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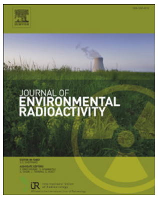

Uranium biosorption from aqueous solution onto *Eichhornia crassipes*

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ABSTRACT

Batch experiments were conducted to investigate the biosorption of U(VI) from aqueous solutions onto the nonliving biomass of an aquatic macrophyte *Eichhornia crassipes*. The results showed that the adsorption of U(VI) onto *E. crassipes* was highly pH-dependent and the best pH for U(VI) removal was 5.5. U(VI) adsorption proceeded rapidly with an equilibrium time of 30 min and conformed to pseudo-second-order kinetics. The Langmuir isotherm model was determined to best describe U(VI) biosorption with a maximum monolayer adsorption capacity of 142.85 mg/g. Thermodynamic calculation results indicated that the U(VI) biosorption process was spontaneous and endothermic. Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy analysis implied that the functional groups (amino, hydroxyl, and carboxyl) may be responsible for the U(VI) adsorption process, in which the coordination and ion exchange mechanisms could be involved. We conclude that *E. crassipes* biomass is a promising biosorbent for the removal of uranium pollutants.

1. Introduction

The increasing pollution of soil and water body by heavy metals is an alarming environmental problem. The occurrence of heavy metals in water is of significant public concern because they cannot degrade biologically like organic contaminants and are readily absorbed and accumulated in organ or tissue. Among all the heavy metals, considerable attention has been focused on radioactive uranium. Large amounts of uranium-bearing effluent were annually produced from various nuclear-associated activities, such as uranium exploration and processing, manufacture of nuclear weapons, production of nuclear power, and geological disposal of radioactive waste. The manufacture of fertilizers from natural phosphate ore and their agricultural applications are also major sources of uranium pollution. The quality of surface water and groundwater was severely threatened by uranium contamination because uranium readily migrates into soil and water bodies. Uranium can enter the body through inhalation or ingestion. Ingestion of uranium exceeding the tolerance level can cause increased cancer risk, congenital abnormality, liver and kidney damage, and dysfunction of the brain and central nervous system. Long-term chronic uptake of radioactive uranium in food, water, or air can lead to inner irradiation and chemical toxicity (ATSDR, 2013). The maximum permitted contaminant level of uranium in drinking water has been established as 30 μg/L by World Health Organization (2004) to protect public health. Considerable attention has been focused on methods for the removal of uranium from wastewater before its discharge into the environment because it poses serious environmental problems and is dangerous to human health.

The existing physicochemical methods, such as chemical precipitation, electrodialysis, reverse osmosis, ion exchange, membrane filtration, evaporation, and solvent extraction, have been proven to be effective in the treatment of radioactive wastewater (Khani, 2011). However, each method has its own limitations, for instance, high energy requirement, incomplete removal of metal, moderate or no metal selectivity, limited tolerance to pH change, and generation of toxic sludge or other products that need further treatment. Thus, these limitations often severely restrict the widespread use of the aforementioned methods in wastewater treatment.

In the past decades, the use of adsorbents of biological origin has emerged as one of the most promising alternatives for the control of heavy metal contamination because of its simplicity, ease of

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operation and handling, sludge-free operation, and regeneration capacity. Metal sequestration may include complicated mechanisms, mainly ion exchange, chelation, physicochemical adsorption, coordination, and microprecipitation. Living and dead biomasses as well as cellular products, such as polysaccharides, can be employed for metal sequestration. Compared with living biomass, dead biomass has many advantages in that it is not only cheap and effective in reducing heavy metals to low levels but also needs less maintenance and is easily regenerated.

Many biosorbents, such as pomelo peel (Li et al., 2012), coir pith (Parab et al., 2005), shrimp shell (Ahmed et al., 2014), wheat straw (Wang et al., 2010), grape stalk (Anagnostopoulos et al., 2015), starfish (Choi et al., 2009), tea waste (Li et al., 2015), *Penicillium citrinum* (Pang et al., 2011), *Arthrobacter* (Carvajal et al., 2012), and *Shewanella oneidensis* (Sheng and Fein, 2013), have been used for uranium removal from water. In recent years, nonliving biomass of freshwater/marine algae or aquatic plant species, such as green algae *Chlorella vulgaris* (Vogel et al., 2010), brown algae (Moghaddam et al., 2013), red algae *Catenella repens* (Bhat et al., 2008), and *Ceratophyllum demersum* (Markich, 2013), was the focus of considerable attention and used for uranium removal.

Eichhornia crassipes is a free-floating aquatic macrophyte growing in lakes, ponds, rivers, marshes, and other types of wetland habitats in China. *E. crassipes* can not only tolerate extremes of water level fluctuations, seasonal variations in flow velocity, nutrient availability, pH, temperature, and toxic substances but can also proliferate ubiquitously and abundantly under favorable temperature and nutrient conditions. However, the large coverage of *E. crassipes* on water would reduce sunlight penetration and lower oxygen content in water, thereby influencing the water ecosystem. The yield of fishes and other water foods could be significantly reduced. Many water areas would be difficult to ship, and many canals would be unsuitable for irrigation and drainage. If *E. crassipes* could be harvested and further employed to eliminate uranium contamination, then we can make waste profitable. However, as far as the authors are aware, no investigation on the application of *E. crassipes* in U(VI) removal has been reported in the literature.

In the present work, *E. crassipes* was used for U(VI) removal from aqueous solution. The U(VI) adsorption behavior of *E. crassipes* was investigated with respect to contact time, pH, temperature, and initial U(VI) concentration through the batch method. The adsorption isotherms, kinetics, and thermodynamics were also examined. The possible mechanisms for the adsorption of U(VI) onto *E. crassipes* biomass were also explored by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS).

2. Materials and methods

2.1. Biosorbent, chemical reagents, and uranium stock solution

E. crassipes biomass used in the present study was purchased from Honghu Liangshui Aquatic Plant Co. Ltd., Jingzhou, China. The fresh biomass (without roots) was rinsed thoroughly with running water to remove silt, sand, diatoms, and other epiphytic organisms and then cut into pieces. The sliced biomass was dried under sunlight for three days 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 placed in a desiccator for subsequent use in the biosorption experiments.

A stock solution of U(VI) (1000 mg/L) was prepared by dissolving 1.1792 g of U_3O_8 in a mixture of HCl and H_2O_2 (Zhang et al., 2014). U_3O_8 was courtesy of the School of Nuclear Resources and Nuclear Fuel Engineering of the University of South China. The other required concentrations (50–300 mg/L) were obtained by diluting the aforementioned standard U(VI) stock solution with distilled water. All other chemical reagents were analytical grade, commercially available, and used as received without any further treatment.

2.2. Batch biosorption experiments

Generally, 0.12 g of adsorbents were added to a series of 250 mL stoppered conical flasks containing 100 mL of uranium solution with the desired initial U(VI) concentrations (50–300 mg/L). The pH of the solutions was adjusted when required by adding HCl (1.0 or 0.1 M) or NaOH (1.0 or 0.1 M) and by using a pH meter. Then, these flasks were shaken on a reciprocal rotary shaker at 140 r/min for specified durations at the desired temperatures (298–318 K). Supernatant samples were collected at suitable time intervals, centrifuged at 5000×g for 5 min, and analyzed for residual U(VI) concentrations by using the standard method described by Xie et al. (2009). The uranium removal efficiency (*Ad%*) and uranium adsorption capacity (*Q*) can be determined according to the following equations:

$$Ad\% = \frac{C_0 - C_t}{C_0} \times 100, \tag{1}$$

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

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

where *Ad%* is the U(VI) removal efficiency; Q_e and Q_t are the adsorption capacity (mg/g) at equilibrium and at time t (min), respectively; C_0, C_t, and C_e are the initial U(VI) concentration, liquid-phase U(VI) concentration at time t, and equilibrium U(VI) concentration (mg/L), respectively; V is the volume of the aqueous solution (L); and W is the mass of the adsorbent (g). All the experiments were conducted in triplicate, and the arithmetic mean values of the calculations were recorded. Blank experiments were conducted to ensure that no adsorption occurred on the walls of the glassware.

2.3. Kinetic modeling

Kinetic models are usually employed to describe the rate-determining step of the adsorption process. Three commonly used kinetic models, namely, pseudo-first-order, pseudo-second-order, and intraparticle diffusion models, were selected to analyze the kinetic data and to understand the rate-determining step of U(VI) adsorption onto *E. crassipes* biomass.

The pseudo-first-order equation is a simple kinetic model describing the kinetic process of liquid–solid phase sorption (Ho and Mckay, 1999), and its linear formula can be written as follows:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t, \tag{4}$$

where k_1 is the rate constant of the pseudo-first-order sorption (min^{-1}). Evidently, k_1 can be calculated from the slope of the plot of $\ln(Q_e - Q_t)$ versus t.

The pseudo-second-order model based on the adsorption equilibrium capacity may be expressed in the following linear form (Ho and Mckay, 2000):