



## Equilibrium, kinetic and thermodynamic studies of uranium biosorption by calcium alginate beads



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### ABSTRACT

Calcium alginate beads are potential biosorbent for radionuclides removal as they contain carboxyl groups. However, until now limited information is available concerning the uptake behavior of uranium by this polymer gel, especially when sorption equilibrium, kinetics and thermodynamics are concerned. In present work, batch experiments were carried out to study the equilibrium, kinetics and thermodynamics of uranium sorption by calcium alginate beads. The effects of initial solution pH, sorbent amount, initial uranium concentration and temperature on uranium sorption were also investigated. The determined optimal conditions were: initial solution pH of 3.0, added sorbent amount of 40 mg, and uranium sorption capacity increased with increasing initial uranium concentration and temperature. Equilibrium data obtained under different temperatures were fitted better with Langmuir model than Freundlich model, uranium sorption was dominated by a monolayer way. The kinetic data can be well depicted by the pseudo-second-order kinetic model. The activation energy derived from Arrhenius equation was 30.0 kJ/mol and the sorption process had a chemical nature. Thermodynamic constants such as  $\Delta H^0$ ,  $\Delta S^0$  and  $\Delta G^0$  were also evaluated, results of thermodynamic study showed that the sorption process was endothermic and spontaneous.

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### 1. Introduction

Because of the increasing environmental contamination caused by human industrial activity (mining industry, enrichment factories, etc.), the removal of radionuclides, including uranium, from water solutions is a real problem. Uranium disposed into the environment can reach the top of the food chain and be ingested by humans (Anke et al., 2009), causing kidney or liver damage (Bleise et al., 2003; Priest, 2001). Hence, it is necessary to treat wastewater containing uranium. Moreover, with the development of nuclear industry, uranium will be used more extensively. As a nonrenewable resource, the removal of uranium from wastewater is important not only for environmental remediation but also for nuclear industry (Genc et al., 2003).

Various techniques are employed for the removal of uranium ions from wastewater and radioactive wastes. Chemical precipitation, membrane processes, ion exchange, solvent extraction, and

sorption are most commonly used (Kryvoruchko et al., 2004; Rahmati et al., 2012; Sodaye et al., 2009; Wang et al., 2009a). Sorption can be an effective way to purify water solutions from radionuclides. There are many natural, organic and inorganic adsorbents that have been used for uranium removal from water solutions (Genc et al., 2003; Naja et al., 1999; Sar et al., 2004). These studies documented that various biomasses from fungi, yeast, algae and unicellular bacteria are capable of uptaking or binding uranium (Kalin et al., 2005; Tykva et al., 2009; Xie et al., 2008). Furthermore, with the development of biosorption technique, some naturally occurring biopolymers are found to have excellent adsorption ability for uranium (Sureshkumar et al., 2010; Wang et al., 2009b). Alginate is one of the naturally biopolymer and an important cell wall component of many algae species especially brown algae (Davis et al., 2003). Alginate, with monovalent ions (alkali metals and ammonium) is soluble in water but adopt a cross-linked structure when encounters with calcium or other divalent cations. Because of this special property, alginate is always used as the entrapment agent to immobilize microorganism. Some advantages of alginate beads are biodegradability, hydrophilicity, presence of carboxyl groups and natural origin. The presence of carboxyl groups indicates its potential use in radionuclides removal from

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waste solutions. However, limited information is available concerning the uptake behavior of uranium by this polymer gel (Gok and Aytas, 2009), especially when sorption equilibrium, kinetics and thermodynamics are concerned.

Sorption equilibrium, kinetics and thermodynamics are major characteristics of a sorption process, the information obtained from these studies are useful for sorption reactor design. In present work, uranium sorption by calcium alginate beads was investigated. The effects of initial solution pH, sorbent amount, initial uranium concentration and temperature on uranium sorption were discussed. More importantly, the equilibrium, kinetic and thermodynamic studies were also performed by using different models.

## 2. Material and methods

### 2.1. Reagents and main instruments

Uranium stock solution of 1 g/L was prepared from  $\text{UO}_2(\text{NO}_3)_2$  provided by Sigma–Aldrich, and this stock solution was diluted to obtain the working solutions. The initial pH of the uranium working solutions were adjusted to the required value with 0.1 M  $\text{HNO}_3$  or 0.1 M  $\text{NaOH}$  and not controlled during the entire experiment. Sodium alginate and  $\text{CaCl}_2$ , Arsenazo III; were purchased from Tianjin Guangfu Fine Chemical Research Institute and Sinopharm Chemical Reagent Co. Ltd, China, respectively. The reagents used in the experiment were of analytical reagent (AR) grade.

Uranium concentration was determined on UV-1801 spectrophotometer (Beijing Rayleigh Analytical Instrument Co. Ltd, China) using the method described before (Bai et al., 2010). Uranium sorption experiments were performed in batch model by using a SHZ-82 thermostable shaker (Shenzhen Guohua Instrument Factory, China). A Hanna pH211 pH meter was used to measure pH. An oven (DHG-9075A, Shanghai Yiheng Instrument Co. Ltd, China) was used to dry the samples.

### 2.2. Preparation of the calcium alginate (CaAlg) beads

The CaAlg beads were prepared as follows. 3% (wt %) sodium solution was added drop wise to a stirred  $\text{CaCl}_2$  solution (4%) using a medical needle, the spherical gel beads were formed. After gently stirring the beads for 30 min at room temperature, the CaAlg beads were placed into a 4 °C refrigerator for 6 h, then separated from the  $\text{CaCl}_2$  solution, washed several times with distilled water and finally dried at 40 °C for 24 h. The loss of weight after drying was determined to be 95%. Dried CaAlg beads were used instead of wet gel type, for the dried ones were easier to handle and store; and greater precision can be obtained during weighting.

### 2.3. Sorption experiments

As pH is an important factor affecting the sorption process (Gok and Aytas, 2009), the effect of pH on uranium sorption by CaAlg beads was conducted first. The investigated pHs were from 2.0 to 7.0. Experiments were carried out in 10 mL polypropylene tubes, where 40 mg dried CaAlg beads were added to 4 mL uranium solution. After shaking the mixture at 200 rpm, 20 °C for 90 min, the supernatants were used for uranium concentration determination. The effect of sorbent amount on uranium sorption was performed in sorbent amount varied between 10 and 80 mg. The effect of initial metal ion concentration on uranium sorption was studied in the uranium concentration range of 10 mg/L to 400 mg/L and to simultaneously got the information about the effect of temperature,

experiments were performed under different temperatures of 20 °C (293 K), 25 °C (298 K), 30 °C (303 K), 40 °C (313 K) and 50 °C (323 K), respectively.

Kinetic experiments were done at the optimal conditions determined before with a constant initial uranium concentration of 100 mg/L but varied temperature. At different time intervals, samples were withdrawn and uranium concentrations were measured using spectrophotometric method.

The amount of adsorbed uranium per unit dry biomass was calculated by Eq. (1):

$$q_t = \frac{(C_0 - C_t) \times V}{m} \quad (1)$$

where  $C_0$  is the initial uranium concentration (mg/L),  $V$  is the volume of uranium solution (mL),  $m$  is the dry weight of the sorbent (mg),  $q_t$  (mg/g) and  $C_t$  (mg/L) are the uranium sorption capacity and the left uranium concentration at time  $t$ , respectively. If  $t = t_e$  ( $t_e$ , equilibrium time, min), that  $C_t = C_e$  ( $C_e$ , equilibrium uranium concentration, mg/L) and  $q_t = q_e$  ( $q_e$ , equilibrium uranium sorption capacity, mg/g). Except for kinetic studies,  $q_e$  was used.

All experiments were performed in duplicate 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. Equilibrium modeling

Several isotherm equations have been used for the equilibrium modeling of biosorption processes. The most commonly used are Langmuir and Freundlich equations. Langmuir equation assumes a monolayer sorption of a solute from a liquid solution (Wang et al., 2012). The linearized mathematical description of this model is given by Eq. (2):

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{q_{\max} K_L} \quad (2)$$

where  $q_{\max}$  (mg/g) and  $K_L$  (L/mg) are the Langmuir constants, which relate to the maximum sorption capacity and sorption energy, respectively.

Freundlich equation is an empirical relationship (Volesky, 2003). The linearized form of Freundlich equation is:

$$\log q_e = \frac{1}{n} \log C_e + \log K_F \quad (3)$$

where  $K_F$  and  $n$  are Freundlich constants and indicators of adsorption capacity and adsorption intensity, respectively.

### 2.5. Kinetics modeling

In order to investigate the mechanism of biosorption and potential rate controlling step, such as mass transport and chemical reaction processes, the pseudo-first-order and pseudo-second-order kinetic models were used to test the kinetic data.

The pseudo-first-order kinetic model is given as (Aksu, 2002):

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (4)$$

where  $K_1$  is the pseudo-first-order rate constant ( $\text{min}^{-1}$ ). A straight line of  $\log(q_e - q_t)$  versus  $t$  suggests the applicability of this kinetic model.

The pseudo-second-order kinetic equation is given by Ho (2003) and Vadivelan and Kumar (2005):

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