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Adsorption of U(VI) on magnetic iron oxide/*Paecilomyces catenlannulatus* composites

Fengbo Li [a,*], Xiaoyu Li [a,b], Pu Cui [a,b]

[a] The School of Life Science and Environmental Science, Huangshan University, Huangshan 245041, P. R. China
[b] The College of Plant Protection, Anhui Agricultural University, Hefei 230036, P. R. China

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ABSTRACT

Development of engineering materials is critical to the improvement of adsorption performance. In this study, the new adsorbent of magnetic iron oxide/biochar (MIO/B) composites was synthesized by one-pot pyrolysis of $FeCl_2$-preloaded *Paecilomyces catenlannulatus* under N_2 conditions. The as-prepared composites were characterized by TEM, XPS, XRD and FT-IR techniques. The characteristic results showed that MIO/B composites presented a variety of nitrogen- and oxygen-containing functional groups. The effect of water chemistry on U(VI) adsorption towards MIO/B composites was investigated by batch techniques. The batch adsorption showed that U(VI) adsorption on MIO/B composites was independent of ionic strength at pH from 2.0 to 11.0, approximate 90% of U(VI) was removed by MIO/B composites at reaction time of 12 h. The maximum adsorption capacity of U(VI) on MIO/B composites calculated from Langmuir mode at pH 4.0 and 293 K was 74.63 mg/g. These findings are crucial for the practical application of biochar-based composites for the high effective enrichment of radionuclides from aqueous solutions in environmental remediation.

1. Introduction

Uranium is a hazardous element in the sub-environments, which is also the most common radionuclide found in the radionuclides-containing waste sites [1]. Uranium pollution in wastewater bodies is an environmental concern in aquatic ecosystems [2–4]. Hexavalent uranium (i.e., UO_2^{2+}) as stable oxidation state interacts strongly with surface of adsorbents due to the high solubility [5]. Therefore, it is mandatory to remove U(VI) from aqueous solution before it discharged into sub-environments. Among various methods, adsorption is an effective approach to remove U(VI) due to its environmentally friendly, low cost and easy operation [6–9]. Many researchers have well-documented the adsorption of U(VI) on various adsorbents such as clay minerals [10–16] and metal (hydr)oxides [17–21]. However, the limited adsorption capacities of these natural adsorbents are hard to apply in environmental cleanup.

Recently, the adsorption of U(VI) on magnetic iron oxides (MIO) have been studied extensively due to natural abundance, environmentally friendly, high effective adsorption performance and single magnetic separation [12,22–27]. However, MIO nanoparticles were easily accumulated together owing to their high surface energy, strong magnetization and small nanoscale size, which limited the practical application in environmental remediation. Incorporation of MIO nanoparticles into biochar matrix could be an effective approach to increase the dispersity of MIO nanoparticles.

Paecilomyces catenlannulatus (*P. catenlannulatus*) is a genus of entomogenous fungus. In this work, $FeCl_2$ was attached on the surface of *P. catenlannulatus* by bioadsorption, and then $FeCl_2$-preloaded *P. catenlannulatus* was decomposed under N_2 conditions and formed a porous biochar matrix with oxygen- and nitrogen-bearing functional groups in the pyrolysis process. $FeCl_2$ was primarily hydrolyzed in the bio-adsorption process and then was decomposed to MIO under N_2 conditions. To the authors' knowledge, no studies regarding interaction mechanism of U(VI) on MIO/biochar (MIO/B) composites were available due to the complicated systems.

The objectives of this study were to (1) synthesize MIO/B composites by pyrolysis method and characterize by TEM, XPS, XRD and FT-IR techniques; (2) investigate the effect of water chemistry on U(VI) adsorption on MIO/B composites by batch technique. These observations offer a new alternative to convert biomass waste into a high effective adsorbent for U(VI) adsorption, which is crucial for the practical application of biochar-based composites in environmental cleanup.

2. Materials and methods

2.1. Materials

P. catenlannulatus was collected from the microbiology laboratory of University of Huangshan, China. Firstly of all, *P. catenlannulatus* was

* Corresponding author.
E-mail address: lfb@hsu.edu.cn (F. Li).

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isolated from infected pupae of the lipidopteran *T. pityocampa* in NE China. Cultures (3.0 g KH_2PO_4, 1.0 g NH_4Cl, 0.2 g $MgSO_4 \cdot 7H_2O$, 0.01 g $FeSO_4 \cdot 7H_2O$ and 10.0 g glucoses) were provided into 1 L distilled water, then the mixtures were sterilized at 120 °C for 30 min. Induction of proteases was carried out in solid media as following procedure: Petri dishes with 0.5% gelatin and 1% (w/v) agar in the above salt solution were prepared. The stock solution of U(VI) were prepared in a glovebox by dissolving $UO_2(NO_3)_2 \cdot 6H_2O$ (99.99% purity, Sigma-Aldrich) into 0.01 mol/L HNO_3 solution purged by Ar gas. The other chemicals (i.e., $FeCl_2$, $NaClO_4$) were of reagent grade commercially purchased from Sigmoph Chemical Ltd.

2.2. Synthesis of MIO/B composites

MIO/B composites were synthesized by fast pyrolysis of $FeCl_2$-preloaded biomass under N_2 conditions [28]. Fast pyrolysis is the thermal decomposition of humic substance under anoxic conditions at very high heating rate at ~500 °C. The biomass was converted into various biochar in this process. Briefly, 10.0 g $FeCl_2$ and 100 mL deionized water were added into hydrolyte biomass were reacted for 24 h under stirring conditions. After centrifugation (8000 rpm for 30 min), Fe(II)-preloaded hydrolyte biomass were heated for 2 s at 500 °C with heating rates of ~600 °C/s and N_2 flow of 0.4 L/min. MIO/B composites were obtained by further carbonizing for 1 h and then cooled down to room temperature with 0.1 L/min nitrogen flow.

2.3. Characterization of MIO/B composites

The nanostructure and morphology of as-prepared MIO/B composites were characterized by TEM (Hitachi H7650 Transmission Electron Microscope). The as-prepared samples were characterized by XPS (Thermo ESCALAB 250 electron spectrometer) using a multidetection analyzer with an Mg Kα radiation source (1253.5 eV) at 15 kV and 5 mA under 10^{-7} Pa pressure. The energy was calibrated by the C 1s peak at 284.5 eV as a reference. The samples of XPS spectra were prepared as following procedures: 10 mL 0.05 mol/L $NaClO_4$ and 20 mL 1.25 g/L suspension of MIO/B composites were mixed primarily, and then 20 mL 25 mg/L U(VI) solutions were added in the suspension under stirring conditions. The values of pH in aqueous solutions were adjusted to 4.0 by adding neglected volume of HNO_3 or NaOH solution. The suspensions were reacted for 48 h under anaerobic conditions. After adsorption equilibrium, the solid phase was separated from liquid phase by centrifuging it at 6000 rpm for 30 min and then filtered through a 0.22 μm nylon membrane. The high resolution spectra were fitted by XPSPEAK41 software. The mineralogy of MIO/B composite was identified by XRD (Rigaku X-ray diffractrometer, Japan) with monochromatized Cu-Kα radiation. A variety of surface functional groups of MIO/B composites were determined by FT-IR (Nicolet 8700 FT-IR spectrometer) in pressed KBr pellets. Typically, 2.0 mg of MIO/B composite and 200 mg KBr were ground by agate mortars and then were pressed into a disc. The surface area and pore size of MIO/B composites were measured by NOVA 4200e instrument (Quantachrome, FL).

2.4. Batch adsorption experiments

The triple adsorption of U(VI) on MIO/B composites was conducted in golvbox conditions. Briefly, 0.6 mL 0.1 mol/L $NaClO_4$ and 1 mL 3 g/L suspension of MIO/B composites were pre-equilibrated 12 h, and then 3 mL 20 mg/L U(VI) solutions were provided in the suspension under stirring conditions. The values of pH in aqueous solutions were adjusted by adding neglected volume of HNO_3 or NaOH solution (1.0–0.1 mol/L) and were monitored with a pH meter. After adsorption equilibrium, the solid phase was separated from liquid phase by centrifuging it at 6000 rpm for 30 min and then filtered through a 0.22 μm nylon membrane. The concentration of U(VI) in the filtrate were determined by Kinetic Phosphorescence Analyzer (KPA-11, USA).

The regeneration and cycle experiments of U(VI) on MIO/B composites were conducted by an five adsorption-desorption cycle. Typically, U-loaded MIO/B composites were desorbed by 0.1 mol/L HNO_3 solution overnight. The solid was centrifuged at 6000 rpm 10 min and then was dried in oven overnight to conduct the next adsorption experiment. The adsorption capacity (q, mg/g) can be calculated with Eq. (1):

$$q = (C_0 - C_e)/(m/v) \quad (1)$$

C_0 and C_e (mg/L) are the U(VI) concentration at initial and equilibration, respectively. v (L) and m (g) are the solution volume and adsorbent mass, respectively.

3. Results and discussion

3.1. Characterization

The morphology of MIO/B composites was illustrated by TEM images (Fig. 1A). MIO/B composite presented an interconnected framework with diameter ~100 nm, magnetic iron oxides were homogenously dispersed on the surface. As shown by photograph inset Fig. 1A, magnetic iron oxides were synthesized using this method. Fig. 1B shows the deconvolution of high resolution C 1s XPS spectra. Four sub-peaks at ~284.5, 286.0, 287.5 and 388.7 eV were corresponded to C—C, C—O/N, C═O and O═C—OH groups, respectively [29,30]. The XPS analysis indicated that the as-prepared MIO/B composites displayed a variety of oxygen/nitrogen-containing function groups. The XRD pattern of MIO/B composites is shown in Fig. 1C. The characteristic peaks at 2θ = 30.15, 35.67, 43.28, 53.66, 57.31 and 62.68° were attributed to the (220), (311), (400), (422), (511) and (440) planes of magnetite, respectively [30]. The multiple characterizations indicated the magnetic iron oxide nanoparticles were uniformed deposited the surface of stable carbon skeleton (biochar) with abundant nitrogen- and oxygen-bearing functional groups. In the pyrolysis process, adsorbed $FeCl_2$ may be decomposed into magnetic Fe_3O_4 under N_2 and high temperature conditions (Eqs. (2)–(4)):

$$FeCl_2 \cdot 6H_2O = FeCl_2 \cdot 2H_2O + 4H_2O \quad (2)$$

$$FeCl_2 \cdot 2H_2O = (FeOH)Cl + H_2O + HCl\uparrow \quad (3)$$

$$3(FeOH)Cl + 1/2O_2 = Fe_3O_4 + 3HCl\uparrow \quad (4)$$

The main components of the biomass were quickly decomposed to volatile species, which can be used for the production of biofuels or valuable chemicals.

Fig. 1D shows the FT-IR spectrum of as-prepared MIO/B composite. The three strong peaks at 1180, 1420 and 1630 cm^{-1} were assigned to the bending vibration of C—OH, stretching vibration of C—OH and bending vibration of C—H groups, respectively [31–33]. The wide peak at 3400 cm^{-1} was ascribed to the stretching vibration of OH from adsorbed water molecular [34,35]. The other peaks at 585, 790 and 1750 cm^{-1} could be attributed to the stretching vibration of Fe—O, Si—O and C═O groups, respectively [36]. The characteristic results indicated that MIO/B composites displayed a variety of oxygen/nitrogen-containing functional groups.

3.2. Adsorption kinetics

Fig. 2A shows the adsorption kinetics of U(VI) on MIO/B composites at different initial U(VI) (10 and 20 mg/L) concentrations. The adsorption rate of U(VI) significantly increased with increasing reaction time from 1 to 12 h, and maintained the high-level adsorption at reaction time >12 h. At 12 h, approximately 99 and 95% of U(VI) were adsorbed