



Mechanisms of antimony adsorption onto soybean stover-derived biochar in aqueous solutions



Meththika Vithanage^{a, b}, Anushka Upamali Rajapaksha^{a, b}, Mahtab Ahmad^c,
Minori Uchimiya^d, Xiaomin Dou^e, Daniel S. Alessi^f, Yong Sik Ok^{a, *}

^a Korea Biochar Research Center, Kangwon National University, Chuncheon 200-701, Republic of Korea

^b Chemical and Environmental Systems Modeling Research Group, Institute of Fundamental Studies, Kandy, Sri Lanka

^c Soil Sciences Department, College of Food & Agricultural Sciences, King Saud University, P.O. Box 2460, Riyadh 11451, Saudi Arabia

^d Southern Regional Research Center, Agricultural Research Service, U.S. Department of Agriculture, 1100 Robert E. Lee Boulevard, New Orleans, LA 70124, United States

^e College of Environmental Science and Engineering, Beijing Forestry University, Beijing 100083, China

^f Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, AB T6G 2E3, Canada

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ABSTRACT

Limited mechanistic knowledge is available on the interaction of biochar with trace elements (Sb and As) that exist predominantly as oxoanions. Soybean stover biochars were produced at 300 °C (SBC300) and 700 °C (SBC700), and characterized by BET, Boehm titration, FT-IR, NMR and Raman spectroscopy. Bound protons were quantified by potentiometric titration, and two acidic sites were used to model biochar by the surface complexation modeling based on Boehm titration and NMR observations. The zero point of charge was observed at pH 7.20 and 7.75 for SBC300 and SBC700, respectively. Neither antimonate (Sb(V)) nor antimonite (Sb(III)) showed ionic strength dependency (0.1, 0.01 and 0.001 M NaNO₃), indicating inner sphere complexation. Greater adsorption of Sb(III) and Sb(V) was observed for SBC300 having higher –OH content than SBC700. Sb(III) removal (85%) was greater than Sb(V) removal (68%). Maximum adsorption density for Sb(III) was calculated as 1.88×10^{-6} mol m⁻². The Triple Layer Model (TLM) successfully described surface complexation of Sb onto soybean stover-derived biochar at pH 4–9, and suggested the formation of monodentate mononuclear and binuclear complexes. Spectroscopic investigations by Raman, FT-IR and XPS further confirmed strong chemisorptive binding of Sb to biochar surfaces.

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1. Introduction

Biochar is a heterogeneous carbon material comprised of a range of functional groups produced by the thermal alteration of organic materials. Biochar has recently received considerable interest as a soil amendment to control the distribution and bioavailability of organic and inorganic contaminants (Lehmann and Joseph, 2009). Biochar can be produced from a variety of waste biomass under different pyrolysis conditions, and are characterized by high carbon content and aromaticity (Sohi et al., 2009). The heterogeneous chemical

composition of biochar translates into complex surface chemistry: acidic to basic, and hydrophilic to hydrophobic (Amonette and Joseph, 2009). Biochar can be used as a sorbent to remove target contaminants such as toxic heavy metals in soil and water (Ahmad et al., 2014).

Recently, biochar has been shown to effectively mitigate the mobility, plant availability and toxicity of heavy metals in soils (Inyang et al., 2012; Shen et al., 2012; Uchimiya et al., 2012, 2010, 2011). Heavy metal ions are strongly bound to specific active sites containing acidic carboxyl groups and other functional groups such as amine, aromatic C–O groups, O-alkylated groups, and anomeric O–C–O carbons at the biochar surface (Fang et al., 2013; Li et al., 2013; Uchimiya et al., 2012; Yuan et al., 2011). Remediation of contaminated soils (e.g., shooting ranges, mining and smelting sites) with biochar can provide a cost-effective alternative to the conventional methods of soil washing and excavation (Lee et al., 2011). The sorption process may control the mobility of metals in these contaminated soils (Ahmad et al., 2012a,b; Uchimiya et al., 2011).

* Corresponding author. Tel.: +82 33 250 6443; fax: +82 33 241 6640. Department of Biological Environment, Kangwon National University, Chuncheon 200-701, Republic of Korea.

E-mail addresses: meththikavithanage@gmail.com (M. Vithanage), anushkaupamali@gmail.com (A.U. Rajapaksha), mah_tabee@yahoo.com (M. Ahmad), Sophie.Uchimiya@ARS.USDA.GOV (M. Uchimiya), alessi@ualberta.ca (D.S. Alessi), soilok@kangwon.ac.kr (Y.S. Ok).

Antimony (Sb) has become an element of growing concern worldwide (Leuz et al., 2006). Elevated aqueous Sb concentration is observed at mining areas, shooting ranges and along roadsides (Filella et al., 2002a). Antimony exists in various oxidation states (-III, 0, III, V) in the environment; the most common oxidation states are Sb(III) and Sb(V). Dominant Sb species in aqueous systems are $\text{Sb}(\text{OH})_3$ and $\text{Sb}(\text{OH})_5$ (Wilson et al., 2010). Similar to As, inorganic Sb compounds are found to be more toxic than the organic species, and of inorganic species, Sb(III) is more toxic than Sb(V) (Filella et al., 2002b). Antimony exposure may cause respiratory irritation, pneumoconiosis, antimony spots on the skin and gastrointestinal symptoms. In addition antimony trioxide is possibly carcinogenic to humans (Sundar and Chakravarty, 2010).

Very few sorption studies of Sb on natural sorbents have been reported to date (Filella et al., 2002b) although several studies have been conducted on adsorption of Sb onto pure mineral phases (Leuz et al., 2006). To our knowledge, biochar has not previously been used to remove Sb from aqueous solutions. Both Sb(III) and Sb(V) bind strongly on Fe and Mn hydroxides, and on clay minerals to a lesser extent; however, the binding mechanism is unclear (Leuz et al., 2006) and references therein). Surface complexation models are used to predict adsorption of metal ions onto a wide range of adsorbents over a fairly extensive set of conditions (Stumm and Morgan, 1996). Hence, this technique can provide parameters for a given adsorbent/adsorbate pair to understand the binding mechanisms.

The objective of this study was to elucidate the mechanisms of interaction between soybean stover-derived biochar (SBC) and Sb in aqueous systems. The experimental results were used to evaluate the feasibility of triple layer surface complexation model to predict sorption as a function of pH and ionic strength. A significant focus of this work was to develop a database of surface complexation modeling (SCM) parameters for SBC-Sb. Experimental and spectroscopic data were used to guide the selection of SCM reactions, and to estimate possible parameters to characterize the adsorption of Sb on SBC.

2. Materials and methods

2.1. Preparation of soybean stover-derived biochar

Air-dried soybean stover was ground and placed in a ceramic crucible covered with a lid and heated in a muffle furnace (MF 21GS, Jeio Tech. Korea). As reported previously (Ahmad et al., 2012a), a slow pyrolysis condition was employed at a 7°C min^{-1} heating rate. Feedstock was held at the peak temperatures (300 or 700 °C) for 3 h, and resulting biochar samples were allowed to cool to room temperature inside the furnace (Chen et al., 2008; Chun et al., 2004). All biochar samples were stored in air-tight containers. Hereafter soybean stover-derived biochar pyrolyzed at 300 and 700 °C are denoted as SBC300 and SBC700, respectively.

2.2. Potentiometric titration

Surface titration was conducted as detailed elsewhere (Vithanage et al., 2006). Briefly, 2 g biochar L^{-1} suspensions were prepared at three different ionic strengths set by NaNO_3 (0.1, 0.01 and 0.001 M). The biochar suspension was N_2 sparged for 1 h and then stirred overnight. The initial pH of the solid suspension was ~ 7.0 ; the pH decreased to 4.0 upon the addition of 0.96 M HNO_3 . Then the titration was carried out using an auto-titrator (Orion 960, Thermo Fisher, USA). Point of zero charge (pH_{zpc}) was calculated based on the equilibrium concentration of protonated and deprotonated surface species (Vithanage et al., 2006).

2.3. Boehm titration

Surface functional groups of SBC300 were determined using the Boehm titration method (Boehm et al., 1964; Goertzen et al., 2010). Details are given in the [Supplementary Materials](#).

2.4. Antimony sorption experiments

Antimony sorption experiments were conducted as a function of pH for soybean stover biomass, SBC300 and SBC700. Adsorption edge experiments were conducted for 5 g L^{-1} SBC300, with $\text{NaNO}_3/\text{KNO}_3$ (0.001, 0.01 and 0.1 M) as the background electrolyte. Sodium antimonite and potassium antimony tartrate stock solutions (1000 mg L^{-1}) were prepared daily. The biochar suspensions were N_2 sparged for 1 h, sealed, and then equilibrated by mixing for 12 h on an orbital shaker (SI-600R, Jeio Tech, Korea) at 100 rpm (25 °C). The pH of the solution was adjusted to 4.0 using 0.1 M HNO_3 before addition of Sb to yield final concentrations of 4.1 and 41 μM . The pH was then increased at 1.0 pH intervals up to pH 10.0 using 0.1 M NaOH, and at each point a 10 mL sample was taken in a polypropylene centrifuge tube. Samples were equilibrated in an orbital shaker (25 °C) for 6 h at 100 rpm on an orbital shaker. After the pH measurements, samples were centrifuged (4000 rpm, 10 min) and filtered (Millipore 0.45 μm). The filtrate was acidified for analysis using inductively coupled plasma optical emission spectrometer (ICP-OES, Optima 7300 DV, Perkin Elmer, USA).

Batch isotherm experiments were carried out at pH ~ 6.5 for SBC300. A suspension of SBC300 with 0.01 M ionic strength was pre-equilibrated for 12 h. Aliquots of the SBC300 suspensions (10 mL) were transferred to polypropylene tubes. The initial Sb concentrations were set to 4–205 μM . The tubes were equilibrated for 6 h at 100 rpm. After centrifugation, the supernatant was transferred through membrane filters (0.45 μm) for analysis using ICP-OES. The Langmuir and Freundlich equations were used for data fitting ([Supplementary materials](#)).

2.5. Surface complexation modeling

Surface complexation modeling was performed to determine the adsorption constants as a function of pH and Sb concentration conditions. A description of Sb sorption onto the SBC300 surface was modeled by calculating the sorption reaction equilibrium constants between the adsorbates and proton active surface functional groups on the adsorbent. This concept has been widely applied, mainly in the case of sorption of hydrated iron oxides and clay minerals (Stumm and Morgan, 1996). In this study, we used 2-pK generalized diffuse double layer model (DDLDM) and Triple Layer Model (TLM) to characterize interactions between sorbent (SBC300) and sorbate (Sb).

Various functional groups such as hydroxyl, carbonyl and carboxyl groups are the putative active sites responsible for sorption capacity of chars towards ionic adsorbates (Corapcioglu and Huang, 1987). The Sb, being a metalloid, is sorbed mainly by chemisorption (Xi et al., 2010). Our model was developed on the basis of experimental results: (a) the predominant surface functional groups are amphoteric; and (b) Sb will adsorb preferentially in neutral/acidic pH (positive surface charge). Additional adsorption sites with different reactivity may exist on the surface, however, we considered only phenolic and carboxylic sites for the DDLDM based on the Boehm titration data. The non-linear least squares optimization program, FITEQL (Herbelin and Westall, 1999) was used for the SCM of Sb. Three aqueous species, $\text{Sb}(\text{OH})_6^-$, $\text{Sb}(\text{OH})_3$ and $\text{Sb}(\text{OH})_4^-$ were considered for model calculations (Leuz et al., 2006), in metal solution phase reactions. The equilibrium constants used for the model are given below (Reactions 1–3) (Leuz et al., 2006):

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