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Competitive adsorption of heavy metals onto sesame straw biochar in aqueous solutions

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HIGHLIGHTS

- Sesame straw biochar demonstrated an excellent adsorption capacity for heavy metals.
- Adsorption fitted best with Langmuir model as compared to the Freundlich model.
- High interference among the metals was observed under multimetal sorption condition.
- The highest reduction in adsorption capacity was found for Cd.
- Adsorption behaviors was well described by three-dimensional simulation.

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ABSTRACT

Objective of this research was to evaluate adsorption of heavy metals in mono and multimetal forms onto sesame straw biochar (SSB). Competitive sorption of metals by SSB has never been reported previously. The maximum adsorption capacities (mg g^{-1}) of metals by SSB were in the order of Pb (102) $\gg$ Cd (86) $\gg$ Cr (65) > Cu (55) $\gg$ Zn (34) in the monometal adsorption isotherm and Pb (88) $\gg$ Cu (40) $\gg$ Cr (21) > Zn (7) $\geqslant$ Cd (5) in the multimetal adsorption isotherm. Based on data obtained from the distribution coefficients, Freundlich and Langmuir adsorption models, and three-dimensional simulation, multimetal adsorption behaviors differed from monometal adsorption due to competition. Especially, during multimetal adsorption, Cd was easily exchanged and substituted by other metals. Further competitive adsorption studies are necessary in order to accurately estimate the heavy metal adsorption capacity of biochar in natural environments.

1. Introduction

Water pollution by heavy metals discharged from industrial effluents has become a worldwide problem during recent years, as most heavy metal species have toxic effects on organisms and accumulate in biota. Thus, wastewater containing heavy metals needs to be purified and recycled in order to secure alternative sources of water (Ali, 2010).

Among various treatment technologies, adsorption is a fast and universal method for treating heavy metals with efficiency and low expense. Various sorbents (natural materials and synthetic products) have been developed (Gupta et al., 2009). Ali (2010) demonstrated that carbon-based adsorbent proved to be the most cost-effective in the removal of inorganic and organic pollutants from wastewater. While activated carbon is ideal for removing contaminants from water it is costly to make, whereas “sustainable” biochar requires less investment. Typical biochar is less carbonized (more hydrogen and oxygen remain in its structure) than activated carbon (Hale et al., 2012; Mohan et al., 2012, 2014). It is a low-cost adsorbent which has recently received increased attention due to its many potential environmental applications and benefits.

Recently, several studies have suggested that biochar can be an effective material for the sorption of heavy metals from wastewater as well as an amendment for immobilization of heavy metals in contaminated soils (Chen et al., 2011; Xu et al., 2013; Inyang et al., 2012). Use of biochar as a sorbent for treating wastewater containing heavy metals is an emerging and promising treatment technology (Ahmad et al., 2014). Biochars derived from plant residues and

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agricultural wastes have been tested for their abilities to sorb various heavy metals (Uchimiya et al., 2010, 2011). Biochar could potentially replace coal- and coconut shell-based activated carbons as a low cost adsorbent for contaminants. However, there is very limited knowledge of the effects of various biochars on metal adsorption processes (Chen et al., 2011). Furthermore, only limited information is available on the competitive adsorption of heavy metals. As heavy metal pollutants often coexist in wastewater and contaminated soil, their competitive sorption as well as the mobilities of single versus multiple heavy metal species have become a global concern (Uchimiya et al., 2011).

Heavy metal adsorption depends not only on biochar characteristics but also on the nature of the metals involved as well as their competitive behavior for biochar sorption sites. Usually, when competitive sorption of metals is compared with their monometal behavior, their adsorption is lower in competitive systems (Harter, 1992). Competitive adsorption of heavy metals has been indirectly assessed either by single sorbate ion or binary system experiments using synthetic minerals (Brummer et al., 1988) and soils (Harter, 1992). There are many studies on the competitive sorption and selectivity sequences of heavy metals using various sorbents (goethite, hydroxyapatite, etc.) and soils, although few studies have examined competitive sorption of heavy metals by biochar. Especially, competitive sorption of metals by sesame straw biochar (SSB) has never been reported previously. Our previous study has demonstrated that sesame straw biochar had an excellent phosphorus adsorption capacity with large surface area and pore volume (Park et al., 2015). Generally, the large surface area and pore volume of biochar can provide sufficient sorption sites available for sorption of contaminants including heavy metals.

The aim of this study was to evaluate the absorption behaviors of heavy metals in mono and multimetal forms by SSB in order to estimate the heavy metal adsorption capacity of biochar in natural environments. The specific objectives were: (1) to analyze raw feedstock and SSB characteristics, (2) to compare monometal and multimetal adsorption characteristics and patterns in a batch experiment, (3) to obtain the distribution coefficients and selectivity sequences for the monometal and multimetal adsorption of metals by biochar, (4) to compare the adsorption capacities of heavy metals in monometal and multimetal adsorption isotherms in the batch experiment using both Freundlich and Langmuir models, (5) to select the optimal adsorption model for exactly predicting the metal retention capacity of biochar, and (6) to develop three-dimensional simulation graphics using the data obtained from the adsorption experiment under single and competitive adsorption conditions in order to estimate the adsorption behaviors of heavy metals under different metal combination conditions in natural environments.

2. Materials and methods

2.1. Sesame straw pyrolysis for biochar production

Sesame straw was collected from a local agricultural field in Geochang-gun, South Korea, and used to produce biochar. A slow pyrolyzer (DK-1015(E), STI tech, Korea) was used to convert the samples into biochar under a limited oxygen conditions. SSB produced at 700 °C for 4 h in a stainless airtight container. Biochar produced by pyrolysis was gently crushed and sieved to <0.5 mm (see the Supporting Information (SI)).

2.2. Characterization of biochar

The pH, BET surface area, elemental composition (C, H, N, S, and O) and spectral properties of raw feedstock and biochar were measured. The details of analysis methods were supplied in the SI.

2.3. Characterization of heavy metal solutions

The following group of metals was used in the studies. Stock solutions (1000 mg L^{-1}) of Cd ($Cd(NO_3)_2 \cdot 4H_2O$), Cr ($Cr(NO_3)_3 \cdot 9H_2O$), Cu ($Cu(NO_3)_2 \cdot 2.5H_2O$), Pb ($Pb(NO_3)_2$), and Zn ($Zn(NO_3)_2 \cdot 6H_2O$) were prepared by dissolving exact quantities of respective salts (GR grade, Fisher Scientific, USA) in double distilled water.

2.4. Batch experiment

Both monometal and multimetal adsorption experiments were conducted to determine the adsorption characteristics of SSB for the heavy metals. Adsorption behaviors of the heavy metals by biochar were evaluated using both the Freundlich and Langmuir adsorption isotherm equations. Monometal adsorption isotherms of heavy metals were obtained by weighing 0.1 g of biochar from each test in glass Erlenmeyer flasks (3 replicates). Thereafter, 50 mL of solution containing specific concentrations of the metals was added to the flask.

Multimetal adsorption isotherms were determined by following the same procedure as the monometal experiment using the same concentration ratio for the selected heavy metals. For each heavy metal with or without biochar, concentration levels of 0, 2.5, 5, 10, 20, 40, 80, 160, and 320 mg L^{-1} were individually evaluated. The initial pH of the solutions were adjusted to 7 by adding either 0.1 M HCl or 0.1 M NaOH solutions. After providing sufficient time for the system to reach equilibrium, all samples were equilibrated for 24 h on a rotary shaker (KASI KSI-200L, Korea) at constant room temperature (25 °C). After settling, a 30 mL aliquot of the supernatant was filtered through a Whatman GF/C filter (0.45 μm) and then analyzed for metal concentrations. The concentrations of heavy metals in the monometal and multimetal adsorption experiments were determined using ICP–OES (Perkin Elmer Optima 4300 DV). The amount of metal adsorption by biochar was calculated from the concentration reduction in solution.

According to Alloway (1995), distribution coefficient (K_d) is a useful parameter for comparing the sorptive capacities of different soils or materials for any particular ion, when measured under the same experimental conditions. The distribution coefficients (K_d) were calculated according to Alloway (1995) (see the SI).

2.5. Adsorption models

Adsorption isotherms were determined using the Freundlich and Langmuir models. The details of Freundlich and Langmuir models were supplied in the SI.

2.6. Statistical analysis

Statistical analysis of data was conducted using SAS software (SAS 9.3, SAS Institute Inc. Cary, NC, USA) (see the SI).

3. Results and discussion

3.1. Characterization of biochar

Major raw feedstock and biochar characteristics were analyzed, and the results are shown in Table S1 (see the SI). The yield of biochar derived from sesame straw at 700 °C was 22.9%. The surface area and total pore volume of biochar were 289.2 m^2 g^{-1} and 0.0411 cm^3 g^{-1}, respectively. SSB had a pH of 10.1 as well as C, H, N, S, and O percentages of 72.6%, 2.1%, 2.9%, 0.42%, and 21.7%, respectively. The FTIR spectra for raw feedstocks and SSB