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Synthesis of porous MgO-biochar nanocomposites for removal of phosphate and nitrate from aqueous solutions

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HIGHLIGHTS

- ▶ A new synthesis method for MgO-biochar nanocomposites was developed.
- ▶ MgO nano-flakes within a biochar matrix have uniform morphologies.
- ▶ Biochar matrix is mesoporous with average pore size of 50 nm.
- ▶ Nanocomposites showed excellent removal efficiencies to phosphate and nitrate.

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ABSTRACT

A new synthesis was developed to create highly porous nanocomposite material consisting of MgO nano-flakes within a biochar matrix that has high sorption ability for ionic contaminations. The synthesis method was used in laboratory to produce MgO-biochar nanocomposites from a variety of carbon-rich biomass. Physical and chemical properties of the synthesized nanocomposites were studied systematically with X-ray powder diffraction, thermogravimetric analysis, scanning electron microscopy, high-resolution transmission electron microscopy, and energy-dispersive X-ray analysis. In addition, batch sorption experiment was conducted to determine the sorption ability of the MgO-biochar nanocomposites to aqueous phosphate and nitrate. The results showed that the MgO nano-flakes have uniform morphologies and disperse uniformly on the surface of the biochar matrix. HR-TEM indicated that the biochar matrix is mesoporous with average pore size of 50 nm and the MgO nano-flakes have spacing between 2 and 4 nm, which can serve as adsorption sites for anions. As a result, all the tested MgO-biochar nanocomposites showed excellent removal efficiencies to phosphate and nitrate in water. Nanocomposites made from sugar beet tailings and peanut shells had the best performances with Langmuir adsorption capacities as high as 835 mg g^{-1} for phosphate and 95 mg g^{-1} for nitrate, respectively, much higher than the reported values of other adsorbents.

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1. Introduction

Excessive phosphorous (P) and nitrogen (N) release into runoff from human activities is considered as the major cause of eutrophication, which degrades fresh water and imposes great risk to the ecosystem [1–5]. Biological, chemical, and physical treatment methods have been developed for various applications to remove P and N from aqueous solutions prior to their discharge into runoff and natural water bodies [6–8]. Because the cost of these treatment technologies is substantial, there is a need to develop more cost effective and high efficiency technologies for P and N removal.

Biochar is a stable solid, rich in carbon and is resistant to decomposition an mineralization [9]. When applied to soils, biochar can increase soil fertility, raise agricultural productivity, increase soil nutrients, and enhance soil water holding capacity [10–12]. In addition, it can also serve as carbon storage to reduce CO_2 emissions and mitigate climate change [13–16]. During the past several years, considerable research effort has also been made on biochar-based adsorbents for removal of aqueous contaminants. In this practice, biochar adsorbents are often made from various precursors, such as wood, grass, manure, without any modifications and then are evaluated in laboratory to select the ones with the best performance for desired application [17–23]. Through this method, a number of biochars have been identified as effective adsorbents for some common water pollutants, such as organic compounds and heavy metals [24–31].

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Recently, Yao et al. [32,33] found that biochar produced from anaerobically digested sugar beet tailing can efficiently adsorb phosphate ions from water. They indicated that anaerobic digestion process can introduce Mg compound into biochar precursors (digested sugar beet tailing) to form colloidal or nanosized MgO particles on the biochar surfaces after pyrolysis [32,33]. Because the resulted MgO-biochar composite showed excellent ability to remove phosphate from water, their findings provided an opportunity to produce biochar-based adsorbents to remove anionic nutrients (e.g., P and N) from aqueous solutions. The application of this new biochar technology, however, requires the anaerobic digestion of feedstock biomass, which need comparatively long processing time and rigorous control of the biological reactions. These definitely complicate and increase the cost of the production of nutrient removal biochars, so facile synthetic nanofabrication techniques of MgO-biochar nanocomposite become extremely meaningful.

The overarching objective of this study is to develop a novel method to produce engineered biochar that can effectively remove phosphate and nitrate from water. For the first time, a facile self-assembly of porous MgO-biochar nanocomposites containing 20-nm-thick flakes of polycrystalline MgO were produced in laboratory from various types of biomass feedstocks. Both the nano-MgO and the biochars showed highly porous structures formed during pyrolysis process by evaporated water and a series of chemical reactions in different phases. As a result, these novel nanocomposites demonstrated exceptional adsorption ability to anions, thus can be used to remove phosphate and nitrate from aqueous solutions to reduce eutrophication in fresh water.

2. Materials and methods

2.1. Feedstocks

Five common biomass feedstocks were used to make the MgO-biochar nanocomposites: sugar beet tailings (SBTs), sugarcane bagasse (SB), cottonwoods (CWs), pine woods (PWs), and peanut shells (PSs). The SBT and SB were provided by the American Crystal Sugar Company (East Grand Forks, MN) and Florida Crystals Corporation (Okeelanta, FL), respectively. The other three feedstocks were obtained locally in Gainesville FL. All feedstocks were air dried and milled into powders of ~2 mm prior to use.

2.2. MgO-biochar nanocomposites

Magnesium chloride hexahydrate ($MgCl_2·6H_2O$) was purchased from Fisher scientific to prepare a magnesium chloride solution to pretreat the biomass feedstocks. All the solutions used in this work were prepared with deionized (DI) water (Nanopure water, Barnstead), which was also used to rinse and clean the samples. The magnesium chloride solution was prepared by dissolving 40 g of $MgCl_2·6H_2O$ in 60 mL of deionized water. Each feedstock was immersed into the solution for 2 h. The mixture of biomass and $MgCl_2$ was then oven dried at 80 °C to remove the water. A dry mixture of biomass and $MgCl_2$ was heated at 10 °C/min up to 600 °C under N_2 flow for 1 h. Maintain the N_2 flow is important because it could bring out byproduct gases including HCl to facilitate the formation of MgO particles in the biochar matrix. The MgO-biochar nanocomposites produced from pyrolysis was gently crushed and sieved into two size fractions: <0.5 and 0.5–1 mm. Only the latter was used in the experiments to minimize the presence of residual ash particles. In addition, the selected samples were washed with DI water for several times, oven dried (80 °C), and sealed in a container for further tests.

2.3. Characterizations

Microscopic features of the MgO-biochar nanocomposites were characterized with both field emission gun scanning electron microscopy (FEG-SEM, JEOL 6335F) equipped with an energy-dispersive X-ray analyzer and high-resolution transmission electron microscopy (HR-TEM, JEOL 2010F). X-ray diffraction (XRD) analysis was carried out to identify any crystallographic structure for the samples using a computer-controlled X-ray diffractometer (Philips Electronic Instruments) equipped with a stepping motor and graphite crystal monochromator. Surface area of all of the MgO-biochar nanocomposites was determined using N_2 sorption isotherms at 77 K run on NOVA 1200 and the Brunauer–Emmett–Teller (BET) method to determine mesopore-enclosed surfaces and using CO_2 sorption isotherms run on a Quantachrome Autosorb measured at 273 K and interpreted using grand canonical Monte Carlo simulations of the non-local density functional theory for micropore-enclosed (<1.5 nm) surfaces. Thermogravimetric analysis (TGA) was conducted with one selected biomass feedstock (SBT). The analysis was carried out under a stream of nitrogen at a heating rate of 10 °C/min for both original and $MgCl_2$-pretreated SBT using a Mettler's TGA/DSC1 thermogravimetric analyzer.

2.4. Adsorption of phosphate and nitrate

Phosphate and nitrate solutions were prepared by dissolving potassium phosphate dibasic anhydrous (K_2HPO_4, certified A.C.S, Fisher Scientific) and sodium nitrate ($NaNO_3$, certified A.C.S, Fisher Scientific) in DI water, respectively. Stock solutions of 1600 mg/L P and 20 mg/L N were prepared. The sorption experiments were carried out in 68 mL digestion vessels (Environmental Express) at room temperature (22 ± 0.5 °C). For each experiment, 50 mL solutions of 20 mg/L sorbate (P or N) and 0.1 g of each adsorbent (MgO-biochar nanocomposite prepared from SBT, SB, CW, PW, or PS) were added into the vessels. After being shaken at 60 rpm in a mechanical shaker for 24 h, the vials were withdrawn and the mixtures were filtered through 0.22 lm pore size nylon membrane filters (GE cellulose nylon membrane). The phosphate concentrations of the liquid phase samples were then determined by the ascorbic acid method (ESS Method 310.1; (USEPA, 1992)) with aid of a spectrophotometer (Thermo Scientific EVO 60). The nitrate concentrations of the liquid phase samples were analyzed by using ion chromatography (IC) (DIONEX-120, USA). The P and N removal rates were calculated based on the initial and final aqueous concentrations.

Adsorption isotherms of selected nanocomposites to aqueous P (SBT nanocomposite) and N (PS nanocomposite) were also determined using the batch sorption experiments at room temperature in the digestion vessels. The adsorbent (0.1 g) was added into 50 mL solutions with concentration ranging from 1.0 to 1600 ppm for P or 0.5 to 20 ppm for N. After being shaken at 60 rpm in a mechanical shaker for 24 h, the vials were withdrawn and the mixtures were filtered to determine the equilibrium concentrations. The amount of P or N on the adsorbents was calculated based on the difference between initial and final aqueous concentrations. All the experimental treatments were performed in duplicate and the average values are reported. Additional analyses were conducted whenever two measurements showed a difference larger than 5%.

3. Results and discussion

3.1. Production of MgO-biochar nanocomposites

The new synthesis successfully produced biochar from all the $MgCl_2$-pretreated biomass feedstocks. The weight-based produc-

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