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The interaction mechanism of Th(IV) on sepiolite investigated by batch and modeling techniques

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ABSTRACT

The effect of *Paecilomyces cateniannulatus* (*P. cateniannulatus*) on Th(IV) adsorption by sepiolite were investigated by batch techniques. The batch adsorption showed that the adsorption of Th(IV) on sepiolite and sepiolite + *P. catenlannulatus* significantly increased with increasing of pH from 3.0 to 6.0, then remained the high-level adsorption. *P. cateniannulatus* significantly facilitated the adsorption of Th(IV) on sepiolite at pH 2.0–5.0, whereas inhibited adsorption was observed at pH > 6.0. The adsorption of Th(IV) on sepiolite + *P. catenlannulatus* was independent of ionic strength at pH from 3.0 to 9.0. The adsorption kinetics of Th(IV) on sepiolite and sepiolite + *P. catenlannulatus* can be satisfactorily simulated by pseudo-second-order kinetic model. The maximum adsorption capacities of sepiolite and sepiolite + *P. catenlannulatus* for Th(IV) calculated Langmuir model at pH 3.0 and 293 K were 50.76 and 57.80 mg/g, respectively. Based on surface complexation modeling, the adsorption mechanism of Th(IV) on sepiocite + *P. catenlannulatus* was cation exchange/outer-sphere surface complexation at low pH, whereas inner-sphere surface complexation dominated the Th(IV) adsorption at high pH conditions. The findings presented in this study are of great importance towards understanding of fate and transport of heavy metals under natural aquatic environments.

1. Introduction

Radionuclide contamination is increasingly concerned issues due to its potential threat to human health [1]. Therefore, investigations on the adsorption of radionuclides at water-mineral interface play a crucial role in controlling the fate and transport of radionuclides in natural aquatic environments [2]. A number of macroscopic investigations of radionuclides adsorption on hydrous metal oxides, clay minerals and humic substances have been extensively investigated in recent years [3–6]. However, to the author's knowledge, little studies on the adsorption of radionuclides on sepiolite are observed [7].

Paecilomyces cateniannulatus (*P. catenlannulatus*), carnivorous fungi specialized in trapping and digesting nematodes, which has been extensively used for controlling nematodes. *P. catenlannulatus* can kill harmful nematodes by pathogenesis [8,9]. It is also demonstrated that *P. catenlannulatus* can be used as a promising adsorbent to remove heavy metals such as As(V) [10], Co(II) [8], Cr(VI) [11,12] and Pb(II) [13]. Li et al. [8] found that the adsorption of Co(II) on *P. catenlannulatus* increased with increasing pH from 3.0 to 7.0, whereas the Co(II) adsorption was independent of ionic strength. However, to the author's knowledge, little information on the effect of *P. catenlannulatus* on the adsorption of radionuclides onto sepiolite is available.

In this study, the Th(IV) was selected as typical representative of radionuclides to evaluate the fate and transport of radionuclides at water-mineral interface in the presence of microorganism. The objectives of this study are (1) to characterize the surface properties of sepiolite and *P. catenlannulatus* by scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform Infrared (FTIR) and potentiometric titration; (2) to investigate the effect of *P. catenlannulatus* on Th(IV) on sepiolite as a function of pH, ionic strength, reaction time and initial Th(IV) concentration by batch techniques; (3) to simulate the adsorption of Th(IV) on sepiolite and sepiolite + *P. catenlannulatus* using surface complexation modeling. This paper gives the highlights into the effect of microorganism on Th(IV) adsorption on sepiolite, which play an initial role in predicting the fate and transport of heavy metals at sub-surface aquatic environments.

2. Materials and methods

2.1. Materials

The stock solution of Th(IV) (1.0 mol/L) was prepared form $ThCl_4$ (99.9% purity) in 0.01 mol/L HCl solution. The sepiolite sample was purchased from Mineralogical Society of America and was purified with 0.1 mol/L HNO_3 solution under vigorous stirring conditions overnight. *P. catenlannulatus* strain was provided from the School of Life Science and Environmental Science, Anhui Agricultural University. *P.*

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catenlannulatus cells were cultured in the 10.0 g/L glucoses solution with various salt solution such as 2.0 g/L KH_2PO_4, 1.0 g/L NaH_2PO_4, 1.0 g/L NH_4Cl, 0.2 g/L $MgSO_4 \cdot 7H_2O$, 0.01 g/L and $FeSO_4 \cdot 7H_2O$ at 303 K overnight [8,9]. Then the cells were harvested by centrifugation (3000 ×*g*, 10 min) during the logarithmic phase and were washed three times using Milli-Q water. All other chemicals used in this work were of analytical grade and were prepared using Milli-Q water. All solutions were sterilized at 120 °C for 30 min.

2.2. Characterization

The morphologies of sepiolite and *P. catenlannulatus* were performed by SEM (JOEL, Japan). FTIR spectra were conducted on JASCO FTIR 410 spectrophotometer in KBr pellet. Briefly, 2.0 mg of sample and 0.2 g KBr were ground, and then pressed into a disc. The spectrum was recorded from 399 to 3999 cm^{-1}. The mineralogy of sepiolite and *P. catenlannulatus* was identified by XRD (Rigaku MiniFlex 600, Japan) with a Cu-Ka radiation source ($\lambda = 1.5406$ Å) form 10 to 70° with a step size of 0.02°. The potentiometric titration experiments were conducted at $I = 0.01$ mol/L NaClO4 using Mettler DL 50× programmable titrator.

2.3. Adsorption experiments

The effect of reaction time on Th(IV) adsorption by sepiolite and sepiolite + *P. catenlannulatus* was conducted at pH 4.5 and 293 K by batch techniques. Briefly, 10 mL 6.0 g/L of sepiolite suspensions were added into 50 mL 10 mg/L Th(IV) solution in the absence and presence of *P. catenlannulatus* (~1.0×10^6 cells/mL), then aliquots of suspension (1.0 mL) were withdrawn from aforementioned suspension periodically. The effect of ionic strength on Th(IV) adsorption under various pH conditions adsorption was performed by adjusting the initial pH of suspension with negligible volume of 0.1–1.0 mol/L HNO_3/NaOH solution. The isothermal adsorption was performed at pH 4.5 and 293 K over wide range of Th(IV) solution from 1.0 to 50 mg/L. The liquid-phase was separated from solid-phase by centrifuging it at 4000 ×*g* for 15 min and then by filtering through 0.1 μm syringe filter. The concentration of Th(IV) in aqueous solution was measured by atomic absorption spectroscopy (AAS-6300, Shimadzu, Japan). The each data was obtained by the average values of triple parallel experiments. The adsorption percentage (R, %) and equilibrium adsorption capacity (Qe, mg/g) of Th(IV) on sepiolite and sepiolite + *P. catenlannulatus* can be calculated as followed by Eqs. (1) and (2), respectively:

$$R(\%) = (C_0 - C_{eq})/C_0 \times 100\% \tag{1}$$

$$Qe(mg/g) = V \times (C_0 - C_{eq})/m \tag{2}$$

where C_0 (mg/L) and C_{eq} (mg/L) are the initial and equilibrated concentration of Th(IV) solution, respectively. V (mL) and m (g) are the volume and mass of adsorbents, respectively.

3. Results and discussion

3.1. Characterization

The morphologies of sepiolite and sepiolite + *P. catenlannulatus* were illustrated by SEM images (Fig. 1A and B). As showed in Fig. 1A, the rod-like sepiolite (10 × 500 nm) was observed, which was consistent with previous study [7,14]. *P. catenlannulatus* displayed the flower-like type macroparticles (Fig. 1B), which agreed with our previous studies [8,9]. The mineralogy of sepiolite was determined by X-ray powder diffraction. As shown in Fig. 1C, the characteristic peaks of sepiolite (such as (110), (131), (060), (331) and (−131)) were observed [15].

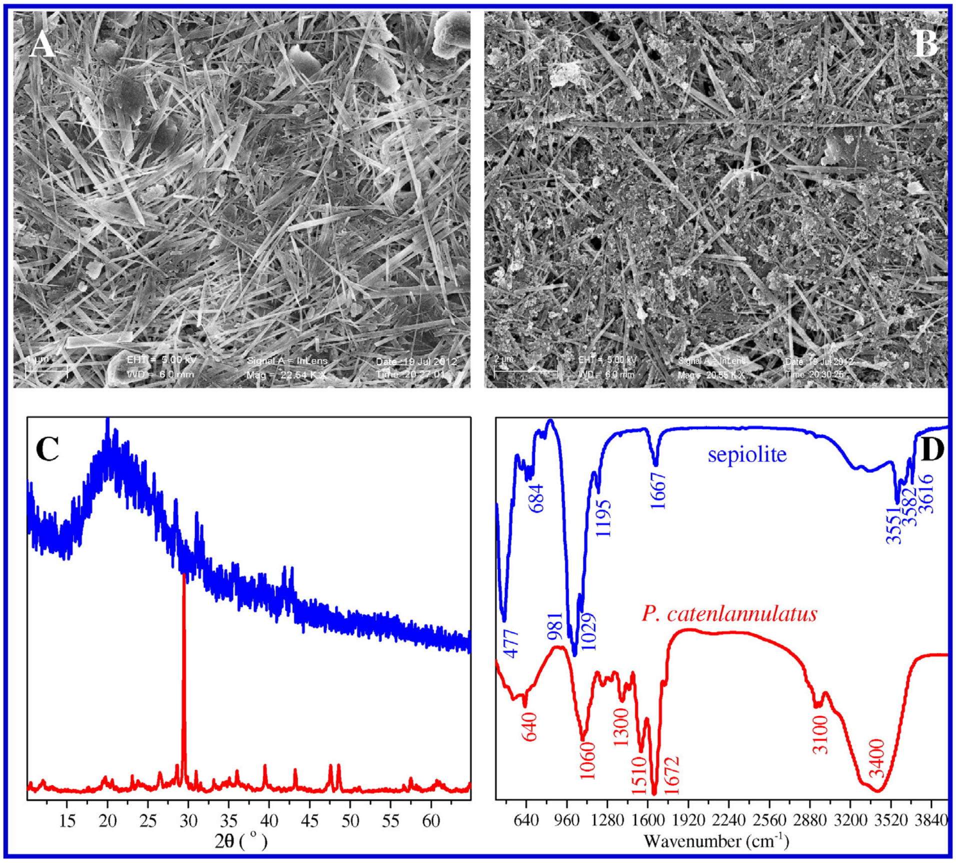

Fig. 1. The characterization of sepiolite and *P. catenlannulatus* used in this study. (A) and (B): SEM images of sepiolite and *P. catenlannulatus*; (C): XRD patterns; (D): FT-IR spectra;