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4 1 **Enhanced Arsenic Removal by Biochar Modified with Nickel (Ni) and Manganese (Mn)**
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12 4 Shengsen Wang¹, Bin Gao^{1*}, Yuncong Li²
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- 19 7 1. *Department of Agricultural and Biological Engineering, University of Florida,*
20
21 8 *Gainesville, FL 32611*
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23 9 2. *Tropical Research and Education Center, Soil and Water Science Department, University*
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25 *of Florida, Homestead, FL 33031*
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48 19 * Corresponding author: phone: (1) 352-392-1864 ext. 285, email: bg55@ufl.edu
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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 NiO and MnO were dominant crystals in NMMF, whereas Ni/Mn-LDHs in NMMB. Sorption experiment showed 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 three desorption-resorption cycles. The As(V) sorption is mainly attributed to anion exchange and surface complexation by NMMB and surface complexation by NMMF.

Keywords: Biochar; Arsenate; Ni/Mn-LDH; NiO; MnO

1. 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 $10 \mu\text{g L}^{-1}$ 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 $[A_xB_{1-x}(\text{OH})_2]^{x+}C^{x-} \cdot n\text{H}_2\text{O}$, where A, B represent divalent and trivalent cations, 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, and 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, 3) evaluate the sorption capacity of wo sorbents and propose the possible mechanisms for As(V) sorption.

2. Experimental

2.1 Reagents

All chemicals of reagent grade were dissolved with ultrapure water (18.2 MΩ cm, herein referred as DI H₂O) (Nanopure water, Barnstead). Sodium arsenate dibasic heptahydrate (Na₂HAsO₄·7H₂O), manganese chloride tetrahydrate (MnCl₂·4H₂O), nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O), sodium nitrate (NaNO₃) and granular sodium hydroxide (NaOH) and hydrochloric acid (HCl) of analytical grades were purchased from Fisher Scientific.

2.2 Biochar preparation

MnO/NiO-biochar composite was derived from pyrolysis of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ modified feedstock (NMMF). The feedstock, loblolly pine (*Pinus taeda*) wood, were oven dried and were ground into < 2mm fragments with a mechanic miller. 25 g of crushed feedstock were mixed into 100 ml solution of $0.1 \text{ mol L}^{-1} \text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (2.0 g) and $0.2 \text{ mol L}^{-1} \text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (5.8g). 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 1h 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 as previously reported methods [22]. The pristine biochars (5g) 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. $\text{Ni}(\text{NO}_3)_2$ (0.02 mol) and $0.1 \text{ mol L}^{-1} \text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.01 mol) were dissolved in biochar suspension. The suspension was transferred to 250 ml 1.5M NaOH preheated at 80°C with continuously 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 < $0.22\mu\text{m}$) and dried at 80°C for 12 h.

2.3 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 -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 a powder CuK α 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).

2.4 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 NaNO₃ 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 analyzed with an inductively coupled plasma-atomic emission spectrometry (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 NaNO₃ containing As(V) (0-20 mg L⁻¹ for FNM and 0-40 mg L⁻¹ for FNB) 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 0.22 μm pore size nylon membrane filters. The As (V)-loaded sorbents were collected and dried in the oven at 80 $^{\circ}\text{C}$ 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 value were reported along with standard deviations.

2.5 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.

2.6 As(V) sorption at different pH

Metal oxide and LDHs are usually hydroxylated and thus may protonated and deprotonated dependent 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 to between 3-9 with 0.1 M NaOH and HCl. The sorption procedure followed the batch experiment described in 2.4. The sorption with 0.05 g sorbents was conducted in 0.05 mM NaNO_3 solutions and followed procedure described in 2.4, and was terminated after 24 h. Sorption at each pH was triplicated.

3. Results and Discussion

3.1 Physical properties of biochar

Ni and Mn contents were 6.01 and 6.63% in NMMF, 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 m² g⁻¹ in NMMF and NMMB, respectively.

XRD diffractogram of NMMF showed diffraction peaks with d spacings of 2.556, 2.220. 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 appearance of two distinct minerals in NMMF (Figure S2, supporting information). XRD diffraction patterns of NMMB with d spacings of 7.752, 4.030, 2.632, 2.310, 1.535 Å matched the Ni/Mn-LDH patterns in previous work [6, 21]. EDS mapping analysis showed that Ni and Mn had similar elemental distribution pattern in NMMB, supporting the conclusion that Ni/Mn based LDH was formed in NFMB. The diffractogram indicated Ni/Mn-LDH in NMMF is better crystalline than that in NMMB, as indicated by the sharper and narrower diffraction peaks. XPS analysis confirmed the appearance of both Ni and Mn in the as-prepared sorbents. Binding energies of Mn 2p 3/2 and 1/2 were 642.02 and 653.81 eV in NMMF, and 643.18 and 654.09 eV in NMMB, corresponding to Mn²⁺ and Mn³⁺ respectively (Figure S3, supporting information) [6]. Ni 2p 3/2 and 1/2 were 856.11-856.45 and 874.10-874.11 eV in both sorbents, ascribing to divalent Ni [6, 21]. Surface morphology was visualized with SEM. The surface topography and mapping

analysis along with XRD and XPS analyses revealed that the LDH was anchored on the biochar surface matrix for NMMB (Figure S4, supporting information).

3.2 As(V) sorption kinetics and isotherm

The kinetics curves show that equilibrium was attained in 8h (Figure 1a). Fast kinetics between 0 and 2h followed by much slower kinetics suggested at least two distinct mechanisms ascribing to As(V) sorption, such as non-specific and specific sorption. Kinetics data were fitted with three commonly used mathematical models which reproduced the data well (Table 2). Fitted models were explained and described elsewhere in our previous work [16]. The As(V) sorption kinetics by NMMF and NMMB were better fitted by first order kinetics model ($R^2=0.991$) and Elovich model ($R^2=0.972$), respectively, suggesting different mechanisms participated in two different sorbents. The first order and second order kinetics indicated that NMMB has faster kinetics (k_1 and k_2) than NMMF, the Elovich model also showed that NMMB has faster initial sorption rate (α) and lower desorption potential (β) than NMMF. The sorption rate of NMMB (1.58 h^{-1}) is about 9 times NMMF (0.173 h^{-1}) obtained from first order kinetics, and initial sorption rate of NMMB (649 g kg^{-1}) is about 464 times than NMMF (1.41 g kg^{-1}) while desorption of NMMB ($\beta=1.68 \text{ g kg}^{-1}$) is 11 times less than NMMF (18.27 g kg^{-1}).

The maximum As(V) sorption is determined by sorption isotherms. The isotherm data were fitted with Langmuir model and Freundlich model. The Langmuir model was a better simulation model, and maximal As(V) sorption capacity by NMMB (6.52 g kg^{-1}) is 12.7 times than NMMF (0.513 g kg^{-1}) (Table 2). Both sorbents have better As(V) sorption than previously-reported un-modified pinewood biochar ($0.200\text{-}0.265 \text{ g kg}^{-1}$) [16, 28] and most of LDHs as summarized in Table 3. L-shaped curves indicated good affinity of As(V) by NMMB. As(V)

removal efficiency decreased as the initial As(V) concentration decreases (Figure 1b). For example, at initial As(V) concentration 1.4, 4.3, 7.6 and 11.5 mg L⁻¹, the removal efficiency were 36.2, 30.1, 23.1 to 10.6 % by NMMF, and 98.1, 99.8, 96.5 and 98.4% by NMMB. This suggests that NMMB has better performance at lower sorbate concentrations, e.g., 15 mg L⁻¹. The robust As(V) removal, e.g., initial As(V) concentration below 15 mg L⁻¹, endows the potential use of NMMB in water treatment.

3.3 As(V) desorption study

Desorption potential of As(V)-loaded sorbents determines the re-use of sorbents in environmental reclamation. 0.1 M NaOH is able to desorb 81.7% and 75.0 % of initially sorbed As(V) onto NMMB and NMMF, respectively. As(V) desorption curves comprise of a very rapid phase (4h) and a slower phase (4- 24h) and steady last phase (Figure 2). Same trend was also observed on Mg/Al LDH, which ascribed As(V) sorption to inner-sphere complexation [11]. The NMMB showed excellent re-sorption capacity, which account for about 98% removal efficiency for the second and third desorb-resorb cycles (data not shown). This indicates NMMB can be recycled and reused in environment reclamation and remediation.

3.4 pH affects As(V) sorption

Metal oxides in NMMF have pH dependent surface charges due to protonation and deprotonation of surface hydroxyl (-OH) groups [3]. As(V) sorption envelopes showed that As(V) sorption by NMMF and NMMB decreased as the solution pH rises (Figure 3). Because As(V) exists mainly as negatively charged oxyanions (H₂AsO₄⁻ and HAsO₄⁻) between pH 3 and 9 (Figure 4), it may be attracted by positively charged metal oxides and/or LDHs surfaces. When pH are below point of zero charges (pHpzc), the sorbent surfaces are more positively charged at lower pH and thus have greater tendency to attract As(V) oxyanions. For NMMF, MnO usually

has low pH_{pzc}, i.e., around 5.5 [29], and thus it may not attract As(V) at pH higher than pH_{pzc}. However, NiO has pH_{pzc} between 8.25-8.53 [30], it may attract As(V) below the pH_{pzc}, which is the dominant sorption sites for As(V) in NMMF. As for NMMB, LDHs usually has high pH_{pzc} [31], accounting for As(V) sorption.

3.5 Sorption mechanisms

Pristine pinewood derived biochars have very low As(V) sorption capacity (0.200- 0.265 g kg⁻¹) [16] and thus the synthesized Ni and Mn oxides or Ni/Mn-LDHs are responsible for the elevated As(V) sorption. As(V) was detected in the XPS spectrum of both NMMF and NMMB after sorption confirming the effective As(V) sorption (Figure S5 and S6, supporting information). As discussed in 3.4, both NiO in NMMF and LDH in NMMB has pH_{pzc} above 8 and therefore are positively charged at experimental pH (8) [28, 31]. It could be possible that both NiO and LDH sorb As(V) by electrostatic attractions.

Electrostatically attracted As (V) may form specific inner-sphere complexation with hydroxyl groups bonded to metals, with different complexation mechanisms such as monodentate mononuclear, bidentate mononuclear, or monodentate mononuclear [11, 32]. The formation of surface complex was supported by change of binding energies of O1s for NMMB. The peaks at binding energy of 531.09 and 532.68 eV were changed to 531.99 and 533.70 eV, respectively (Figure S7, supporting information) [3, 33]. The peaks at binding energy of 531.09, 531.99, and 532.68 eV can be assigned to O bonded to metals, hydroxyl bonded to metal and to H₂O, respectively. Thus, HAsO₄²⁻ may complex with –OH (bonded to metals) which explains disappearance of hydroxyl peaks in As(V)-loaded NMMB. No change of O1s binding energies pre and post-sorption in NMMF suggest surface complexation with –OH was not supported.

Besides, two phases in kinetics and isotherms models indicate multiple mechanisms may be involved in the NMMB. Anion exchange may be involved in As(V) sorption [7, 10, 11]. The d spacing of NMMB at 7.752 Å decreased to 7.581 Å after As(V) sorption, respectively. This may suggest oxyanionic HAsO_4^{2-} may be trapped in the interlayer of adjacent layers, by the anions (Cl^- and NO_3^-) in the interlayers of Ni/Mn-LDH in both NMMB. Previous work also found that d spacings of Mg/Al -LDH changed after As(V) sorption due to exchange of HAsO_4^{2-} ($\text{pK}_{a2}=7.03$) with NO_3^- [11].

Thus, the dominant mechanisms for As(V) sorption by NMMF is electrostatic attraction, while anion exchange and surface complexation for NMMB.

4. Conclusions

Mn and Ni bimetal oxide and hydroxides modified biochars were prepared. The NiO and MnO are the dominate crystals in sorbent produced by pyrolysis of Mn/Ni treated biomass (NMMF), and Ni/Mn-LDH is dominant crystalline forms in Ni/Mn-LDHs modified biochars (NMMB). As(V) removal was improved by both composites, while maximum As(V) sorption by NMMB was about 12 times that of NMMF. The As(V) was mainly sorbed via anion exchange and surface complexation by NMMB. The NMMB has excellent As(V) removal efficiency of more than 98% at low As(V) concentrations (e.g., below $\sim 12 \text{ mg L}^{-1}$). The NMMB can be desorbed easily by NaOH and attached more than 98% efficiency in the second and third desorption-resorption cycles. Thus, NMMB is an excellent sorbent for As(V) removal from aqueous solutions.

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Tables

Table1. Elemental composition, surface area and pore volume of loblolly pine wood biochar (PB), NMMF and NMMB

	C	N	Mn	Ni	BET Surface area
			%		m ² g ⁻¹
NMMF	55.14	0.52	6.01	6.63	125.0
NMMB	54.90	0.41	10.90	22.03	282.8

Table 2. Kinetics and isotherm models and best-fit parameters for As(V) sorption onto PB, NMMF and NMMB

Model/Equations	Sorbents	Parameter1	Parameter2	R ²
Kinetics				
First-order	NMMF	q _e =0.432 g kg ⁻¹	k ₁ =0.173 h ⁻¹	0.991
$q_t = q_e(1 - e^{-k_1 t})$	NMMB	q _e =5.59 g kg ⁻¹	k ₁ =1.58 h ⁻¹	0.917
Second-order	NMMF	q _e =0.506 g kg ⁻¹	k ₂ =0.383 kg g ⁻¹ h ⁻¹	0.979
$q_t = k_2 q_e^2 t / (1 + k q_e t)$	NMMB	q _e =5.94 g kg ⁻¹	k ₂ =0.410 kg g ⁻¹ h ⁻¹	0.971
Elovich	NMMF	α=1.41 g kg ⁻¹	β=18.27 g kg ⁻¹	0.975
$q_t = \beta^{-1} \ln(\beta \alpha t + 1)$	NMMB	α= 649 g kg ⁻¹	β=1.68 g kg ⁻¹	0.972
Isotherm				
Langmuir	NMMF	S _{max} =0.549 g kg ⁻¹	K=0.513 L g ⁻¹	0.995
$S = S_{\max} KC / (1 + KC)$	NMMB	S _{max} =6.52 g kg ⁻¹	K=4.59 L g ⁻¹	0.969
Freundlich	NMMF	n=0.340	K _f =0.201 g ⁽¹⁻ⁿ⁾ L ⁿ kg ⁻¹	0.985
$S = K_f C^n$	NMMB	n=0.187	K _f =4.02 g ⁽¹⁻ⁿ⁾ L ⁿ kg ⁻¹	0.848

Table 3. Comparison of maximum As(V) sorption capacities of various sorbents

Sorbents	Sorption (g kg^{-1})	pH	References
PB	0.265	7	[16]
Mg/Al-LDH	6.13	7	[34]
Mg/Fe-LDH	11-16	7	[5]
Mg/Al-LDH	11	7.5	[7]
Ni/Fe-LDH/Biochar	4.38	7.5	[18]
Ni/Mn-LDH/Biochar	6.52	8	This work
Ni/Mn-LDH	18	8	This work

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Figure captions

Figure 1. As(V) sorption kinetics (a) and isotherm (b)

Figure 2 As(V) desorption curves as a function of time from As(V) loaded NMMF and NMMB

Figure 3 As(V) sorption by NMMF and NMMB at different pH

Figure 4 As(V) species distribution diagram between pH 2-12. Initial As(V)=0.67 mM, I=0.01M

Figure 1

Figure 2

Figure 3

Figure 4

Synthesis → Characterization → As(V) Sorption → Sorption mechanisms