1$ the rate constant of pseudo first-order sorption (min$^{-1}$). The value of the rate constant $k_1$ and $Q_e$ for the pseudo-first-order adsorption process can be derived by plotting $Q_t$ versus $t$ as well as
further nonlinear regression analysis. The correlation coefficient for the pseudo-first-order kinetic model ($R^2=0.995$) is close to 1.0. Furthermore, there is little difference in the equilibrium adsorption capacity ($Q_e$) between the experimental value (ca. 269 mg/L) and calculation value (277.72 mg/L). These findings suggest that the adsorption of uranyl ions by *Potamogeton pectinatus L.* follows the pseudo-first-order kinetic model.

$$Q_e = 277.72 \text{ mg/L}$$  
$$k_1 = 0.0413$$  
$$R = 0.995$$

**Fig. 1 Effect of contact time on U(VI) adsorption**

**Effect of pH value.** Adsorption of heavy metal ions from aqueous solution is strongly affected by the solution pH in that it influenced the dissociation state of adsorbent site and the solution chemistry of soluble metals as well. In order to ascertain the best pH for the U(VI) adsorption process and whether the *Potamogeton pectinatus L.* exhibits a good U(VI) uptake at extreme pH values, metal uptake was studied over the pH range from 3.0 to 6.5 (Fig. 2). Obviously, the initial solution pH markedly affected the equilibrium U(VI) adsorption capacity. Over the pH range examined, an acid condition (pH 3.0–4.0) was not favorable to the U(VI) adsorption. When the pH increased, adsorption of U(VI) increased and the maximum U(VI) adsorption capacity ($Q_{max}$) was reached at pH 5.5. A further pH increase beyond the optimum caused a decrease of U(VI) adsorption. This phenomenon could be explained that at higher pH values, the non-ion dissolved solid schoepite formed in the solution. The decrease in the U(VI) concentration retarded its adsorption.

$$C_{0}(\text{UO}_2^{2+}) = 120 \text{ mg/L}$$  
$$M(\text{biomass}) = 0.04 \text{ g}$$  
$$\text{pH} = 5.5$$  
$$\text{Temp} = 25 \degree \text{C}$$  
$$V = 100 \text{ mL}$$

**Fig. 2 Effect of pH on U(VI) adsorption**
**Adsorption isotherm modeling.** The empirical Langmuir adsorption model was employed to correlate the isotherm data obtained. The relative parameters could be calculated out finally by linear regression analysis using the Origin 9.0 software. The linear Langmuir equation could be described with the following Eq. (4).

$$\frac{C_e}{Q_e} = \frac{1}{Q_{\text{max}}}C_e + \frac{1}{bQ_{\text{max}}}$$  \tag{4}

where $Q_e$ represents the equilibrium adsorption capacity (mg/g); $Q_{\text{max}}$ represents the maximum monolayer adsorption capacity (mg/g); $C_e$ represents the equilibrium concentration of U(VI) (mg/g); $b$ represents the affinity constant related to the energy of adsorption (L/mg).

In order to gain an insight into the adsorption capacity of *Potamogeton pectinatus L.*, the adsorption experiments were performed over the initial U(VI) concentration range from 30 to 210 mg/L and the equilibrium data were fitted using the Langmuir model. Fig. 3 shows the curve of Langmuir isotherm models for the U(VI)–*Potamogeton pectinatus L.* biosorption system. The parameters of models are calculated out from fitting the adsorption equilibrium data and shown in Fig. 3. The correlation coefficient ‘$R$’ value of Langmuir isotherm model is much closer to 1.0. This result suggests that Langmuir isotherm is more suitable to describe the adsorption process. Furthermore, the theoretical saturated adsorption capacity of Langmuir isotherm ($Q_{\text{max}}=268.82$ mg/g) is very close to experimental data (ca. 263 mg/g), which also indicates the best description of the U(VI) uptake by Langmuir model. Since Langmuir isotherm is a monolayer adsorption model, the adsorption of U(VI) on *Potamogeton pectinatus L.* probably belongs to monolayer adsorption rather than multilayer one. It should be pointed out that $Q_{\text{max}}$ is an important parameter for describing the adsorption ability of adsorbents. Previous investigations have reported the $Q_{\text{max}}$ values of two low-cost adsorbents for U(VI) adsorption, such as 42.84 mg/g for polyvinyl alcohol-g-amidoxime [9], 20.76 mg/g for montmorillonite/carbon composite [10]. Apparently, comparison of these $Q_{\text{max}}$ values demonstrated that the *Potamogeton pectinatus L.* has a greater uranium adsorption capacity than some other adsorbents.

![Fig. 3 Langmuir adsorption isotherm of U(VI) on *Potamogeton pectinatus L.*](image)

**SEM analysis of the biosorbent.** The morphology of *Potamogeton pectinatus L.* was characterized through SEM observation (Fig. 4). Obviously, the surface of *Potamogeton pectinatus L.* was rough and irregular, and many depressions could be clearly observed (Fig. 4). Since the diameter of the U(VI) ion was picometer-scale (ca. 92 pm), these micrometer-scale concave on the biosorbent surface could accommodate many uranyl cations.
Conclusions

The U(VI) biosorption onto *Potamogeton pectinatus L.* was investigated via batch experiments. The adsorption capacity was highly pH-dependent and the best adsorption performance for U(VI) was observed at pH 5.5. The adsorption reached equilibrium within 60 min and followed pseudo-first-order kinetics. *Potamogeton pectinatus L.* can adsorb U(VI) in terms of Langmuir model with a maximum adsorption capacity of 268.82 mg/g. *Potamogeton pectinatus L.* dry biomass could be used as an efficient biosorbent for the treatment of U(VI) contaminants in aqueous solutions.

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