JOURNAL OF ENVIRONMENTAL SCIENCES XX (2018) XXX–XXX

Available online at www.sciencedirect.com
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www.elsevier.com/locate/jes

JES
JOURNAL OF ENVIRONMENTAL SCIENCES
www.jesc.ac.cn

Mechanistic insights into sequestration of U(VI) toward magnetic biochar: Batch, XPS and EXAFS techniques

Qingyuan Hu[1], *Yuling Zhu*[1], *Baowei Hu*[1,*], *Songhua Lu*[2], *Guodong Sheng*[1,*]

1. *College of Life Science, College of Chemistry and Chemical Engineering, Shaoxing University, Zhejiang 312000, China*
2. *Institute of Plasma Physics, Chinese Academy of Science, Hefei 230031, China*

ARTICLE INFO

Article history:
Received 14 November 2017
Revised 15 January 2018
Accepted 16 January 2018
Available online xxxx

Keywords:
Magnetic biochar
Uranium
X-ray absorption spectroscopy
Sequestration

ABSTRACT

The magnetic iron oxide (Fe_3O_4) nanoparticles stabilized on the biochar were synthesized by fast pyrolysis of Fe(II)-loaded hydrophyte biomass under N_2 conditions. The batch experiments showed that magnetic biochar presented a large removal capacity (54.35 mg/g) at pH 3.0 and 293 K. The reductive co-precipitation of U(VI) to U(IV) by magnetic biochar was demonstrated according to X-ray diffraction, X-ray photoelectron spectroscopy and X-ray absorption near edge structure analysis. According to extended X-ray absorption fine structure analysis, the occurrence of U-Fe and U-U shells indicated that high effective removal of uranium was primarily inner-sphere coordination and then reductive co-precipitation at low pH. These observations provided the further understanding of uranium removal by magnetic materials in environmental remediation.

Introduction

Uranium (U) pollution in contaminated sites is an environmental concern due to radioactive and toxic effects on human health and aquatic eco-environments (Gu et al., 2004; Sun et al., 2016b). Therefore, it is imperative to fast and effectively remove uranium from aqueous solutions (Liu et al., 2017a). Adsorption approach is demonstrated to be an effective method to high efficiently eliminate uranium among various methods (Liu et al., 2017c; Sheng et al., 2016; Sun et al., 2014b). Magnetic iron oxides (*i.e.*, maghemite and magnetite) has been used as a desirable and effective adsorbent for U(VI) removal due to its ubiquitous, environmentally friendly, strong redox ability and easily magnetic separation (Crane et al., 2011; Ilton et al., 2010; Latta et al., 2012, 2013; Singer et al., 2012; Yuan et al., 2015). However, these magnetic iron oxides, especially synthetic magnetite, displayed the accumulation tendency due to their high surface energy and nanoscale size, resulting in the limit of their practical application (Ding et al., 2015b; Jin et al., 2015; Sun et al., 2014a).

Owing to low-cost, ubiquitous and porous structure, biochar has been widely used as a promising adsorbent for removing various environmental contaminants in recent years (Lu et al., 2012; Park et al., 2016; Vázquez et al., 2009; Yang et al., 2014). However, raw biochar displayed relatively low removal capacity and required prolong equilibrated time due to its limited surface function groups and poor porous structure (Liu et al., 2015). Recently, surface modification can endow biochar with abundant surface functional groups and significantly improve removal performance. The incorporation of magnetic iron oxide nanoparticle into biochar is promising approach for increasing removal performance to increase the dispersity of Fe_3O_4 nanoparticles. In recent years, magnetic biochar derived from biomass have

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* *Corresponding authors.*
E-mail addresses: hbw@usx.edu.cn (B. Hu), gdsheng@usx.edu.cn (G. Sheng).

https://doi.org/10.1016/j.jes.2018.01.013
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Please cite this article as: Hu, Q., et al., Mechanistic insights into sequestration of U(VI) toward magnetic biochar: Batch, XPS and EXAFS techniques, J. Environ. Sci. (2018), https://doi.org/10.1016/j.jes.2018.01.013

extensively investigated to various organic pollutants (Dong et al., 2017; Jung et al., 2016; Reguyal et al., 2017) and heavy metals such as Cr(VI) (Han et al., 2016; Wang et al., 2014; Zhang et al., 2015), Pb(II) (Reddy and Lee, 2014; Yan et al., 2015; Yap et al., 2017), Cd(II) (Ruthiraan et al., 2015; Trakal et al., 2016; Yap et al., 2017) and As(V) (Liu et al., 2017c; Wang et al., 2015). To the authors' knowledge, few studies regarding the interaction mechanism between U(VI) on magnetic biochar was available.

The objectives of this study are to (1) synthesize magnetic biochar composites and characterize their surface properties by scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FT-IR) techniques; (2) investigate the effect of water chemistry (*i.e.*, reaction time, pH and initial concentration) on U (VI) removal onto magnetic biochar by batch tests; (3) demonstrate the interaction mechanism of U(VI) on magnetic biochar using XPS, X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) analysis. The highlight of this study is to turn waste into wealth, change scrap into resource.

1. Experimental section

1.1. Materials

The hydrophyte biomass with high N content used in this study was harvested from eutrophicated water of Chao Lake (Hefei, China), which is effective method for preventing the release of N into water bodies during withering periods (Xu et al., 1999). Briefly, the natural hydrophyte biomass was washed by distilled water and then was dried it at 378 K overnight to remove the adsorbed H_2O. The dried biomass was ground by agate pestle and then was sieved less than 60 mesh. The stock solutions of U(VI) (60 mg/L) and Fe(II) (0.1 mol/L) was prepared by dissolving $UO_2(NO_3)_2{\cdot}6H_2O$ (>99.99% purity, Sigma-Aldrich) and $FeCl_2{\cdot}4H_2O$ (analytical grade, Aladdin, Shanghai) into deoxygenated water under the glovebox, respectively. Other chemicals (*e.g.*, $NaClO_4$, NaOH) of analytical grade were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

1.2. Synthesis and characterization of magnetic biochar

Magnetic biochar was synthesized by fast pyrolysis of Fe(II)-loaded hydrophyte biomass under mixed gas ($V_{N2}/V_{O2} = 95/5$) at 700°C in a very fast heating rate (Ling et al., 2017). Firstly of all, Fe(II)-loaded hydrophyte biomass was obtained by biosorption of $FeCl_2$ on hydrophyte biomass. Then, Fe(II)-loaded hydrophyte biomass was converted the raw biomass into porous biochar matrix in the fast pyrolysis process. After fast pyrolysis, the solid residue was further heated at 700°C for 1 hr to further carbonize the remained biochar and Fe_3O_4 NPs were formed during the hydrolysis and decomposition of $FeCl_2$ under the N_2 flow (0.5 L/min). To compare removal performance, the magnetite nanoparticles and raw biochar were synthesized in this study by chemical precipitation of Fe (II) + Fe(III) and fast pyrolysis of hydrophyte biomass under N_2 conditions, respectively.

The morphology of magnetic biochar was conducted using a Sirion 200 scanning electron microscope (FEI Electron Optics Company, USA) with the energy dispersive X-ray spectrometry (EDX) at 5.0 kV of acceleration voltage. The mineralogy of magnetic biochar before and after U(VI) removal was identified by TTR-III X-ray diffractometer (Rigaku, Japan) with a scan rate of 0.05°/sec using Cu-Kα radiation (λ = 1.5406 Å, 35 kV/150 mA). The surface functional groups of magnetic biochar were qualitatively demonstrated by FT-IR (VERTEX 70, Brucker Corporation, Germany) in a range of 400–4000/cm. Briefly, approximately 2 mg of samples and 200 mg of KBr were ground and then pressed disc. The specific surface area and porous structure of magnetic biochar was analyzed through N_2 adsorption–desorption isotherms by ASAP 2020 Micromeritics Gemini Apparatus (Micromeritics Co. USA). The elemental compositions of magnetic biochar (C, H, N, O, Fe) were analyzed using VARIO EL III elemental analyzer (Elementar Inc., Germany).

1.3. Batch removal experiments

The triple removal of U(VI) on magnetic biochar was conducted in the glovebox as follows: 20 mg of magnetic biochar was added into 50-mL polycarbonate centrifuge tubes containing 10 mL of 50 mg/L U(VI) solutions. The ionic strength was set 0.01 mol/L by adding the desired amount of $NaClO_4$ solution. The pH of suspension were adjusted to the desired values by adding neglected volume of 5.0 mol/L of aqueous HCl or NaOH solution and monitored with a pH meter. The removal kinetics and isotherms were conducted at pH 3.0 in the presence of 0.01 mol/L $NaClO_4$ under different reaction time and U(VI) concentration, respectively. After reaction equilibrium, the solid phase was separated from liquid phase by centrifuging it at 6000 r/min for 20 min and then filtered by a 0.22-μm nylon membrane. The concentration of U (VI) in the filtrate was determined by kinetic phosphorous analyzer (KPA 11, Maryland, USA). The removal amount of U (VI) was calculated by the difference in the initial and finial U (VI) concentrations.

The recycle experiments of U(VI) on magnetic biochar was carried out through adsorption- desorption process (Ding et al., 2015a; Liu et al., 2017a; Sun et al., 2015). Briefly, the U-loaded magnetic biochar after adsorption was added into 50-mL polycarbonate centrifuge tube containing 20 mL of 1.5 mol/L Na_2CO_3 solution (as an effective agent for U(VI) desorption to form a soluble $UO_2(CO_3)_2^{2-}/UO_2(CO_3)_3^{4-}$) for 6 hr under a constant-temperature oscillator. After desorption, the magnetic biochar was separated from desorption mixture for another cycle and then dried it oven overnight. The adsorption–desorption cycles were performed 5 times, and the removal capacity of uranium was calculated for the evaluation of its cycle performance.

1.4. Preparation and analysis of XPS, XANES and EXAFS

The samples for XPS, XANES and EXAFS analysis were prepared as the similar batch experiments. Briefly, 20 mg of magnetic biochar and 10 mL of 50 mg/L U(VI) solutions was added into 50-mL polycarbonate centrifuge in glovebox

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