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Fast nitrate and fluoride adsorption and magnetic separation from water on α-Fe_2O_3 and Fe_3O_4 dispersed on Douglas fir biochar

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ABSTRACT

α-Fe_2O_3 and Fe_3O_4 dispersed on high surface area (663 m^2/g) Douglas fir biochar (BC) was prepared for fast nitrate and fluoride ion removal from water using magnetic separations. This biochar, made originally at 900 °C, was impregnated with $FeCl_3$ and converted by pyrolysis at 600 °C to magnetic (494 m^2/g) biochar (MBC). MBC and its precursor BC were characterized using SEM, SEM-EDX, STEM, S_{BET}, PZC measurements, XRD analysis, and XPS. Dispersed α-Fe_2O_3 and Fe_3O_4 particles caused magnetization and generated most adsorption sites, causing more nitrate and fluoride uptake than BC. Both nitrate and fluoride adsorption on MBC remained high over a pH range from 2 to 10. Sorption was evaluated from 298 to 318 K using the Langmuir and Freundlich isotherm models. Langmuir adsorption capacities were 15 mg/g for nitrate and 9 mg/g for fluoride, higher capacities than those reported for other biochar and iron oxide adsorbents.

1. Introduction

Ground water contamination by toxic heavy metals (Pb^{2+}, Cd^{2+}, Hg^{2+}, As^{3+}), inorganic anions (NO_3^-, F^-, PO_4^{3-}, CrO_4^{2-}), and organic compounds (carbamazepine, nonylphenol, estrone), has recently increased in many locations (Blowes et al., 2000; Hashim et al., 2011; Lapworth et al., 2012). Application of nitrate-containing fertilizers satisfies the demand for nitrogen, an essential primary plant nutrient (Crawford, 1995), but creates major nitrate run-off problems (Hester et al., 1996). Agricultural nutrients migrate into the world's lakes, rivers, and oceans. Massive nitrate and phosphate run-off feeds algae blooms, leading to eutrophication and ultimately "dead zones" (Diaz and Rosenberg, 2008). Excess human nitrate ingestion can induce "blue-baby syndrome" (methemoglobinemia) (Majumdar and Gupta, 2000). The US Environmental Protection Agency (USEPA) National Pesticides Survey found 1.2% of public water systems and 2.4% of private drinking water wells have nitrate concentrations above the USEPA's maximum nitrate contaminant level (MCL) of 44 ppm (Spalding and Exner, 1993).

Fluoride ground water contamination is caused by weathering of rocks and soils enriched by fluoride (CaF_2) and fluorapatite (FAP) [$Ca_5(PO_4)_3F$] (Banerjee, 2015). Excess fluoride in drinking water causes dental and skeletal fluorosis affecting millions of people worldwide. The maximum fluoride limit in drinking water is 1.5 ppm set by World Health Organization (WHO) regulations (WHO, 1985). Prolonged water intake with > 1.5 ppm of fluoride causes dental fluorosis, whereas consumption > 4 ppm of fluoride results in skeletal fluorosis (Kundu et al., 2001). Effective treatments are available to decontaminate nitrate and fluoride from water but are often accompanied by significant costs. Lower cost fluoride treatments being studied or applied in Africa have been recently reviewed (Kut et al., 2016). Fluoride adsorption is applied due to its ease of application and cost effectiveness. The need for low cost and highly efficient nitrate and fluoride adsorbents has spurred extensive research during the past decade (Loganathan et al., 2013; Mohapatra et al., 2009).

Biochar is a made by pyrolysis of biomass. Large amounts of by product biochar from bio oil production from future biorefineries could enhance its availability. A decade of research has demonstrated biochar's potential as a low cost adsorbent to remove contaminants from water (Mohan et al., 2014b; Peiris et al., 2017). Many biochars have been modified, enhancing their adsorption properties (Rajapaksha et al., 2016).

Rapid magnetic separation of pollutant-laden biochar from treated water can be achieved when chemical coprecipitation (Fe^{2+}/Fe^{3+}, NaOH) deposits Fe_3O_4 onto biochar generating a magnetic material (Karunanayake et al., 2016). Contaminated water is usually run through columns or filter beds of adsorbent. However, small particle-sized, high surface area sorbents cause pressure drops, slowing flow

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rates. Magnetic attraction enables separation from batch processes of small particle sorbents, avoiding slow filtration. Magnetic biochars can also be prepared by impregnating biomass with iron ions and pyrolyzing this to biochar, during which Fe^0 or magnetic iron oxides form on the chars (Reddy and Lee, 2014). α-Fe_2O_3 and Fe_3O_4 have been used as adsorbents to remove environmental contaminates (Cao et al., 2012; Liu et al., 2008). Incorporating of α-Fe_2O_3 and Fe_3O_4 into biochar forms a magnetic hybrid biochar/α-Fe_2O_3/Fe_3O_4 composite containing active α-Fe_2O_3 and Fe_3O_4 surface sites to remove contaminates. Moreover, α-Fe_2O_3 and Fe_3O_4 particle aggregation is reduced on biochar surfaces. This dispersion increases iron oxide surface areas and adsorption capacities. Finally, by depositing the small iron oxide particles on larger biochar particles, flow through columns is improved. A hybrid adsorbent's properties can exceed those of its individual components (Zhang et al., 2013). Other biochar/α-Fe_2O_3 and biochar/Fe_3O_4 composites were used to adsorb Cr(VI) (Ruan et al., 2015) and pharmaceuticals (Shan et al., 2016).

We now report preparing a biochar/α-Fe_2O_3/Fe_3O_4 adsorbent by pyrolyzing a porous, high surface area, waste Douglas fir biochar from a bio-syn gas plant, which rapidly adsorbed nitrate and fluoride from water. Nitrate removal is difficult due it's high water solubility. MgO-biochar sorption of nitrate has been studied (Zhang et al., 2012). Both magnetized and nonmagnetic corn stover, pine wood and bark biochars have been used for fluoride sorption (Mohan et al., 2014a, 2012). Biochar/α-Fe_2O_3/Fe_3O_4 composites might provide an effective adsorbent that can be magnetically removed from stirred tank batch processes or speed flow through columns by supporting tiny iron oxide particles or larger biochar supports.

2. Experimental

2.1. Chemicals and equipment

GR or AR grade reagents were used (Sigma Aldrich, Saint Louis, MO) unless otherwise specified. Aqueous stock solutions of 1000 ppm NO_3^- and F^- were prepared by dissolving KNO_3 and NaF in deionized (DI) water. The pH was adjusted using 0.1 M H_2SO_4 and 0.1 M NaOH. pH measurements were conducted using a Hanna HI 2211 pH meter.

2.2. Preparation of Douglas fir biochar

Douglas fir biochar, obtained from Biochar Supreme (Everson, WA), is a by-product from waste wood gasification to syn gas. Green Douglas fir chips (~3 in. lengths) were Auger-fed to an updraft gasifier at 900–1000 °C for a ~1 s residence time. The resulting biochar was thoroughly water-washed several times removing ash and other impurities, dried in air, ground, sieved to a 75 μm–150 μm particle size range, and stored in closed vessels. This biochar is designated as BC.

2.3. Preparation of magnetic biochar

The preparation of this biochar/α-Fe_2O_3/Fe_3O_4 was similar a reported method (Zhang et al., 2013). BC (50 g) was immersed with stirring into aqueous 2, 3.5, and 5 M $FeCl_3$ (500 mL) for 24 h and then were filtered (Whatman No. 1 filter paper). The wet biochar was pyrolyzed in a furnace at a heating rate of 10 °C/min to 600 °C under N_2 and held at 600 °C for 1 h. The hot biochar was then cooled to 200 °C under N_2 followed by cooling in air to room temperature. The biochar/α-Fe_2O_3/Fe_3O_4 composite was thoroughly washed with DI water and dried under air for 24 h at 70 °C. This magnetized adsorbent is designated as MBC. The overall yield was 89.8%, calculated based on the original raw biochar (BC).

2.4. Biochar characterization

The BC and MBC surface morphologies were examined by Scanning Electron Microscopy (SEM) using a JEOL JSM-6500F FE-SEM operated at 5 kV. SEM/EDX samples were applied to a carbon stub attached to carbon tape, and then attached to a sample holder. EDX analysis employed a Zeiss EVO 40 scanning electron microscope containing a BRUKER EDX system. Scanning Transmission electron microscopy (STEM) analysis was conducted using a JEOL model 2100 TEM operated at 200 kV. Samples (~10 mg) were mixed with ~0.5 mL of 100% ethanol, sonicated for about 4 min, deposited on carbon film on a 300-mesh copper grid, and allowed to stand overnight before analysis.

Surface areas and pore size distributions were determined using nitrogen physisorption at 77 K on a Micromeritics Tristar II Plus surface area analyzer. Samples (~100 mg) were pre-dried on a Micromeritics FlowPrep 060 degas system at 180 °C under N_2 for 1 h. Surface area and average pore diameter were determined using the Brunauer-Emmett-Teller (BET) method, employing Micromeritics Tristar II Plus software version 2.03, assuming the presence of uniform cylindrical pores. Quantitative biochar iron analysis was determined by atomic absorption spectroscopy (AAS) (Shimadzu AA-7000) using an iron solution standard. Complete acid digestion used 0.1 g of biochar in 50.0 mL of aqua regia (1:3 70% HNO_3/37% HCl) for 1 h at 60 °C with stirring dissolved iron. Solutions were diluted 15 fold with deionized water prior to AAS analysis.

The point of zero charge (PZC) of BC and MBC was determined using 0.01 M NaCl aqueous solutions adjusted to pH values from 3 to 11 with 0.1 M NaOH or 0.1 M HCl. About 0.05 g of adsorbent was added to 25 mL of these solutions. They were agitated for 5 min and the filtrate's pH were measured. Plotting the initial solution pH versus the final solution pH provided the PZC. Crystallographic phases were analyzed by X-ray diffraction (XRD) using a Rigaku ultima III X-ray diffraction system by scanning 2θ from 0° to 80° at 4°/min. An XRD spectrum was also obtained using a Rigaku SmartLab X-ray diffraction system under the same conditions.

Surface and near surface MBC analysis was performed by X-ray photoelectron spectroscopy (XPS). A Thermo Scientific K-Alpha XPS system equipped with a monochromatic X-ray source at 1486.6 eV (Al Kα line) was used. High resolution spectra were obtained for C, O, Fe, N, and F. High-resolution data plots were deconvoluted by assigning different numbers of peaks to get the best fit (the highest correlation coefficient) to the experimental values by applying a Gaussian method employing OriginPro 2017 software.

2.5. Adsorption studies

Batch sorption studies were conducted to determine solution pH, contact time, and adsorbate concentration effects on uptake. Kinetic studies were carried by adding 0.05 g of MBC to 25 mL solutions of adsorbate and swirling samples at 200 rpm for from 5 min to 2 h. Vials were periodically withdrawn and the adsorbent was immediately removed magnetically. Fluoride concentrations in the remaining adsorbate solutions were analyzed with a double beam UV–Vis spectrophotometer using SPADNS reagent (Clesceri et al., 1996) at 580 nm. Nitrate was quantified by LC-UV at 210 nm. Equilibria were achieved within 10 to 15 min for all fluoride and nitrate adsorptions. All the experiments were repeated in triplicate. Standard errors were calculated using the standard deviations of these replicates. Standard error bars were included in all plots. Very small deviations were observed, which confirm that using 0.05 g of adsorbent samples is reasonably representative of the full MBC sample.

Nitrate adsorption isotherms were determined using solution concentrations from 10 to 100 ppm with 0.05 g of MBC. Samples were mechanically shaken for 10 min (equilibration occurred in < 10 min as demonstrated in kinetic experiments) at 298, 308, and 318 K. Solution nitrate concentrations after adsorption were then analyzed. Fluoride adsorption isotherms were determined similarly for all three temperatures, at 1–60 ppm concentrations after 5 min of shaking (equilibration was completed in < 5 min during kinetic experiments).