



Removal of arsenic by magnetic biochar prepared from pinewood and natural hematite



Shengsen Wang^{a,b}, Bin Gao^{c,*}, Andrew R. Zimmerman^d, Yuncong Li^{a,b}, Lena Ma^b, Willie G. Harris^b, Kati W. Migliaccio^{a,c}

^a Tropical Research and Education Center, University of Florida, Homestead, FL 33031, United States

^b Soil and Water Science Department, University of Florida, Gainesville, FL 32611, United States

^c Department of Agricultural and Biological Engineering, University of Florida, Gainesville, FL 32611, United States

^d Department of Geological Sciences, University of Florida, Gainesville, FL 32611, United States

HIGHLIGHTS

- Magnetic biochar was prepared from pine wood and natural hematite.
- Hematite modified biochar showed greater ability to remove aqueous As.
- γ -Fe₂O₃ particles on the biochar served as sorption sites for As.

ARTICLE INFO

Article history:

Received 20 August 2014

Received in revised form 19 October 2014

Accepted 20 October 2014

Available online 28 October 2014

Keywords:

Biochar

Hematite

γ -Fe₂O₃

Nanocomposite

Arsenate

ABSTRACT

There is a need for the development of low-cost adsorbents to removal arsenic (As) from aqueous solutions. In this work, a magnetic biochar was synthesized by pyrolyzing a mixture of naturally-occurring hematite mineral and pinewood biomass. The resulting biochar composite was characterized with X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDS). In comparison to the unmodified biochar, the hematite modified biochar not only had stronger magnetic property but also showed much greater ability to remove As from aqueous solution, likely because the γ -Fe₂O₃ particles on the carbon surface served as sorption sites through electrostatic interactions. Because the magnetized biochar can be easily isolated and removed with external magnets, it can be used in various As contaminant removal applications.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Arsenic (As) is a carcinogenic trace metal that is toxic to human and animals. It occurs naturally in soils and can be mobilized by weathering reactions and biological activity and may lead to contamination of surface or groundwater aquifers (Mohan and Pittman, 2007). In addition, anthropogenic As contamination by discharge and disposal of As-containing compounds may lead to even greater As concentrations (Mandal and Suzuki, 2002). Because of the severe toxicity of As to humans, a very strict drinking water allowance limit of 10 $\mu\text{g L}^{-1}$ was prescribed by the US Environmental Protection Agency.

Various removal techniques such as precipitation, adsorption, membrane separation, ion exchange and permeable reactive

barriers, have been developed to treat As contaminated water and soils (Tuutjarvi et al., 2009). Among them, adsorption is the one of the most commonly used method for the removal of As from aqueous solutions (Mohan and Pittman, 2007). Many low-cost sorbents such as carbonaceous materials, clay minerals and metal oxyhydroxides, have been successfully applied for As sorption (Goldberg, 2002; Zhou et al., 2014). Several studies have demonstrated that As tends to accumulate on the surface of metal oxyhydroxides and clay minerals containing Fe, Mn, Al, Cu, and Co (Ferguson and Gavis, 1972; Mandal and Suzuki, 2002). Strong sorption of As from aqueous solution by Fe, Al, and Mn oxides and naturally occurring clay minerals, such as kaolinite, montmorillonite, and illite, has been reported frequently in the literature (Gimenez et al., 2007; Goldberg, 2002).

Hematite is one of the most abundant natural iron oxide minerals and shows good As sorption ability (Gimenez et al., 2007). The sorption behaviors and mechanisms of As on hematite have been investigated for various solution chemistry conditions (Goldberg and Johnston, 2001). Using X-ray scattering analysis, Catalano

* Corresponding author at: Department of Agricultural and Biological Engineering, University of Florida, Gainesville, FL 32611, United States. Tel.: +1 352 392 1864x285.

E-mail address: bg55@ufl.edu (B. Gao).

et al. (2008) found that the sorption of As on hematite was mainly controlled by electrostatic interactions to form inner and outer sphere surface complexes. Surface complex models have also successfully simulated experimental sorption data (Goldberg, 2002). Several studies have synthesized iron oxides to mimic the natural hematite and found that the synthesized hematite showed better As sorption ability because of higher purity and larger surface area (Auffan et al., 2008). In addition, thermal treatment has also been used to 'activate' hematite to enhance its sorption ability to As in aqueous solution (Ramirez-Muniz et al., 2012).

Biochar is a pyrogenic carbon material produced by combustion of biomass under oxygen limited conditions. Because of its unique properties such as high surface area and cation exchange capacity, biochar can be used for such applications as soil improvement, fertility enhancement and carbon sequestration (Mohana et al., 2014; Zimmerman et al., 2011). It also has shown great potential to remove heavy metals from aqueous solution and to reduce their mobility and bioavailability in soils (Ahmad et al., 2014; Zhou et al., 2013). Because the surfaces of most of the biochars are predominantly net negatively charged (Mukherjee et al., 2011; Yao et al., 2012), their sorption of aqueous As, which is in anionic forms of either arsenate (As(V)) or arsenite (As(III)), is relatively low (Beesley and Marmiroli, 2011). Several methods have thus been developed to modify biochar to enhance its sorption of As. In particular, biochar modified with colloidal and nano-sized oxyhydroxides showed strong ability to remove As from aqueous solution (Chen et al., 2011; Zhang and Gao, 2013). For example, iron oxide-biochar composites prepared by either pyrolyzing iron chloride (FeCl₃)-modified biomass or precipitating Fe³⁺/Fe²⁺ on biochar surfaces greatly enhanced the As sorption ability of the biochars (Chen et al., 2011; Zhang et al., 2013). However, the methods used to create these biochar nanocomposites are relatively complex and costly. Thus, additional investigations thus are needed to develop simple and cost-effective methods to modify biochars with iron oxide particles, particularly with natural iron oxide minerals.

The objective of this work was to develop and evaluate a new method to prepare iron-oxide biochar composites from biomass and natural hematite. Hematite-treated pinewood was used as the feedstock to produce the biochar through pyrolysis. Physico-chemical properties of the resulting biochar were measured in laboratory and sorption ability of the biochar to As was assessed through batch sorption experiments.

2. Methods

2.1. Reagents

All chemicals used in this work were analytical grade and were dissolved in deionized (DI) water (18.2 MΩ) (Nanopure water, Barnstead). Sodium arsenate dibasic heptahydrate (Na₂HAsO₄·7H₂O) was purchased from Fisher Scientific. A natural hematite mineral specimen was obtained from Wards Natural Science Establishment, Inc. (Minnesota, USA) and X-ray diffraction (XRD) analysis confirmed it to be nearly pure, with only trace amounts of kaolinite and quartz. The mineral was crushed with hammer and ground with a pestle and mortar and sieved to particle sizes of between 38 and 75 μm for use in subsequent experiments. Commercial loblolly pine (*Pinus taeda*) wood was oven dried overnight at 80 °C and then chopped with a mechanic mill. The crushed feedstock was then sieved to between 0.425 and 1 mm.

2.2. Biochar preparation

The method of preparing hematite modified biochar was similar to that used by Yao et al. (2014). A hematite suspension was

prepared by mixing 2 g of crushed mineral particles in 40 mL of DI water. The suspension was stirred and sonicated for 30 min with an ultrasonicator (3510R-DTH, Branson Ultrasonics Corporation) to form a stable suspension. About 10 g of the feedstock was well mixed with the suspension for 2 h and was then oven-dried at 80 °C. The hematite-treated biomass was pyrolyzed in a tube furnace (MTI, Richmond, CA) under N₂ at a peak temperatures of 600 °C for one hour. Feedstock without modification procedure was used as control and went through the same pyrolysis process. The biochars produced were sieved to obtain particles between 0.075 and 0.425 mm and rinsed with DI water several times. Biochar was then oven dried overnight at 80 °C and saved in a sealed container for later use. The biochars with and without hematite modification were denoted as HPB and PB, respectively.

2.3. Characterizations

Total carbon (C), nitrogen (N), and hydrogen (H) content in the biochar samples were analyzed with a CHN Elemental analyzer (Carlo-Erba NA-1500). The inorganic element content of the biochar samples were determined using acid digestion method and analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Perkin-Elmer Plasma 3200). Oxygen was determined as the weight difference between the raw dried biochar and sum of C, H, N, and other non-volatile elements.

Total surface area was measured using N₂ sorption on a NOVA 1200 analyzer and calculated using Brunauer-Emmett-Teller (BET) method. Scanning electron microscope (SEM) images were obtained with a JEOL JSM-6400 Scanning Microscope. Energy dispersive X-ray spectroscopy (EDS, Oxford Instruments Link ISIS) was coupled with SEM to examine surface elemental composition and obtain surface elemental distribution maps.

Surface elemental composition was also analyzed by X-ray photoelectron spectroscopy (XPS) with a PHI 5100 series ESCA spectrometer (Perkin-Elmer). An Al X-ray source was used with a 93.90 eV passing energy between 0 and 1400 eV binding energy. High-energy resolution scans of Fe2p and C1s peaks were obtained with pass energy of 23.50 eV in the 705–734 eV and 281–293 eV binding energy ranges, respectively.

Surface crystallinity was analyzed to identify Fe-bearing minerals using an X-ray diffractometer (XRD) (Philips Electronic Instruments) equipped with a stepping motor, a graphite crystal monochromator, and a CuKα radiation source.

Thermal stability of PB and HPB was examined using thermogravimetric analysis (TGA) with a Mettler Toledo's TGA/DSC1 analyzer. Temperature was increased by 10 °C per minute between 25 and 700 °C under air atmosphere.

2.4. Sorption kinetics and isotherm

Sorption kinetics of As at a constant concentration (20 mg L⁻¹) onto biochar were examined using the method of Zhang and Gao (2013). Briefly, about 0.05 g of biochar (2.5 g L⁻¹) was added to 20 mL As solutions (pH ~7) in 68 mL digestion vessels (Environmental Express) at room temperature (22 ± 0.5 °C). The vessels with sorption mixtures were placed on a shaker and agitated at 50 rpm until sampling. At each sampling time (0.5, 1, 2, 4, 8, 12, 24 and 48 h), the suspensions were immediately filtered through 0.22 μm pore size nylon membrane filters (GE cellulose nylon membrane). Concentrations of As in the filtrates were determined with an inductively coupled plasma-atomic emission spectrometry (ICP-AES, Perkin-Elmer Plasma 3200) and the residues were examined spectroscopically as described above. Sorbed As(V) was calculated as the difference in As concentration between initial and final solution. Kinetics data were fitted using various kinetic models (detailed in Supporting Information).

Download English Version:

<https://daneshyari.com/en/article/680275>

Download Persian Version:

<https://daneshyari.com/article/680275>

[Daneshyari.com](https://daneshyari.com)