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Biosorption of uranium by magnetically modified *Rhodotorula glutinis*

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ABSTRACT

Adsorption of uranium from aqueous solution onto the magnetically modified yeast cell, *Rhodotorula glutinis*, was investigated in a batch system. Factors influencing sorption such as initial solution pH, biomass dosage, contact time, temperature, initial uranium concentration and other common cations were analyzed. Sorption isotherm, kinetic and thermodynamic studies of uranium on magnetically modified *R. glutinis* were also carried out. The temperature dependent equilibrium data agreed well with the Langmuir model. Kinetic data obtained at different temperatures were simulated using pseudo-first-order and pseudo-second-order kinetic models, the pseudo-second-order kinetic model was found to describe the data better with correlation coefficients near 1.0. The thermodynamic parameters, ΔH°, ΔS° and ΔG° were calculated from the sorption data gained at different temperatures. These thermodynamic parameters showed that the sorption process was endothermic and spontaneous. All results indicated that magnetically modified *R. glutinis* can be a potential sorbent for uranium wastewater treatment.

1. Introduction

Uranium mining and mineral processing for nuclear power plants and for nuclear weapon production have resulted in the generation of significant amounts of radioactive wastewater containing uranium [8]. As uranium is highly toxicity and has long half-life, its impact on environment is tremendous. Uranium disposed into the environment can eventually enter the food chain and be ingested by humans, causing severe kidney or liver damage [1,2]. Therefore, it is necessary to treat wastewater containing uranium.

Biosorption can be used to bind and concentrate heavy metals or radionuclides from aqueous solutions. It has been regarded as an innovative technology to remove contaminants from industrial effluents [3,4]. Compared with the conventional methods, the biosorption process offers several advantages, such as low operating cost, high efficiency in detoxifying very dilute effluents and a minimal volume of disposable sludge. Studies on uranium biosorption have already been performed using various microorganisms, viz. fungi, yeast, algae and bacteria [5–7]. *Rhodotorula glutinis*, a common yeast, was found to be a good sorption material for uranium [8]. However, in real use, disadvantages like post-separation, clogging, washout, etc. of the biomass appear. Among these disadvantages, the most troublesome is the post-separation of biosorbent from metal solution. Usually, centrifugation and filtration are used, which definitely increase the treatment cost. Magnetic separation is a new separation technique and has recently been found many interesting applications in various areas of bioscience and biotechnology. The essence of this technique is to incorporate a discrete magnetic phase into the weakly or non-magnetic target particles to increase their magnetic susceptibility and then separate these particles by magnetic separation. Magnetic adsorbents can be efficiently used for the separation of various compounds from both solutions and suspensions. With this method, heavy metal ions, such as Cu^{2+}, Pb^{2+}, Cd^{2+}, Hg^{2+}, Sr^{2+} [9–12], were successfully removed by magnetically modified biomass. Biosorption of water soluble dyes with magnetic sorbents was also studied [13,14].

Compared with the standard separation process, magnetic separation techniques offer several advantages. The most attractive one for radioactive wastewater treatment is its good performance in difficult-to-handle samples. By using the magnetic separation techniques rather than centrifugation or filtration, it will reduce the chances of contacting with radiations. However, so far only limited knowledge exists concerning the removal of radioactive substances by magnetic separation method, especially uranium removal by magnetically modified biomass, which is meaningful from the purification, environmental and radioactive waste disposal point of view.

In this work, magnetically modified *R. glutinis* was prepared, the effects of initial solution pH, biomass dosage, contact time,

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temperature, initial uranium concentration and other cations on uranium sorption by this magnetic biosorbent were studied. Moreover, isotherm, kinetic and thermodynamic modeling were performed to predict the feasibility of this biomass in real radioactive wastewater treatment.

2. Materials and methods

2.1. Materials

R. glutinis was cultured in the sterilized medium used before [8] at 30 °C for 24 h, further incubation was performed by adding 5 mL cell suspension to 100 mL of the same fresh culture medium. Cells at the stationary growth phase were harvested by centrifugation at 4390 × *g* for 5 min and washed several times with distilled water until the biomass looked whitish. The obtained cells were used as thoroughly washed *R. glutinis* and stored at 4 °C for further magnetic modification process.

Stock solution of uranium was prepared by dissolving an accurately weighed amount of $UO_2(NO_3)_2$ (purchased from Beijing Sigma–Aldrich Co. LLC, China) in distilled water so as to yield a metal ion concentration of 1.0 g/L. This stock solution was diluted to obtain the uranium working solutions. The initial pH of the uranium working solutions were adjusted to the desired values with 0.1 M HCl or 0.1 M NaOH and not monitored during the experimental process. 0.05% Arsenazo III solution was prepared by dissolving 5 g of the reagent in 100 mL water. All the reagents used were of analytical grade unless otherwise stated.

Water based ionic magnetic fluid (MF) stabilized with perchloric acid was prepared using the standard Massart procedure [15]. This ferrofluid was composed of magnetic iron oxides nanoparticles with diameters ranging between 10 and 20 nm (scanning electron microscopy measurements, not shown).

2.2. Preparation of magnetically modified yeast cells

Thoroughly washed *R. glutinis* cells were further washed two to three times with acetate buffer (pH 4.6), then centrifuged and resuspended in acetate buffer to obtain a yeast suspension of 33% (v/v; yeast volume obtained after centrifuge at 4390 × *g* for 5 min). Magnetic modification of the yeast cells was performed by mixing 3 mL of the yeast suspension with 1 mL of the MF sample. The mixture was then kept at room temperature for 2 h without further mixing. Then the residual MF and nonmagnetic yeast cells were removed by repeated washing with distilled water until the supernatant was clear. The magnetized cells were captured using a permanent magnet with surface magnetic field of 0.3 T, suspended in water and stored at 4 °C. The determined dry weight of the magnetically modified yeast cell suspension was 51.5 ± 0.2 mg/mL.

2.3. Adsorption of uranium by magnetically modified yeast cells

The magnetically modified yeast cell suspension of known volume was sampled, added to a polypropylene centrifuge tube, then 4 mL uranium solutions of required concentration was mixed with the suspension and shaken on a rotary shaker at 250 rpm for 30 min. After that the magnetically modified biomass was separated from the mixture by a permanent magnet and the clear supernatant was used for uranium concentration measurement. The amount of adsorbed uranium per unit yeast biomass (mg metal ions/g dry yeast biomass) was calculated using the following expression,

$$q = \frac{C_i \times V_U - C_e(V_U + V_m)}{m} \quad (1)$$

where q is the amount of uranium adsorbed onto the unit amount of the biomass (mg/g), C_i is the initial uranium concentration (mg/L), C_e is the equilibrium uranium concentration (mg/L), V_U is the volume of added uranium solution, and V_m and m are the volume and dry weight of the added magnetically modified biomass, respectively.

The uranium sorption ratio (r) can be calculated by Eq. (2)

$$r = \frac{C_i \times V_U - C_e(V_U + V_m)}{C_i V_U} \times 100\% \quad (2)$$

All the experiments were performed twice and mean values were used in the analysis of data. Control experiments without biomass were carried out to determine the degree of uranium removal by plastic tube.

2.4. Analytical methods

Uranium concentration was determined using the spectrophotometry method with Arsenazo III as chromomeric reagent [16]. 100 μL uranium solution, 500 μL 0.3 M HCl and 300 μL 0.05% Arsenazo III aqueous solution were added to a glass flask and the mixture was filled up to 10 mL by distilled water, then the absorbance of the solution was analyzed at 650 nm on an UV-1801 spectrophotometer (Beijing Rayleigh Analytical Instrument Co., Ltd., China). Mixed solution prepared in the same way but without uranium was used as reference. Uranium concentrations were calculated from the calibration curve. The detection limits and sensitivity of this method were 7.02 mg/L and 3.16 mg/L, respectively.

3. Results and discussion

3.1. Effect of initial solution pH

Earlier studies on heavy metal biosorption have shown that solution pH is an important parameter affecting the biosorption process [17]. The effect of pH on uranium removal was analyzed over the initial pH range from 2.0 to 10.0 and initial uranium concentration of 100 mg/L, temperature of 20 °C. The used volume of magnetically modified yeast cell suspension was 0.1 mL (dry weight = 51.5 mg/mL × 0.1 mL = 5.15 mg). As can be seen from Fig. 1, uranium sorption capacity (q) and uranium sorption ratio (r) varied with pH and showed the same trend. Maximum uranium sorption was observed at an initial solution pH of 6.0. This result was consistent with the earlier study when using free *R. glutinis* as biosorbent [8]. At pH lower than 4.0, q and r decreased sharply with decreasing pH, which could be due to the competition between uranyl ions and hydrogen ions [18]. However, as pH increased, the metal ion uptake increased. It has been reported in the literature that, pH affects both the solubility of metal ions and the binding sites present on the biomass surface [19,20]. Carboxyl and amino groups were important functional groups involved in uranium sorption by *R. glutinis* [8]. As pH increased, these groups deprotonated and existing negative charges resulted in a higher uranium uptake. In the pH range of 6.0–10.0, q and r stayed nearly constant. As much higher initial solution pH may lead to the precipitation of uranium [21], therefore, no experiments were carried out at pH above 10.0. The optimal initial solution pH used for magnetically modified *R. glutinis* to absorb uranium was selected as 6.0.

3.2. Effect of biomass dosage

The effect of biomass dosage on uranium sorption was investigated using different biomass dosage from 0.5 mg to 10 mg and an initial uranium concentration of 100 mg/L, pH of 6.0 and temperature of 20 °C. The obtained results are presented in Fig. 2. As shown in Fig. 2, the uranium sorption ratio (r) increased with an increase in biomass dosage but uranium sorption capacity (q) showed an opposite trend. r was 55% when 0.5 mg, and 95% when 5.15 mg biomass was added, respectively. Then r became nearly constant. An increase of biomass dosage at lower values (<5.15 mg) meant increasing the surface area and binding sites of the biosorbent, so r increased [22]. However, at higher biomass dosage (>5.15 mg), partial aggregation of the biomass occurred, resulting in constant r value [18,23]. The decrease of q was due to an increase

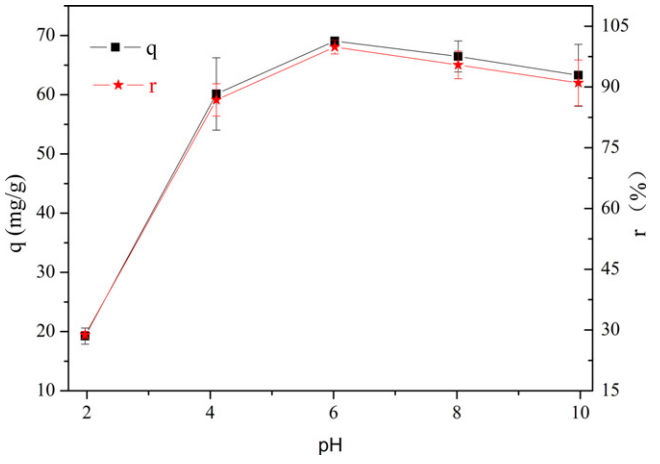

Fig. 1. Effect of initial solution pH on uranium sorption by magnetically modified *Rhodotorula glutinis*. *q*, uranium sorption capacity (mg/g); *r*, uranium sorption ratio (%).