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Removal of radiocobalt from aqueous solutions using titanate/graphene oxide composites

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The titanate/graphene oxide composites were synthesized by thermal treatment using graphene oxides and TiO_2 powder (P25), and were characterized using FTIR, SEM and XRD. The as-prepared titanate/graphene oxide composites were used as adsorbents to eliminate radiocobalt (^{60}Co) from aqueous solutions as a function of contact time, ionic strength and pH values. The sorption of ^{60}Co to titanate/graphene oxide composites was strongly dependent on pH and ionic strength at pH < 8, and was independent of ionic strength at pH > 8. The sorption of ^{60}Co was mainly dominated by inner-sphere surface complexation at high pH and by ion exchange and/or outer-sphere surface complexation at low pH values. The sorption of ^{60}Co on titanate and on graphene oxides was also compared, and the results indicated that the titanate/graphene oxide composites were suitable materials for the preconcentration and solidification of ^{60}Co and/or other radionuclides/heavy metal ions from large volumes of aqueous solutions in environmental pollution cleanup in real applications.

1. Introduction

With the rapid development of nuclear power energy, large volumes of radioactive wastewater and spent fuels are produced. In the spent fuel treatment process, large amounts of radionuclides are inevitably released into the environment, and thereby results in environmental pollution and are dangerous to human health [1–5]. Among the fission products, radionuclides ^{60}Co and ^{58}Co are present in liquid wastes which are released from the pressurized water nuclear power reactors, and radiocobalt is one of the most serious radionuclides because it is non-degradable and can be accumulated through food chain [6]. ^{60}Co is also widely used in medical applications. The permissible limits of cobalt in irrigation water and livestock wastewater are 0.05 and 1.0 mg/L, respectively [6,7]. Thereby, it is necessary to remove radiocobalt from aqueous solutions. Various techniques such as (co)precipitation, ion exchange, membrane filtration, bio-remediation, solvent extraction and sorption have been used to eliminate radionuclides from large volumes of aqueous solutions [8–12]. Although these methods are efficient for the preconcentration of radionuclides from solutions, sorption technique has been widely used for the removal of radionuclides from aqueous solutions due to its simple operation and low cost [13–15]. The sorption of Co(II) on many materials has been extensively studied [16–19], and the results indicated that Co(II) sorption was mainly dependent on pH and ionic strength at low pH, and independent of ionic strength at high pH. The sorption was mainly attributed to outer-sphere surface complexation or ion exchange at low pH, and was mainly dominated by inner-sphere surface complexation and/or surface (co)precipitation at high pH.

Since the innovative work of Kasuga et al. [20,21], titanate has come under multidisciplinary study as ion-exchange materials and superior adsorbents due to their fascinating microstructures and excellent properties. In the past few years, the titanate has been applied as adsorbent to remove heavy metal ions [22,23]. Graphene oxide, a new two dimensional carbon allotrope with one or several atomic layers with abundant oxygen-containing functional groups to various sites, has been studied extensively to remove heavy metal ions and radionuclides from aqueous solutions [24–26]. Although the graphene oxide and titanate have been studied extensively for the elimination of pollutants from aqueous solutions, the synthesis of titanate/graphene oxide composites and their application for the removal of radionuclides are still not available, which are crucial for the application of the composites in nuclear waste management.

In this paper, we reported a simple method to synthesize the titanate/graphene oxide composites and applied them to remove radiocobalt from aqueous solutions. The effect of pH, ionic strength, and solid contents on radiocobalt sorption to the composites was investigated, and the sorption of radiocobalt on titanate and graphene oxides was also studied as a comparison. The interaction mechanism was also discussed in detail.

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2. Experimental

2.1. Synthesis of graphene and titanate/graphene oxide composites

The graphene oxides were synthesized by the oxidation of expanded graphite using the modified Hummers method [12,13]. 4.0 g graphite and 3.0 g $NaNO_3$ were added into 300 mL concentrated H_2SO_4 under vigorous stirring and ice-water bath conditions. Then 18.0 g $KMnO_4$ was slowly added into the suspension, stirred for 5 days, and 560 mL 5.0 wt.% H_2SO_4 was dropwise added into the suspension with vigorous stirring at 98 ± 1 °C. After the temperature was decreased to 60 °C, 24 mL H_2O_2 (30 wt.%) was added into the suspension to eliminate the excess $KMnO_4$. At last, the suspension color was converted from dark brown to yellow and the solid phase was separated from solution using ultracentrifugation at 20,000 rpm for 30 min.

The titanate/graphene oxide composites were synthesized by a simple thermal treatment. 0.2 g graphene oxide was dispersed in 140 mL 10 M NaOH under ultrasonication for 1 h. Then, 2.0 g of TiO_2 powder (P25, Degussa AG, Germany) was added into the suspension, and stirred for 10 min. The resulting suspension was transferred into a Teflon-lined stainless steel autoclave, followed by thermal treatment at 130 °C for 72 h. The precipitate was rinsed with Milli-Q water until pH ~ 12 and then rinsed with ethanol to remove the residual surface Na^+ and OH^-. The powder was dried at 80 °C overnight, and the titanate/graphene oxide composites were prepared. As comparison, the bare titanate was also synthesized by the aforementioned method without graphene oxides.

2.2. Characterization

The materials were characterized by Fourier transformed infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), and X-ray diffraction (XRD). The FT-IR spectra were recorded on a Nicolet Magana-IR 750 spectrometer using KBr pellets over a range from 350 to 4000 cm^{-1}. The SEM images were measured using a JEOL JSM-6330F instrument operated at the beam energy of 15.0 kV. The powder XRD patterns were measured using a Philips X'Pert Pro Super X-ray diffractometer with Cu Kα source ($\lambda = 1.54178$ Å).

Radionuclide ^{60}Co(II) was used as a radiotracer and the concentration of ^{60}Co(II) was measured by liquid scintillation counting using a Packard 3100 TR/AB Liquid Scintillation Analyzer (PerkinElmer). The scintillation cocktail was ULTIMA GOLD AB (Packard).

2.3. Sorption experiments

The sorption of radiocobalt on titanate, graphene oxides, and titanate/graphene oxide composites was studied using the batch technique. The solid suspension, Milli-Q water and $NaClO_4$ solutions were mixed in test tubes for 24 h to achieve the interaction equilibration of Na^+ ions with solid phases. Then the radiocobalt solution was added into the suspension and the pH was adjusted using negligible volumes of $HClO_4$ and/or NaOH. After shaken for 48 h, the solid phase was separated from solution by centrifugation at 18,000 rpm for 30 min. The amount of Co(II) adsorbed on solid phase (i.e., titanate/graphene oxide composites, titanate or graphene oxides) was calculated from the initial concentration (C_0) and the final one (C_e). The sorption percentage (%), the amount of Co(II) adsorbed on solid phase (C_s) and the distribution coefficient (K_d) were calculated as:

$$\text{Sorption}(\%) = \frac{C_0 - C_e}{C_0} \times 100\% \tag{1}$$

$$C_s = \frac{C_0 - C_e}{m} V \tag{2}$$

$$K_d = \frac{C_0 - C_e}{C_e} \times \frac{V}{m} \tag{3}$$

where V is the volume of solution and m is the mass of the solid phase. All the experimental data were the average of duplicate experimental results, and the relative errors of the data were about 5%.

3. Results and discussion

3.1. Characterization

The morphologies of the as-prepared graphene oxides, titanate and titanate/graphene oxide composites were characterized by FE-SEM. Fig. 1A shows the SEM image of titanate and the inset figure is the SEM image of graphene oxides. One can see that the titanates appear as typical nanofibers, which are very similar to the morphology of reported titanate [27]. In the synthesis process, the P25 nanoparticles were firstly transformed into 2D lamellar structure, and then followed by rolling to form 1D structure of titanate. The inset figure in Fig. 1A (SEM image of graphene oxides) shows the wrinkled and aggregated nanosheets throughout the morphology of graphene oxides. In the SEM image of titanate/graphene oxide composites (Fig. 1B), it is clear that titanate nanofibers are well distributed on graphene oxides. However, the sizes of titanate nanofibers are smaller than those of the pure titanates. The graphene oxides could provide more binding sites, and thereby result in the formation of titanate easily.

The surface functional groups and the structures of the titanate, graphene oxides and titanate/graphene oxide composites were analyzed by FTIR and XRD. The XRD pattern of titanate/graphene oxide composites showed the characteristics of diffraction peaks at 10°, 25°, 29° and 48°, which were in good agreement with the results of XRD characterization of bare titanate (Fig. 2A) [28]. The interlayer distance of titanate at around 10° was 0.848, which are larger than the value of titanate/graphene oxide (0.831 nm). The interaction of graphene oxide with titanate nanofibers reduces the interlayer distance of titanate. Comparing to the XRD patterns of standard anatase and rutile (Fig. 2B), one can see that the titanate sample is not similar to the anatase and rutile. The XRD patterns indicate that a single phase of either anatase or rutile used in this experiments. The FTIR spectra of the titanate, graphene oxides and titanate/graphene oxide composites were shown in Fig. 3. In the FTIR spectrum of graphene oxides, various oxygenated functional groups, such as C–OH (broad peak at ~3400 cm^{-1}), —COOH group (at ~1700 cm^{-1}), C═O group (at ~1400 cm^{-1}) and C–O–C group (at ~1050 cm^{-1}) were found on graphene oxide surfaces [27,29]. The strong peak at ~3400 cm^{-1} was attributed to the stretching vibration of the –OH groups associated with the layered structure of titanate and graphene oxides [14,15]. The absorption peak appearing at ~900 cm^{-1} was ascribed to the stretching vibration of short Ti–O bonds from disordered TiO_6 octahedron [27]. The characteristic peaks of graphene oxides were not found in the FTIR spectra of titanate/graphene oxide composites, which may be due to the low content of graphene oxides in the composites and the coverage of graphene oxides by titanate nanofibers.

3.2. Kinetic sorption

The sorption of ^{60}Co(II) on the titanate/graphene oxides as a function of contact time was shown in Fig. 4A. The sorption of ^{60}Co(II) on titanate/graphene oxides increased quickly with increasing contact time in the first contact time of 2 h, and then increased very slowly with increasing contact time. The fast sorption of ^{60}Co(II) on titanate/graphene oxides indicates that chemical sorption or surface complexation rather than physical adsorption is the main mechanism for the sorption of ^{60}Co(II) to titanate/graphene oxides [1,30,31]. In the following experiments, 24 h of contact time was applied to achieve the sorption equilibration.

From the two inset figures in Fig. 4A, one can see that the sorption increases very quickly and then very slowly with increasing contact time. The two-step sorption processes follow the general sorption