Interaction between U(VI) with sulfhydryl groups functionalized graphene oxides investigated by batch and spectroscopic techniques

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GRAPHICAL ABSTRACT
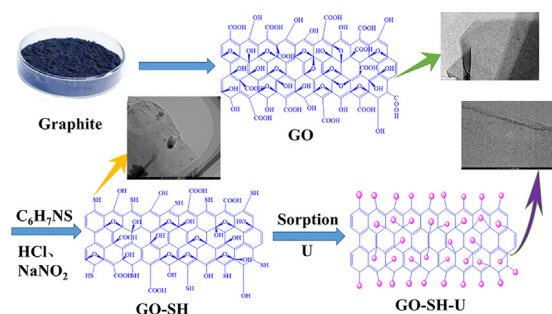
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ABSTRACT

A novel 4-aminothiophenol functionalized graphene oxide composite (GO-SH) was prepared by an easy reaction route. Chemical structure and element analysis showed that the sulfhydryl groups (-SH) were successfully decorated on GOs. The sorption capacity toward U(VI) from aqueous solution was conducted by batch experiments. The results indicated the maximum sorption capacity of GO-SH composite toward U(VI) at pH = 5.5 and T = 298 K could reach 281.69 mg·g^{-1} on the base of the Langmuir model. The sorption kinetic curve for U(VI) fitted well with the pseudo-second-order model. X-ray photoelectron spectroscopy and infrared analysis demonstrated that the surface-grafted sulfhydryl groups contributed to the sorption of U(VI) by forming the surface complexation. The GO-SH also showed high stability and excellent reuse capability. Therefore, GO-SH can be regarded as a potential sorbent for the efficient removal of U(VI) from aqueous solutions.

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1. Introduction

Uranium (U), as a primary raw material for the nuclear reactor, can lead to a serious environmental pollution [1,2], making uranium a common contaminant to soils, surface and groundwater. Therefore, the removal of U(VI) from waste water is extremely important [3–5]. Various technologies have been used to eliminate U(VI) pollution including chemical precipitation, ion exchange,

membrane separation, bio-treatment, electrochemical treatment and sorption [6–11]. Among these methods, sorption has been demonstrated to be superior to other techniques owing to its low cost, efficient and wide adaptability [12,13]. However, owing to low sorption capacity or poor efficiency, the direct application of traditional sorbents in the removal of U(VI) is still limited. Various types of sorbents such as carbon materials [14], biomaterials [15], metal–organic frameworks [16] and nanometer materials have been applied for the removal of U(VI).

Due to its good dispersibility and high surface area, graphene oxide (GO) is being used as a sorbent in the removal of radionuclides [17], heavy metal ions [18–20], organic contaminations and anions [21,22]. Furthermore, the oxidation process of graphite to GO can introduce plenty of functional groups on GO surface that can be used as active attachment sites for the functionalization and as anchoring sites for metal ion complexation [23–25]. However, the limited amount of functional groups on GO do not completely remove U(VI) from solution, and also the oxygen-containing functional groups are introduce to provide strong coordination with U(VI). Thus it is urgent and interesting to explore novel functional composites to solve these problems.

In this study, GO-SH was successfully prepared by introducing functional groups (-SH) on the surface of GO with 4-aminothiophenol. The morphologies, structures and properties of GO-SH were investigated. The effects of pH value, contact time and temperature on U(VI) removal were also studied. The kinetic and thermodynamic parameters of the sorption process were evaluated. The sorption mechanisms of U(VI) onto GO-SH were explored.

2. Experimental section

2.1. Chemicals and materials

Graphite powder, 4-aminothiophenol (C_6H_7NS), hydrochloric acid (HCl), hydrogen peroxide (H_2O_2, 30%), sodium nitrite($NaNO_2$), potassium permanganates ($KMnO_4$), acetone (CH_3COCH_3), concentrated sulfuric acid (H_2SO_4, 98%) and absolute ethyl alcohol (C_2H_5OH) were purchased in analytical grade from Sinopharm Chemical Reagent Co. Ltd. The standard stock solution (2.38 g/L) of U(VI) was prepared by dissolving uranium nitrate ($UO_2(NO_3)_2$·$6H_2O$, spectral purity, Sigma-Aldrich) into deionized water in N_2 conditions. All of the reagents were of AR grade and used without further purification.

2.2. Preparation of GO-SH

GO was prepared according to modified Hummers method [26,27]. Generally, 2.0 g graphite powder was added into 50.0 mL of concentrated H_2SO_4 solution in a 250 mL conical click under vigorous stirring and ice-water bath conditions. Then 6.0 g $KMnO_4$ was slowly added to the GO dispersion for 3 h or more time. To keep the reaction temperature below 15 °C, the temperature should be controlled carefully. After another 24 h stirring at 35 °C, a portion of H_2O_2 (15 mL) was added into the mixture to neutralize the unreacted $KMnO_4$. For refinement, the reaction production was separated by centrifugal machine (8000 rpm for 10 min) and washed repeatedly with 0.1 M HCl and deionized water for several times. The obtained product was at 35 °C under vacuum drying oven for three days.

For preparation GO-SH, a simple method was carried out to prepare GO-SH [28], firstly, 2.5 g 4-aminothiophenol and 60 mL hydrochloric acid (1mol/L) were stirred for 1 h at 50 °C. $NaNO_2$ solutions were cautiously added under ice bath condition, followed by addition of GO (1.25 g GO suspended in 50 mL of deionized

water). The temperature of the mixture was kept 0 °C for another 10 h. The mixture was washed by acetone, absolute ethyl alcohol and deionized water several times. The obtained products were dried at 60 °C for 48 h under vacuum.

2.3. Characterization

The morphology of the samples was characterized by using JAPAN JSM-6700 scanning electron microscope (SEM) and JAPAN JEOL-2010 transmission electron microscope (TEM). The Fourier transform infrared spectroscopy (FTIR) spectrum was recorded on a Nexus 670 Fourier transform infrared spectrometer. The powder X-ray diffraction (XRD) characterization was carried out using X-ray diffraction (Bruker, D8 Focus) with Cu Kα radiation (40 kV, 60 mA). The Raman spectrum was recorded with a Tokyo Instruments Model Nano finder 30R spectroscopy at room temperature. The X-ray photoelectron spectra (XPS) were measured with ESCA-LAB 250 electron energy spectrometer (Thermo Fisher Scientific, USA). The Brunauer-Emmett-Teller (BET) areas were measured on a Nova 100 (Quantachrome Instrument, USA) by using N_2 as the adsorption gas. Thermo gravimetric analysis (TGA) curves were examined (Shimadzu TGA-50) by heating the sample at the rate of 10 °C/min from room temperature to 800 °C under N_2 atmosphere. A Zeta sizer Nano ZS instrument (Malvern Instrument Co., UK) was used to measure the zeta potential at various pH values.

2.4. Batch sorption experiments

In the batch sorption experiments, several parameters that affect the U(VI) sorption has been investigated, such as solution pH, contact time and temperature. The pH was adjusted to values between 2 and 10 by adding 0.01–0.1 M HCl and NaOH solution for each experiment. The solutions were separated from the sorbent by centrifugation at 8000 rpm for 10 min and then the supernatants were then filtered with 0.45 μm. The concentration of U(VI) was determined by an ICP-MS (Agilent 7900, USA). The sorption efficiency (SE% = $(C_0 − C_e)/C_0 \times 100\%$) and equilibrium sorption amount ($q_e = (C_0 − C_e) \times V/m$) were calculated, where C_0 and C_e (mg/L) refer to the initial concentration and equilibrium concentration, respectively. V is the volume of solution (L), and m is the mass of the sorbent (g).

3. Results and discussion

3.1. Characterization

Fig. 1(A, B) shows the typical SEM and TEM images of GO. In the SEM image (Fig. 1A), GO is partially transparent with a thin, smooth surface, and crumpled sheets. The morphology of GO is similar to the flower shape. The TEM image of GO (Fig. 1B) corroborated that GO clearly existed in the sheet-like shapes and edges of the graphene sheets. As shown in Fig. 1(C, D), GO-SH presents layered structure with aggregated thin, wrinkled nanosheets and low agglomeration rate, which is similar to that of the GO. Moreover, it is worth noting that the GO-SH almost keeps its original structure after the sorption of U(VI) (Fig. 1E), compared to Fig. 1D. Fig. 1F is HRTEM image of GO-SH after sorption (GO-SH-U). We can easily find that the GO-SH-U presents lamellar folds structure and keeps previous stabilized structure without evident change.

The wide-angle XRD patterns of GO and GO-SH are shown in Fig. 2A. A sharp diffraction peak is observed at 2θ = 10.7°, corresponding to the typical diffraction peak of GO nanosheets. For GO-SH, the broad and relatively weak diffraction peak is emerged at 2θ = 17.2°, corresponding to the presence of -SH [28]. Fig. 2B presents