High efficiency and selectivity of MgFe-LDH modified wheat-straw biochar in the removal of nitrate from aqueous solutions

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Abstract:

Mg-Fe layered double hydroxide (MgFe-LDH) particles were incorporated into wheat-straw biochar by liquid-phase deposition. The obtained biochar/MgFe-LDH composite was used to remove nitrate from aqueous solutions. X-ray diffraction patterns demonstrated that LDH particles were successfully deposited onto the carbon surface within the biochar matrix. Adsorption kinetic and isotherm studies and the effects of co-existing anions and adsorbents dosages were investigated using laboratory batch sorption experiments. The biochar/MgFe-LDH composite showed a strong sorption ability to nitrate in aqueous solutions with the Langmuir maximum adsorption capacity of 24.8 mg/g. A high selectivity for nitrate of the biochar/MgFe-LDH composite was also observed irrespective of the co-existence of sulfate and phosphate. The biochar/MgFe-LDH composite can thus be potentially used as an alternative adsorbent for the treatment of nitrate-contaminated waters as well as a soil amendment for the reduction of soil nitrate leaching.

Keywords: engineered biochar; layered double hydroxides; nitrate adsorption; ion selectivity

1. Introduction

Excess levels of nitrate in water have become a serious concern worldwide. Nitrate contamination from both point and non-point sources include agricultural and urban runoff, disposal of untreated sanitary and industrial wastes in unsafe manners, leakages in septic systems, landfill leachates, and animal manure. Due to its high water solubility and low adsorption affinity to soils, nitrate is perhaps the most widespread groundwater contaminant in the world, posing a serious threat to drinking water supplies [1]. High concentrations of nitrate in drinking water may cause methemoglobinaemia, or blue baby syndrome, which has been cited as a risk factor in developing gastric and intestinal cancer. The maximum contamination level set by the US Environmental Protection Agency (EPA) for drinking water is 10 mg/L of $\text{NO}_3\text{-N}$, while the guideline value of the World Health Organization (WHO) for drinking water is 50 mg NO_3^-/L .

Numerous techniques for the removal of nitrate from water and wastewater have been reported [2]. These techniques can remove nitrate from water with varying levels of efficiency, cost, and ease of operation. Adsorption is generally considered an effective water treatment technique because of its convenience, ease of operation, and simplicity of design [2]. The adsorption process can remove/reduce different types of organic and inorganic pollutants from water or wastewater. Efficiency of nitrate removal from aqueous solutions by adsorption depends largely on the adsorbent used [3].

Biochar, a renewable, low cost, and sustainable adsorbent, has received extensive attention for the removal of contaminants from water and wastewater, including nitrate [4]. Mizuta et al.

[5] found that bamboo powder charcoal can adsorb more nitrate than commercial activated carbon and thus can serve as an attractive option for in situ treatment of nitrate-contaminated groundwater and surface water. Several studies [6-9] have reported that porous MgO-biochar nanocomposites have high nitrate adsorption capacities. Furthermore, spent biochar loaded with ammonium, nitrate, and phosphate can potentially be used as a slow-release fertilizer to enhance soil fertility and sequester soil carbon.

Layered double hydroxide (LDH), known as one of the most promising inorganic anion-exchangeable materials used for removing toxic anions from polluted water, has lately been studied for the removal of nitrate [10-12]. Research showed that varying the metal composition of LDH can change the anion selectivity, with Ni/Fe-LDH and Mg/Fe-LDH being reported to have a relatively high selectivity for nitrate ions [11, 13]. Use of LDHs as a slow release fertilizer or anionic exchanger has also been proposed for increasing the nitrogen use efficiency as well as nitrate buffering capacity of soils [14]. However, granular/bulk LDHs may have limited sorption ability to anion contaminants due to the very tight stacking of layers [15]. Composite materials with colloidal and/or nanosized LDHs have thus been developed to maximize the sorption ability of LDHs to various aqueous contaminants [16, 17]. However, research on combining biochar with colloidal and/or nanosized LDHs was limited in the literature with the exception of Zhang et al [7, 18], who reported that biochar/MgAl-LDH ultrafine composite can be successfully obtained by liquid-phase deposition or hydrothermal self-assembly for enhanced uptake capacity of phosphate. To the best of the authors' knowledge,

none of previous studies have examined the sorption ability of LDH-biochar composites to nitrate in aqueous solutions. Although various engineered methods have been developed to modified biochars for contaminants removal [19, 20], only few studies have examined that sorption of nitrate onto biochars [21, 22]. It is therefore crucial to develop novel biochar-based sorbents that can effectively remove nitrate from aqueous solutions.

The overarching objective of this study was to evaluate the potential application of biochar-LDH composite in the removal of nitrate from aqueous solutions. Biochar was derived from wheat straw through slow pyrolysis and then modified with MgFe-LDH through liquid-phase deposition. A range of laboratory experiments were then conducted to characterize the physicochemical properties and sorptive ability of the MgFe-LDH modified biochar to nitrate under various conditions. The specific objectives were as follows: (1) synthesize and characterize biochar/MgFe-LDHs composite; (2) study the nitrate adsorption characteristics of the composite; and (3) evaluate the efficiency and selectivity of the composite in the removal of nitrate ions.

2. Materials and methods

2.1. Materials

Analytical grade magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), potassium hydroxide (KOH), potassium nitrate (KNO_3), and potassium sulfate (K_2SO_4) were purchased from Fisher Scientific and used as received. All

experimental solutions were prepared using deionized (DI) water (18.2 MX) (Nanopure water, Barnstead), which was also used to rinse and clean the samples. Wheat straw (WS) obtained locally in Gainesville, FL was used as the biomass feedstock for biochar production. It was dried and milled into small pieces (2 mm) before use.

2.2. Preparation of samples

Biochars were produced from the WS feedstock through slow pyrolysis at 600 °C for 1 h under N₂ flow conditions following the procedure outlined in previous studies [23, 24]. MgFe-LDH deposited biochar composite was synthesized by the liquid-phase deposition method according to Zhang et al. [7]. Briefly, the pH of 100 mL aqueous solution containing MgCl₂ (0.03 mol), FeCl₃ (0.01 mol), and biochar (10.0 g) was adjusted to about 10 with 1 mol L⁻¹ NaOH aqueous solution. The obtained slurry was aged for 3 d at 70 °C, then filtered, and washed with DI water. Biochar/MgFe-LDH sample was then obtained by drying the filtrate at 70 °C in an oven.

2.3. Characterizations

Specific surface areas of the samples were measured with a Quantachrome Autosorb-1 surface area analyzer using N₂ (BET) sorption methods. Thermogravimetric (TG) curves for the sorbents were determined by using a Mettler TGA/DSC thermogravimetric analyzer (TGA/ DSC 1, STARe System, METTLER TOLEDO, USA) at a heating rate of 10 °C/min from 50°C to

700 °C under air flow. X-ray diffraction (XRD) analysis was carried out to identify crystallographic structures in the samples using a computer-controlled X-ray diffractometer (Philips Electronic Instruments) equipped with a stepping motor and graphite crystal monochromator.

2.4. Batch sorption experiments

Pre-experiment showed that the pristine biochar had no detectable sorption of the nitrate, so all the batch sorption experiments were only conducted with the modified biochar. Adsorption kinetics of nitrate on the biochar/MgFe-LDH samples were examined by mixing 0.1 g sorbent with 50 mL nitrate solution (45 mg/L nitrate) in 68 mL digestion vessels (Environmental Express) at room temperature (22 ± 0.5 °C). The vessels were then shaken at 50 rpm in a mechanical shaker. At appropriate time intervals, the vessels were withdrawn and the mixtures were immediately filtered through 0.22 µm pore size nylon membrane filters (GE cellulose nylon membrane).

The adsorption isotherm of nitrate on the biochar was determined similarly by mixing 0.1 g of biochar with 50 mL of nitrate solutions of different concentrations ranging from 0 to 88 mg/L in the digestion vessels. The vessels were shaken in the mechanical shaker for 24 h at room temperature (sufficient to reach adsorption equilibrium). The samples were then withdrawn and filtered through 0.22 µm pore size nylon membrane filters (GE cellulose nylon membrane) to determine nitrate concentrations. In addition, pH values of solutions before and after nitrate

sorption were measured with a pH meter (Fisher Scientific Accumet Basic AB15).

Adsorption of 45 mg/L of nitrate solution by different adsorbent doses (2 – 20 g/L) for biochar/MgFe-LDH samples was also carried out using the same procedure as the adsorption isotherms. The samples were shaken for 24 h at room temperature and then filtered. The nitrate concentrations of the filtrates were measured.

The effects of competing compounds on nitrate sorption by the biochar/MgFe-LDH composite were investigated by adding a common coexisting anion in natural water bodies (SO_4^{2-} , HCO_3^{-1} , PO_4^{3-} , or NH_4^+) to the 50 mg/L nitrate solutions. The concentration of each of the ions added was also 50 mg/L. The ratio of adsorbent to initial nitrate solution was the same as in the kinetics/isotherm experiment. The vessels were shaken in the mechanical shaker for 24 h at room temperature. The same procedures were used to determine aqueous and adsorbed nitrate concentrations.

Nitrate was analyzed using the ultraviolet spectrophotometric screening method outlined in the standard methods of examination of water and wastewater using spectrophotometry [25]. All the adsorption experiments were conducted in duplicate, and the averages of the experimental data were reported. Additional measurements were obtained when the duplicates had a difference larger than 5%.

3. Results and Discussion

3.1. Morphological structure of biochar/MgFe-LDH composite

Specific surface areas were $182 \text{ m}^2 \text{ g}^{-1}$ for the pristine biochar and $3.9 \text{ m}^2 \text{ g}^{-1}$ for MgFe-LDH impregnated biochar, suggesting that the impregnation filled pores or clogged pore-openings on biochar surfaces. Thus, specific surface areas may not be considered the key parameter in determining nitrate sorption onto biochar.

The XRD pattern in the range of $10\text{-}70^\circ$ of the biochar/MgFe-LDH sample is shown in Fig. 1. The pattern shows diffraction peaks of both the LDH structure and the MgFe_2O_4 (magnesioferrite) spinel structure (JCPDS 17-0465), which is supported by the results that some of the MgFe-LDH microcrystals were converted into spinel ferrite when the aging temperature was higher than 40°C [26]. The basal spacing d of the biochar/MgFe-LDH sample was about 0.75 nm , indicating that MgFe-LDH incorporated some CO_3^{2-} anions [11]. The weaker peak intensity of the spinel ferrite component compared to that of the LDH suggests that LDH is still the dominant component in the sample. Also, diffraction peaks owing to impurities were observed at $2\theta = 16.8^\circ, 26.7^\circ, 39.2^\circ$ and 56° , which corresponded to akaganeite ($\text{Fe}^{3+}\text{O}(\text{OH},\text{Cl})$). This indicates that the sample was a composite of MgFe-LDH, spinel ferrite, and akaganeite. Some patterns of quartz were also found in the XRD due to the existence of Si in wheat straw. The specific surface area for the biochar/MgFe-LDH sample was $3.9 \text{ m}^2 \text{ g}^{-1}$, which is within the range of a typical LDH powder with a single component, such as Mg/Al-, Co/Al-, and Ni/Al-LDH(Cl), whose specific surface areas are usually several square meters per gram [11].

Thermal decomposition showed a greater mass loss in the temperature range of about $350\text{-}500^\circ\text{C}$ for wheat straw biochar (WC) than for MgFe-impregnated biochar (Fig. 2). The

mass remaining, compared to the initial mass, was 8% for wheat straw biochar and 12% for the biochar/MgFe-LDH composite, further confirming the impregnation of LDH into the biochar.

3.2 Adsorption Kinetics

The adsorption rate of nitrate was studied at room temperature using the initial nitrate concentrations (45 mg/L) up to a contact time of 24 h (Fig.3). It appears from Fig. 3 that the kinetics of nitrate adsorption for biochar/MgFe-LDH composite consist of two phases: an initial rapid phase with fast reactions where 74% of the adsorption is completed within 3 h of contact time, followed by a slow phase with an adsorption rate of about 0.086 mg/g/h before reaching equilibrium. The initial high rate of nitrate uptake is probably due to the greater anion exchange ability of LDH. The slow phase is perhaps associated with the pore network and surface of the biochar which help the dispersion of LDH flakes to efficiently increase their reaction with nitrate [7].

The experimental results were fitted to the kinetic models of pseudo-first-order, pseudo-second -order, and Elovich defined in Table 1. While the pseudo-first-order and Elovich model fit to the data well, the pseudo-second-order model is the most suitable one in describing the adsorption kinetics of nitrate on the biochar/MgFe-LDH composite as it had the highest R^2 , lowest standard error of estimate (SSE), and closest match of q_e with the experimental results (7.22 mg/g) (Table 1). Similar results were also reported by other studies [7, 12, 27, 28].

3.3 Adsorption isotherms

Freundlich, Langmuir and Redlich-Peterson isotherms were used to describe the adsorption characteristics of nitrate anions [12, 27, 28]. All three models described the sorption isotherm well with the Langmuir model providing a slightly higher R^2 value (Table 1, Fig. 4), which is consistent with the results obtained by [7, 27, 28]. The maximum Langmuir nitrate adsorption capacity for biochar/MgFe-LDH composite was 24.8 mg/g, greater than that of some previously reported activated carbon and biochar (Table 2) [5, 22, 28, 29], but lower than the 31.6 mg/g of pure MgFe-LDH (3:1) reported by Sasai et al [11] and 118.11 mg/g of pure MgAl-LDH (4:1) reported by Halajnia et al.[12]. According to the results of the TGA analysis, the amount of the MgFe-LDH loaded onto the biochar was only about 4% of the total weight. The converted maximum nitrate adsorption capacity for the pure MgFe-LDH of the composite thus should be much higher (~620 mg/g), conforming that biochar can distribute and stabilize ultrafine LDH particles for better sorption of contaminants [7, 18].

Also of note was that the R^2 values of all three models were very close to one another (Table 1), suggesting that the adsorption of nitrate on the biochar/MgFe-LDH composite may be controlled by multiple processes. This is consistent with findings from previous studies of phosphate sorption on LDHs, which noted that both surface adsorption and interlayer anion exchange mechanisms govern the sorption processes [7, 30]. Because surface adsorption and interlayer anion exchange are both reversible processes, it is anticipated that the adsorbed nitrate on the biochar/MgFe-LDH composite desorb back into aqueous phase and become bioavailable if

the spend adsorbent is applied as soil amendment [9]. In addition, the existence of akaganeite in the biochar/MgFe-LDH composite, which has a large tunnel-type structure, could allow nitrate to easily enter the tunnel and form a new Fe(III) oxyhydroxynitrate, $\text{FeO}(\text{OH})_{1-x}(\text{NO}_3)_x$ [31].

3.4 Effect of coexisting ions

In real systems, other ions can be present and compete with nitrate for adsorption sites. Figure 5 shows the effects of the coexistence of phosphate, sulfate, bicarbonate, and ammonium ions on nitrate adsorption in terms of adsorption capacity at equilibrium (q_e) and nitrate removal efficiency (RE). It can be seen that the influence of phosphate and sulfate on nitrate removal efficiency was very small and could be negligible. Mg/Fe-LDH(Cl) can incorporate nitrate anions, but not sulfate and phosphate anions, into its interlayer space via anion exchange. This is due to the ion-sieve effect produced by the spatial limits between the brucite layers [13]: the ion diameters of SO_4^{2-} (0.46nm) and PO_4^{3-} (0.476nm) were larger than those of Cl^- (0.33nm) or nitrate (0.29 nm) [11, 32]. Tezuka et al. [13] also reported that Mg-Fe LDHs have relatively higher selectivity for nitrate adsorption than MgAl-LDH, even in sea water with overwhelmingly high levels of SO_4^{2-} and Cl^- . They attributed the high anion adsorption capacity but low selectivity for nitrate of MgAl-LDH to the more expansive interlayer character. Furthermore, the tunnel size of akaganeite can only let nitrate enter and replace Cl^- , but not large enough for sulfate and phosphate anions [33]. This study also found that nitrate removal was greatly influenced by HCO_3^- (Fig. 5). This may be explained by the smaller ion diameter of bicarbonate

(0.243nm) [34]. If a chloride LDH is used as a starting material, the chloride can be largely replaced by bicarbonate and nitrate. Similarly with a nitrate LDH, a certain quantity of the nitrate can be replaced by bicarbonate [35].

In general, anions of higher valence have a more significant interfering effect than monovalent anions in the oxyanion adsorption by LDH [30]. While the interfering effects of competing anions on nitrate adsorption by biochar/Mg/Fe-LDH composite follow the order of $\text{HCO}_3^- > \text{HPO}_4^{2-} > \text{SO}_4^{2-}$, such an unusual anion-exchange behavior cannot be explained simply by the Coulomb interaction between the anion and the anion exchange site on LDH nanosheets [11].

Besides these anions, ammonia is another important form of N in natural waters and can have some effect on nitrate removal. The nitrate removal efficiency of biochar/MgFe LDH composite decreased from 30.6% to 22.2% in the mixture of NH_4^+ and NO_3^- (Fig.5), indicating that some absorption sites on the biochar were taken by ammonia. But the data still exhibited a high nitrate removal capacity of 8.37 mg g^{-1} , suggesting that biochar/MgFe LDH composite can remove ammonia and nitrate simultaneously. Previous studies have demonstrated that, in addition to anion pollutants, LDHs can also effectively remove various positively charged compounds such as ammonia from aqueous solution and the sorption mechanisms including precipitation, surface complexation, isomorphic substitution, and chelation with anions in the interlayers of LDHs [36].

3.5 Effect of adsorbents dosages

Applying an optimum dosage of suitable adsorbent for adsorbate removal in a batch adsorption system is crucial for its cost-effective application. Fig. 6 shows the removal of nitrate as a function of adsorbent dosage in the 50 mg/L nitrate solution. In general, an increase in adsorbent dosage increased the percent removal of nitrate, likely due to the increase in adsorbent surface area and the total amount of active adsorption sites [37, 38]. When the sorbent dosage increased from 2 g/L to 5 g/L, the removal efficiency of nitrate increased linearly from 19.1% to 43.6% and the adsorption capacity remained at about the same level. After that, the nitrate removal efficiency increased with increasing dosage to 80.2%, but the adsorption capacity decreased from 3.88 mg/g to 1.84 mg/g. This indicates that the optimum dosage for nitrate removal should be between 5-10 g/L. The adsorption capacities of the adsorbent (Q_e) were higher at lower adsorbent loadings, which may be attributed to the fact that, at higher adsorbent loadings, some of the adsorption sites remain unsaturated during the adsorption process [39].

4. Conclusions

Nitrate adsorption properties of biochar/MgFe-LDH composite prepared by liquid-phase deposition were examined in this study. XRD analysis demonstrated that LDH particles were successfully deposited onto the carbon surface within the biochar matrix. The obtained biochar/MgFe-LDH composite showed a strong sorption ability to nitrate in aqueous solutions with the maximum uptake capacity at 24.8 mg/g, which is higher than most of the unmodified

activated carbon (AC)/biochar adsorbents. Furthermore, the biochar/MgFe-LDH composite showed a high selectivity for nitrate due to its suitable interlayer spacing for fixing NO_3^- ion, irrespective of the existence of sulfate and phosphate. The increase of adsorbent dosage increased the percent removal of nitrate while the adsorption capacity decreased, making 5-10 g/L the optimum dosage for nitrate removal. Because biochar is a low-cost material commonly derived from waste biomass, using biochar as a support to distribute and stabilize LDH creates an environmentally friendly adsorbent. Findings from this work demonstrated potential applications of biochar/MgFe-LDH composite as a green adsorbent for nitrate removal from water and as a soil amendment for reduction of soil nitrate leaching.

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Table 1. Summary of kinetic and isotherm models and their best-fit parameters for the adsorption of nitrate onto the biochar/MgFe-LDH composite

Parameters	Kinetic Models				Isotherm Models	
	First-order:	Second-order:	Elovich:	Langmuir:	Freundlich:	Redlich-Peterson:
	$q_t = q_e(1 - e^{-kt})$	$q_t = \frac{kq_e^2 t}{1 + kq_e t}$	$q_t = \frac{1}{\beta} \ln(\beta \alpha t + 1)$	$q_e = \frac{q_{\max} K C_e}{1 + K C_e}$	$q_e = K_f C_e^n$	$q_e = \frac{q_{\max} K C_e}{1 + K C_e^n}$
Parameter 1	k=0.607	k=0.109	$\alpha = 17.357$	K=0.012	K=0.55	K=0.0133
Parameter 2	q _e =6.6	q _e =7.4	$\beta = 0.767$	q _{max} =24.8	n=0.718	q _{max} =22.72
Parameter 3	-	-	-	-	-	n=0.983
R ²	0.960	0.986	0.938	0.977	0.969	0.977
SEE	0.986	0.334	1.532	1.585	2.15	1.591

Table 2. Comparison of the Langmuir maximum nitrate sorption capacity of various sorbents (LDH and unmodified AC/biochar)

sorbents	Max. sorption capacities(mg/g)	Experiment condition	references
Mg-Al LDH(4:1)	118.11	20°C, 5g/L absorbents, 0.02-5mmol L ⁻¹ nitrate	[12]
Mg-Fe LDH(3:1)	31.6	26.85°C, 2g/L absorbents, 0.01mol L ⁻¹ nitrate	[11]
Ni-Fe LDH	20.46	room temperature, 1g/L absorbents, 0.1mol L ⁻¹ nitrate, Seawater	[10]
Mg-Fe LDH	5.022	room temperature, 1g/L absorbents, 0.1mol L ⁻¹ nitrate	[13]
Activated carbon from sugar beet bagasse	9.14	25°C, 2g/L absorbents, 10-200mg/L nitrate	[28]
Charcoal of wheat straw (WSC) and mustard straw(MSC),commercial activated charcoal(CAC)	4.87 (WSC), 5.40 (MSC), 5.76 (CAC)	15°C, 8-80g/L absorbents, 0-105mg/L nitrate	[29]
Activated Bamboo charcoal(BPC) and CAC	5.54 (BPC) ; 4.83 (CAC)	10°C, 1.25g/L absorbents, 0-45mg/L nitrate	[5]
Sugarcane bagasse biochar at 600°C	0.64	22°C, 2g/L absorbents, 34mg/L nitrate,	[22]
MgFe-LDH biochar	24.8	room temperature, 2 g/L absorbents, 0-88 mg/L nitrate	This study

Figure Captions

Fig. 1 XRD patterns of the biochar/ MgFe LDH composite

Fig. 2 TGA curves for the wheat straw biochar (WC) and biochar/MgFe-LDH composite
(MgFe-LDH/WC)

Fig. 3 Adsorption kinetic data and modeling for nitrate onto the biochar/MgFe-LDH composite
(2 g/L absorbents and 45 mg/L nitrate)

Fig. 4 Adsorption isotherm for nitrate onto the biochar/MgFe-LDH composite (2 g/L absorbents
and 0-68 mg/L nitrate)

Fig. 5 Effect of coexisting ions on nitrate removal by the biochar/MgFe-LDH composite (2 g/L
absorbents, the ion concentration were all 50 mg/L)

Fig. 6 Effect of adsorbent dosage on removal efficiency and adsorption capacity of nitrate by the
biochar/MgFe-LDH composite (45 mg/L nitrate)

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6