Full Length Article

Phosphoryl functionalized mesoporous silica for uranium adsorption

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ABSTRACT

Phosphoryl functionalized mesoporous silica (TBP-SBA-15) was synthesized by modified mesoporous silica with γ-amino propyl triethoxy silane and tributyl phosphate. The obtained samples were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), small angle X-ray diffraction (SAXRD), thermo-gravimetric/differential thermalanalyzer (TG/DTA), N_2 adsorption–desorption (BET) and Fourier transform infrared spectroscopy (FT-IR) techniques. Results showed that TBP-SBA-15 had large surface areas with ordered channel structure. Moreover, the effects of adsorption time, sorbent dose, solution pH, initial uranium concentration and temperature on the uranium adsorption behaviors were investigated. TBP-SBA-15 showed a high uranium adsorption capacity in a broad range of pH values. The U(VI) adsorption rate of TBP-SBA-15 was fast and nearly achieved completion in 10 min with the sorbent dose of 1 g/L. The U(VI) adsorption of TBP-SBA-15 followed the pseudo-second-order kinetic model and Freundlich isotherm model, indicating that the process was belonged to chemical adsorption. Furthermore, the thermodynamic parameters (ΔG^0, ΔH^0 and ΔS^0) confirmed that the adsorption process was endothermic and spontaneous.

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1. Introduction

Nowadays, the demand for uranium resources has been increasing with the rapid development of nuclear power industry in the world. At the same time, the uranium radiation has become a global threat of human health through water pollution [1]. Therefore, the removal and enrichment have attracted lots of attention in the past decades. A variety of methods have been used to U(VI) removal and enrichment process, including chemical precipitation, extraction, ion exchange and membrane method, etc [2–6]. Compared with above methods, the adsorption method [7–12] is dominant for simple process, high efficiency and low cost. At present, U(VI) sorbents mainly include inorganic sorbents and organic sorbents. The inorganic sorbents have fast adsorption kinetics, easy manufacture, low cost and easy recycling and elution. But the complex adsorption mechanism and poor directional adsorption properties have limited the application of inorganic sorbents [13]. On the contrary, the organic sorbents have strong directional adsorption capacity,

which is attributed to N, P, O and other relative elements in the functional groups [14,15]. However, the development of organic sorbents is restricted by the low adsorption rate and complex stripping process. In this context, the organic and inorganic composite materials have become a hot research topic, which can utilize both the advantages comprehensively.

Due to the strong chelation of phosphoryl group on U(VI) ions, lots of organics with phosphorus function group have been used in U(VI) adsorption process [16]. Among these, excellent properties of strong chelating capacity and high selectivity on uranium element render tributyl phosphate (TBP) a promising uranium extraction agent extensively applied in the hydrometallurgical process [17,18]. Meanwhile, the high U(VI) adsorption selectivity, wide pH values range and low cost make TBP an ideal function part of U(VI) adsorption materials.

The unique structure and properties make mesoporous materials ideal materials for radionuclide adsorption [19–21]. Among these, mesoporous silica (SBA-15) has been used for U(VI) adsorption owing to its high specific surface area, large pore size, regular structure and significant hydrothermal stability [22]. In addition, the surfaces and channels of SBA-15 have abundant hydroxyl groups, which can be combined with organic functional groups [18].

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In this paper, SBA-15 was chosen as the inorganic matrix. Then γ-amino propyl triethoxy silane and TBP were added to SBA-15 for the further preparation of phosphoryl functionalized mesoporous silica. The synthesized composite materials were used for removing U(VI) from aqueous solutions. Experimental parameters, such as time, sorbent dose, solution pH and initial concentration were studied and optimized. In addition, the adsorption isotherm and thermodynamics studies were used to analyze the mechanism of U(VI) adsorption onto TBP-SBA-15.

2. Experimental

2.1. Starting materials

A standard stock U(VI) solution was prepared by dissolving 1.18 g of U_3O_8 in nitric acid solution. Then the mixture was diluted to 1000 mL with deionized water. The main raw materials were listed in Table 1.

2.2. Preparation of TBP-SBA-15

The TBP-SBA-15 was synthesized as follows steps and the schematic representation of the preparation of the SBA-15, ammonia functionalized SBA-15 and TBP-SBA-15 was shown in Fig. 1.

Step 1: Preparation of SBA-15

SBA-15 was prepared by template synthesis method as the following steps. Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (marked P123) used as the template was dissolved in deionized water with hydrochloric acid (2 mol/L). After P123 completely dissolved, tetraethylorthosilicate (TEOS) was added to the solution. Then the mixture was continue stirred at 40 °C for 24 h and aged at 110 °C for a day in reactors. After drying, the mixture was washed in ethyl alcohol for 2–3 times at 40 °C to remove the template. The resulting product was filtered and dried at 60 °C and the obtained powders were SBA-15.

Step 2: Preparation of ammonia functionalized SBA-15

SBA-15 was dispersed in toluene with γ-amino propyl triethoxy silane and subsequently stirred for 24 h at 80 °C. The mixture was filtered and washed in ethyl alcohol for 2–3 times and dried at 80 °C for 24 h. The final products were ammonia functionalized SBA-15 (mark as SBA-15-NH$_2$).

Step 3: Modification of TBP

TBP and phosphoric acid were stirred for 1 h at 80 °C, and then epichlorohydrin was added gently. After stirring for 4 h at 90 °C, the mixture was washed by acetone and benzene to remove impurities. The obtained oily liquids were dibutyl-(3-chloro-2-hydroxy)-propyl phosphate (mark as DPP).

Step 4: Preparation of TBP-SBA-15

SBA-15-NH$_2$ and DPP were stirred for 12 h at 60 °C with methyl-benzene as solvent reaction medium. The filtered products were washed by ethyl alcohol and deionized water. After drying at 80 °C, the obtained powders were phosphoryl functionalized mesoporous silica (TBP-SBA-15).

2.3. Characterization of materials

The obtained products were characterized by scanning electron microscopy (SEM, RIGAKU ULTIMA IV), high resolution transmission electron microscopy (TEM, Tecnai-20U-TWIN) small angle X-ray diffraction (SAXRD, EVO-18, CARL ZEISS SMT Ltd), thermo-gravimetric/differential thermalanalyzer (TG/DTA, DSC 404) and N$_2$ adsorption-desorption isotherms using the BET equation (V-Sorb 2800P). Infrared spectra analysis was carried out by Fourier transform infrared spectroscopy (FT-IR, TENSOR 37) in a wave number from 400 to 4000 cm^{-1}. The concentrations of U(VI) solutions were determined by Ultraviolet and Visible Spectrophotometer (UV-3850) with arsenazo III as chromogenic agent [23].

2.4. Adsorption experiments

The adsorption experiments were carried out under different conditions to investigate the U(VI) adsorption performances of TBP-SBA-15. The adsorption capacity (q) and percentage E (%) of U(VI) were calculated by Eqs. (1) and (2):

$$q = \frac{(C_0 - C_e) \times V}{m} \tag{1}$$

$$E(\%) = \frac{C_0 - C_e}{C_0} \times 100\% \tag{2}$$

Here, q (mg g^{-1}) is the adsorption capacity; C_0 (mg L^{-1}) and C_e (mg L^{-1}) represent the initial concentration and residual equilibrium concentration of U(VI) solution, respectively; V (L) and m (g) represent the volume of U(VI) solution and the amount of the sorbent, respectively.

2.5. Adsorption data calculation

2.5.1. Adsorption kinetics

The kinetic study of the adsorption process is mainly used to describe the adsorption rate and the adsorption mechanism was explored by fitting the kinetic data. The adsorption kinetics of U(VI) adsorption onto TBP-SBA-15 were analyzed by using the pseudo-first-order kinetics and pseudo-second-order kinetics models as the following Eqs. (1) and (2), respectively [24]. The pseudo-first-order kinetics model is established on the direct proportion of adsorption rate and the un-adsorbed amount on the surface. However, the pseudo-second-order kinetics model considers that the main control step of the adsorption rate is chemical reaction or chemical adsorption based on electronic sharing and gain-loss.

$$\ln(q_e - q_t) = \ln q_e - \frac{k_1 t}{2.303} \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

where k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) is the adsorption rate constant of the pseudo-first-order and pseudo-second-order kinetics, respectively, t (min) is the adsorption time, q_e (mg g^{-1}) and q_t (mg g^{-1}) are the adsorption quantity at equilibrium and time t, respectively.

2.5.2. Adsorption isotherm

The adsorption isotherms of TBP-SBA-15 were analyzed with different concentrations (10–400 mg/L, T = 288 K, sorbent dose = 1 g/L, t = 30 min). The experimental values were used to correlate with the Langmuir and Freundlich sorption isotherm models.

The Langmuir isotherm model assumes the adsorption process is monolayer absorption and all the adsorption sites are equal and uniform [25]. The equation of Langmuir model is given as following:

$$q_e = \frac{q_m b_L c_e}{1 + b_L c_e} \tag{5}$$

where q_m (mg g^{-1}) is the saturated monolayer adsorption capacity, b_L (L g^{-1}) is the Langmuir constant relating to the adsorption strength.

The Freundlich isotherm model is suitable for the monolayer and multilayer adsorption. It is established on the un-uniform surface and active sites [26]. The Freundlich model is expressed by the following equation:

$$q_e = K_F c_e^{1/n_F} \tag{6}$$