Investigation of U(VI) sorption on silica aerogels: Effects of specific surface area, pH and coexistent electrolyte ions

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ABSTRACT

The very large surface associated with aerogels made them attractive in the field of sorption. Herein, silica aerogels were characterized and used for the sorption of U(VI) in solution. The effects of specific surface area (SSA), pH and coexistent electrolyte ions on the surface site density, aggregation and sorption properties have been carefully investigated. The site distributions of silica aerogels were calculated with Visual MINTEQ. The sorption of U(VI) is affected significantly by the solution pH. The sorption increases with increasing SSA due to the increased amount of surface active sites of silica aerogels. Electrolyte ions (Na^+, K^+, NO_3^-, Cl^-) were added to investigate the competition ability to U(VI) adsorbed on active sites. The influence of humic acid (HA), silicate and phosphate on U(VI) sorption in multiphase systems were also discussed. The kinetics data were used to investigate the sorption process and pseudo-second-order model was used to simulate the kinetic data. Spectroscopic analyses were also utilized to explain the role of —OH groups in the U(VI) sorption.

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1. Introduction

The removal and recovery of the hazardous radionuclides from larger amounts of nuclear wastes are urgent required due to the fast growing of the nuclear industry [1,2]. The pollution of U(VI) dispersed in mine tailings or concentrated on spent fuel is a serious environmental concern. The free U(VI) ions have significant mobility, which can be easily released to the natural environment. The radioactive U(VI) ions can do seriously harm to living beings. Therefore, it is crucial to eliminate of U(VI) from the wastewater before it enters into the environment [3–5].

The sorption is regarded as an efficient way to remove radionuclides due to its most economically favorable, simple operation and high efficiency. The choice of adsorbent should meet some criteria such as having large surface area, mechanical stability, possibility of recycling and biodegradability. Natural minerals usually own the features as environmentally friendly and simple use. To enhance the performance as adsorbent, some manmade materials have been used to eliminate radionuclides from wastewaters, such as aerogels, which were usually made of renewable materials and had constituted an interesting class of adsorbents as their low density, large surface area and resilience properties [6–9]. Thus, many research results have been concentrated on developing its potential applications as adsorbent recently [6,7,10]. The sorption of uranyl ions (UO_2^{2+}) on silica gel at different environmental conditions have been reported [11]. The effects of the particle size and the porosity of silica gel on U(VI) sorption were also discussed [12]. Actually, physicochemical parameters of silica aerogels such as specific surface area (SSA), aggregation properties, surface functional groups as well as external environmental factors such as pH, coexistent electrolyte ions and so on could influence the sorption performance of silica aerogels in the natural environments.

Increasing SSA may increase the amount of active sites as well as the reaction rates [13]. Besides, the accurate analysis of surface functional groups is necessary for the effective utilization of the silica aerogels. The hydroxylated groups are of particular importance in the utilization of silica aerogels due to the complexation ability between U(VI) and protonation/deprotonation sites [14]. Many researchers have studied the surface properties of minerals with the aid of potentiometric titration [15]. In the natural environments, the coagulation of silica aerogels in the presence of electrolyte ions will strongly influence the migration and chemical behaviors of silica aerogels in watery environment.

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However, the aggregation of the adsorbents and the relationship between SSA and concentration of protons consumed have been investigated scarcely, which need to be further discussed.

In general, natural environments are multi-component systems and the effect of coexistent ions and humic substances on the aggregation and sorption properties of adsorbents should be considered. Due to the dissolution of clays and biodegradation of organic matter, soluble humic acids (HA), silicate and phosphate exist in the environment, and the interactions with U(VI) have great influence on the behavior of radionuclides [16]. Moreover, HA, silicate and phosphate can significantly change the aggregation of silica aerogels in aquatic environment and reduce the efficiency of remediation [17,18]. Changes in particle size upon aggregation may alter the transport and reactivity properties of solid materials [19]. Sorption of natural organic matter could lead to large amounts of negative charges on the surface of materials, stabilize the particle suspensions and then affect the U(VI) sorption on silica aerogels [20]. However, the aggregation of silica aerogels and its influence on the interactions among HA, silicate and phosphate and U(VI) ions, are still not very clear.

Therefore in this study, silica aerogels were utilized to investigate the sorption behavior of U(VI) in multi-system to simulate the natural environments. The effects of SSA, pH and coexistent electrolyte ions on the surface site density, aggregation and sorption properties have been investigated. The surface site density and the site distributions of silica aerogels were elucidated with the aid of Visual MINTEQ based on the diffuse layer model (DLM). The aggregation and the particle size distribution of silica aerogels in the multi-systems were detected to give the better understanding of the physicochemical behaviors of silica aerogels in the natural environments. The sorption of U(VI) on silica aerogels as a function of pH, temperature, U(VI) concentration and co-existent electrolyte ions and so on were investigated by batch experiments. Spectroscopic techniques were used to obtain insights into the mechanism of U(VI) adsorbed on silica aerogels.

2. Experiments

2.1. Chemical

All chemicals were derived from the Sinopharm Chemical Reagent Beijing Co. Ltd. (Beijing, China). All stock solutions of chemicals could be obtained by dissolving chemicals with Milli-Q water. The HA used in the experiments is a commercialized product bought from Sinopharm Chemical Reagent Co., Ltd., and was purified by a strong acid to remove bund iron and decrease the ash content prior to use [21]. Silicate and phosphate stock solutions were prepared by dissolving $Na_2SiO_3 \cdot H_2O$ and $NaH_2PO_4 \cdot H_2O$ in Milli-Q water, respectively.

2.2. Synthesis

The silica aerogels throughout the study were prepared by sol-gel process. The detailed information about the synthesis of silica aerogels was well-documented in preliminary reports [6]. Briefly, the synthesis procedure contains these steps as follows: (1) 210 ml $NH_3 \cdot H_2O$ (25% NH_3 in water) solution with 270 ml water and 0.855 g sodium dodecyl sulfate were added with stirring 1 h to obtain homogeneous mixture solution; (2) 1.145 g hexadecyl trimethyl ammonium bromide was added to the mixed solution; (3) after 30 min, tetraethyl orthosilicate was added, causing the white slurry; (4) after 2 h, the resulting product was washed with ethanol, dried at 65 °C, and followed by calcinations in air at 550 °C for 5 h. The silica aerogels with different SSA (76, 360, 609, 631, 850 m^2/g) were synthesized through controlling the reaction condition.

2.3. Characterization

The morphology of silica aerogels was characterized by field emission scanning electron microscope (FESEM, FEI Sirion-200). X-ray diffraction (XRD) analysis was conducted on TTRAX3 theta/2theta rotating anode X-ray diffractometer (Rigaku, Japan). A multi-point BET method was adopted to obtain the N_2 sorption-desorption isotherms by a sorption instrument (Micromeritics ASAP 2010 system) for calculating the SSA. The size distributions of the silica aerogels were analyzed on a ZETASIZER Nano-ZS90 system from Malvern. The surface functional groups of silica aerogels were analyzed on Fourier transformed infrared spectroscope (FT-IR) (PerkinElmer 100 spectrometer). The X-ray photoelectron spectroscopy (XPS) measurements were performed by a Thermo ESCALAB 250 electron spectrometer.

2.4. Potentiometric titration

The potentiometric acid-base titrations were performed on a DL50 Automatic Titrator (Mettler Toledo). 5.5 mg silica aerogels were suspended in 50 ml of $NaNO_3$ solution in a 100 ml flask. We added HNO_3 into the suspension of silica aerogels sample (40.0 ml) for the acidification of suspension to achieve pH ~ 2.8 and then started to be titrated with 4 mM NaOH until pH of suspension exceeded 11.4.

2.5. Sorption experiments

The U(VI) sorption experiments were conducted in polypropylene centrifuge tubes at room temperature (25 ± 2 °C) in triplicates. In these experiments, powdered silica aerogels were mixed with Milli-Q water to achieve desired sold/liquid ratio and the prepared U(VI) concentration was 240 mg/L. The volume of 0.05 mol/L HNO_3 or NaOH used to adjust pH is negligible. After 24 h shaking time, high-speed centrifuge was used to separate the solid and liquid phases under 9000 rpm for 40 min and a kinetic phosphorescence analyzer (KPA-11, Richland) was employed to measure the equilibrium concentration of U(VI).

The amounts of U(VI) adsorbed on silica aerogels (q_e (mg/g)) and the sorption percent were calculated by Eqs. (1) and (2), respectively, as follows [22–24]:

$$q_e = (C_0 - C_e)/m \times V \tag{1}$$

$$Sorption\ (\%) = (C_0 - C_e)/C_0 \times 100\% \tag{2}$$

where C_0 (mg/L) and C_e (mg/L) denote the initial and equilibrium concentrations of U(VI) in solution, m (g) is the mass of adsorbent and V (L) denotes the volume of the solution. Experiments regarding effects of different conditions were conducted in the similar manner to clarify interactions between U(VI) and silica aerogels.

3. Results and discussion

3.1. Characterization

FESEM image of silica aerogels (Fig. 1A) shows the sponge-like microstructure and three-dimensional nanoporous network structure. And the silica aerogels with different SSA have the similar structures. To analyze the crystalline structure of silica aerogels, the XRD pattern was investigated (Fig. 1B). There is no obvious narrow peak found in the spectrum. Only a broad peak was found in the range from 20° to 30°, which indicates the amorphous structure of the silica aerogels. The N_2 sorption-desorption isotherm of silica aerogels with SSA of ~360 m^2/g is shown in Fig. 1C. It could be observed clearly that the isotherm exhibits the typical *IV* curve, suggesting the existence of predominantly mesoporous structure [25]. The average pore diameter of silica aerogels is centered at 50 Å (Fig. 1D).

3.2. Aggregation of silica aerogel

The size distribution of silica aerogels as a function of concentration of silica aerogels particles is shown in Fig. 2A. The average diameters