Organic modification of bentonite and its application for perrhenate (an analogue of pertechnetate) removal from aqueous solution

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ABSTRACT

Technetium-99 (^{99}Tc) is an important fission product of nuclear industry. Its characteristics can be predicted by studying rhenium (Re), a chemical analogue of technetium, thus avoiding the use of radioactive elements at high concentrations. The present work focused on the sorption of Re(VII) by hexadecyl trimethylammonium cation (HDTMA) modified bentonite. Our experimental results show that the bentonite sample has been successfully modified. The stability of HDTMA in the sample is satisfactory with the increasing of calcination temperature ($<200\,^\circ$C). The uptake rate of Re(VII) is relatively rapid and the sorption kinetics of Re(VII) can be successfully described by the pseudo-second-order model. Thermodynamic studies reveal that the sorption process is more favorable at low temperature. The uptake ratio of Re(VII) on HDTMA modified bentonite was enhanced significantly compared with the unmodified one, the surface precipitate between HDTMA and Re(VII) is the main mechanism for Re(VII) uptake by HDTMA modified bentonite.

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1. Introduction

Technetium-99 (^{99}Tc) (a soft β-emitter, $E_{max} = 294$ keV) is a product of thermal fission of uranium-235 (^{235}U) and plutonium-239 (^{239}Pu) with a high yield of around 6% [1,2]. It is particularly mobile once released to the environment, since ^{99}Tc is present in aqueous in its stable heptavalent state as pertechnetate anionic complex, TcO_4^-. This oxoanion is highly soluble in groundwater under oxidizing conditions and difficult to eliminate, posing concern as a significant environmental hazard [3–5].

In the geologic disposal of high-level nuclear waste, sorption is treated as an effective way to evaluate the migration of radionuclides in the environment [6]. The investigation on the sorption behavior of TcO_4^- on natural mineral is therefore significant. Bentonite, with various outstanding physicochemical properties, *i.e.*, large specific area, low permeability, low cost, high cation exchange capacity, accessibility and ubiquitous presence in most soils, has been suggested for use in the construction of storage facilities for the disposal of spent nuclear fuel and fission products as

a host or as the principal component of engineered barrier materials [7,8]. Based on the permanently negatively charged surface like other aluminosilicate minerals and a pH-dependent negative surface charge caused by deprotonation of the surface hydroxyl group under high pH conditions, bentonite is often characterized by excellent sorbents capabilities for cationic pollutants [9,10] but are usually ineffective sorbents for anionic contaminants such as iodine and TcO_4^- [11,12].

With the development of surface modification technologies, materials (including natural mineral and artificial materials) with eximious sorption abilities have been synthetized and applied for pollutants removal [13–19]. Studies have shown that the absorptive capabilities of bentonite for anionic radionuclides can be substantially improved by converting the surface charge of bentonite from negative to positive using cationic surfactants [15]. Choung and coworkers investigated the sorption of iodine by surfactant-modified bentonite and found that the sorption abilities of bentonite can be enhanced with the increase of surfactant content loaded [12]. Although a few studies have been conducted TcO_4^- sorption experiment with organo-modified bentonite [11], the comprehensive investigations on the various environmental parameters which affect the sorption abilities of TcO_4^- are limited. Furthermore, the sorption mechanism of ^{99}Tc on organo-modified bentonite is still not clear, which hinders the application of such kind of materials for the immobilization of ^{99}Tc.

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Owing to the similar electronic configuration, stereochemistry and thermodynamic properties, rhenium (Re) is often treated as a nonradioactive surrogate of ^{99}Tc and applied for the evaluation of ^{99}Tc behavior [20–22]. Accordingly, the objectives of this work are to provide fundamental information for Re(VII) sorption on HDTMA modified bentonite and to investigate the main mechanisms of Re(VII) uptake. The results are expected to help better elaborate and evaluate the migration behavior of ^{99}Tc in the environment.

2. Materials and methods

2.1. Chemicals

A Re(VII) stock solution (in ReO_4^- form) was prepared with NH_4ReO_4 salt (> 99.99%) which was purchased from STREM CHEMICALS. All other chemicals used were of analytical grade. High purity water (18 MΩ·cm) was used in all experiments.

2.2. Bentonite modification and characterization

The raw bentonite was obtained from Gaomiaozi Mine (Xinghe County, Inner Mongolia, China), which has been selected as the candidate of backfill material for potential Chinese nuclear waste repository [8,23]. Before organic modification, the samples were purified and transformed into Na-form with the method mentioned in our previous work [23].

The procedure for organic modification of bentonite is as follows: 10 g Na-bentonite sample was dispersed in 200 ml H_2O and the suspension was heated to 60 °C under magnetic stirring. At the same time, 1.8223 g hexadecyl trimethylammonium bromide (HDTMA) was dissolved in 500 ml H_2O and heated to 60 °C. Then the HDTMA solution was transferred into the Na-bentonite suspension with continually stirring. The mixed suspension was placed for 3 h at 60 °C, and then made it cool down to room temperature and centrifuged at 4000 rpm for 15 mins. After removing supernatant, the residue was washed with high purity water. The washing step was repeated until Br^- cannot be detected with $AgNO_3$ solution. Then the precipitate was filtered, dried and grinded. After sifting by 160 mesh sieve, the sample was stored in desiccator for further use.

The sorbent was characterized using scanning electron microscopy (SEM), X-ray powder diffraction (XRD), Fourier transform infrared (FTIR) and potentiometric titration. The surface area of the sample was determined by N_2 sorption/desorption isotherms.

2.3. Sorption experiment

Sorption experiments were carried out at room temperature (25 ± 2 °C) using batch techniques. The general procedure was as follows: suitable amount of sorbent was dispersed in 0.1 mol/L NaCl solution in a polyethylene tube with a solid-to-liquid ratio of 10 g/L. The pH of suspensions was adjusted to desired values with small amount of NaOH/HCl solution. The suspensions with Re(VII) were then shaken for 3 days so as to make sure that the steady state was reached (the pH was monitored during these periods). After that, the pH of the suspension was measured and the suspension was separated by centrifugation at 18,000 g for 30 mins to get the concentration of Re(VII) in aqueous phase. The amount of Re(VII) sorbed on bentonite samples (q, mol/g) can be calculated by Eq. (1):

$$q = (C_0 - C_{aq}) \cdot \frac{V}{m} \tag{1}$$

where V (L) is the volume of aqueous solution, m (g) is the mass of sorbent, C_{aq} (mol/L) is the concentration of Re(VII) in aqueous phase, C_0 (mol/L) the total concentration of Re(VII) added.
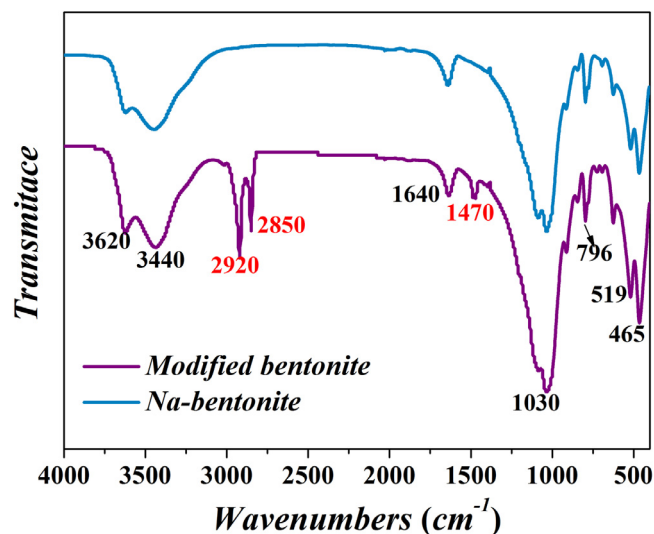

Fig. 1. FTIR spectrums of Na-bentonite and HDTMA modified bentonite.

2.4. ReO_4^- measurement using spectrophotometry

The concentration of ReO_4^- in solution was measured using spectrophotometry. The amount of calculated $SnCl_2$ (10 g/L) was added in the target solution to adjust the oxidation state of Re. To prevent Sn(II) ion hydrolysis, the pH of solution was adjusted to less than 1 with 3 mol/L HCl. Then excessive amount of diacetyldioxime (10 g/L) was added in the mixture. The solution was then stayed for 30 mins to ensure that the color reaction has completed. After that, the absorbance of solution was measured at 450 nm using spectrophotometer (7230G-N) and the concentration of Re(VII) in solution was calculated according to the standard carve of Re(VII) obtained.

3. Results and discussion

3.1. Characterization of bentonite samples using FTIR, XRD, SEM, BET and potentiometric titration

The FTIR spectrum of two kind samples (Na-bentonite and HDTMA modified bentonite) is showed as Fig. 1. Among which, 3440 cm^{-1} and 3620 cm^{-1} represent for stretching vibration peak of –OH from H_2O [24], and 1030 cm^{-1} for stretching vibration peak of Si–O–Si, which is the typical composition of bentonite. There are at least three new sorption peaks (marked as the green number) present in the modified bentonite. The peaks at 2850 cm^{-1} and 2920 cm^{-1} are assigned to the stretching vibration peak of –CH$_2$, and 1470 cm^{-1} should be the bending vibration peak of it [25,26]. Two inconspicuous sorption peaks at 2960 cm^{-1} and 725 cm^{-1} might be the stretching vibration peak of –CH$_3$ and the bending vibration peak of carbon chain (n-CH$_2$ > 4) respectively. Accordingly, it can be deduced that there is a certain amount of HDTMA which had been connected to bentonite samples.

Through the characterization of sample by XRD, it can be known that the dominant component of bentonite is montmorillonite, and quartz is the main impurity by comparing with the standard spectrum of montmorillonite and quartz (Fig. 2a). The peaks at 2θ degree of 21.9 and 26.5 represent for quartz. Peak at 7.104 degree is mainly for montmorillonite (Fig. 2a), the value could vary with the change of interlayer spacing [26]. The most obvious change for bentonite after HDTMA modification is the peak at 7.104 which moved to 4.413 (see Fig. 2b), the interlayer spacing (d_{001}) corresponded changed from 1.244 nm to 2.002 nm. It can be deduced that some HDTMA molecules have been inserted