Uptake of uranyl (UO$_2^{2+}$) in water body by sago pondweed

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Abstract. Uranium pollution is posing severe threat to the human environment. In the current research, we studied the applicability of *Stuckenia pectinata* (sago pondweed) powder as a new sort of biosorbent for uranyl removal from effluent. A series of batch experiments were conducted to explore impact of shaking time, solution pH, and initial U(VI) level upon U(VI) biosorption onto *Stuckenia pectinata* powder. The results show that the biosorption process is highly dependent upon pH value in the range of 3.0-6.5. The pH value of 5.5 is preferable to uranium elimination. The U(VI) biosorption equilibrium can be achieved after 60 min. The *Stuckenia pectinata* has a maximum uranium biosorption capacity of 268.82 mg·g$^{-1}$. In brief, the obtained results suggest that *Stuckenia pectinata* may be utilized as a promising biosorbent for efficient removal of U(VI) from effluent.

1. Introduction

Although nuclear energy has become one of the alternatives to alleviate the energy shortage, the production of nuclear weapons and the mining and processing of uranium have also brought serious uranium pollution. In actual fact, lots of uranium-bearing wastewater is annually produced. Uranium as one of the most serious radionuclides has great effect on environment, natural water resources and public health due to its long half-life, biological toxicity and high radioactivity [1, 2]. Besides, uranium commonly existing as uranyl (UO$_2^{2+}$) under oxic conditions, is extremely soluble which is unable to be eliminated. Hence, the removal and recovery of uranium are very significant. So far, some treatment approaches, such as ion-exchange, evaporation concentration, chemical precipitation and biosorption have been widely adopted to eliminate uranium from wastewater. Among these approaches, biosorption seems to be the most effective choice due to its cheap and easy-operation characteristics for removing trace levels of uranyl ions.

Over the past few years, the application of dead freshwater macrophytes for uranium removal has gained increasing concern [3-6]. But few studies have been done to date about the utilization of *Stuckenia pectinata* (sago pondweed) in the removal of uranyl. *Stuckenia pectinata* is a submersed plant growing in fresh, brackish, and saline waters. It occurs in spring-fed rivers, stagnant pools, and slow-flowing wetlands. It can proliferate ubiquitously under optimum temperature and nutrient conditions. If *Stuckenia pectinata* could be obtained and used to eliminate radionuclide contamination, we are able to make waste profitable.

In short, the goal of this research is to gain an insight into the biosorption ability of *Stuckenia pectinata* to sequestrate uranyl cations. The uranium biosorption characteristics of *Stuckenia pectinata*
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.

2. Materials and methods

2.1. Adsorbent pretreatment and U(VI)-bearing stock solution preparation

The Stuckenia pectinata biosorbent utilized in this research was bought from Honghu Liangshui Aquatic Plant Company, Jingzhou, China. The fresh biomass could be washed enough using tap water to remove sand, mud, diatoms. Afterwards, the biomass was sundried for two days and further dehydrated at eighty degrees centigrade for twenty four hours in a heating oven. The dried organisms were ground into fine powder and permitted to pass through an eighty mesh sieve. The sieved biomass was put in an exsiccator for following experiments.

The uranium stock solution (1000 mg/L) was confected by dissolving triuranium octoxide in a mixture of hydrochloric acid, hydrogen peroxide and nitric acid [7]. The other concentrations were prepared from those stock solutions by proper dilution. All of the chemical reagents utilized in the current research were analytical pure.

2.2. Uranyl biosorption tests

As to all the biosorption experiments, a hundred mL of uranium solution was mixed with a certain amount of dry Stuckenia pectinata powder in a series of 250 mL conical flasks. The solution pH was adjusted as needed with diluted NaOH and HNO₃ solution before mixing with the Stuckenia pectinata powder. After that, the biosorption experiments proceeded on a rotary oscillator (140 r/min). The supernatant sample was taken out periodically and centrifuged at 10000 xg for fifteen minutes, and the U(VI) concentration was measured by using a standard method proposed by Xie et al [8]. Finally, the U(VI) removal efficiency as well as equilibrium adsorption capacity (mg U/g dry Stuckenia pectinata weight) was calculated using the following equations:

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

\[ Q = \frac{(C_0 - C) \times V}{m} \]

where \( C_0 \) and \( C \) (mg/L) represent the U(VI) levels in the solution before and after biosorption, respectively; \( Q \) (mg/g) represents the amount of U(VI) adsorbed onto the unit amount of the biosorbent; \( V \) (L) represents the aqueous solution volume; and \( m \) (g) represents the biosorbent dry weight.

3. Results and discussion

3.1. Influence of sorption time and sorption kinetics

Sorption time is a pivotal factor for a designed sorption process. As seen from Fig. 1, the U(VI) removal elevated with the lapse of time in the beginning. A great amount of U(VI) could be removed rapidly within the first thirty minutes during which approximately 70% of U(VI) was removed. Then the U(VI) adsorption rate became slowly. The uranium adsorption attained equilibrium within sixty minutes after which no more uranyl was further attached to Stuckenia pectinata. Therefore, 60 minutes was chosen as uniform adsorption time in this investigation.

To explore the kinetics of U(VI) binding onto Stuckenia pectinata powder, kinetic data were fitted with pseudo-first-order [9] as well as pseudo-second-order equations [10], which could be described as the following two equations:
where $Q_t$ and $Q_e$ represent adsorbed amount of metal cation per gram of biomass at any time $t$ (min) and at equilibrium (mg/g), respectively; $k_1$ and $k_2$ represent the pseudo-first-order and pseudo-second-order kinetic rate constant, respectively. The rate constant $k_1$ and $Q_e$ for pseudo-first-order adsorption process could be derived by plotting $Q_t$ versus $t$ and further nonlinear regression analysis. The correlation coefficient for pseudo-first-order kinetic model ($R=0.995$) is close to 1.0. Furthermore, there is little difference between the experimental equilibrium adsorption capacity ($Q_e, \text{exp}=269 \text{ mg/g}$) and theoretical calculation value ($Q_e, \text{cal}=277.72 \text{ mg/g}$) (Fig. 1). But it is not the same case for pseudo-second-order kinetic model in which $R=0.976$ deviates from 1.0. Meanwhile, there is much difference between experimental $Q_t$ value and theoretical value (Fig. 2). These results indicate that adsorption of U(VI) by *Stuckenia pectinata* conforms to pseudo-first-order kinetic model.

$$Q_t = Q_e (1 - e^{-k_1 t})$$  \hspace{1cm} (3)

$$\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{k_2 Q_e^2}$$  \hspace{1cm} (4)
3.2. Influence of pH value

Uptake of heavy metals from wastewater is greatly affected by solution pH in that it influences the ionized state of adsorbent site as well as the water chemistry of soluble metals. To ascertain the optimum pH for the U(VI) binding process and whether Stuckenia pectinata exhibits a good U(VI) uptake under very acidic pH conditions, U(VI) biosorption was investigated over the pH range from 3.0 to 6.5 (Fig. 3). Evidently, the initial pH of solution greatly affected $Q_e$ value. In the examined pH range, the acidic medium (pH 3.0–4.0) was unfavorable to the U(VI) adsorption. When the solution pH rose, uranyl adsorption increased and the $Q_{max}$ was reached at pH 5.5. A further pH increase beyond the optimum caused a decline of U(VI) adsorption. This finding might be expounded that non-ion dissolved solid paraschoepite formed in solution at higher pH values. The decrease in the U(VI) level retarded its adsorption.

![Graph](https://example.com/graph.png)

Figure 3. Influence of solution pH on uranyl uptake.

3.3. Adsorption isotherm fitting

The empirical Langmuir adsorption model was used to fit the obtained isotherm data. The corresponding parameters could be calculated finally by linear regression treatment with the help of Origin 9.0 software. The linear Langmuir model could be written as follows [11]:

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

(5)

where $C_e$ represents the equilibrium concentration of uranyl (mg·g$^{-1}$); $Q_e$ represents the equilibrium adsorption capacity (mg·g$^{-1}$); $Q_{max}$ represents the maximum monolayer adsorption capacity (mg·g$^{-1}$); $b$ represents the affinity constant associated with the adsorption energy (L·mg$^{-1}$).

To examine the adsorption capacity of Stuckenia pectinata, the adsorption experiments were performed over the initial U(VI) concentration range from 30 to 210 mg/L and the experimental data were fitted using the Langmuir model. Fig. 4 shows the curve of Langmuir isotherm model for the uranium–Stuckenia pectinata adsorption system. The parameters of Langmuir equation was calculated out and exhibited in Fig. 4. The correlation coefficient ‘$R$’ value for Langmuir isotherm model is much closer to 1.0. This result suggests that Langmuir isotherm is preferable to characterize the adsorption process. Besides, the theoretical saturated adsorption capacity of Langmuir isotherm ($Q_{max}$=268.82 mg/g) is very close to experimental data (ca. 263 mg/g), which also indicates the best description of the U(VI) binding by using Langmuir model. Since Langmuir isotherm is a monolayer adsorption model, the adsorption of U(VI) on Stuckenia pectinata likely should be monolayer adsorption instead of multilayer one. It should be noted that $Q_{max}$ is a key parameter for describing the sorption process.
Some other researches documented the $Q_{\text{max}}$ values of two inexpensive fungus sorbents for uranium uptake, such as 19.95 mg·g$^{-1}$ of Pleurotus ostreatus [12], 83.40 mg·g$^{-1}$ of inactive Aspergillus niger [13]. Obviously, comparison of these $Q_{\text{max}}$ values reveals that the Stuckenia pectinata has a better U(VI) adsorption performance in comparison with some other sorbents.

3.4. Biosorbent surface observation

The structural feature of Stuckenia pectinata surface was observed by means of SEM (Fig. 5). Evidently, the surface of Stuckenia pectinata is irregular and rough, and considerable concaves can be obviously seen (Fig. 4). Since the diameter of uranyl cation is picometer-sized (approx. 92 pm), these micrometer-sized concaves on the biosorbent surface could accommodate many uranyl cations.
4. Conclusions
The U(VI) biosorption onto *Stuckenia pectinata* 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. *Stuckenia pectinata* can adsorb U(VI) in terms of Langmuir model with a maximum adsorption capacity of 268.82 mg/g. *Stuckenia pectinata* dry biomass could be used as an efficient biosorbent for the treatment of U(VI) contaminants in aqueous solutions.

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