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



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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 Jospeh, 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).

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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 Sb(OH)₃ and Sb(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 NaNO₃ (0.1, 0.01 and 0.001 M). The biochar suspension was N₂ 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 HNO₃. 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 NaNO₃/ KNO₃ (0.001, 0.01 and 0.1 M) as the background electrolyte. Sodium antimonite and potassium antimony tartrate stock solutions $(1000 \text{ mg } \text{L}^{-1})$ 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 HNO₃ before addition of Sb to yield final concentrations of 4.1 and 41 μ M. 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 μ m). 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 μ M. The tubes were equilibrated for 6 h at 100 rpm. After centrifugation, the supernatant was transferred through membrane filters (0.45 μ m) 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 2pK generalized diffuse double layer model (DDLM) 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 DDLM 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, $Sb(OH)_{6}^{-}$, $Sb(OH)_{3}$ and $Sb(OH)_{4}^{-}$ 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):

 $Sb(OH)_5 + H_2O \Leftrightarrow Sb(OH)_6^- + H^+ \quad \text{log } K = -2.7 \tag{R1}$

$$Sb(OH)_3 + H_2O \Leftrightarrow Sb(OH)_4^- + H^+ \quad \text{log } K = -11.82$$
 (R2)

$$Sb(OH)_2^+ + H_2O \Leftrightarrow Sb(OH)_3 + H^+ \quad \log K = -1.42$$
 (R3)

2.6. Surface complex formation

Our foremost aim of using SCM in this study was an accurate representation of the experimental data over all variations in the suspension composition. A small set of adjustable parameters was used due to the lack of equilibrium constant data on antimony adsorption. Both DDLM and TLM met these requirements well. Based on Boehm titration results, we modeled SBC300 surface as a set of ionizable functional groups that acquire charge through protonation and deprotonation (C_1 OH and C_2 OH).

For the amphoteric sites of the hydrated SBC300, surface reactions were written as follows (Reactions 4-5);

$$\equiv C_i OH + H^+ \Leftrightarrow \equiv C_i OH_2^+ \tag{R4}$$

$$\equiv C_i O H \Leftrightarrow \equiv C_i O^- + H^+ \tag{R5}$$

where C is the reactive surface active sites including graphitic carbon (Corapcioglu and Huang, 1987; Gabaldon et al., 1996). Based on these reactions, the surface titration data was optimized to calculate the surface protonation and deprotonation constants. The optimized surface area, protonation and deprotonation constants, and site density values obtained from potentiometric titration were used for optimization of Sb adsorption constants.

The TLM was used for modeling SBC300-Sb interaction due to the possibility of outer sphere complex formation. According to the concept of surface complex formation, the adsorption reactions between SBC300 and Sb were tested in many different combinations using monodentate mononuclear, binuclear and bidentate mono nuclear and binuclear, however, fitting was possible by the following expressions for antimonite (Reaction 6) and antimonate (Reaction 7):

$$(\equiv C_i)_2 OH + Sb(OH)_3 \Leftrightarrow (\equiv C_i)O - Sb(OH)_2^0 + H_2O$$
(R6)

$$\equiv C_i OH + Sb(OH)_6^- \Leftrightarrow \equiv C_i OSb(OH)_5^- + H_2 O$$
(R7)

2.7. Spectroscopic investigations

Antimony–SBC300 interface interactions were investigated using different spectroscopic techniques: FTIR, Raman and XPS. The FT-IR spectrograms of the vacuum dried SBC300 samples pellets prepared with fused-KBr were obtained using FT-IR spectrophotometer (Bio-Rad FTS 3000MX, USA) with a resolution of 1 cm⁻¹ between 4000 and 400 cm⁻¹. First derivatives of the FTIR spectra were obtained with 5-segment length Norris derivative smoothing technique. The spectra were analyzed using OMNIC version 7.3 software. The XPS spectra of the adsorbent before and after metal adsorption were recorded by a PHI Quantera spectrometer (USA). The binding energies were referenced to the C1s line at 284.8 eV.

3. Results and discussion

3.1. Surface properties of SBC300

Surface functional groups quantified by Boehm titration, BET surface area and other characteristics of SBC300 are given in Table 1.

Table 1

Properties of SBC300 used in FITEQL optimization.

Parameter	Value	Reference
Surface area	20.23 m ² g ⁻¹	This study
pH _{zpc} for SBC300	7.10	This study
pH _{zpc} for SBC700	7.75	This study
Surface functional groups from Boehm	titration data	
Total acidic groups	1884.82 μ mol g $^{-1}$	This study
Total basic groups	1614.87 μ mol g ⁻¹	This study
Carboxylic groups	199.35 µmol g ⁻¹	This study
Lactonic groups	230.92 μ mol g $^{-1}$	This study
Phenolic groups	1454.65 μ mol g ⁻¹	This study
Antimonate and antimonite protonation	on constants	
$Sb(OH)_5 + H_2O = Sb(OH)_6^- + H^+$	-2.7	(Baes and
		Mesmer, 1976)
$Sb(OH)_3 + H_2O = Sb(OH)_4^- + H^+$	-11.82	(Baes and
		Mesmer, 1976)
$Sb(OH)_{2}^{+} + H_{2}O = Sb(OH)_{3} + H^{+}$	-1.42	(Baes and
		Mesmer, 1976)

Potentiometric titration results (Figure S1) indicated that the SBC300 surface will be positively charged below pH 7.5 (point of zero charge, pH_{zpc}). Data from the potentiometric titrations were modeled to determine the intrinsic surface acidity constants (pKa) of SBC using the FITEQL fitting program. Computations were made for all three ionic strengths since no data have been previously reported for biochar. Figure S1 shows that experimental data are in high agreement with modeled data. Simulated pKa of Sb values are also given in Table 1.

The cross polarization ¹³C NMR spectrum of SBC300 was dominated by 2 peaks (Figure S2). The most prominent groups were aromatic C–H (126 ppm) and CH₃ groups (36 ppm). These bands at 126 and 36 ppm indicated that both aromatic and aliphatic carbons existed in biochar (Chun et al., 2004). Small peaks observed in the range of 160–190 ppm were attributed to phenolic and carboxyl groups (Braida et al., 2003). Few peaks were observed in the range of 190–225 ppm, indicating aromatic C–O and carbonyl (C=O and COO) groups (Braida et al., 2003).

3.2. Batch antimony adsorption experiments as a function of pH

Preliminary experiments demonstrated higher adsorption of Sb on SBC300 than raw soybean stover and SBC700 (Fig. 1a). This may be due to the higher surface area of SBC300 compared to the raw soybean stover, and the greater amount of –OH functional groups on SBC300 than SBC700 (Ahmad et al., 2012a). Furthermore, SBC300 contained 0.04% S that can facilitate the formation of water insoluble thioantimony species (Planer-Friedrich and Scheinost, 2011). Hence, SBC300 was used for further studies. The effect of pH and ionic strength on Sb retention on SBC300 is shown in Fig. 1b. The adsorption edges revealed a higher retention capability (>92%) of Sb(III) than Sb(V) at 4 µM. No pH dependency was observed for Sb(V) while Sb(III) adsorption was slightly parabolic, and reached the maximum adsorption around pH 6-7 (Fig. 1a). This difference in pH dependence clearly demonstrates the difference of adsorption behavior between Sb(V) and Sb(III). Antimonite is considered to be a stronger Lewis base, and hence, it can deprotonate sites at the SBC300 surface. In addition, the lower adsorption ratio of Sb(V) to SBC300 may have resulted from the large size of the Sb(V) molecules compared to those of Sb(III). Hence, the adsorption ability of Sb(V) is low compared to that of Sb(III).

No ionic strength dependency was observed, regardless of the initial Sb(III) concentration (4 and 40 μ M), suggesting an inner sphere complexation mechanism (Hayes et al., 1988). Similar observations were made for Sb(V) sorption on SBC300 (Fig. 1c).



Fig. 1. Variation of Sb(III) adsorption on raw biomass, SBC300 and SBC700 as a function of pH (a); adsorption based on pH and ionic strength at 4 and 40 μ mol L⁻¹ for SBC300 (b); and adsorption of Sb(III) and Sb(V) on SBC300 (c). Suspension density: 5 g L⁻¹. The lines represent TLM model calculations where the symbols illustrate experimental data for 0.1, 0.01, and 0.001 M ionic strength.

3.3. TLM modeling of Sb adsorption on biochar

In the proposed TLM in SCM, below the pH of metal precipitation, all antimony ions were assumed to be adsorbed by forming monodentate or bidentate complexes with SBC surface sites. As shown in Fig. 1b and c, modeling results of Sb(III) and Sb(V) fitted well with TLM, whereas weaker DDLM fits were observed at low concentrations (4.1–41 μ M). Calculated values of equilibrium concentrations are presented in Table 2. The goodness-of-fit was quantified by the overall variance (the weighted sum of squares of residuals divided by the degree of freedom, WSOS/df) and the standard deviation $\sigma_{\log K}$ for each adjustable parameter was provided in the FITEQL program. In Table 2, the WSOS/df values of 0.1 < V(Y) < 20 indicated a good fit (Herbelin and Westall, 1996).

Due to the steric hindrance, 1-1 complexes are used to describe metal ion binding by organic matter (Ravat et al., 2000). This study focused on the monodentate mononuclear complexes to model antimony sorption on SBC300; bidentate complexes were not considered. For antimonite adsorption, the addition of monodentate binuclear complexes improved model fits. The proton surface site concentrations and intrinsic surface acidity constants were maintained as they were in some cases, being slightly adjusted to enhance the fitting. Model predictions are represented as lines in Fig. 1b and c, and all the experimental data were reasonably well described by the TLM (Table 2). The intrinsic surface complexation constants, as calculated on the basis of inner sphere antimony adsorption at both phenolic and carboxylic groups of SBC300, are given in Table 2.

3.4. Effect of antimony loading on SBC300

Antimony sorption decreased as a function of initial concentration as shown in the constant pH isotherm plot (Fig. 2). The experimental data revealed that Sb(III) attained a sorption maximum at an initial Sb(III) concentration of 165 μ M. Similarly, Sb(V) showed a maximum adsorption around the same initial concentration as in the case of Sb(III), but beyond that formation of multilayer complexation was depicted on the SBC surface. When

Table 2

Optimized FITEQL results from potentiometric titration and adsorption edges.

Surface complexation reactions					0.1 M	0.01 M	0.001 M	Weighted mean ^a
Surface sites used for FITEQL optimization $\equiv C_1 OH \equiv C_2 OH$					$\begin{array}{c} 1.002 \times 10^{-3} \\ 1.168 \times 10^{-3} \end{array}$	$\begin{array}{l} 9.946 \times 10^{-3} \\ 1.644 \times 10^{-3} \end{array}$	$\begin{array}{l} 5.411 \times 10^{-4} \\ 1.291 \times 10^{-3} \end{array}$	$\begin{array}{l} 3.173 \times 10^{-3} \\ 1.320 \times 10^{-3} \end{array}$
	Protonantion constants				Dissociation con	istants		
	0.1 M	0.01 M	0.001 M	Weighted mean ^a	0.1 M	0.01 M	0.001 M	Weighted mean ^a
$=C_1 OH$ =C_2 OH	9.599 13.78	9.559 13.84	10.866 14.47	5.497 14.190	-1.122 -7.220	-1.148 -7.148	-1.261 -7.261	-3.611 -3.743
For surface sites Antimonate adsorption constants					0.1 M	0.01 M	0.001 M	Weighted mean ^a
Monodentate mononuclear reactions $ \equiv C_1 OH + Sb(OH)_{\overline{6}}^- \rightarrow \equiv COSb(OH)_{\overline{5}}^- + H_2 O$ $ \equiv C_2 OH + Sb(OH)_{\overline{6}}^- \rightarrow \equiv COSb(OH)_{\overline{5}}^- + H_2 O$ Antimonite adsorption constants	4 μΜ				1.142 4.700 40 μM	0.814 4.694	0.578 4.735	0.821 4.707
	0.1 M	0.01 M	0.001 M	Weighted mean ^a	0.1 M	0.01 M	0.001 M	Weighted mean ^a
$\begin{array}{l} \text{Monodentate binuclear reactions} \\ (\equiv\!C_1)_2\text{OH} + \text{Sb}(\text{OH})_3 \!\rightarrow\! (\equiv\!C_1)\text{O} - \text{O} - \text{Sb}(\text{OH})_2^0 + \text{H}_2\text{O} \\ (\equiv\!C_2)_2\text{OH} + \text{Sb}(\text{OH})_3 \!\rightarrow\! (\equiv\!C_2)\text{O} - \text{O} - \text{Sb}(\text{OH})_2^0 + \text{H}_2\text{O} \end{array}$	1.375 12.66	1.320 12.47	2.648 12.98	9.354 0.934	1.287 17.75	1.287 17.75	1.911 16.75	0.310 5.276

^a Weighted averages were calculated from logK = Σwi (logK)*i*, where $wi = (1/\sigma \log K)i/(\Sigma(1/\sigma \log K)i$, where $\sigma \log K$ is the standard deviation obtained from FITEQL calculations.



Fig. 2. Adsorption isotherms for Sb on SBC300 at 0.01 M NaNO₃ at pH = 5.0. The symbols show the experimental results and the solid line represents the calculated results using non-linear least square fit. The continuous line is attributed to Langmuir adsorption isotherm for Sb(III) and Sb(V) species at 0.01 M NaNO₃, while short dashes represent the Freundlich fit for Sb(V)–SBC300 interaction at 0.01 M NaNO₃.

the level of solution ions increases, the adsorbed amount increases, however, the monolayer capacity corresponding to complete surface coverage can be reached in some cases. Depending on the surface and the adsorbing ion, adsorption beyond monolayer formation can take place in the form of condensation of multi-layers, which is equivalent to surface precipitation or to the development of a three dimensional phase. This was observed from the experimental data and fitting of the Sb(V) isotherm to Langmuir and Freundlich models (Fig. 2).

The measured isotherm fitting for Sb(V) with a simple Langmuir equation fit was not successful. The disagreement at the higher concentrations was probably caused by the surface precipitation reaction occurring in those regions. However, the calculated values agreed well, when we add two Langmuir equations for two different sections (Ishiguro et al., 2006). It represents the sum of the adsorption at both the stronger and weaker adsorption sites in multilayer formation. The constants k_f and n were calculated from Freundlich adsorption isotherm (Table 3). The value of n below unity (0.78) implies a favorable chemisorption process for the Sb(V) adsorption.

3.5. Spectroscopic investigations of Sb adsorption

Raman spectroscopic investigations were conducted for SBC300 using G and D bands where the G band at 1590 cm⁻¹ mainly represents aromatic ring system vibration and the D band at 1300 cm⁻¹ represents defect structures in the highly ordered

Table 3 Isotherm constants for Sb(III) and Sb(V) adsorption on SBC300 at pH 6.0.

Isotherm constants							
Freundlic	1	$k_f ((\text{mol } \text{m}^{-2})/((\text{mol } \text{dm}^{-3})^n))$	Ν	R ²			
Sb(V)		5.37×10^{-3}	0.78	0.95			
Langmuir	$I'_{max1} \pmod{m^{-2}}$	$K_{L1} ({\rm dm^3}{ m mol^{-1}})$	$I'_{max2} (mol \ m^{-2})$	$K_{L2} ({\rm dm^3}{ m mol^{-1}})$			
Sb(V) Sb(III)	$\begin{array}{l} 1.74 \times 10^{-6} \\ 1.88 \times 10^{-6} \end{array}$	$\begin{array}{l} 6.26 \times 10^4 \\ 2.12 \times 10^5 \end{array}$	1.00×10^{-5}	5.64×10^3			

aromatics with not less than 6 rings (Kim et al., 2011) (Fig. 3). However, the resulting spectrum showed two broad bands in the areas of 1500–1660 cm⁻¹ and 1000–1500 cm⁻¹. The overlap between the D and G bands has been deconvoluted into two pseudosub bands (data not shown) at 1617 and 1422 cm⁻¹. The band at 1422 cm⁻¹ represents –CH₃ groups (Kim et al., 2011). It is likely that the band at 1617 cm⁻¹ is due to the aromatic ring breathing of C=C (carbonyl group), for rings containing more than two fused aromatic rings, as observed by Kim et al. (2011) for pine wood and switch grass biochars, as typical structures in amorphous carbon (Chen et al., 2008). Hence, the bands observed from the Raman spectroscopy can be assigned to cellulose, hemi-cellulose and lignin derived from undecomposed carbonaceous materials.

Only slight changes were observed in Raman spectra after Sb sorption to the SBC300 (Fig. 3). The two broad bands recorded at 1617 and 1422 cm⁻¹ showed a slight shift after Sb(III) and Sb(V) adsorption. Interestingly the shifts were opposite to each other, in that the carbonyl group exhibited a red shift while the $-CH_3$ band exhibited a blue shift at 1422 cm⁻¹. The red shift was high at Sb(V)-SBC300, while the blue shift was higher for Sb(III)-SBC300.

The FT-IR spectra of SBC300 are shown in Fig. 4a. The appearance of a broad band at the 3500 cm⁻¹ region of the spectrum is attributed to -OH functional groups, indicating the presence of tightly bound water molecules in SBC300. No band appeared near to 1630 cm⁻¹, which indicates that there was no physically sorbed water on the sorbent. Major bands found in all 3 spectra around 3382, 2924 and 1595 cm⁻¹ are attributed to H – bonded OH, CH₃ – stretch and C=O stretch (Schnitzer et al., 2007). Small peaks at 3775–3640 cm⁻¹ are possibly due to free and bonded NH in SBC samples (Schnitzer et al., 2007). Another broad band was observed in the 1500–1000 cm⁻¹ region, and it may be due to the extensive overlapping of individual bands. The bands can be assigned to carboxylic stretch, C=C, C=O and C–O stretching vibrations in 1700–1200 cm⁻¹ region (Kim et al., 2011).

To better understand Sb adsorption affinity to individual surface functional groups of SBC300 FT-IR analysis was conducted by first derivatives (with 5-segment length Norris derivative smoothing) for Sb(III) and Sb(V) adsorbed SBC, as shown in Fig. 4b, and c. After the treatment of SBC300 with Sb(III), the appearance and disappearance of some peaks was observed, while for Sb(V), treatment



Fig. 3. Raman spectra at 532 nm of SBC300 before and after antimony adsorption.



Fig. 4. Diffuse-reflectance FT-IR spectra of SBC300 and the first derivative of 3 spectra of SBC300, before and after adsorption of Sb(III) and Sb(V).



Fig. 5. XPS spectra of Sb(V) and Sb(III) adsorbed on SBC300 samples.

induced a new visible band formation (2300–1800 cm⁻¹). Similarly, the appearance of broad bands in the metal oxide region (700–400 cm⁻¹) for both Sb(III) and Sb(V) treated SBC300 indicated inner sphere bond formation on the SBC300 surface. Bands at 2910 and 2840 cm⁻¹ (aliphatic C–H stretching of CH₃ and CH₂ groups respectively), show an increase in –H bonding after Sb sorption. The band at 780 cm⁻¹ is assigned as the –OH vibration (McComb et al., 2007). Chemisorption of Sb(III) and Sb(V) likely influences the frequencies of the –OH related adsorptions, and this is evident by the wavenumber shifting and increase of absorbance.

XPS spectra of Sb(V) and Sb(III) adsorbed on SBC300 are shown in Fig. 5. From the results, it can be seen that $Sb3d_{3/2}$ peaks appeared after Sb(V) and Sb(III) adsorption on the surface of SBC300, and Sb(V) showed a stronger binding affinity than Sb(III) to the surface groups from the more intense $Sb3d_{3/2}$ peaks for Sb(V). This could be due to the precipitation of Sb(V) on SBC surface. This was also evidenced from the results of the isotherm study (Fig. 2).

4. Conclusions

This study evidenced that biochar produced from soybean stover at a low pyrolysis temperature (300 °C) was able to bind both antimonite and antimonate strongly. With a lower affinity, antimonate was also absorbed well to the SBC forming inner-sphere complexes similar to that of antimonite. Both monodentate mononuclear and binuclear complexes are predicted as mechanisms of antimony adsorption on SBC300 using a triple layer model surface complexation approach. Antimony adsorption by low temperature SBC may act as a potential candidate to clean mine waste water or storm water through shooting ranges, depending on the antimony concentration and speciation.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jenvman.2014.11.005.

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