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Enhanced arsenic removal by biochar modified with nickel (Ni) and manganese (Mn) oxyhydroxides

Shengsen Wang [a], Bin Gao [a,*], Yuncong Li [b]

[a] Department of Agricultural and Biological Engineering, University of Florida, Gainesville, FL 32611, United States
[b] Tropical Research and Education Center, Soil and Water Science Department, University of Florida, Homestead, FL 33031, United States

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ABSTRACT

Two biochar composites were synthesized by either pyrolysis of Ni/Mn oxide-modified pinewood feedstock (NMMF) or precipitation of Ni/Mn-LDHs onto pristine biochars (NMMB). Both sorbents were characterized and results indicated that NiO and MnO were dominant crystals in NMMF, whereas Ni/Mn-LDHs in NMMB. Sorption experiment showed that the maximum As(V) sorption capacity were 0.549 and 6.52 g kg^{-1} for NMMF and NMMB, respectively. The As(V)-loaded sorbents can be easily desorbed with 0.1 NaOH, and NMMB maintained 98% removal efficiency after two to three desorption–resorption cycles. The As(V) sorption is mainly attributed to anion exchange and surface complexation by NMMB and surface complexation by NMMF.

Introduction

Arsenic (As) is a primary contaminant in drinking water and wastewater in many places such as in Asia and North America [1]. The prolonged consumption of As contaminated water may cause severe health problems. A stringent regulation has been announced to prescribe the maximum permissible levels as 10 μg L^{-1} in drinking water [2]. Previous studies have shown that adsorptive As(V) removal by effective sorbents is a prevailing approach [1,3,4].

In recent decades, layered double hydroxides (LDHs) attract much attention in treatment of environmental contaminants [5]. LDHs can be formulated as $[A_xB_{1-x}(OH)_2]^{x+}C^{x-}\cdot nH_2O$, where A and B represent divalent and trivalent cations, and C is anion [6]. They are naturally occurring minerals with two positively charged metal hydroxides sheets and anions in the interlayers to compensate the positive charges [7]. LDHs with different cation combinations can also be synthesized by wet chemistry such as exfoliation [8] and reverse micelle method [9]. LDHs of different metal combinations have been widely studied for removal of As(V). Greatly enhanced As(V) removal capacity have been achieved by Mg/Fe-LDHs [5,10] and Mg/Al-LDHs [7,11,12]. The retention mechanisms may include anion exchange and surface complexation [7,10,11]. Furthermore, different from other sorbents, the LDHs are prepared at high pH and high point of zero charge (pHpzc), and demonstrate good performance at higher pH such as 7 or above [7,12].

Colloidal or nano scaled LDHs tend to agglomerate which reduce the surface area and active sites for As(V) removal. Biochar is a pyrolyzed carbon enriched material, with large surface area, abundant surface functional groups and are recalcitrant to degradation, which make them ideal support framework for nano-sized particles. For example, graphitic materials such as activated carbon [13], graphene oxides [14], carbon nanotubes [15] and biochars [16–18], and alginate beads [19] have been used as support materials for higher As(V) removal efficiency. Although Ni/Mn based LDHs have been successfully synthesized [20,21], they are mainly used in energy storage, catalysts, etc. To the best of the authors' knowledge, Ni/Mn-LDH has never been applied in environmental applications such as removal of oxyanions. Furthermore, using biochar as an inexpensive support framework for the Ni/Mn-LDH to prepare a composite adsorbent has never been reported in the literature. The combination of the advantages of Ni/Mn-LDH and biochar may introduce a novel sorbent that has high efficiency to removal oxyanions including As(V). Nevertheless, biochar-supported Ni/Mn LDHs or Ni/Mn oxides have not been studied for their As(V) removal capacity.

The overall objectives were to prepare Ni/Mn-LDH-biochar composites with two synthetic methods and evaluate its performance for As(V) removal. The specific objectives included: (1) compare two preparation methods for biochar/metal, (2) characterize the two as-prepared composites, and (3) evaluate the sorption capacity of two sorbents and propose the possible mechanisms for As(V) sorption.

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* Corresponding author. Tel.: +1 352 392 1864x285; fax: +1 352 392 4092.
E-mail address: bg55@ufl.edu (B. Gao).

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Experimental

Reagents

All chemicals of reagent grade were dissolved with ultrapure water (18.2 MΩ cm, herein referred as DI H_2O) (Nanopure water, Barnstead). Sodium arsenate dibasic heptahydrate ($Na_2HAsO_4{\cdot}7H_2O$), manganese chloride tetrahydrate ($MnCl_2{\cdot}4H_2O$), nickel nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$), sodium nitrate ($NaNO_3$), granular sodium hydroxide (NaOH) and hydrochloric acid (HCl) of analytical grades were purchased from Fisher Scientific.

Biochar preparation

MnO/NiO-biochar composite was derived from pyrolysis of $MnCl_2{\cdot}4H_2O$ and $Ni(NO_3)_2{\cdot}6H_2O$ modified feedstock (NMMF). The feedstock, loblolly pine (*Pinus taeda*) wood, were oven dried and were ground into <2 mm fragments with a mechanic miller. 25 g of crushed feedstock were mixed into 100 ml solution of 0.1 mol L^{-1} $MnCl_2{\cdot}4H_2O$ (2.0 g) and 0.2 mol L^{-1} $Ni(NO_3)_2{\cdot}6H_2O$ (5.8 g). After 2 h soaking in solution, 0.08 mol NaOH and 0.04 mol Na_2CO_3 were added, leading to the formation of a precipitate, which was rinsed with DI water and dried at 80 °C overnight. The dried feedstock was pyrolyzed at peak temperature of 600 °C for 1 h in a tube furnace (MTI, Richmond, CA) under constant N_2 gas protection.

Post-pyrolysis Ni/Mn-LDH-modified biochar (NMMB): Ni/Mn-LDH was synthesized onto the biochars using previously reported methods [22]. The pristine biochars (5 g) produced at peak temperature of 600 °C was added to 25 ml DI water and agitated vigorously with a magnetic stirrer and continuously purged with N_2 gas. $Ni(NO_3)_2$ (0.02 mol) and 0.1 mol L^{-1} $MnCl_2{\cdot}4H_2O$ (0.01 mol) were dissolved in biochar suspension. The suspension was transferred to 250 ml 1.5 M NaOH solution preheated at 80 °C with continuous N_2 gas protection. The resulting biochars composite was washed with DI water several times to remove excess ions. The composite was then vacuum filtered through nylon membrane filter (pore size <0.22 μm) and dried at 80 °C for 12 h.

Biochar characterization

Total C, nitrogen (N) and hydrogen (H) contents in both biochars composites were determined with a CHN Elemental analyzer (Carlo-Erba NA-1500). AOAC method was used to prepare NMMF and NMMB and total Ni and Mn contents were analyzed by an inductively coupled plasma-atomic emission spectrometry (ICP-AES, Perkin-Elmer Plasma 3200).

Brunauer-Emmett-Teller (BET) surface area was determined with a NOVA 1200 analyzer [23,24]. Thermal stability between 25 and 700 °C under air atmosphere was evaluated by using thermogravimetric analysis (TGA) with a Mettler Toledo's TG/DSC1 analyzer. Elemental composition and surface reactions between sorbents and sorbates were determined with a PHI 5100 series ESCA spectrometer (Perkin-Elmer) which is an Al X-ray photoelectron spectroscopy (XPS) with binding energy between 0 and 1400 eV. Crystalline forms of metals were obtained by powder CuKα X-ray diffractometer (XRD) (Philips Electronic Instruments), with diffraction peaks between 2° and 80°. Surface morphology was scanned with scanning electron microscope (SEM) (JEOL JSM-6400 Scanning Microscope). Distribution of Mn, Ni and O on biochar surface was obtained by an energy dispersive X-ray spectroscopy (EDS, Oxford Instruments Link ISIS).

Adsorption kinetics and isotherm

Adsorption kinetics was determined for As(V) sorption as a function of sorption time. Sorption was initiated with 0.05 g sorbent in 20 ml 0.01 M $NaNO_3$ containing As(V) (20 mg L^{-1}) solution in 68 ml digestion vessels (Environmental Express) at room temperature (22 ± 0.5 °C). The vessels were agitated at 40 rpm on a rotary shaker and sampled at 0, 0.5, 1, 2, 4, 8, 12, 24 and 48 h. At each sampling, the suspension was immediately filtered through 0.22 μm pore size nylon membrane filters (GE cellulose nylon membrane). As(V) concentration in filtrate was analyzed with an inductively coupled plasma-atomic emission spectrometer (ICP-AES, Perkin-Elmer Plasma 3200).

Adsorption isotherm was used to determine saturated sorption by increasing ratios of As(V) concentration and sorbents. 20 ml 0.01 M $NaNO_3$ containing As(V) (0–20 mg L^{-1} for NMMF and 0–40 mg L^{-1} for NMMB) solution containing 0.05 g biochar were kept in 68 ml digestion vessels (Environmental Express). At the end of experiments, the sorption was terminated and final suspension was passed to 0.22 μm pore size nylon membrane filters. The As(V)-loaded sorbents were collected and dried in the oven at 80 °C for surface characterization.

The initial sorption solutions for both kinetics and isotherms study was adjusted with diluted NaOH and HCl to pH 8. All the experiments in this study were triplicated and the mean values were reported along with standard deviations.

Desorption and regeneration studies

As(V) was sorbed onto NMMF and NMMB by placing 0.1 g of sorbents into 40 ml of 40 mg L^{-1} As(V) solution. The As(V)-loaded sorbents were separated from the suspensions by 10 min centrifugation at 5000 rpm. The spent sorbents desorbed in 40 ml of 0.1 M NaOH solution for 48 h. An aliquot of 2 ml desorption solution was collected at intervals and filtered to predict desorption curves. After desorption, sorbents were rinsed with DI water several times, and used for As(V) re-sorption (40 ml of 40 mg L^{-1} As(V), pH 8). The desorption and resorption process was repeated three times to assess the regeneration potential.

As(V) sorption at different pH

Metal oxide and LDHs are usually hydroxylated and thus may protonate or deprotonate depending on pH. The surface charges resulting from hydroxyl (–OH) groups may affect As(V) sorption. In this study, pH of As(V) (50 mg L^{-1}) solution was adjusted between 3 and 9 with 0.1 M NaOH and HCl. The sorption procedure followed the batch experiment described in 'Adsorption kinetics and isotherm'. The sorption with 0.05 g sorbents was conducted in 0.05 mM $NaNO_3$ solutions and followed procedure described in 'Adsorption kinetics and isotherm', and was terminated after 24 h. Sorption at each pH was triplicated.

Results and discussion

Physical properties of biochar

Ni and Mn contents were 6.01 and 6.63% in NMMF, and 10.90 and 22.03% in NMMB respectively, equivalent to molar ratio of Ni/Mn as 1.04 and 1.92 (Table 1). C content in both sorbents was decreased after addition of Mn and Ni, i.e., C content in NMMF and NMMB were 55.1 and 69.8%, respectively. Surface area was also reduced to 128 and 281 m^2 g^{-1} in NMMF and NMMB, respectively.

XRD diffractogram of NMMF showed diffraction peaks with *d* spacings of 2.556 and 2.220 Å. 1.566 Å can be assigned to manganosite (MnO) [25], and 2.036, 1.761 and 1.246 Å to NiO [25,26] (Figure S1, supporting information). The originally formed $Ni(OH)_2$ before pyrolysis can be completely converted to NiO at pyrolysis temperature of 600 °C [27]. Mn and Ni distribution map as revealed by EDS elements showed some discrepancy, indicating