ELSEVIER

Contents lists available at ScienceDirect

Journal of Hazardous Materials

Aurona and a second and a secon

journal homepage: www.elsevier.com/locate/jhazmat

Enhanced sulfamethazine removal by steam-activated invasive plant-derived biochar



Anushka Upamali Rajapaksha^{a,b}, Meththika Vithanage^b, Mahtab Ahmad^c, Dong-Cheol Seo^d, Ju-Sik Cho^{d,*}, Sung-Eun Lee^e, Sang Soo Lee^a, Yong Sik Ok^{a,**}

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

^b Chemical and Environmental Systems Modeling Research Group, National 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 Department of Biological Environment, Sunchon National University, Sunchon 540-742, Republic of Korea

^e School of Applied Biosciences, Kyungpook National University, Daegu 702-701, Republic of Korea

HIGHLIGHTS

• Steam activation of biochar enhanced sulfamethazine removal from aqueous media.

• Biochar properties varied drastically by the activation with steam.

• Solution pH and biochar properties had strong effect on sulfamethazine sorption.

• The steam activated biochar produced at 700 °C had the highest sorption capacity.

ARTICLE INFO

Article history: Received 23 October 2014 Received in revised form 10 February 2015 Accepted 15 February 2015 Available online 17 February 2015

Keywords: Activated carbon Black carbon Charcoal Emerging contaminants Slow pyrolysis Veterinary antibiotics

ABSTRACT

Recent investigations have shown frequent detection of pharmaceuticals in soils and waters posing potential risks to human and ecological health. Here, we report the enhanced removal of sulfamethazine (SMT) from water by physically activated biochar. Specifically, we investigated the effects of steam-activated biochars synthesized from an invasive plant (*Sicyos angulatus* L.) on the sorption of SMT in water. The properties and sorption capacities of steam-activated biochars were compared with those of conventional non-activated slow pyrolyzed biochars. Sorption exhibited pronounced pH dependence, which was consistent with SMT speciation and biochar charge properties. A linear relationship was observed between sorption parameters and biochar properties such as molar elemental ratios, surface area, and pore volumes. The isotherms data were well described by the Freundlich and Temkin models suggesting favorable chemisorption processes and electrostatic interactions between SMT and biochar. The steamactivated biochar produced at 700 °C showed the highest sorption capacity (37.7 mg g⁻¹) at pH 3, with a 55% increase in sorption capacity compared to that of non-activated biochar produced at the same temperature. Therefore, steam activation could potentially enhance the sorption capacities of biochars compared to conventional pyrolysis.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Water contamination by antibiotics is becoming a worldwide environmental issue [1,2]. Sulfamethazine (SMT), which belongs to the sulfonamide group of antibiotics, is commonly used in veterinary medicine to control diseases and in livestock feeds for cattle

http://dx.doi.org/10.1016/j.jhazmat.2015.02.046 0304-3894/© 2015 Elsevier B.V. All rights reserved. and swine [3]. Previous studies have shown that, SMT does not sorb to soil well and hence, can be detected at high concentrations in water [4]. Remediation of antibiotic-contaminated water has been achieved by sorption processes using various sorbents, including natural sorbents, clays, chitosan derivative, activated carbon, and more [5–8]. It has been shown that sorption of SMT by clays decreases with increasing pH of solution and increases with increasing ionic strength and surface charge density. Various SMT sorption mechanisms including cation exchange, hydrophobic partitioning, and surface complexation reactions (H-bonding and other polar interactions) between the functionalities (amino, carboxyl,

^{*} Corresponding author. Tel.: +82 61 750 3297.

^{**} Corresponding author. Tel.: +82 33 250 6443; fax: +82 33 241 6640.

E-mail addresses: chojs@sunchon.ac.k (J.-S. Cho), soilok@kangwon.ac.kr (Y.S. Ok).

and phenol) of the SMT molecules have been purposed [9–10]. Even though materials such as activated carbon are suitable for removing contaminants from water, they may not be economically feasible [11] due to the high energy requirements of their production.

Low-cost biochar, a solid material obtained from the carbonization of biomass in an oxygen-limited environment [12], has recently received major attention as a very effective environmental sorbent of many organic and inorganic contaminants in soil and water [11,13–16]. Biochar can be produced from various waste materials as a feedstock, which is advantageous as a waste management option [17]. Previous studies have focused on producing biochar from invasive plant species, thereby providing a useful way of eliminating them from the environment [18–20].

However, little work has been done to examine the mechanisms and effectiveness of SMT removal by biochars [6,9,21]. Previously, biochars produced by conventional slow pyrolysis showed potential as adsorbents of organic contaminants, although the reported sorption capacities were much lower than those of other adsorbents such as activated carbon (AC) for practical applications [22]. Hence, the production of biochar can be a good alternative to AC for environmental remediation, even though more studies are needed to enhance the removal efficiencies of biochars to match the sorption capacities with AC [23]. Thus, in this study, we developed a simple method for increasing the (maximum) sorption capacities of biochars by steam activation after slow pyrolysis. Ippolito et al. [24] recently demonstrated the potential of steam-activated pecan shell biochar to sorb excess Cu (inorganic metal ions) from waste waters. Despite this, the significance of steam-activated biochar in the sorption of organic compounds has not been studied in detail and requires continued research.

Here, we converted the biomass of an invasive plant species (Burcucumber; *Sicyos angulatus* L.) into biochar in order to simultaneously address two environmental issues i.e., (a) economically feasible removal of invasive plants will generate a valuable source of biomass for biochar production and (b) production of innovative and environmentally friendly material in pollutant removal. The physiochemical properties of steam-activated biochars were compared with those of conventional slow pyrolysis biochars. The potential applicability of steam-activated biochars for the removal of veterinary antibiotics was evaluated by conducting a series of batch experiments. The specific objectives of this study were (1) to produce invasive plant-derived steam-activated biochars, (2) to evaluate the effectiveness of steam-activated biochars on SMT sorption from water, and (3) to determine the factors governing SMT removal by biochars.

2. Experimental

2.1. Preparation of biochars and steam activation

Burcucumber plants were collected from Chuncheon city in Gangwon province, Korea. The dried plants were crushed and ground to <1.0 mm particle size. Portions of this biomass were pyrolyzed at two temperatures (300 and 700 °C) in a pyrolyzer (N11/H Nabertherm, Germany) under a limited supply of air. Slow pyrolysis was achieved at a rate of $7 \,^{\circ}C \min^{-1}$. A holding time of 2 h was applied for each peak temperature for complete carbonization of biomass. Then, the pyrolyzed samples were steam-activated at a flow rate of $5 \,\text{mL} \min^{-1}$ for 45 min, under the peak temperature (i.e., 300 or 700 °C) [25,26]. Steam may change the properties of biochar by removing the trapped products of incomplete combustion during pyrolysis [27]. The typical reactions involved in the steam activation [28] are as below:

 $C + H_2O \rightarrow CO + H_2$

$$2C + H_2 \rightarrow 2CH$$

$$CO + H_2O \rightarrow CO_2 + H_2$$

Steam oxidizes the C surface generating H_2 and CO_2 which may activate the surface of biochar. In other words, the rate of gasification is inhibited due to these water-gas shift reactions. Burcucumber biochars (BBC) produced at 300 and 700 °C without steam activation were denoted as BBC-300 and BBC-700, whereas biochars produced by steam activation were designated as BBC-300S and BBC-700S.

2.2. Characterization of biomass and biochars

Proximate analysis, including moisture, mobile matter, ash, and residual matter contents, were determined according to the modified thermal analysis methods of McLaughlin et al. [29]. Briefly, moisture content was calculated based on weight loss after heating biochars at 105 °C for 24 h to a constant weight. Mobile matter content was determined by calculating weight loss after heating in a covered crucible at 450 °C for 30 min, whereas ash content was determined as the residue remaining after heating at 700 °C in an open-top crucible. The pH levels of produced biochars were estimated in a suspension of 1:5 BBC/de-ionized water using a digital pH meter (Orion, Thermo Electron Corp., Waltham, USA). Elemental (C, H, N, S, O) analyses were conducted by dry combustion using an elemental analyzer (EA1110, CE Instruments, Milan, Italy).

Structural analysis was performed using Fourier transform infrared spectroscopy (FTIR) (Bio-Rad Excalibur 3000MX spectrophotometer, Hercules, CA, USA). The spectra were obtained at $4 \,\mathrm{cm^{-1}}$ resolution by measuring the absorbance from 400 to $4000 \,\mathrm{cm^{-1}}$ using a combined 190 scans. Surface areas of sorbents were measured by nitrogen adsorption isotherms at 77 K using a gas sorption analyzer (NOVA-1200; Quantachrome Corp., Boynton Beach, FL, USA). Specific surface areas were determined from adsorption isotherms using the Brunauer–Emmett–Teller (BET) equation. The Barret–Joyner–Halender (BJH) method was used to determine pore volume and pore diameter from the N₂ adsorption data.

2.3. Batch sorption studies

Ultrapure water with a resistivity of 18.2 M Ω was used for all procedures. SMT was obtained from Sigma–Aldrich Chemical Co. (99% purity). Acid dissociation constants and physical properties of SMT are given in Table S1 of the supplementary data. Stock solution (100 mgL⁻¹) was prepared in 1% methanol and was used to obtain the starting SMT concentrations in batch sorption studies. Batch sorption isotherm studies were carried out in the concentration range of 2.5 ~ 50 mg L⁻¹ at pH 3, 5, 7 and 9 (10 mM ammonium phosphate for pH 3, 7 and 9, and 10 mM ammonium acetate for pH 5) [10]. A sorbent dose of 1 g L⁻¹ was used for all sorption experiments at an ionic strength of 0.1 M (adjusted by ammonium chloride). During the experiments, the pH values were checked and readjusted using conjugated acids and bases if required. The mixtures were shaken at 100 rpm in an incubator shaker (Jeio Tech, SI-600R) for 72 h at 25 °C.

After equilibrium, an aliquot from each vial was filtered through a 0.45 µm syringe filter, after which the SMT concentration was determined by high performance liquid chromatography (HPLC; SCL-10A, Shimadzu, Japan) equipped with an auto-sampler (SIL-10AD, Shimadzu, Japan) and UV–vis detector (SPD-10A, Shimadzu, Japan). A reverse-phase Sunfire C18 column (4.6 mm by 250 mm; Waters, USA) was employed in a column oven (CTO-10AS, Shimadzu, Japan). Mobile phase A was composed of HPLC grade water and formic acid (99.9:0.1 v v⁻¹) while mobile phase B was composed of HPLC grade acetonitrile and formic acid (99.9:0.1 v v⁻¹). The gradient was maintained as 70% mobile phase A and 30% mobile phase B at a rate of 0.5 mL min⁻¹. The injection volume was 20 μ L. The absorbance was measured at 265 nm [5]. Blanks containing no adsorbents showed no SMT loss during the equilibration time.

2.4. Experimental data modelling and calculations

The equilibrium sorption capacities of the biomass and biochars were calculated by using Eq. (1) [30]:

$$q_{\rm e} = [C_{\rm o} - C_{\rm e}] \times V/M \tag{1}$$

where q_e is the equilibrium SMT solid phase concentration (mgg^{-1}) , C_o and C_e are the SMT concentrations of the initial and equilibrium aqueous phases (mgL^{-1}) , respectively, *V* is the volume of solution (*L*), and *M* is the mass of adsorbent (*g*). Two parameter-based equilibrium isotherm models, viz Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich (D–R), were applied to determine effective SMT adsorption. The Freundlich (Eq. (2)) and Langmuir isotherms (Eq. (3)) are given as follows [30,31]:

$$q_{\rm ads} = K_{\rm F} C_{\rm e}^{\ n} \tag{2}$$

$$q_{\rm ads} = \frac{q_{\rm max} K_{\rm L} C_{\rm e}}{1 + K_{\rm L} C_{\rm e}} \tag{3}$$

where, q_{ads} is the amount of adsorbate adsorbed per unit mass $(mgg^{-1}), K_F((mgg^{-1})/(mgL^{-1})^n)$ is the Freundlich affinity – capacity parameter, n is the Freundlich exponent, K_L is the Langmuir affinity parameter (Lmg^{-1}) , and q_{max} is the Langmuir capacity parameter (mgg^{-1}) .

The Temkin model is related to heat of sorption and assumes that the adsorption energy decreases linearly with surface coverage due to adsorbent–adsorbate interactions (Eq. (4)).

$$q_{\rm ads} = \frac{RT}{b} \ln(AC_{\rm e}) \tag{4}$$

where *R* is the universal gas constant $(8.314 \text{ J K}^{-1} \text{ mol}^{-1})$, *T* is the absolute temperature, *b* is the heat of adsorption, and *A* is the binding constant (Lmg^{-1}) .

The Dubinin–Radushkevich model deals with sorption onto the porous structure of the sorbent, assuming that the adsorption has a multilayer character, involving Van der Waals forces, and is applicable for physical adsorption processes. It can be expressed as follows [32]:

$$q_{\rm ads} = q_{\rm D} \exp(-B_{\rm D} [RT \ln(1 + \frac{1}{C_{\rm e}})]^2$$
(5)

where q_D is the adsorption capacity (mg g⁻¹) and B_D is the mean free energy of sorption. From this model, bonding energy of the ion-exchange mechanism (*E*) can be calculated as follows:

$$E = \frac{1}{(2B_{\rm D})^{0.5}} \tag{6}$$

All modeled parameters were determined by non-linear regression.

The separation factor (R_L), which is based on Langmuir parameters, can be used to determine whether the sorption system is favorable or unfavorable, and is given by Eq. (7):

$$R_{\rm L} = \frac{1}{1 + K_{\rm L} C_0} \tag{7}$$

2.5. Best-fitting isotherm model estimation

The best fit among the isotherm models is commonly assessed by mathematical expressions. The chi-square (χ^2) test measures the difference between the experimental and model data. The mathematical form of this test statistic can be expressed as [33]:

$$X^2 = \frac{\Sigma (q_{\rm ex} - q_{\rm m})^2}{q_{\rm m}} \tag{8}$$

where q_{ex} is the experimental equilibrium capacity (mg g⁻¹), q_m is the model calculated equilibrium capacity (mg g⁻¹).

The percent deviation was calculated as follows:

Percent deviation=
$$\frac{q_{\rm ex} - q_{\rm m}}{q_{\rm m}} \times 100$$
 (9)

The average relative error (ARE) function attempts to minimize the fractional error distribution across the entire concentration range [34].

$$ARE = \frac{100}{N} \frac{\Sigma q_{\rm ex} - q_{\rm m}}{q_{\rm e}} \tag{10}$$

where N is the number of experimental points.

The sum of the squares of the errors (*SSE*) can be expressed as [35],

$$SSE = \Sigma (q_{\rm m} - q_{\rm ex})^2 \tag{11}$$

2.6. Statistical analysis

Isotherm regression curves were plotted using non-linear regression. Pearson's correlation coefficient (r) and probability (P) values between the various parameters were calculated by linear regressions and SAS ver. 9.1, (SAS Institute, Cary, NC, USA).

3. Results and discussion

3.1. Biochar properties

The pH of biochar increased with elevation of the pyrolysis temperature due to separation of alkali salts from the organic matrix in the feedstock as well as removal of acidic functional groups (Table 1) [36,37]. Biochar yield was 52% at 300 °C and was reduced to 28% at 700 °C, and this further decreased to 19% upon steam activation. This can be attributed to greater loss of volatile matter at high temperatures [19]. Conversely, total C contents of biochars increased with elevation of pyrolysis temperature. High C contents (69.41%) were observed in BBC-700, which was about 60% higher compared to that of the biomass. This increase in C content was related to the higher carbonization of biomass at high pyrolysis temperature (700 °C). Molar H/C and O/C ratios have been used to predict the aromaticity and polarity of biochars, respectively [38]. Reduction of the molar O/C ratio with elevation of pyrolysis temperature (Table 1) may cause biochars to be less hydrophilic [37,39]. In this study, molar H/C ratios were 1.68, 1.00, 0.89, 0.23, and 0.39 for biomass, BBC-300, BBC-300S, BBC-700, and BBC-700S, respectively, indicative of highly aromatic structures for biochars produced at high temperature but not at low temperatures.

The high pyrolysis temperature slightly increased the surface area of BBC-700 compared to that of BBC-300 due to elevation of the micropore volume caused by removal of volatile materials. The observed low surface areas corroborate the findings of Ahmad et al. [19], who observed relatively low surface areas ($9.27 \text{ m}^2 \text{ g}^{-1}$) for plant biomass-derived biochars produced at 700 °C. This may be due to the formation of tars during the biomass thermal decomposition process [37]. In general, steam application enhances the surface areas of biochars [38,40,41], whereas in the case of BBC, only a slight increase in surface area was observed upon steam application. The surface area of BBC-700S was found to be 7.10 m² g⁻¹. Compared to woody biochars having low ash contents, this invasive plant-derived biochar showed a high ash content,

Table 1

Proximate and ultimate analyses of biomass (BM), biochar at 300 °C (BBC-300), biochar at 700 °C (BBC-700), steam activated biochar at 300 °C (BBC-300S) and steam activated biochar at 700 °C (BBC-700S).

a 1	224			22.2.2.2	
Sample	BM	BBC-300	BBC-300S	BBC-700	BBC-700S
pH ^a	8.45 ± 0.01	10.86 ± 0.04	11.14 ± 0.05	12.32 ± 0.03	11.72 ± 0.01
Proximate analysis ^a					
Yield (%)	_	51.83 ± 1.57	50.21 ± 3.01	27.52 ± 0.29	18.90 ± 1.36
Moisture (%)	8.44 ± 0.10	0.36 ± 0.04	1.69 ± 0.06	0.33 ± 0.05	2.12 ± 0.30
Mobile matter (%)	64.96 ± 1.10	33.63 ± 2.98	31.76 ± 1.24	13.55 ± 4.67	13.17 ± 0.87
Resident matter (%)	13.07 ± 1.09	40.62 ± 3.27	37.44 ± 2.05	42.40 ± 4.82	14.05 ± 0.37
Ash (%)	13.53 ± 0.09	25.40 ± 0.32	28.67 ± 2.61	43.72 ± 0.09	70.66 ± 0.79
Ultimate analysis					
C ^b (%)	43.38	65.98	68.10	69.41	50.55
H ^b (%)	6.12	5.55	5.11	1.31	1.66
O ^b (%)	46.81	23.09	21.43	24.45	44.88
N ^b (%)	3.26	5.08	5.10	4.61	2.54
Molar H/C	1.68	1.00	0.89	0.23	0.39
Molar O/C	0.81	0.26	0.24	0.26	0.67
Molar (O + N)/C	0.38	0.33	0.30	0.32	0.71
Surface area (m ² g ⁻¹)	2.28	0.85	1.22	2.31	7.10
Pore volume ($cm^3 g^{-1}$)	0.006	0.004	0.003	0.008	0.038
Pore diameter (nm)	3.628	3.070	5.418	6.780	8.393

^a Mean ± standard deviation (SD) in triplicate determinations.

^b Ash and moisture free.



Fig. 1. Pore size distribution of the biomass (BM), biochar at 300 $^{\circ}$ C (BBC-300), biochar at 700 $^{\circ}$ C (BBC-700), steam activated biochar at 300 $^{\circ}$ C (BBC-300S) and steam activated biochar at 700 $^{\circ}$ C (BBC-700S).

and its steam application resulted in elevated ash production. High ash-producing biochars tend to have low surface areas [42,43]. Correlation analysis between surface area and ash content showed a positive correlation between BET area and ash content (Fig. S1). This may imply that the surface area determined by N_2 gas adsorption technique may primarily represent the surface of minerals in biochars with high ash content [44].

Pore size distribution curves were constructed in order to understand the effects of pore size and pore surface chemistry on SMT removal (Fig. 1). Clearly, introduction of steam had remarkable effects on the pore size distributions of BBC, as pore volume increased after steam application. In the pore size distribution curve, all biochars and biomass exhibited heterogeneous pore structures (Fig. 1). The FTIR spectra of the four biochars and biomass with their spectroscopic assignments are illustrated in Fig. S2. There was a remarkable reduction in the volume of peaks associated with O–H stretching (3200–3500 cm⁻¹) and aliphatic C–H stretching (2820–2980 cm⁻¹) vibrations due to loss of labile aliphatic compounds in high temperature-derived biochars (BBC-700 and BBC-700S). The peaks between 750 and 885 cm⁻¹ for BBC-700 and BBC-700S can be attributed to out-of-plane deformations of aromatic C–H [45]. This confirms the highly aromatic nature of



Fig. 2. Adsorption isotherm fittings of biomass (BM), biochar at 300 °C (BBC-300), biochar at 700 °C (BBC-700), steam activated biochar at 300 °C (BBC-300S) and steam activated biochar at 700 °C (BBC-700S) to (a) Langmuir and Freundlich (b) D–R model and Temkin fitting. The symbols represent experimental results at pH 5 and the solid line represents the calculated results using non-linear least square fit.

BBC-700 and BBC-700S compared to that of BBC-300 and BBC-300S. These changes in biochar properties based on production conditions are consistent with the detailed explanation given by Manyà et al. [46], who highlighted changes in biochar properties according



Fig. 3. Langmuir separation factors for biomass (BM), biochar at 300 °C (BBC-300), biochar at 700 °C (BBC-700), steam activated biochar at 300 °C (BBC-300S) and steam activated biochar at 700 °C (BBC-700S) at pH 5.

to changes in production parameters (i.e., peak temperature, heating rate, physical activation process using oxidizing agents such as steam and carbon dioxide). Overall, these characterization results confirm that production conditions affect biochar properties and may lead to different sorption capacities towards contaminants.

3.2. SMT sorption

BBC-700S exhibited the highest SMT adsorption capacity while biomass showed the lowest (Fig. 2). The maximum sorption capacity simulated by the Langmuir equation for the biomass was $6.69 \,\mathrm{mgg^{-1}}$, which was lower than that of BBC-300 (15.66 $\mathrm{mgg^{-1}}$) or BBC-700 (18.87 m g g^{-1}). Biochars produced at high temperatures have shown high capacity for adsorbing organic pollutants [11,47]. This may be due to the high aromaticity and low polarity of biochars derived at higher temperatures compared to biomass and biochars derived at 300 °C. After steam activation, however, the Langmuir maximum SMT sorption capacity of BBC increased almost 5-fold to 32.19 mg g^{-1} compared to that of biomass. Based on the model fitting for the Langmuir isotherm equation, adsorption capacity increased in the order of biomass <BBC-300S < BBC-300 < BBC-700 < BBC-700S at pH 5 (Table 2). The fact that pore volume of BBC-300S was less than that of BBC-300 might explain the lower sorption capacity of BBC-300S.

The relationship between the Langmuir separation factor (R_L) and C_0 is given in Fig. 3, which shows the essential features of the

Langmuir isotherm. The R_L value indicates the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$). In our study, calculated R_L values for biomass and biochars were less than 1 and greater than zero, indicating favorable adsorption. The R_L values indicate that sorption was more favorable at high initial SMT concentrations than at low initial SMT concentrations. BBC-700S was the most favorable, having the lowest R_L values over the entire concentration range (Fig. 3).

The magnitude of the Freundlich exponent (n) indicates the favourability of sorption. In agreement with the Langmuir model predictions, the *n* values were less than 1, indicating favorable sorption to heterogeneous biochar surfaces. Freundlich K_f values plotted against pH of the media for BBC-700 and BBC-700S demonstrate that SMT sorption was high at low pH levels (Fig. 4(a)). For both BBC-700 and BBC-700S, SMT sorption decreased with increasing pH. This pH dependency of sorption is due to SMT solution speciation. As pH increases, an anionic form of SMT is increasing, thereby increasing electrostatic repulsion between SMT and biochar surfaces [9,18]. Although BBC-700 and BBC-700S showed similar Freundlich K_f values with pH, high K_f values (~ 2 fold) were reported for BBC-700S over the entire pH range studied (Table 2).

Non-linear plots for the Temkin adsorption isotherm (Fig. 2b), which considers chemisorption of an adsorbate onto an adsorbent [48], fit quite well with the correlation coefficients >0.895 for all sorbents (Table 2). This further supports the findings that adsorption of SMT onto biochars is a chemisorption process. The SMT sorption data were not described well by the D-R model, and this was confirmed by the correlation coefficients as shown in Table 2. In agreement with the Langmuir maximum sorption capacities, BBC-700S showed the maximum calculated q_D values, indicating highest sorption.

Surface complexation in mechanistic modeling approaches [49] is not applicable to such systems due to the high amount of organic matter and the hydrophobicity of biochar. Hence, various empirical models were used to understand the mechanisms of SMT removal.

The percentage SMT removal by BBC-700S at different pH values is given in Fig. 4(b). The amount of SMT sorption decreased with increasing initial SMT concentration; >95% at low initial concentration and >64% at high initial concentration at pH 5. Moreover, pH dependency was negligible at low initial SMT concentrations (>95%) while distinct pH dependency was observed at high initial concentrations. The percentage of SMT removal at high initial SMT concentrations and low pH values was around ~95% and decreased to ~46% at high pH values. It should be noted that these removal percentages would be changed in the environment, as they are tempered by several factors such as competitive ions.

Various mechanisms such as hydrophobic, electrostatic, hydrogen bond, and π - π interactions may simultaneously participate

Table 2

Isotherm parameters for sulfamethazine (SMT) adsorption onto biomass (BM), biochar at 300 °C (BBC-300), biochar at 700 °C (BBC-700), steam activated biochar at 300 °C (BBC-300S) and steam activated biochar at 700 °C (BBC-700S). All parameters were calculated by non linear regression.

isotnerm parameters													
Adsorbent	pН	Langmuir			Freundlich			Temkin			Dubinin-Radushkevish		
		$q_{\rm max} ({ m mg}{ m g}^{-1})$	$K_{\rm L} ({\rm L}{ m mg}^{-1})$	r ²	$K_{\rm F} ({\rm mg^{1-n}}{\rm L^n}{\rm g^{-1}})$	п	r ²	Ā	b	r ²	$q_{D} (mg g^{-1})$	$E(kJg^{-1})$	r ²
BM	5	6.688	0.011	0.940	0.089	0.840	0.922	0.267	0.801	0.911	2.373	0.002	0.995
BBC-300	5	15.656	0.045	0.959	1.156	0.590	0.909	0.564	3.110	0.941	10.160	0.004	0.958
BBC-300S	5	14.681	0.031	0.939	0.697	0.670	0.939	0.471	2.652	0.951	7.292	0.006	0.877
BBC-700	3	20.559	0.893	0.869	10.601	0.208	0.895	26.555	3.150	0.916	18.487	1.682	0.687
	5	18.776	0.794	0.883	7.995	0.262	0.921	16.817	3.029	0.913	16.760	0.035	0.721
	7	18.591	0.342	0.984	6.556	0.298	0.958	9.599	3.025	0.946	15.380	0.957	0.654
	9	10.451	0.456	0.921	4.081	0.266	0.912	9.244	1.770	0.942	8.994	1.267	0.767
BBC-700S	3	37.731	1.289	0.943	18.599	0.292	0.973	20.433	6.739	0.984	32.700	2.425	0.814
	5	32.192	0.935	0.927	14.989	0.274	0.975	97.814	3.957	0.895	27.682	0.040	0.800
	7	30.015	1.211	0.931	15.117	0.244	0.947	23.799	4.948	0.962	27.126	2.020	0.815
	9	25.226	0.490	0.966	9.676	0.292	0.956	9.474	4.376	0.981	21.537	1.103	0.837



Fig. 4. Adsorption capacity variations with pH (a) Freundlich adsorption coefficients for biochar at 700 °C (BBC-700) and steam activated biochar at 700 °C (BBC-700S) (b) Percentage removal of SMT by steam activated biochar at 700 °C (BBC-700S) with initial SMT concentrations.

in SMT sorption [6,50] and may be explained by pH dependencies. The effect of pH on sorption capacities correlated well with the pH-regulated distribution of SMT species, which highlights the importance of SMT species in the sorption process (Fig. 4(a) and (b)). SMT molecules may interact with biochar via $\pi - \pi$ electron donor-acceptor (EDA) interactions between the protonated aniline ring of the SMT molecule and the π -electron rich graphene surface of biochars [9]. This strong π - π EDA interaction has previously been verified between SMT molecules and carbon black [6,9]. Electrostatic cation exchange could be another possible mechanism [7]. Since SMT molecules contain several moieties capable of hydrogen bonding as hydrogen acceptors or donors, SMT may bind through hydrogen bonding depending on the pH of the media. For instance, in an alkaline environment where SMT is dominant, the sorption process is governed mainly by a near stoichiometric proton exchange process known as negative charge-assisted hydrogen bonding [9,51]. At high pH values, anionic SMT species may increase electrostatic repulsion between SMT and BBC surfaces, possibly leading to reduced K_f values.

3.3. Comparison of isotherm sorption models

Correlation of adsorption data with theoretical or empirical equations can be used to gain further insights into the adsorption behavior of solutes with the sorbent. Degrees of applicability of the different isotherm equations were compared by calculating percent deviation as well as ARE and SSE values. According to χ^2 values, adsorption isotherm data showed good fit with the Temkin model, followed by the Freundlich model. The lowest calculated SSE suggested that the data fit better with the Freundlich model in

comparison to the other models (Table 3). ARE values were the lowest for the D–R model. Further, the distribution of average percent deviation was reduced from more than 6.6% in the D–R model to <0.4% and 1.6% in the Temkin and Freundlich models, respectively, for BBC-700S at pH 3 (Fig. S3). This trend held for all pH values. In comparison with the isotherms studied, the Freundlich and Temkin models were most suitable for illustrating the sorption behavior of BBC. Hence, the order of best fit for the isotherm models of biochars was determined to be Temkin \approx Freundlich > Langmuir > D–R. This suggests a favorable chemisorption process as well as electrostatic interactions between SMT and biochar.

3.4. SMT sorption and biochar properties

Correlation test was performed to evaluate the adsorption parameters versus biochar properties. Positive correlation was observed for surface area and Langmuir adsorption capacity (P<0.01) (Table S2 and Fig. 5). Similarly, surface area was positively correlated with Freundlich K_f, D–R Q values and Temkin A values. The relatively higher surface area of BBC-700S (7.10 m² g⁻¹; Table 1) compared to that of BBC-700 $(2.31 \text{ m}^2 \text{ g}^{-1})$ can explain its high adsorption capacity, as emphasized by positive correlations between surface areas of the sorbents and adsorption modeled parameters (Table S2). This result suggests that surface area is a key property of biochar affecting adsorption capacity. Similarly, a strong positive correlation (r > 0.99; P < 0.005) was observed between pore volume and Langmuir adsorption capacity (Fig. 5). Furthermore, Temkin parameter A showed a much stronger correlation (P<0.001) with pore volume (Table S2). A similar linear relationship between surface area and Freundlich parameters was

Table 3

Values of three different error analyses of isotherm models for sulfamethazine (SMT) adsorption onto the biomass (BM), biochar at 300 °C (BBC-300), biochar at 700 °C (BBC-700), steam activated biochar at 300 °C (BBC-300S) and steam activated biochar at 700 °C (BBC-700S).

isoulerins													
Adsorbent	pН	Langmuir			Freundlich			Temkin			Dubinin-Radushkevish		
		X ²	SSE	ARE	$\overline{X^2}$	SSE	ARE	$\overline{X^2}$	SSE	ARE	X ²	SSE	ARE
BM	5	0.581	0.287	144.658	0.648	0.366	138.932	0.016	0.419	83.578	2.020	0.023	16.896
BBC-300	5	0.621	3.079	14.174	1.446	6.806	24.847	0.832	4.446	8.569	2.030	3.143	31.933
BBC-300S	5	2.271	8.387	132.450	1.951	4.101	152.48	0.318	6.232	79.521	6.690	13.676	20.364
BBC-700	3	1.056	18.515	0.269	0.549	9.168	0.716	0.513	9.554	0.446	2.035	35.434	1.042
	5	2.032	27.295	3.529	1.055	14.845	2.651	0.865	15.895	0.368	10.254	53.810	6.969
	7	1.073	16.751	7.780	0.265	3.481	0.751	0.554	7.421	0.784	2.521	43.443	12.130
	9	1.028	5.380	3.916	0.906	5.952	4.998	0.488	3.904	0.506	17.129	15.775	8.231
BBC-700S	3	2.118	45.737	3.335	0.476	6.821	1.544	0.398	10.632	0.303	6.136	120.009	2.618
	5	2.227	44.556	2.663	0.697	14.915	1.281	2.736	45.103	9.346	7.740	82.806	2.498
	7	1.099	27.344	0.837	0.880	11.233	1.582	0.535	13.297	0.508	4.151	53.749	2.149
	9	91.330	737.31	59.290	1.250	14.916	0.727	0.530	45.103	2.143	2.252	82.806	0.459



Fig. 5. Correlation among Langmuir maximum adsorption capacity, q_{max} versus (a) surface area, (b) pore volume and (c,d) molar ratios of O/C and (O+N)/C. Lines represent linear regression.

observed by Uchimiya et al. [38] and Ahmad et al. [37]. However, molar H/C ratio as an indication of aromaticity showed a negative correlation with modeled parameters, whereas molar O/C ratio showed a positive correlation. This result indicates that the less polar sites in biochars produced at high pyrolysis temperatures favor SMT adsorption. Furthermore, O-containing functional groups in biomass and biochars pyrolyzed at low temperatures adsorbed water as a result of hydrogen bonding, thereby preventing SMT adsorption [36]. This indicates that steam-activated biochar can be an effective sorbent to remove SMT from water.

4. Conclusions

Biochar properties showed drastic changes due to steam activation. For instance, steam-activated biochars at 700 °C had a larger surface area and pore volume compared to a non-activated counterpart. Although all four adsorption isotherm models (namely, Langmuir, Freundlich, Temkin, and Dubinin-Radushkevish) adequately described biochar adsorption, the best models were Freundlich and Temkin, suggesting the importance of electrostatic interactions among heterogeneous sites in biochars. Chemisorption is the major process in SMT sorption through electrostatic interactions, while various mechanisms such as hydrophobic, hydrogen bond, and π - π interactions may simultaneously participate in SMT sorption. Therefore, steam activation of biochar can be used to enhance the removal of SMT, and use of steam-activated burcucumber biochars could be an economic method to remove invasive plants from the environment as well as to remove SMT from aqueous media.

Acknowledgements

This research was supported by the Basic Science Research Program, through the National Research Foundation of Korea (NRF), funded by the Ministry of Education, Science and Technology (Project number: 2012R1A1B3001409) and 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.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhazmat. 2015.02.046.

References

- [1] Y.S. Ok, S.C. Kim, K.R. Kim, S.S. Lee, D.H. Moon, K.J. Lim, J.K. Sung, S.O. Hur, J.E. Yang, Monitoring of selected veterinary antibiotics in environmental compartments near a composting facility in Gangwon Province, Korea, Environ. Monit. Assess. 174 (2011) 693–701.
- [2] K.R. Kim, G. Owens, S.I. Kwon, K.H. So, D.B. Lee, Y.S. Ok, Occurrence and environmental fate of veterinary antibiotics in the terrestrial environment, Water Air Soil Pollut. 214 (2011) 163–174.
- [3] M.O. Aust, S. Thiele-Bruhn, J. Seeger, F. Godlinski, R. Meissner, P. Leinweber, Sulfonamides leach from sandy loam soils under common agricultural practice, Water Air Soil Pollut. 211 (2010) 143–156.

- [4] S. Wegst-Uhrich, D. Navarro, L. Zimmerman, D. Aga, Assessing antibiotic sorption in soil: a literature review and new case studies on sulfonamides and macrolides, Chem. Cent. J. 8 (2014) 5.
- [5] L. Ji, W. Chen, S. Zheng, Z. Xu, D. Zhu, Adsorption of sulfonamide antibiotics to multiwalled carbon nanotubes, Langmuir 25 (2009) 11608–11613.
- [6] L. Ji, Y. Wan, S. Zheng, D. Zhu, Adsorption of tetracycline and sulfamethoxazole on crop residue-derived ashes: implication for the relative importance of black carbon to soil sorption, Environ. Sci. Technol. 45 (2011) 5580–5586.
- [7] W. Yang, F. Zheng, X. Xue, Y. Lu, Investigation into adsorption mechanisms of sulfonamides onto porous adsorbents, J. Colloid Interface Sci. 362 (2011) 503–509.
- [8] H. Chen, B. Gao, H. Li, Removal of sulfamethoxazole and ciprofloxacin from aqueous solutions by graphene oxide, J. Hazard. Mater. 282 (2015) 201–207.
- [9] M. Teixidó, J.J. Pignatello, J.L. Beltrán, M. Granados, J. Peccia, Speciation of the ionizable antibiotic sulfamethazine on black carbon (Biochar), Environ. Sci. Technol. 45 (2011) 10020–10027.
- [10] M.K. Richter, M. Sander, M. Krauss, I. Christl, M.G. Dahinden, M.K. Schneider, R.P. Schwarzenbach, Cation binding of antimicrobial sulfathiazole to leonardite humic acid, Environ. Sci. Technol. 43 (2009) 6632–6638.
- [11] D. Mohan, A. Sarswat, Y.S. Ok, C.U. Pittman Jr., Organic and inorganic contaminants removal from water with biochar a renewable, low cost and sustainable adsorbent – a critical review, Bioresour. Technol. 160 (2014) 191–202.
- [12] IBI, Standardized product definition and product testing guidelines for biochar that is used in soil, International Biochar Initiative, April 2012 (2012).
- [13] M. Ahmad, S.S. Lee, A.U. Rajapaksha, M. Vithanage, M. Zhang, J.S. Cho, S.-E. Lee, Y.S. Ok, Trichloroethylene adsorption by pine needle biochars produced at various pyrolysis temperatures, Bioresour. Technol. 143 (2013) 615–622.
- [14] D. Moon, J.-W. Park, Y.-Y. Chang, Y. Ok, S. Lee, M. Ahmad, A. Koutsospyros, J.-H. Park, K. Baek, Immobilization of lead in contaminated firing range soil using biochar, Environ. Sci. Pollut. Res. 20 (2013) 8464–8471.
- [15] R. Bian, S. Joseph, L. Cui, G. Pan, L. Li, X. Liu, A. Zhang, H. Rutlidge, S. Wong, C. Chia, C. Marjo, B. Gong, P. Munroe, S. Donne, A three-year experiment confirms continuous immobilization of cadmium and lead in contaminated paddy field with biochar amendment, J. Hazard. Mater. 272 (2014) 121–128.
- [16] M. Zhang, M. Ahmad, S. Lee, L. Xu, Y. Ok, Sorption of polycyclic aromatic hydrocarbons (PAHs) to lignin: effects of hydrophobicity and temperature, Bull. Environ. Contam. Toxicol. 93 (2014) 84–88.
- [17] K. Lu, X. Yang, J. Shen, B. Robinson, H. Huang, D. Liu, N. Bolan, J. Pei, H. Wang, Effect of bamboo and rice straw biochars on the bioavailability of Cd, Cu Pb and Zn to Sedum plumbizincicola, Agric. Ecosyst. Environ. 191 (2014) 124–132.
- [18] M. Vithanage, A.U. Rajapaksha, X. Tang, S. Thiele-Bruhn, K.H. Kim, S.E. Lee, Y.S. Ok, Sorption and transport of sulfamethazine in agricultural soils amended with invasive-plant-derived-biochar, J. Environ. Manage. 141 (2014) 95–103.
- [19] M. Ahmad, D.H. Moon, M. Vithanage, A. Koutsospyros, S.S. Lee, J.E. Yang, S.E. Lee, C. Jeon, Y.S. Ok, Production and use of biochar from buffalo-weed (*Ambrosia trifida* L.) for trichloroethylene removal from water, J. Chem. Technol. Biotechnol. 89 (2014) 150–157.
- [20] A.U. Rajapaksha, M. Vithanage, J.E. Lim, M.B.M. Ahmed, M. Zhang, S.S. Lee, Y.S. Ok, Invasive plant-derived biochar inhibits sulfamethazine uptake by lettuce in soil, Chemosphere 111 (2014) 500–504.
- [21] Y. Yao, B. Gao, H. Chen, L. Jiang, M. Inyang, A.R. Zimmerman, X. Cao, L. Yang, Y. Xue, H. Li, Adsorption of sulfamethoxazole on biochar and its impact on reclaimed water irrigation, J. Hazard. Mater. 209–210 (2012) 408–413.
- [22] S. Hale, K. Hanley, J. Lehmann, A. Zimmerman, G. Cornelissen, Effects of chemical biological, and physical aging as well as soil addition on the sorption of pyrene to activated carbon and biochar, Environ. Sci. Technol. 45 (2011) 10445–10453.
- [23] D.W. Tsang, J. Hu, M. Liu, W. Zhang, K.K. Lai, I.C. Lo, Activated carbon produced from waste wood pallets: Adsorption of three classes of dyes, Water Air Soil Pollut. 184 (2007) 141–155.
- [24] J.A. Ippolito, D.A. Laird, W.J. Busscher, Environmental benefits of biochar, J. Environ. Qual. 41 (2012) 967–972.
- [25] I.M. Lima, A.A. Boateng, K.T. Klasson, Physicochemical and adsorptive properties of fast-pyrolysis bio-chars and their steam activated counterparts, J. Chem. Technol. Biotechnol. 85 (2010) 1515–1521.
- [26] A.U. Rajapaksha, M. Vithanage, M. Zhang, M. Ahmad, D. Mohan, S.X. Chang, Y.S. Ok, Pyrolysis condition affected sulfamethazine sorption by tea waste biochars, Bioresour. Technol. 166 (2014) 303–308.
- [27] J.J. Manyà, Pyrolysis for biochar purposes: a review to establish current knowledge gaps and research needs, Environ. Sci. Technol. 46 (2012) 7939–7954.

- [28] M.T. Bach, Impact of Surface Chemistry on Adsorption: Tailoring of Activated Carbon, University of Florida, 2007, 2015, pp. 132.
- [29] B.A. McCarl, C. Peacocke, R. Chrisman, C.C. Kung, R.D. Sands, Economics of biochar production, utilization and greenhouse gas offsets, in: J. Lehmann, A.S. Joseph (Eds.), Biochar for Environmental Management: Science and Technology, Earthscan, London, 2009, pp. 341–358.
- [30] Y.S. Ok, J.E. Yang, Y.-S. Zhang, S.-J. Kim, D.-Y. Chung, Heavy metal adsorption by a formulated zeolite-Portland cement mixture, J. Hazard. Mater. 147 (2007) 91–96.
- [31] M. Liu, D. Tsang, J. Hu, K. Ng, T. Liu, I. Lo, Adsorption of methylene blue and phenol by wood waste derived activated carbon, J. Environ. Eng. 134 (2008) 338-345.
- [32] Y.S. Ho, J.F. Porter, G. McKay, Equilibrium Isotherm studies for the sorption of divalent metal Ions onto peat: copper, nickel and lead single component systems, Water Air Soil Pollut. 141 (2002) 1–33.
- [33] Y.-S. Ho, W.-T. Chiu, C.-C. Wang, Regression analysis for the sorption isotherms of basic dyes on sugarcane dust, Bioresour. Technol. 96 (2005) 1285–1291.
- [34] A. Kapoor, R.T. Yang, Surface diffusion on energetically heterogeneous surfaces, AICHE J. 35 (1989) 1735–1738.
- [35] Y.C. Wong, Y.S. Szeto, W.H. Cheung, G. McKay, Adsorption of acid dyes on chitosan—equilibrium isotherm analyses, Process Biochem. 39 (2004) 695–704.
- [36] L. Li, P.A. Quinlivan, D.R.U. Knappe, Effects of activated carbon surface chemistry and pore structure on the adsorption of organic contaminants from aqueous solution, Carbon 40 (2002) 2085–2100.
- [37] M. Ahmad, S.S. Lee, X. Dou, D. Mohan, J.K. Sung, J.E. Yang, Y.S. Ok, Effects of pyrolysis temperature on soybean stover- and peanut shell-derived biochar properties and TCE adsorption in water, Bioresour. Technol. 118 (2012) 536–544.
- [38] M. Uchimiya, I.M. Lima, K.T. Klasson, L.H. Wartelle, Contaminant immobilization and nutrient release by biochar soil amendment: roles of natural organic matter, Chemosphere 80 (2010) 935–940.
- [39] Y. Chun, G. Sheng, C.T. Chiou, B. Xing, Compositions and sorptive properties of crop residue-derived chars, Environ. Sci. Technol. 38 (2004) 4649–4655.
- [40] I.M. Lima, A.A. Boateng, K.T. Klasson, Physicochemical and adsorptive properties of fast-pyrolysis bio-chars and their steam activated counterparts, J. Chem. Technol. Biotechnol. 85 (2010) 1515–1521.
- [41] A.U. Rajapaksha, M. Vithanage, M. Zhang, M. Ahmad, D. Mohan, S.X. Chang, Y.S. Ok, Pyrolysis condition affected sulfamethazine sorption by tea waste biochars, Bioresour. Technol. 166 (2014) 303–308.
- [42] F. Karaosmanoğlu, A.A. Işıgigür-Ergü denler, Sever, Biochar from the straw-stalk of rapeseed plant, Energy Fuels 14 (2000) 336–339.
- [43] A. Enders, K. Hanley, T. Whitman, S. Joseph, J. Lehmann, Characterization of biochars to evaluate recalcitrance and agronomic performance, Bioresour. Technol. 114 (2012) 644–653.
- [44] K. Sun, K. Ro, M. Guo, J. Novak, H. Mashayekhi, B. Xing, Sorption of bisphenol A, 17α-ethinyl estradiol and phenanthrene on thermally and hydrothermally produced biochars, Bioresour. Technol. 102 (2011) 5757–5763.
- [45] B. Chen, D. Zhou, L. Zhu, Transitional adsorption and partition of nonpolar and polar aromatic contaminants by biochars of pine needles with different pyrolytic temperatures, Environ. Sci. Technol. 42 (2008) 5137–5143.
- [46] J.J. Manyà, Pyrolysis for bochar purposes: a review to establish current knowledge gaps and research needs, Environ. Sci. Technol. 46 (2012) 7939–7954.
- [47] M. Ahmad, A.U. Rajapaksha, J.E. Lim, M. Zhang, N. Bolan, D. Mohan, M. Vithanage, S.S. Lee, Y.S. Ok, Biochar as a sorbent for contaminant management in soil and water: a review, Chemosphere 99 (2014) 19–33.
- [48] K. Biswas, S.K. Saha, U.C. Ghosh, Adsorption of fluoride from aqueous solution by a synthetic iron(III)-auminum(III) mixed oxide, Ind. Eng. Chem. Res. 46 (2007) 5346–5356.
- [49] M. Vithanage, A.U. Rajapaksha, X. Dou, N.S. Bolan, J.E. Yang, Y.S. Ok, Surface complexation modeling and spectroscopic evidence of antimony adsorption on iron-oxide-rich red earth soils, J. Colloid Interface Sci. 406 (2013) 217–224.
- [50] M. Keiluweit, M. Kleber, Molecular-level Interactions in soils and sediments: the role of aromatic π-systems, Environ. Sci. Technol. 43 (2009) 3421–3429.
- [51] H. Haham, A. Oren, B. Chefetz, Insight into the role of dissolved organic matter in sorption of sulfapyridine by semiarid soils, Environ. Sci. Technol. 46 (2012) 11870–11877.