RESEARCH ARTICLE

Acid-activated biochar increased sulfamethazine retention in soils

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Received: 14 March 2014 / Accepted: 10 August 2014 © Springer-Verlag Berlin Heidelberg 2014

Abstract Sulfamethazine (SMZ) is an ionizable and highly mobile antibiotic which is frequently found in soil and water environments. We investigated the sorption of SMZ onto soils amended with biochars (BCs) at varying pH and contact time. Invasive plants were pyrolyzed at 700 °C and were further activated with 30 % sulfuric (SBBC) and oxalic (OBBC) acids. The sorption rate of SMZ onto SBBC and OBBC was pronouncedly pH dependent and was decreased significantly when the values of soil pH increased from 3 to 5. Modeled effective sorption coefficients ($K_{D,eff}$) values indicated excellent sorption on SBBC-treated loamy sand and sandy loam soils for 229 and 183 L/kg, respectively. On the other hand, the low sorption values were determined for OBBC- and BBC700-treated loamy sand and sandy loam soils. Kinetic modeling demonstrated that the pseudo second order model was the best followed by intra-particle diffusion and the Elovich model, indicating that multiple processes govern

Responsible editor: Zhihong Xu

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SMZ sorption. These findings were also supported by sorption edge experiments based on BC characteristics. Chemisorption onto protonated and ligand containing functional groups of the BC surface, and diffusion in macro-, meso-, and micro-pores of the acid-activated BCs are the proposed mechanisms of SMZ retention in soils. Calculated and experimental q_e (amount adsorbed per kg of the adsorbent at equilibrium) values were well fitted to the pseudo second order model, and the predicted maximum equilibrium concentration of SBBC for loamy sand soils was 182 mg/kg. Overall, SBBC represents a suitable soil amendment because of its high sorption rate of SMZ in soils.

Keywords Emerging contaminant · Charcoal · Black carbon · Amendment · Pharmaceuticals · Activated carbon

Introduction

Antibiotics are increasingly prevalent environmental pollutants (Boxall 2012). Its elevated concentrations are being observed in the environment in many parts of the world, with particular attention being focused on soil, water, and plants (Kim et al. 2011; Ok et al. 2011). Veterinary medicines and their metabolites are released into soils, directly from animals and indirectly from manure or slurry as a fertilizer (Boxall et al. 2004) and leachate near animal carcass sites in special cases. Many studies have reported the release of diverse antibiotics into soil and groundwater in many countries around the world, including Germany, Denmark, USA, Korea, China, Vietnam, etc. (Kwon et al. 2011; Ok et al. 2011; Gao et al. 2012; Awad et al. 2013a). Excessive antibiotic presence in the environment may lead to the development of antibiotic-resistant microorganisms (Heuer and Smalla 2007).

Once antibiotics are released into soil or water systems, they may be degraded by biological, physical, or chemical processes, adsorbed to soil particles, taken up by plants, leached to groundwater, or transported to surface waters through runoff and drainage water (Kim et al. 2010b). The extent to which any of these processes happen depends on the properties of the soil, characteristics of the compound, and climatic and environmental conditions. Among many different veterinary antibiotics which are in common usages, sulfonamides, i.e., sulfamethazine (SMZ), have been frequently reported in high concentration (García-Galán et al. 2010; Kim et al. 2011; Li et al. 2012). Especially, sulfonamides are considered to be nonreactive with the mineral matrix of soils and, hence, quite mobile in the environment. Although extensive research has been conducted on the sorption of different SMZ compounds into soils, results have shown that sorption behavior varies widely in different soil types. These differences in the sorption of sulfonamides in soils were not well explained by variations in soil organic carbon levels or soil mineral matrices, but were better explained by the polar nature of the sulfonamides (Thiele-Bruhn et al. 2004; Kurwadkar et al. 2007; Teixidó et al. 2011).

A broad variety of sorptive surfaces has been investigated in the recent past, many of which focused on the retention of SMZ, due largely to its mobility in the environment. It has been revealed that pH, ionic speciation, and soil organic carbon (SOC) may influence the sorption of sulfonamides to soils (Kahle and Stamm 2007; Richter et al. 2009; Kim et al. 2010a). However, the adsorption observed by various soils remained low. Biochar (BC) produced by the thermal decomposition of the carbon-rich biomass has enormous potential as a sorbent for organic contaminants (Tsang et al. 2007; Ahmad et al. 2012b, 2013b, d; Awad et al. 2012, 2013b; Almaroai et al. 2014). The few studies that explored the effects of BC in soil systems with respect to antibiotics have shown a high sorption capacity of BC, which is dependent on the temperature and feedstock used in black carbon production as well as on the ionic speciation of sulfonamides (Teixidó et al. 2011; Rajapaksha et al. 2014; Yao et al. 2012).

Many invasive plants are ecologically problematic; therefore, it should be eliminated from the environment. These invasive plants can be a valuable source of biomass for BC production, and this practice may be an economically viable operation (Ahmad et al. 2013c). Burcucumber, *Sicyos angulatus* L., is one of the wide-spread invasive plants in Korea and the worst invasive alien species (Kil et al. 2006). Burcucumber plant has impacted agriculture as well as natural ecosystems and presents a serious threat to biodiversity. Hence, the Ministry of Environment in Korea has adopted many regulations controlling burcucumber, including the encouragement of the general public to eliminate. As antibiotic pollution is widespread in Korea (Kim et al. 2011, 2012), our attention has been drawn to the adsorption kinetics of SMZ in soils treated with burcucumber BC. Currently, little information exists in literatures on approaches for using BC production as a method of adding economic viability to the widespread harvesting of such invasive species. Acid activation of activated carbon and BC has promised better removal rate of different pollutants by adsorption mechanisms because of a relatively high surface area obtained from protonation of surface sites (Soleimani and Kaghazchi 2007; Uchimiya et al. 2012). Although few studies have shown that the sulfuric and oxalic activation enhance sorption of pollutants through ligand- and proton-promoted processes (Sewwandi et al. 2012; ShamsiJazevi and Kaghazchi 2010), the BCs activated with sulfuric or oxalic acids have not been employed. No data is available on the kinetics of veterinary antibiotics sorption within BC-treated soil systems. It has been studied for the pure mineral phases (Kahle and Stamm 2007). Also, no reports on the distribution coefficients and pH effects of acid-activated BC for antibiotic retention in soils have been identified. Acid activation has been shown to have a potential for enhancing the adsorption capacities of BCs for different pollutants (Liu et al. 2008; Choppala et al. 2012). Regarding the frequent use and detection of SMZ as well as its mobility, our focus was to examine the effect of pH on speciation and distribution coefficients as well as kinetic aspects of SMZ retention in soils treated with burcucumber-derived biochar (BBC). The potential of acid-activated BBC for enhanced SMZ sorption was also evaluated.

Materials and methods

Soil and biochar preparation

Two soils were collected from agricultural fields in Bonghwagun, Gyeongsangbuk-do Province, and Jeongseon-gun, Gangwon Province, Korea. The soils were sieved through a 2-mm mesh, dried in an oven overnight, and sealed in an airtight container prior to use. The general physicochemical characteristics of the soils were tested based on standard methods. Burcucumber plants were collected and air-dried under the strong sunshine, and then in an oven at 60 °C for 24 h. The dried shoots were crushed and ground to <1.0-mm particle size. This biomass was then pyrolyzed at 300 and 700 °C in a muffle furnace under no air supply, resulting in slow pyrolysis (Ahmad et al. 2012a). Biomass was heated at a rate of 7 °C/min and a holding time of 2 h for the complete carbonization. The BBCs produced at 300 (BBC300) and 700 °C (BBC700) were allowed to cool inside the furnace overnight. The BBCs were then crushed and sieved, yielding a uniform 2-mm-size fraction. The pure SMZ was purchased from Fluka Analytical Ltd., and all other chemicals were also achieved from Sigma-Aldrich as analytical reagents.

Activation of biochar

Acid activation of BBC700 was done using 30 % sulfuric and oxalic acids. Sulfuric acid is a diprotic acid which can be effective in terms of H^+ activity, whereas oxalic acid is high in ligand activities (Rajapaksha et al. 2012). The 5 g of BBC700 was mixed with 100 mL of 30 % sulfuric (SBBC) or oxalic (OBBC) acids and shaken for 4 h using an orbital shaker. The SBBC and OBBC were filtered and washed thoroughly with distilled water five times, and then were dried using a fan oven at 40 °C.

Soil and biochar characterization

Soil pH and electrical conductivity (EC) were determined in a 1:5 soil/water suspension (w/v) using deionized water, whereas soil organic matter was determined using the loss-onignition method (Sparks 1996). The standard textural classification guide was adopted from the U.S. Department of Agriculture, Soils, and Agricultural Engineering (USDA). The results of soil characterization are presented in Table 1. The elemental composition (C, H, N, S, and O) of BCs was determined using an elemental analyzer (Flash EA 1112 series, CE Instruments, UK). The surface physical morphology was examined using a field emission scanning electron microscope (FE-SEM) equipped with an energy dispersive spectrometer (SU8000, Hitachi, Tokyo, Japan).

Batch sorption experiments

The sorption of SMZ in two soil types was determined by procedures of the Organization for Economic Co-operation and Development (OECD) Test Guideline 106 (OECD 2000) at four different pH values of 3, 5, 7, and 9 under ammonium phosphate and ammonium acetate-buffered conditions (Richter et al. 2009). Experiments were conducted to calculate solid-water distribution coefficients (K_d). All samples were treated with 10 mg/L SMZ in 50 g/L soil. Kinetic experiments were conducted at pH 5 and

using acetic buffer, as it is most appropriate for soil environments. Experiments were carried out for bare soils, 2 % BBC700 (w/w), and acid-treated BBC700 with a similar w/w ratio to that of all BC soil mixtures at room temperature (25 °C). The mixtures were shaken in an incubator shaker at 100 rpm for 24 h. For the kinetics study, samples were taken at appointed times and were filtered through Whatman 0.45-µm PVDF disposable filters and collected in Agilent amber color vials prior to high-performance liquid chromatography (HPLC) analysis. SMZ concentrations in samples were determined using a HPLC system (SCL-10A, Shimadzu, Tokyo, Japan) equipped with an auto-sampler (SIL-10AD, Shimadzu) and a UV-VIS detector (SPD-10A, Shimadzu). A reverse-phase Sunfire C18 column (4.6 mm×250 mm, Waters, USA) was employed in a column oven (CTO-10AS; Shimadzu, Japan). The mobile phase A was composed of HPLC grade water and formic acid (99.9:0.1 v/v), while mobile phase B was HPLC grade acetonitrile and formic acid (99.9:0.1 v/v). Mobile phase A of 70 % together with 30 % mobile phase B was then maintained for 20 min. The absorbance was measured at 265 nm.

Solid-water distribution coefficients

Effective sorption coefficients ($K_{D,eff}$) and individual K_D values were simulated for cationic, anionic, and zwitterionic species for soil-BC systems and were calculated through experimental data. The proportions of speciated forms (cationic, anionic, and neutral species) of SMZ were calculated as a function of pH and pKa values (Eqs. 1, 2, and 3; Kurwadkar et al. 2007):

$$\alpha_0 = \frac{1}{1 + 10^{(pH-pK_1)} + 10^{(2pH-pK_1-pK_2)}} \tag{1}$$

$$\alpha_1 = \frac{1}{1 + 10^{(pK_1 - pH)} + 10^{(pH - pK_2)}}$$
(2)

$$\alpha_2 = \frac{1}{1 + 10^{(pK_2 - pH)} + 10^{(pK_1 + pK_2 - 2pH)}}$$
(3)

Table 1 Selected physiochemical properties of soil

Soil sample	рН ^а	EC dS/m	CEC ^b cmol/kg	Sand %	Silt %	Clay %	TC ^c %	TN ^d %	Avail. P ₂ O ₅ mg/kg	SOM ^e g/kg	SOC ^f g/kg	DOC ^g mg/kg
Loamy sand soil (S1)	5.95	24.3	2.07	84.1	6.2	9.7	0.28	0.02	23	4.33	7.46	61
Sandy loam soil (S2)	6.38	35.9	2.34	64.1	26.1	9.8	4.68	0.11	579	29.4	50.8	207

a 1:5 soil/water ratio

^b Cation exchangeable capacity

^c Total carbon

^d Total nitrogen

e Soil organic matter

^fSoil organic carbon

g Dissolved organic carbon

where pK_1 and pK_2 are kept as 2.07 and 7.49, respectively and α_0 , α_1 , and α_2 represent fractions of cationic, anionic, and neutral species, respectively (Qiang and Adams 2004).

Individual sorption coefficients for different forms (cationic, neutral, and anionic) of SMZ were determined using nonlinear regression analysis of experimental versus modeled weighted averages of $K_{D,eff}$ (below), where K_{D0} , K_{D1} , and K_{D2} values were calculated using Microsoft Excel 2007 according to Eq. 4 (Kurwadkar et al. 2007):

$$K_{\rm D,eff} = K_{\rm D0}\alpha_0 + K_{\rm D1}\alpha_1 + K_{\rm D2}\alpha_2 \tag{4}$$

where K_{D0} , K_{D1} , and K_{D2} represent individual K_D values for the different SMZ forms.

Kinetic models

Various kinetic models were used to investigate the sorption mechanism of SMZ on soils and BCs. The pseudo first order equation (also known as the Lagergren equation) can be written as follows, assuming nondissociating molecular adsorption (Lagergren 1898; Naiya et al. 2009):

$$\frac{dq}{dt} = k_1(q_e - q_t) \tag{5}$$

where q_t is an amount adsorbed per kilogram of adsorbent at time t (mg/kg), q_e is an amount adsorbed per kilogram of the adsorbent at equilibrium (mg/kg), k_1 is Lagergren rate constant (h⁻¹), and t is time (h).

The integrated form of Eq. 5 can be written as below:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$$
(6)

The kinetic parameters as well as correlation coefficient (R^2) and chi square (χ^2) were obtained from the plot $\log(q_e - q_t)$ vs *t*. Eq. 6 was used for data fitting. The pseudo second order adsorption kinetic rate equation is based on the assumption of chemisorption of the adsorbate on the adsorbents and is expressed as below (Ho and McKay 1999; Ahmad et al. 2013a):

$$\frac{dq}{dt} = k_s (q_e - q_t)^2 \tag{7}$$

where q_t is an amount adsorbed per kilogram of adsorbent at time t (mg/kg), q_e is an amount adsorb per kilogram of the adsorbent at equilibrium (mg/kg), k_s is a pseudo second order constant (kg/mg h), and t is time (h). The integrated form of the above equation becomes (Eq. 8):

$$\frac{t}{q_t} = \frac{1}{k_s q_e^2} + \frac{t}{q_e} \tag{8}$$

The initial sorption rate, $h \pmod{kg}$ h), as $t \rightarrow 0$ can be defined as in Eq. 9 (Ho and Ofomaja 2005):

$$h = k_{\rm s} q_e^{-2} \tag{9}$$

A process is diffusion-controlled if its rate is dependent upon the rate at which components diffuse towards one another, and this process was explored by the intra-particle diffusion model (Eq. 10) (Srivastava et al. 2006):

$$q_t = k_{\rm id} t^{1/2} + C \tag{10}$$

where q_t is mass adsorbed per kilogram of adsorbent at time *t* (mg/kg), k_{id} is an intra-particle diffusion rate constant (mg/kg h^{1/2}), and *C* is boundary layer effect (mg/kg). Different kinetic parameters obtained for different models are listed in Table 4.

The Elovich equation can be expressed as Eq. 11 (Almaroai et al. 2012):

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \left(\frac{1}{\beta}\right) \ln t \tag{11}$$

where α is the initial sorption rate (in mg/kg h) and β is the sorption constant.

Results and discussion

Characteristics of soils and biochars

Soils were categorized as loamy sand (soil 1) and sandy loam (soil 2) based on their textures. The physicochemical characteristics of soils are presented in Table 1. In the case of biomass and BCs, the ultimate analysis provides composition of C, H, and O as well as S and N. The physicochemical characteristics and elemental data for BBC700 and acid-activated BCs (i.e., SBBC and OBBC) have been reported in Table 2. In general, the pH of the BBC700 was much higher than other BCs mainly due to the separation of alkali salts from the organic matrix (Shinogi and Kanri 2003).

Molar ratios of elements were calculated to estimate the aromaticity (H/C) and polarity (O/C) of the BCs (Uchimiya

Sample	pH (1:5)	Ultimate	analysis ^a					BET surface area (m^2/q)	BJH adsorption pore volume (cm^3/q)
		С	0	Н	Ν	H/C	O/C	area (III /g)	volume (em /g)
Biomass	8.45	43.37	46.81	6.12	3.26	1.68	0.81	2.28	0.0062
BBC700 ^b	12.56	78.07	14.66	2.48	4.78	0.38	0.14	2.31	0.0084
SBBC ^c	5.04	65.65	22.56	2.73	4.40	0.49	0.26	571	0.1338
OBBC ^d	5.65	60.76	32.09	3.65	3.49	0.72	0.39	411	0.1180

Table 2 Characteristics of burcucumber biomass and different BBCs

^a Moisture and ash free basis

^b Burcucumber biochar produced at 700 °C

^c Burcucumber biochar produced at 700 °C activated with sulfuric acid

^d Burcucumber biochar produced at 700 °C activated with oxalic acid

et al. 2010). Noticeably, lower molar ratios were obtained in BCs produced at the higher temperature. The molar H/C ratios of BBC700, SBBC, and OBBC were 0.38, 0.49, and 0.72, respectively. Indirect information on the bonding arrangement of C to protons connected through -OH groups may be obtained based on the molar ratios of H/C (Knicker et al. 2005). The OBBC showed an increase in H and O (Table 2). Oxidation of BBC700 by oxidizing agents such as sulfuric acid and oxalic acid may have added oxygen containing surface functional groups to the BC surface. This could be the reason behind the increase of oxygen percentage and H/C and O/C ratio in acid-activated BCs. An increase in the H/C ratio with acid activation may be attributed to a reduction of carbonization and aromaticity. A considerable increase in the molar O/C and H/C ratios of OBBC indicates a decrease in hydrophobicity (Chun et al. 2004). The effects of acid activation were observed from the BET and pore volume data (Table 2). An extensive increase in the BET surface area and pore volume was observed in acid-activated BCs compared to those of both the untreated biomass and BBC700. The surface area was increasing 205- to 285-fold whereas pore volume was increasing only 19-fold. This phenomenon may be explained by the oxidation of ashes (Uchimiya et al. 2012).

Scanning electron microscopic (SEM) images showed the morphological and physical changes in BCs produced at the high temperature (Fig. 1). Oxidized ashes were observed, especially in the case of OBBC (Fig. 1d) after acid activation.

Speciation and distribution coefficients

Sorption edge experimental results demonstrated that the adsorption was higher at lower pH values and decreased with increasing pH in all types of BCs (Fig. 2). A considerably high sorption was observed in both soils treated with acid-activated BCs compared to soils treated with BBC700. This may be due to the development of protonated and ligand-containing surface functional groups and increase in the surface areas as well as the formation of amorphous carbon at the BC surface by acid (Toles et al. 1999). About 30 and 50 % decreases of sorption were observed with the increase of pH from 3 to 9 for loamy sand and sandy loam soils, respectively (Fig. 2a, b). However, still with buffers, pH of the BBC700-treated soils showed high pH values (pH 6 for pH 3 buffer) whereas control soil and acid-activated BBC-treated soils showed no change in pHs. This decrease was more prominent in sandy loam soil, which may be due to the complexation of SMZ with high DOC or phosphates in the soil (Table 1), which is through van der Waals bonding, and release of this physisorbed SMZ may occur to a greater degree at lower soil pH values (Haham et al. 2012).

In order to obtain quantitative estimates of species-specific sorption with pH, experimental data were fitted with Eq. 1, incorporating experimental $K_{\rm D}$ values. Beforehand, the relative contributions of each proportion of the speciated forms were calculated based on Eqs. 2–5. Table 3 reports the $K_{\rm D}$ values calculated by multiple regression analysis. The dependence of $K_{\rm D}$ values with the changes in pH for loamy sand and sandy loam soils treated with BBC700 and acid-activated BBC are plotted in Fig. 3. Sorption of SMZ greatly increased as the pH of the aqueous phase decreased for the pH range and soils investigated due to the ionic speciation of SMZ. At pH 3, a high sorption of SMZ may be primarily due to cation exchange process of dominant cationic forms as well as the sorption of zwitterionic forms. From pH 5 to 7, the dominant zwitterionic species in aqueous media play major roles in sorption (Gao and Pedersen 2005; Kahle and Stamm 2007; Kurwadkar et al. 2007). With the increase of pH, low $K_{\rm D}$ values may be attributed to the dominant anionic species of the SMZ.

In past studies, it has been observed that both SMZ^+ and SMZ^0 , which are dominant in the low pH values, are responsible for sorption, the inclusion of anionic species does not improve model fitting, and also, zwitterionic forms have been excluded from many models (Gao and Pedersen 2005; Kahle and Stamm 2007). However, our modeling attempt demonstrated that all three species are responsible for the sorption of



Fig. 1 Scanning electron micrographs showing morphological and physical changes due to temperature and acid activation of biochars produced from burcucumber. (a) BBC300. (b) BBC700. (c) Sulfuric acid-activated BBC700 (SBBC). (d) Oxalic-acid-activated BBC700 (OBBC)

SMZ in BC-treated soils, based on the approach supported by recent studies (Kurwadkar et al. 2007; Teixidó et al. 2011).

Data showed a significant correlation (α =0.01) between the experimental and simulated data for $K_{\rm D}$. Our results can be



Fig. 2 Adsorption edges of SMZ in (a) loamy sand and (b) sandy loam soils treated in different biochars. The concentration of SMZ used in these experiments was 10 mg/L, as applied to a 50 g/L soil solution

Sample	pH range	K_{D0}	K_{D1}	K_{D2}	$K_{D,eff}$ at pH 3
			L/k	g	
S1a+BBC700b	3.10-9.02	390.239	31.104	19.866	68.861
S1+SBBC ^c	2.91-9.11	943.525	93.627	19.306	229.371
S1+OBBC ^d	2.94-9.04	194.965	51.433	13.070	137.187
S2e+BBC700	3.03-9.16	390.239	31.104	19.866	50.448
S2+SBBC	2.99-9.01	1006.233	138.104	34.149	182.987
S2+OBBC	3.01-9.20	716.568	69.119	12.599	66.522

Table 3 Simulated batch sorption coefficients for cationic, zwitterionic and anionic forms of SMZ

^a Loamy sand soil

^b Burcucumber biochar produced at 700 °C

^c Burcucumber biochar produced at 700 °C activated with sulfuric acid

^d Burcucumber biochar produced at 700 °C activated with oxalic acid

^e Sandy loam soil

directly compared to the results from Kurwadkar et al. (2007). Similar pH dependency was observed by those authors. For cationic species of SMZ, the cation exchange mechanism is plausible; however, since it has been determined through modeling that both SMZ⁺ and SMZ⁰ ions dominate at pH 3, the π - π electron donor-acceptor interaction of the protonated aniline with the π electron-rich graphene surface may also result in the high $K_{D,eff}$ values for loamy sand (68 L/kg) and sandy loamy soils (50 L/kg) (Teixidó et al. 2011).

Acid-activated BC-treated soils showed the highest K_{D0} values for both soils (Table 3). Simulated K_{D1} values demonstrated a significant reduction compared to K_{D0} , which may be due to the dominating effect of cationic forms of SMZ in sorption. Loamy sand soil showed the highest K_{D0} value for sulfuric-activated BC (about 2.5 times that of BBC700-treated soil) whereas the increase was lower for oxalic-activated BC (1.8 times). However, in the alkali region, at pH 9, as anionic form of SMZ prevailed in the aqueous phase, low $K_{D,eff}$ values were observed for all samples (Table 3). At pH 3, the $K_{D,eff}$ for SBBC-treated soils showed high values (229 and 182 L/kg); however, $K_{D,eff}$ for OBBC-treated loamy sand and sandy loam soils were 137 and 66 L/kg, respectively. This indicates that SBBC are more effective in SMZ adsorption than either BBC700 or OBBC.

Kinetics of SMZ sorption

Time-dependent SMZ sorption data revealed that the soils reached pseudo-equilibrium at 4 h; however, the adsorption was very low compared to that of BC-treated soils, which attained pseudo-equilibrium status at about 24-h contact at pH 5 (Fig. 4). Loamy sand soil demonstrated a somewhat higher SMZ sorption compared to sandy loam soil, even though it is rich in organic matter, silt, and clay, which may be due to the

competition with phosphates. Additions of BBC300 slightly increased SMZ retention; however, a contrast increase was observed by the addition of BBC700. Hence, the BBC300 system was not modeled. Specifically, in the case of BC-applied soils, a rapid SMZ sorption was observed for both soils during the first 1 h (44 and 38 % for soils 1 and 2 with 2 % BBC700, respectively) followed by slow SMZ removal. Finally, at 24 h, about 69 to 71 % SMZ retention was observed for loamy sand and sandy loam soils treated with 2 % BBC700. The two-phase adsorption indicates the reduction of surface sites available for adsorption with increasing contact time.

In the case of acid-treated BCs, a considerable increase in sorption was observed which is primarily due to the increase



Fig. 3 Experimental and modeled sorption coefficients for SMZ of different pH values for loamy sand and sandy loam soils. *Squares* represent loamy sand soil (S1), *circles* represent sandy loam soil (S2), and *lines* represent modeled data. The concentration of SMZ used in these experiments was 10 mg/L, as applied to a 50 g/L soil solution







Fig. 4 (a) Time dependency of SMZ sorption (10 mg/L) on loamy sand and sandy loamy soils (50 g/L), biochar-treated soils with BBC300 and BBC700 (b) modeled data with pseudo second order absorption (c) intraparticle diffusion and (d) Elovich models. *Symbols* represent

in the surface area by the acid activation (Fig. 5). Although the sulfuric and oxalic activations have increased surface area by 285 and 205 times, respectively, the adsorption capacities have not increased concurrently which may be due to the

experimental data and *lines* represent modeled results. *Solid* symbols are for bare soils; half solid symbols (**a**) for BBC300-treated soils and *crossed symbols* represent BBC700-treated soils. *Squares* represent loamy sand (S1) while *circles* represent sandy loam soil (S2)

size-exclusive effect. Acid activation created micro-pores and increased the surface area of BC. However, these micropores were not available for SMT due to its molecular size is larger than pore diameter. Similar two-phase sorption was



Fig. 5 (a) Time dependency of SMZ sorption (10 mg/L) on loamy sand (S1) and sandy loamy soils (S2) (50 g/L), sulfuric and oxalic acidactivated biochar-treated soils, (b) modeled data with pseudo second

order and (c) Elovich models. *Symbols* represent experimental data and *lines* represent modeled results. *Squares* represent loamy sand while *circles* represent sandy loam soil

observed for the acid-activated BCs. Compared to the soils treated with BBC700, the acid-activated BCs showed a higher rate of sorption for SMZ. In the case of BBC700, the maximum SMZ sorption at 24 h was around 140 mg/kg from all treatments, whereas in acid-activated BCs, the maximum sorption reported was around 190 mg/kg. Hence, acid activation of BCs shows a greater increase in the adsorption ability of SMZ in soil systems.

Kinetic data were modeled into pseudo first order, pseudo second order, intra-particle diffusion, and Elovich models. The results were then used to predict mechanisms of sorption, which include the transport of sorbate into sorbent, diffusion through the boundary layer, chemisorption or intra-particle diffusion of ions or molecules, or combinations of these processes (Thiele-Bruhn et al. 2004; Tsang et al. 2013). The best fitting model results are shown in Figs. 4 and 5 and Table 4 by considering the calculated correlation coefficient (R^2) and chi-square. The kinetic data were best described by the pseudo second order model (Fig. 5).

Since the sorption system fitted the pseudo second order model, the rate limiting factor of chemical sorption in nature involves valence forces through sharing electrons between sorbate and sorbent and is valid for the SMZ-BC systems investigated (Ho and McKay 1999; Plazinski et al. 2009). Hence, SMZ indicated a strong interaction on BC surfaces in the soil system. The initial adsorption rate, as denoted by h, demonstrated rather high values for acid-activated BCs, indicating a quick sorption of SMZ to activated BCs. This may be due to the strong chemisorption process involved between the acidified black carbon surfaces and anionic SMZ under acidic conditions. These findings corroborate recent work on BCs and carbonaceous materials (Plazinski et al. 2009; Qiu et al. 2009).

The Elovich model followed by the intra-particle diffusion model fitted considerably well to the absorption profile of BBC700-treated soils. However, in the case of acid-activated BCs in soils, a better fit was observed for the Elovich model than for the intra-particle diffusion model. Although the Elovich equation does not provide any mechanistic evidence, it has proven to be a suitable representation of the highly heterogeneous systems of adsorption of different pollutants onto biosorbents. A clear difference was observed between the two soils for the initial rate of adsorption, where loamy sand soil (4.04) showed a value which was about 8.4 times higher than that of sandy loam soil (0.48). The reason for this may be due to the competition of DOC or phosphate for the sorption of sites in the sandy loam soil (Table 1), which contains a high amount of soil organic matter (Haham et al. 2012). Between the two different acid treatments, sulfuric activation showed the highest initial rate of sorption of SMZ, as about twice that of oxalic activation for both soils (Table 4), even though there were no considerable differences in the adsorption process observed for the two different acid activation processes.

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s obtained from different model fittings	
Kinetic parameters	
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Sample		Pseudo 1	st order			Pseudo 21	nd order				Intra-particle	diffusion			Elovic	Ч		
	q _{e (exp)} (mg/kg)	q _{e (cal)} (mg/kg)	k_1 (/h)	R^{2}	χ^2	ge (cal) (mg/kg)	$k_2 \pmod{({ m mg/kg}\ { m h}^{0.5})}$	h (mg/kg h)	R^{2}	χ^{2}	$k_{ m id}$ (mg/kg ${ m h}^{0.5}$)	C (mg/kg h)	R^2	χ^2	α	β	R^2	χ^2
S1 ^a	31.5	2.90	0.029	0.414	4.5×10^{3}	40.6	0.01	10.2	0.982	33.9	4.35	15.3	0.807	1.89	4.04	39.7	0.617	3.44
S1+2 % BBC700 ^b	129	2.90	0.029	0.95	4.1×10^{4}	147.3	0.004	77.5	0.998	8.93	10.9	47.8	0.878	9.58	23.3	0.78	0.962	10.23
S1+2 % SBBC ^c	176.4	74.49	0.348	1.000	1.5×10^{5}	181.8	0.005	174.3	0.995	9.75	14.9	114	0.758	7.79	83.4	17.5	0.924	30.28
S1+2 % OBBC ^d	155.1	86.46	0.267	0.994	7.8×10^4	163.9	0.008	190.4	0.999	13.68	20.3	75.3	0.826	20.3	16.2	0.45	0.971	51.78
$S2^{e}$	14.2	2.71	0.038	0.049	1.0×10^{3}	11.1	0.16	22.5	0.928	7.16	0.35	11.8	0.019	2.10	0.48	4×10^{3}	0.086	35.40
S2+2 % BBC700	132	58.4	0.226	0.958	6.1×10^4	166.0	0.005	81.9	0.996	17.6	15.8	70.7	0.889	3.67	0.45	16.2	0.982	38.16
S2+2 % SBBC	176.7	64.45	0.198	0.997	1.5×10^{5}	169.5	0.007	231.4	0.996	9.48	17.4	108	0.971	7.75	48.6	18.5	0.978	30.02
S2+2 % OBBC	158.8	60.69	0.196	0.995	1.0×10^{5}	175.4	0.005	141.3	0.996	46.02	18.9	85.0	0.972	22.1	16.2	0.45	0.989	56.75
^a Loamy sand soil																		
^b Burcucumber bioch	nar produce	ed at 700 ⁰0	C															
^c Burcucumber bioch	nar produce	sd at 700 °€	C activate	ed with s	sulfuric acic	Ŧ												
^d Burcucumber biocł	nar produce	ed at 700 ⁰0	C activat	ed with (oxalic acid													
^e Sandy loam soil																		

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The rate of surface reaction may not only govern the chemisorption process. Another assumption involved in the rate kinetics of sorption is the assumption of a two-step process (Plazinski et al. 2009). The first (initial) kinetic process is governed mainly by the rate of surface reaction, and when the adsorbed amount reaches a certain ratio of equilibrium surface coverage, another kinetic process can become dominant, which is governed mainly by the rate of solute diffusion through macro-, meso-, and micro-pores of the sorbent, expressed by the intra-particle diffusion model (IDM). Interestingly, it was observed that the intra-particle rate constants of BBC700 soil systems were lower than the acidactivated BC-treated systems, indirectly indicating that chemical activation may have an effect on the kinetic process governed by the diffusion process. Intra-particle rate constants in soils were in the order of OBBC>SBBC>BBC700>S2. The minimum rate reported was that of sandy loam soil, as 0.35 mg/kg h^{0.5}, and the highest was that observed for loamy sand soil treated with OBBC, as 20.3 mg/kg h^{0.5}. The intercept of the plot, C, reflects the boundary layer effect. The high boundary layer effect, C, in the soil systems treated with activated BCs, shows an increase in the diffusion governing adsorption, which may be due to the increase in the porosity of BCs. In the soil systems, C was low (around 12–15), whereas in the acid-activated systems, it reached a maximum of around 114. However, the intra-particle rate constants of bare soils are remarkably low, which highlights that the diffusion kinetic process is solely due to the application of BCs to the soil systems.

Conclusions

Acid activation showed an extensive increase in the BET surface area of BBC, which may be due to the increase of micro-pores. Sulfuric-activated BC indicated the highest BET surface area, which was more than 250 times that of BBC700. Acid activation showed an obvious enhancement in the sorption of SMZ, especially SBBC. The results of the edge experiments and species-specific modeling demonstrated that the pH of the media greatly affected the speciation of SMZ and would thereby influence fate and transport. The sandy loam soil showed a lower SMZ retention ability as compared to the loamy sand soil, which is likely due to the competition of soil DOC for sorption sites. Soils treated with acid-activated BCs showed the highest K_{D0} values due to the dominating effect of cationic forms of SMZ in sorption. The highest K_{D0} value for SBBC-treated soil was about 2.5 times that of BBC700treated soil, whereas it was lower for OBBC-treated soil (1.8 times that of BBC700). Kinetic data indicated the possible prediction of involvement of two step processes in adsorption, chemisorption, and intra-particle diffusion. In particular, it can be concluded that acid activation, especially sulfuric treatment, increases SMZ adsorption, and hence, can be used as a potential amendment for soils contaminated with SMZ.

Acknowledgments This work was supported by the Korea Ministry of Environment as a Geo-Advanced Innovative Action Project (G112-00056-0004-0). Instrumental analyses were supported by the Korea Basic Science Institute, the Environmental Research Institute and the Central Laboratory of Kangwon National University, Korea. The Ministry of Technology, Research and Atomic Energy in Sri Lanka partially supported the first author.

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