



Macroscopic and molecular investigations of immobilization mechanism of uranium on biochar: EXAFS spectroscopy and static batch

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ABSTRACT

A new environmentally friendly and low-cost adsorbent was produced from the camphor tree leaves (BC@CTL) and used to remove U(VI) from waste water via batch capture experiments under varying pH, time, and U(VI) concentration. The resultant biochar was characterized by SEM, BET, zeta-potentials, and FTIR spectroscopy. The capture process was strongly dependent on pH and independent of ionic strength. The capture experimental results indicated that U(VI) was quickly captured to BC@CTL with a maximum capture capacity of 0.41 mmol U(VI) g⁻¹ obtained by Langmuir model fitting. The results of EXAFS analysis revealed that the interaction mechanism of U(VI) on the BC@CTL was primarily controlled by inner-sphere surface complexation. The investigation was meaningful for the “treating wastewater with wastes” strategy implementation, especially biochar can be regarded as a promising candidate for the pre-concentration and immobilization of radionuclides from aqueous solutions in environmental remediation.

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1. Introduction

With the rapid development of nuclear industry, excessive amounts of uranium (U) have been discharged into the soil and water environment through various processes such as ore mining, nuclear fuel production, nuclear power generation, nuclear weapon manufacturing, etc. [1–5]. When released into the environment, uranium is predominantly in the hexavalent form (U(VI)) under normal environmental conditions, and has high and long-term radioactivity as well as strong complexation affinity for organic ligands [6]. The pollution of U(VI) could pose serious threats to aquatic life and human health due to its potential toxic [7]. Excess exposure to U(VI) can trigger toxicological effects and serious diseases such as diarrhea, spasm, thyroiditis, lymphatolysis, hepatitis, nephritis, neurological disorder and even cancers [8,9]. For the sake of public health and ecosystem stability, it is crucial to eliminate the radioactive U(VI) ions from the wastewater before it is released into the natural environment [10]. Therefore, the highly efficient and safety treatment removal of radioactive U(VI) ions from aqueous solutions has become an issue of great concern [11,12].

Different kinds of methods such as ion exchange, membrane filtration, surface precipitation, sorption, and solidification, have been

applied to remove U(VI) ions from aqueous solutions [13–16]. Of the as-proposed traditional techniques, sorption strategy has been widely used for the remediation of polluted environment due to its diverse advantages such as simplicity of design, ease of operation, low cost and general applicability to hazardous pollutants [17–19]. Thus, a variety of adsorbents have been utilized in the efficient capture of radionuclides like U(VI), including diatomite [20], Na-bentonite [21], hematite [22,23], natural clinoptilolite zeolite [24], zerovalent iron nanoparticles [25], Mn-oxyhydroxides [26], carbonaceous nanofibers [27], functionalized graphene oxides [28,29]. However, it is highly desirable to explore novel nanomaterials with huge capture capacities and low-cost. Carbon materials, such as activated carbon, fullerene, and graphene, have been widely used in pollution control because of their stability and large surface area [30–32]. Biochar, produced from agricultural and forest residues, has recently received increasing attention as a novel adsorbent in environmental remediation process because of its unique features, such as higher surface area, novel porous structure, and functional groups on the surface [33–35]. Several studies have suggested that biochar can be used as an effective material for the capture of heavy metals from wastewater as well as an amendment for immobilization of heavy metals in contaminated soils [36,37]. Use of biochar for treating wastewater containing heavy metals is an emerging and promising technology due to that is less carbonized (more hydrogen and oxygen remain in its structure) than activated carbon [38,39]. However, there is very

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limited knowledge on the treatment of uranium containing waste water using biochar from agricultural and forestry waste, and the study of the interaction mechanism of between uranium and capture materials is not yet adequately understood. Because of that investigation on the interaction of metal ions with the biochar surface active groups are of particular interest and fundamental for the development of wastewater treatment technologies based on capture/release processes. In this context the use of spectroscopic methods of analysis is of particular importance because these methods can provide direct information about the capture mechanism at molecular level.

The aim of this study was what in order to estimate the radionuclide capture capacity of biochar in natural environments by means of which to elucidate the interaction mechanism and to evaluate the capture behaviors of U(VI). The specific objectives are the following: (1) to characterize the morphology and nanostructures of the BC@CTL using SEM, specific surface area (BET) and zeta-potential techniques, as well as FTIR spectra of the BC@CTL with prior and after U(VI) capture; (2) to investigate the effect of reaction time, pH, temperature, and initial concentration on the capture of U(VI) on the BC@CTL using batch techniques; (3) to probe structure, surface functional groups and coordination environments of U(VI) on BC@CTL by the extended X-ray absorption fine structure (EXAFS) studies in order to reveal the mechanism of U(VI) on the surface of BC@CTL. This paper highlights that the BC@CTL can be used as promising adsorbents for the pre-concentration and removal of radionuclides in environmental pollution cleanup.

2. Experimental section

2.1. Materials

The camphor tree leaves were obtained from author's campus in Shaoxing, China. All reagents used here were of analytical grade without further purification and provided by Shanghai Chemical Corp, China, and high-purity water from a Millipore Milli-Q water purification system was employed in the experiment for solution preparation. U(VI) stock solution was prepared by dissolving uranyl nitrate hexahydrate ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) in Milli-Q water. The stock solution was kept at pH 3 and used in the following capture experiments.

2.2. Biochar preparation

The camphor tree leaves were collected from author's campus, and washed with Milli-Q water for several times, and then dried at 80 °C. The dried raw material was pulverized and passing through 100-mesh sieve to obtain the fine leaf powder for biochar preparation. The passed powder was soaked in 1.6 mol L⁻¹ KOH in a crucible for 3 h. The use of KOH removes loose organic matter from the pore structure, increasing pore volume, surface area, and possibly reactive surface functional groups [40]. Then the material was subjected to the pyrolysis process in a tubular furnace at 350 °C for 6 h. For ensuring oxygen-free environment and uniform heating conditions, nitrogen was used as flush gas. The products were filtered off and washed with Milli-Q water and ethanol for several times until the rinse water reached near neutral pH, and finally dried at 80 °C for at least 3 h in a vacuum oven.

2.3. Batch capture experiments

The capture properties of biochar were studied as a function of pH, contact time, initial concentration and temperature in polyethylene centrifuge tubes under ambient conditions by using batch conditions. The BC@CTL suspension and KCl solution were pre-equilibrated for 24 h, then U(VI) stock solution was added in BC@CTL suspension to achieve the desired concentrations of different components. The pH of the suspension was adjusted with 0.001–1.0 mol L⁻¹ HClO₄ or KOH. Then the suspensions were shaken for 20 h to ensure the capture

equilibration. After centrifugation and filtration, the concentrations of U(VI) in the filtrate were determined. Capture capacity ($q_e = (C_0 - C_e)V/m$, mg·g⁻¹) and removal rate ($R(\%) = ((C_0 - C_e)/C_0) \times 100\%$, %) for U(VI) by BC@CTL at equilibrium were calculated by conducting a mass balance of cations before and after capture [41,42]. Where C_0 (mol L⁻¹) is the initial concentration of cations in suspension, C_e (mol L⁻¹) is the concentration in supernatant after centrifugation, respectively, m (g) is the mass of adsorbent, and V is the volume of the suspension. And the distribution coefficient (K_d) are calculated from the equations: $K_d = (C_0 - C_e)V/mC_e$. The capture of U(VI) without BC@CTL was determined under the same experimental conditions to minimize the effect of the radionuclide sticking on the tube walls. It was necessary to emphasize that the sticking of U(VI) on the tube wall was negligible according to the test of U(VI) capture in the absence of BC@CTL. Capture kinetics of U(VI) on the BC@CTL were conducted at $I = 0.01$ mol L⁻¹ KCl and three pH (i.e., 6.58, 5.63, 4.59), and capture isotherms were conducted at pH 6.46 and $I = 0.01$ mol L⁻¹ KCl solution at different concentrations, respectively. The detailed description of the EXAFS analysis is shown in the Supplementary Information (SI).

3. Results and discussion

3.1. Characterization of BC@CTL

The SEM image for the sample of biochars obtained by pyrolysis of horticultural wastes (camphor tree leaves) is shown in Fig. 1A. As can be seen from the presented micrographs, a lot of carbon particles were observed in the surface of BC@CTL, which indicated the camphor tree leaves were hydrolyzed and carbonized. The particles of all investigated biochar retained most of the shape of flake aggregation which is similar to the parent materials, used as precursors for its preparation with slight differences in shape and size. Small particles were randomly distributed with diameters from few microns to ~10 μm and big blocks with diameters could also be observed. In addition, the specific surface area of BC@CTL was determined to be 65.91 m² g⁻¹ (Fig. 1B) and the micropore volume of BC@CTL is 15.14 cm³ g⁻¹. The large surface area and mesoporous structure of BC@CTL can provide much more sorption sites to make the sufficient contact between the adsorbent and adsorbate. The pH_{pzc} value is determined to be 5.76 (Fig. 1C), which indicates that the BC@CTL displays a great binding capacity. At $\text{pH} < \text{pH}_{\text{pzc}}$, the BC@CTL surface charge is positive, whereas the BC@CTL surface charge is negative at $\text{pH} > \text{pH}_{\text{pzc}}$.

3.2. FTIR spectroscopy

Fig. 2 shows FTIR spectra of BC@CTL with prior and after U(VI) capture at different pH. The spectrum of BC@CTL shows characteristic IR absorption bands at ~3434 cm⁻¹ was assigned to the O—H stretching vibration, the peak appeared at ~2928 cm⁻¹ may be due to the —CH₂ stretching vibration, the band at ~1389 cm⁻¹ was due to the vibration of —CH₂ or —CH₃ groups, the band observed at ~1637 cm⁻¹ was caused by the adsorption of stretching vibration C=O and C=C, and the broad band appeared at ~1053 cm⁻¹ could be as a results of the stretching vibration of C—O bonds, respectively [43–46]. Besides, the intensity of the peak at ~900 cm⁻¹ increases with increasing pH of solution and indicates clearly that this peak corresponds to the stretching vibration of the O=U=O moiety [44]. Specifically, the characteristic peak of the O=U=O stretching vibration is shifted only slightly to lower wavelengths. The intensity increases attributed to the increase in the amount of captured U(VI) on BC@CTL with increasing pH of solution.

3.3. Capture properties

3.3.1. pH and ionic strength studies

Solution pH has a significant influence on the migration and transformation behaviors of environmental contaminants at solid/water

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