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Nitrate sorption and desorption in biochars from fast pyrolysis

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ABSTRACT

Increasing the nitrate (NO_3^-) sorption capacity of Midwestern US soils has the potential to reduce nitrate leaching to ground water and reduce the extent of the hypoxia zone in the Gulf of Mexico. The objective of this study was to determine the sorption and desorption capacity of non-activated and chemically activated biochars from microwave pyrolysis using selected biomass feedstocks of corn stover (*Zea mays* L.), Ponderosa pine wood chips (*Pinus ponderosa Lawson* and *C. Lawson*), and switchgrass (*Panicum virgatum* L.). Surface characteristics such as surface area and net surface charge have shown significant effects on nitrate sorption and desorption in biochars. Freundlich isotherms performed well to fit the nitrate sorption data ($R^2 > 0.95$) of biochars when compared to Langmuir isotherms. Nitrate sorption and desorption was significantly influenced by solution pH and presence of highly negative charged potential ions such as phosphate (PO_4^{3-}) and sulfate (SO_4^{2-}) in aqueous solution. Chemical activation with concentrated HCl had significant effect on surface characteristics of biochars and enhanced the nitrate sorption capacity. The first order model fit the nitrate desorption kinetics of biochars with a high coefficient of determination ($R^2 > 0.95$) and low standard error (SE).

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1. Introduction

In Midwestern US agriculture, ammonium (NH_4^+) based fertilizers are routinely applied to meet the nitrogen (N) requirement of agricultural crops. Nitrogen fertilizers generally undergo chemical transformations such as ammonification, nitrification, de-nitrification, nitrogen fixation, and immobilization in soil [1,2]. Nitrification is one of the quickest reaction pathways. It results in the formation of nitrate ion, which is plant available but also highly mobile due to its weak affinity to form surface complexes and therefore prone to leaching [3–5] or is subject to denitrification. Increasing nitrate concentrations in surface and groundwater resources across the world have been attributed to agricultural and industrial inputs [6,7]. Several nitrate removal technologies have been developed such as anion exchange [8], biological denitrification [9], chemical denitrification [10,11], catalytic denitrification [12], reverse osmosis [13], and electrodialyis [14]. These available physico-chemical and biological technologies may be expensive, generate additional by-products and toxic wastes, and have limited applicability in large scale remediation scenarios [15]. For instance, chemical denitrification (reduction) using reductants such as zero-valent iron (ZVI) have been extensively used to reduce nitrate (NO_3^-) in ground water. But this process requires reduced pH and produces ammonia as by-product [16]. Biological denitrification is slow and inefficient to remove nitrate from highly concentrated systems, and also requires additional organic substrates as electron donors [17]. Reverse osmosis and ion exchange resins are not economical for large scale nitrate removal. Ion exchange resins are not selective and also retain other anions (such as SO_4^{2-} and HCO_3^-) which cause the disequlibrium in the ionic composition of soil and water systems and also release chloride (Cl^-) ions during the exchange process [18]. Among these nitrate removal technologies, adsorption has been found less expensive and more effective in removal of nitrate from water systems. Adsorption technologies have evolved as highly efficient remediation tools with lesser energy input to produce sorbent materials; adsorption is easy to apply at large scales [15].

Control of nitrate mobility at its source would eliminate the need for remediation. Various sorbents have been identified which have potential to reduce of nitrate ion mobility in soil and water ecosystems [19,20]. The success of adsorption techniques depends on the selection of appropriate sorbents, their removal efficacy, and economic feasibility. Sorbents (either naturally available or synthetically produced) to remove nitrate from water and waste water systems include functionalized mesoporous siliceous and non-siliceous materials [21–23], metal organic frame works [24], mesoporous carbon materials [25], red mud [26], agricultural waste [27,28], polypropylene-g-N,N-dimethylaminoethyl

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methacrylate [29], poly (dimethylaminoehtyl methacrylate/2-hydroxy ethyl methacrylate) [30], poly (dimethyl diallyl ammonium chloride)/polyacrylamide [31], sepiolite [19], bentonite [32,33], slag [19], activated carbon [19,34], chitin and chitosan derivatives [35,36], and M^{II}-Al-Cl layered double hydroxides [37,38]. In recent years, the depletion of petroleum oil reserves and growing demand for energy across the world has initiated the development of sustainable alternative energy technologies based on renewable biomass. Biochar is the by-product of biomass conversion using pyrolysis to produce bio-oil and syngas. The scientific community has found opportunities to develop these biochar materials as climate change mitigation tools due to their ability to store carbon in soil for long periods. Biochar based materials have the potential to sorb anionic nutrients such as nitrogen (N) and phosphorus (P) from aqueous solutions [39]. Several studies have described that biochars can also supply nutrients to crop plants and reduce the leaching of nutrients in soil [40,41]. Unlike other existing nitrate removal sorbents, biochar can be produced by a simple, cost effective process and its application to agricultural lands may improve soil quality and health.

The sorption capacity of highly carbon rich biochars have been found to be excellent due to their unique surface characteristics such as high surface area, pore volume, and surface functional groups [42]. The surface area and porosity of biochars can be enhanced by either physical or chemical activation methods [43]. The activation of biochars from agricultural products has been increased in recent years due to its use in environmental pollution control [44,45]. Among the activation methods, chemical activation is more economical with higher yield at lower temperature and less production of burn-off char [46]. Slowing the rate at which of nitrate is leached from surface to subsurface soils could improve water quality and reduce greenhouse gas generation. The sorption capacity of soils is critical along with the water flow to determine the leaching rate of nitrate in soil. Cation transport is slowed by sorption on soils with negative charge, while anion transport is slowed by sorption on positively charged soil particles [47]. Most Midwestern United States soils have relatively low anion sorption capacity. For example, the anion exchange capacity of Kranzburg silty clay loam soil (fine-silty, mixed, superactive, frigid, Aeric Calciaquoll) was ranged from -0.25 to 0.27 $\text{cmol}_c\ \text{kg}^{-1}$. This relatively minor anion sorption capacity must be compared with the soil cation exchange capacities that ranged from 27.9 to 33.127 $\text{cmol}_c\ \text{kg}^{-1}$ [47].

Batch experiments are often used to quantify the ionic retention of biochar and other sorbents [48]. The determination of sorption coefficients (K_d) and sorption maxima (q_{max}) of these sorbents help in developing them as remediation tools to control contaminant transport in soil and water eco-systems. In this context, it is important to investigate the interaction of biochar-based sorbents from agricultural products with highly mobile anionic nutrient such as nitrate is essential. Therefore this study was designed with the following objectives: (1) determine the surface characteristics of non-activated and activated biochars produced from microwave pyrolysis using corn stover (*Zea mays* L.), Ponderosa pine (*Pinus ponderosa Lawson* and *C. Lawson*) wood residue, and switchgrass (*Panicum virgatum* L.); and (2) determine the nitrate sorption and-desorption potential of non-activated and activated biochars.

2. Materials and methods

2.1. Production of non-activated and activated biochar materials

Using corn stover, Ponderosa pine wood chips and switchgrass as feedstocks, three biochars were formed as co-products of bio-oil production using microwave pyrolysis at 650 °C and residence time of 18 min. These biochars were activated by heating with concentrated hydrochloric acid (HCl). Air dried biochar (25 g) was placed in a conical flask covered with a watchglass and treated with 250 ml of concentrated HCl. The biochar mixed with concentrated HCl was heated on hot plate at 200 °C (placed in laboratory hood) for 24 h. After heating, the biochars were washed with deionized water four times and then washed with 1% sodium bicarbonate ($NaHCO_3$) solution (1:500 solid-solution ratio) four times to remove acid residues. Later the biochar materials were washed with deionized water several times until the pH of the supernatant was 7.0. The washed biochars were oven dried at 105 ± 5 °C for 8 h and considered as acid activated biochars [49]. These non-activated and activated biochar materials were homogenized and ground to pass through a 0.2 mm sieve and used for characterization and batch studies.

2.2. Characterization of non-activated and activated biochar materials

Specific surface area of biochars, were determined using the iodine absorption method [50]. The biochar acidity, pH, and EC (electrical conductivity) were measured at 1:1 water to solid ratio after shaking for 30 min in deionized water [51]. The cation exchange capacity (CEC) of biochar samples were measured using 1 M ammonium acetate (CH_3COONH_4) at pH 7.0 [51]. The quantitative analysis of volatile organic compounds (VOCs) in biochar samples were determined [52]. Total carbon and total nitrogen were analyzed by Elementar Vario MAX CNS analyzer [53]. Biochar samples were wet digested using concentrated nitric acid (HNO_3) in a pressurized (200 psi) microwave oven (MARS 5, CEM Corp., USA) [54,55] equipped with teflon closed vessels. The wet digested samples were diluted with distilled water to measure nutrient composition (total P, Ca, Mg, Na, and K) using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) (Varian, Australia) [56]. All these determinations were conducted in four separate biochar samples from different pyrolysis runs.

2.3. Infrared spectroscopic analysis of non-activated and activated biochars

Infrared spectrums were recorded for biochar samples using Fourier Transform Infrared Spectroscopy (Thermo Scientific NICOLET 6700 FT-IR spectrometer). Samples were prepared and pressed into pellets using 10 wt% potassium bromide (KBr). The spectrum had wave number (cm^{-1}) on *x*-axis and transmittance (%) on *y*-axis with resolution using 40 scans. The peaks of the spectrum were studied to understand the surface functionality of non-activated and activated biochar samples.

2.4. Surface charge characteristics of non-activated and activated biochars

The point of zero net charge (PZNC) was measured by determining the cation exchange capacity (CEC) and anion exchange capacity (AEC) simultaneously at eight pH values (pH 2–10) [57]. The PZNC was the pH at which CEC and AEC were equal on sorbent surface. Biochar samples were initially saturated with 0.01 M KCl and the pH was adjusted with 1 M HCl and 1 M KOH. For the pH adjustment, biochar samples (10 g) were weighed in triplicate. These biochar samples were suspended in 100 ml of 0.01 M KCl to prepare subsequent pH levels. These biochar suspensions were adjusted to different pH by adding predetermined amounts of 1 M HCl and 1 M KOH. These predetermined quantities were calculated by using regression equations fitted to the potentiometric titration curves of these biochar materials. The biochar samples were shaken for 12 h and the pH was measured every day until the pH values were constant. Then suspensions were filtered and washed

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