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Pyrolysis condition affected sulfamethazine sorption by tea waste biochars

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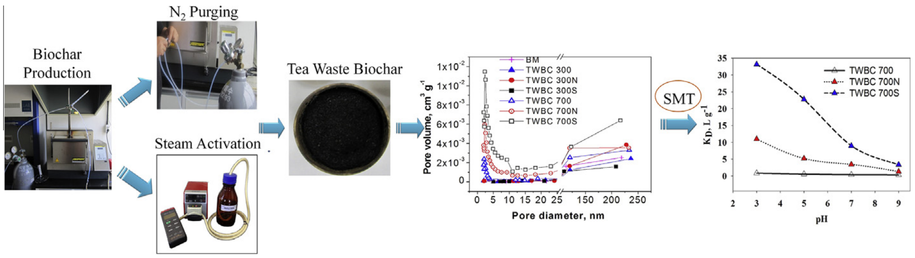
HIGHLIGHTS

- Sulfamethazine (SMT) removal by activated tea waste biochar was investigated.
- Steam activation showed a pronounced effect on biochar properties.
- Biochar properties played a significant role in determining SMT sorption capacities.
- Highest sorption of 33.81 mg g^{-1} was observed at lowest pH value, pH 3.

GRAPHICAL ABSTRACT



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ABSTRACT

Sulfamethazine (SMT) as a veterinary drug has been detected frequently in the environment. In this study, six biochars produced from tea waste (TW) at 300 and 700 °C with or without N_2 and steam activation were characterized and evaluated for SMT sorption in water. The sorption of SMT was interpreted as a function of biochar production condition, SMT concentration, pH and physicochemical characteristics of biochar. Distribution coefficient data showed high sorption of SMT at low pH (~3) and the highest sorption density of 33.81 mg g^{-1} was achieved by the steam activated biochar produced at 700 °C. The steam activation process increased the adsorption capacity by increasing the surface area of the biochar. The π–π electron donor–acceptor interaction, cation–π interaction and cation exchange at low pH were the primary mechanisms governing SMT retention by biochars. Overall, steam activated tea waste biochar could be a promising remedy of SMT removal from water.

1. Introduction

Veterinary pharmaceuticals enter the environment through various processes, such as through manure application and/or input of leachate from animal mass burial sites (Kim et al., 2012; Haller et al., 2002). There are serious concerns for high concentrations of antibiotics in soil and water, as antibiotic resistant bacteria can potentially form in such environments. Sulfonamides (SAs) are a widely used antibiotic group in the veterinary industry and are most frequently detected in water and soil (Kim et al., 2011; Ok et al., 2011). Sulfonamide is a generic name for p-aminobenzenesulfonamide (sulfanilamide) derivatives which vary in their amide substitution (Haham et al., 2012). It is extensively used in the swine industry to promote animal growth and to control infectious

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diseases. Sulfonamides concentrations up to 20 mg kg^{-1} in swine manure have been reported (Haller et al., 2002).

Sulfonamides are less sorptive, not readily biodegradable, but leachable (Kim et al., 2010; Thiele-Bruhn, 2003). Sulfonamide adsorptions have been studied on clays, humic substances, soils, nano materials and black carbon (Ji et al., 2011; Kahle and Stamm, 2007). Their ionization (cationic, anionic and zwitterionic) depends on the pH of the media as is shown in Fig. S1 (Teixidó et al., 2011). Hence, the adsorption of SAs is complex. Generally, the SA sorption decreases with increase in pH for both loamy sand and loam sediments due to the ionization (Vithanage et al., 2014). The adsorption of SAs is known to be governed by surface complexation or cation exchange mechanisms (Ji et al., 2011; Kahle and Stamm, 2007). Among many different parameters, pH, ionic speciation, ionic strength, soil texture, cation exchange capacity (CEC), and soil organic carbon (SOC) were considered as the most important factors influencing the sorption of SAs to clays and soils (Kahle and Stamm, 2007; Richter et al., 2009; Kim et al., 2010). However, the adsorption on various soils has been reported to be low (Thiele-Bruhn, 2003; Vithanage et al., 2014). The sorption of SAs onto graphene oxide was mainly thorough the π–π EDA interaction on the basal planes of graphene oxides and solution pH and ionic strength strongly affected the removal of SAs (Chen et al., 2014).

Very few publications reported the adsorption of SAs onto biochar, even though sulfonamide adsorption has been shown to increase with increasing aromaticity and electronegativity of biochar (e.g., Yao et al., 2012). The high SMT retention was proposed to be caused by the high surface area, micro-, meso- and macropores of BC and pH of the media; the pH of the media affects the ionization of SMT (Rajapaksha et al., 2014; Vithanage et al., 2014). Biochar is produced by pyrolysis under limited or no oxygen at moderate temperatures (300–700 °C) (Ahmad et al., 2013; Lehmann and Joseph, 2009). The properties of biochars depend on the feedstock type, pyrolysis temperature, and residence time (Ahmad et al., 2014b; Uchimiya et al., 2012). Biochar has been applied to improve soil quality, enhance C sequestration, and immobilize contaminants (Ahmad et al., 2014a; Rajapaksha et al., 2014). Many studies have focused on the development of biochars, their characterization and applications in water/soil decontamination (Ahmad et al., 2012, 2014b; Teixidó et al., 2011). However, only few studies were carried out on biochar activation (Azargohar and Dalai, 2008; Uchimiya et al., 2012). The relative importance of the surface functional groups on biochars, that are influenced by the production conditions such as N_2 purging (Manyà, 2012) and steam activation, in the sorption of SAs to biochar has not previously been evaluated. It is speculated that activation of biochar by steam and/or N_2 purging may enhance its sorption tendency. Particularly, the oxidizing agent such as steam may increase the surface area and pore volume of the biochar by removing the trapped products of incomplete combustion during thermal treatment.

In this study, biochars were made from tea waste at different temperatures and some were further activated under steam to improve the capacity for SA sorption and removal. The effect of surface functional groups, which depend on the temperature used and whether steam was used during biochar production, in the sorption of SAs onto biochar was investigated. Possible SA sorption mechanism(s) are discussed in this paper.

2. Experimental

2.1. Chemicals

Deionized water (resistivity of 18.2 MΩ) was used to prepare various solutions. SMT was obtained from Sigma Aldrich Chemical Co. (99% purity). Stock solution (100 ppm) was prepared in 1% methanol and was used to obtain the starting SMT concentrations in batch sorption studies.

2.2. Biochar production and characterization

Biochar samples were produced from tea waste, which contains approximately 31.05% holocellulose, 25.68% lignin, and 13.97% extractives (Uzun et al., 2010). Tea waste was collected after tea infusion, and was then washed several times with distilled water and air dried. The dried biomass was crushed and ground to <1.0 mm in particle size. Tea waste was pyrolyzed at 300 and 700 °C with a heating rate of 7 °C min^{-1} for 2 h under limited O_2, N_2 and steam in a modified N11/H Nabertherm (Germany) furnace (Ahmad et al., 2012). Gaseous N_2 was purged at a rate of 5 mL min^{-1}. For steam activation, samples were treated with 5 mL min^{-1} of steam for an additional 45 min under the peak temperature after the 2 h pyrolysis period had elapsed. A total of six biochars (BCs) viz., TWBC-300, TWBC-300N, TWBC-300S, TWBC-700, TWBC-700N and TWBC-700S were produced. The letters "TW", "BC", "N" and "S" represent tea waste (TW), biochars (BC) produced under N_2 (N) and steam (S), respectively.

Elemental compositions (C, H, N, S and O) of biochars and biomass were determined by dry combustion, using an elemental analyzer (model EA1110, CE Instruments, Milan, Italy). The H/C and (O + N)/C atomic ratios were calculated to evaluate the aromaticity and polarity, respectively. Moisture, mobile matter, ash and residual matter contents were determined using the methods described in Ahmad et al. (2013). The pH of the produced BCs was determined in a suspension of 1:5 (w/v) BC/de-ionized water using a digital pH meter (Orion, Thermo Electron Corp., Waltham, MA, USA). The surface functional groups in biochar and biomass were characterized by Fourier-transform infrared spectroscopy (FTIR) (Bio-Rad Excalibur 3000MX spectrophotometer, Hercules, CA, USA). Surface morphologies of all biochars were examined using a field emission scanning electron microscope (FE-SEM; 15.0 kv × 5.0 k) equipped with an energy dispersive spectrophotometer (SU8000, Hitachi, Tokyo, Japan). Brunauer–Emmett–Teller (BET) specific surface areas (S_{BET}), total pore volumes, and pore diameters were determined using a gas sorption analyzer (NOVA-1200; Quantachrome Corp., Boynton Beach, FL, USA).

2.3. Batch sorption experiments

Batch SMT sorption studies were carried out in the concentration range of 0–50 mg L^{-1} at pH 3.0, 5.0, 7.0 and 9.0 (10 mM ammonium phosphate for pH 3, 7, 9 and 10 mM ammonium acetate for pH 5) and ionic strength of 0.1 M (adjusted by ammonium chloride) (Richter et al., 2009). During the experiments, the pH was checked and adjusted with the conjugated acids and bases if required. A sorbent dose of 1 g L^{-1} was used for all sorption experiments. An equilibrium time of 72 h was chosen based on preliminary kinetic experiments. The solutions were equilibrated at 25 °C at 100 rpm in an incubator shaker (SI-300/300R/600/600R, JEIO TECH, Korea). The samples were then filtered using Whatman 0.45 μm PVDF disposable filters, and kept in Agilent amber color vials prior to HPLC analysis. All experiments were conducted at 25 °C. Losses of SMT during the filtration were determined to be negligible based on the blank samples which contained only the SMT solution. The SMT concentration in samples was determined by HPLC (SCL-10A, Shimadzu, Tokyo, Japan) equipped with an auto-sampler (SIL-10AD, Shimadzu) and UV–VIS detector (SPD-10A, Shimadzu). A reverse-phase Sunfire C18 column (4.6 mm × 250 mm, Waters, USA) was used in a column oven (CTO-10AS; Shimadzu, Japan). The column was maintained at 25 °C with a flow rate of 0.5 mL min^{-1}. 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 ramped from 96% mobile phase A and 4% mobile phase B, to 70% mobile phase A and 30% mobile phase B respectively in the first minute, and was then maintained for 19 min. The injection volume was 20 μL. The absorbance was measured at 265 nm (Ji et al., 2009).

2.4. Experimental data modeling

The SMT batch sorption data were analyzed using Freundlich (Eq. (S1)) and Langmuir (Eq. (S2)) isotherms.

The occupied area per adsorbed SMT molecule (A_m) was calculated for TWBC-700, TWBC-700N and TWBC-700S using Eq. (1) (Yang et al., 2011b):

$$A_m = \frac{S_{\mathrm{BET}} \times M_W}{q_{\max} \times N_A} \tag{1}$$

where S_{BET} is the biochar surface area ($m^2\ g^{-1}$), M_W is the molecular weight of SMT, N_A is the Avogadro constant (6.023×10^{23}), and $q_{\max}$ is the maximum amount absorbed per unit weight of biochar ($g\ g^{-1}$) at pH 5.

The volume occupied by SMT molecules (V_{SMT}) was calculated on the basis of molecular volume (M_V) of SMT (199.8 $cm^3\ mol^{-1}$) (Bao et al., 2014) as given in Eq. (2). The surface coverage of SMT (S_{SMT}) was calculated using the cross sectional area (A_d as 70.35 Å) of the SMT molecule using Eq. (3) (Ferrero, 2010):

$$V_{\mathrm{SMT}} = \frac{q_{\max} \times M_V}{M_W} \tag{2}$$

$$S_{\mathrm{SMT}} = \frac{q_{\max} \times N_A \times A_d}{M_W} \tag{3}$$

Pearson's correlation coefficient (r) and probability (P) values were calculated using the SAS ver. 9.1 (SAS Institute, Cary, NC, USA).

3. Results and discussion

3.1. Biochar characterization

The properties of the tea waste biomass substantially changed upon pyrolysis; the effect of the pyrolysis process on tea waste properties varied with temperature and addition of N_2 or steam. The molar O/C ratio decreased with increasing pyrolysis temperature (Table 1), and thus biochars produced under high-temperature were less hydrophilic (Ahmad et al., 2012). The decrease in the polarity index (O + N)/C with increasing pyrolysis temperature indicates a reduction in the surface polar functional groups. The relatively lower H/C values of 0.28, 0.32 and 0.29 for TWBC-700, TWBC-700N and TWBC-700S, respectively, than TWBC-300 (0.89), indicate that biochars produced under high temperature were highly carbonized, and exhibited a highly aromatic structure, which was supported by the FTIR data (Fig. S2).

All peak assignments in the FTIR spectra of all biochars and feedstock shown in Fig. S2 were based on published data in the literature (Cao and Harris, 2010). Different spectra were obtained between biochars produced under low (TWBC-300, TWBC-300N, TWBC-300S) and high temperatures (TWBC-700, TWBC-700N, TWBC-700S). With the high pyrolysis temperature, the broad O—H stretching band from 3200 to 3500 cm^{-1} and the aliphatic C—H stretching band from 2820 to 2980 cm^{-1} decreased markedly, indicating the loss in labile aliphatic compounds. The bands around 1000–1100 cm^{-1} and 1410–1490 cm^{-1} were possibly due to the presence of PO_4^{3-} and CO_3^{2-}, respectively (Cao and Harris, 2010). The bands appeared at 885 and 750 cm^{-1} for TWBC-700, TWBC-700N and TWBC-700S were possibly due to out-of-plane deformation of aromatic C—H (Ahmad et al., 2012). Thus, biochars produced at 700 °C were more aromatic than those produced at 300 °C (Fig. S2). However, biochars produced under the same temperature but in a different environment (N_2 or steam) did not show any significant difference, indicating lack of significant compositional changes (Ippolito et al., 2012).

Scanning electron microscopic (SEM) images confirmed the amorphous and heterogeneous structure of tea waste biochars. The presence of both open and closed vesicles at high temperatures indicates the formation and release of volatile components and the gradual deformation of the cells, with a gradual melting of various cellular components with increasing temperature (Uzun et al., 2010). The morphology of the biochar particles produced under high temperature showed indirect evidence of the violent release of volatile compounds during pyrolysis. The release of volatile compounds as a result of the build-up of substantial internal pressures leads to the coalescence of the smaller pores, enlargement of internal cavities, and the rupturing of various structures (Ahmad et al., 2014a; Uzun et al., 2010).

Furthermore, SEM images showed morphological changes in biochars produced at the same temperature under different conditions (e.g., TWBC-700 vs. TWBC-700N vs. TWBC-700S) (Fig. S3). A considerable increase in surface area (2.28–342.22 $m^2\ g^{-1}$) was observed with increasing pyrolysis temperature. The surface area was further increased by steam activation under high temperature (576.09 $m^2\ g^{-1}$) (Table 1). Adding steam to the pyrolysis reaction would have liberated additional syngas from the biochar, mainly in the form of hydrogen, thereby increasing pore volume and surface area (Fig. 1) (Demirbas, 2004). These characteristics clearly indicate that only physical changes occurred due to N_2 and/or steam treatments but not compositional changes.

3.2. SMT sorption and distribution coefficients

The sorption data fits the Freundlich model with high regression coefficients (r^2) (Fig. 2, Table 2). The K_F values for the BCs produced at 700 °C were higher than those produced at 300 °C, indicating their higher capacity for SMT adsorption. The Freundlich parameter, n, was always less than 1 (Table 2), suggesting that the sorption sites on biochars were not homogeneous.

The Langmuir adsorption capacity or $q_{\max}$ values for TWBC-700N and TWBC-700S at pH 5 were ~50 and ~58 times higher than that for BM (Table 2). More interestingly, biochars produced under the same temperature with different conditions, i.e., TWBC-700, TWBC-700N and TWBC-700S, had different sorption capacities. The sorption capacity at pH 5 was BM < TWBC-300S < TWBC-300 < TWBC-300N < TWBC-700 < TWBC-700N < TWBC-700S. The sorption capacities were positively correlated with specific surface area ($r = 0.92$, $P = 0.004$) and pore volume ($r = 0.96$, $P = 0.001$) (Table 1), indicating that the interaction between the sorbate and biochars was surface area-dependent (Yang et al., 2011b). The calculated separation factor (R_L) as an indicator of favorability for SMT sorption is shown in Fig. 2(b). The R_L values were <1 for all sorbents investigated through this study, indicating that SMT sorption was favorable. Steam activated biochar produced at 700 °C (TWBC-700S) was the most favorable.

In order to better explain the biochars sorption affinities, the sorption distribution coefficient, K_D, was calculated at pH 5.0 (Fig. 3) at low equilibrium concentrations. Within the tested concentration, K_D was in the order of 10^4 ($L\ kg^{-1}$) for TWBC-700S and TWBC-700N. The observed values were remarkably larger than those reported in the literature for natural geo-sorbents, including soils ($K_D < 10\ L\ kg^{-1}$), humic substances, and clay minerals ($K_D < 100\ L\ kg^{-1}$) (Ji et al., 2009) and less than those recorded for black carbon ($K_D < 10^6\ L\ kg^{-1}$) (Teixidó et al., 2011). The deter-

Table 1
Proximate and ultimate analyses, surface areas, pore volumes and pore diameters of tea waste biomass (BM) and its biochars produced at 300 and 700 °C with different conditions. “S” represents steam activated biochars, whereas “N” represents biochars produced under N_2 flow.

Sample	Proximate analysis[a]					
	pH	Yield (%)	Moisture (%)	Mobile matter (%)	Resident matter (%)	Ash (%)
BM	5.14 ± 0.02		10.86 ± 0.02	62.47 ± 0.41	23.44 ± 0.33	3.22 ± 0.10
TWBC-300	7.93 ± 0.05	55.52 ± 1.23	2.80 ± 0.06	39.75 ± 0.52	51.76 ± 0.44	5.69 ± 0.01
TWBC-300N	6.74 ± 0.03	55.82 ± 0.13	0.87 ± 0.12	35.73 ± 2.95	57.52 ± 2.53	5.87 ± 0.29
TWBC-300S	8.64 ± 0.01	53.26 ± 1.34	0.18 ± 0.07	30.82 ± 5.90	62.58 ± 5.13	6.42 ± 0.69
TWBC-700	11.05 ± 0.04	28.35 ± 1.90	4.23 ± 0.07	16.82 ± 2.03	68.07 ± 2.22	10.87 ± 0.26
TWBC-700N	9.97 ± 0.06	22.35 ± 0.25	9.02 ± 0.01	26.12 ± 3.74	53.24 ± 3.08	11.60 ± 0.67
TWBC-700S	10.48 ± 0.04	18.42 ± 0.32	1.40 ± 0.48	18.62 ± 3.92	63.23 ± 3.29	16.73 ± 0.14

	Ultimate analysis										
	C^b (%)	H^b (%)	N^b (%)	O^b (%)	S^b (%)	Molar H/C	Molar O/C	Molar (O + N)/C	Surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Pore diameter (nm)
BM	51.74	6. 63	3.69	37.74	0.20	1.53	0.55	0.61	2.23	0.0059	3.022
TWBC-300	70.05	5.24	4.97	19.62	0.12	0.89	0.21	0.27	2.28	0.0059	4.323
TWBC-300N	68.53	3.96	5.48	21.91	0.12	0.69	0.24	0.31	0.90	0.0074	7.511
TWBC-300S	71.47	4.75	5.48	18.16	0.14	0.79	0.19	0.26	1.46	0.0042	4.676
TWBC-700	85.11	1.98	3.92	8.88	0.09	0.28	0.08	0.12	342.22	0.0219	1.756
TWBC-700N	79.91	2.17	4.28	13.54	0.11	0.32	0.13	0.17	421.31	0.0576	1.904
TWBC-700S	82.37	2.06	3.89	11.57	0.10	0.29	0.11	0.15	576.09	0.1091	1.998

[a] Mean ± standard deviation (SD) in triplicate determinations.
[b] Ash and moisture free.

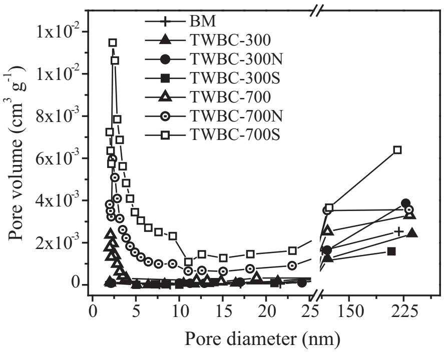

Fig. 1. Pore size distributions of the biochars (BC) and the biomass (BM) of tea waste (TW). “S” represents steam activated biochars, whereas “N” represents biochars produced under N_2 flow.

mined sorption was much higher for TWBC-700S than those produced at 700 and 300 °C, which is also consistent with the surface area accessibility of the sorbent. Fig. S4 shows the dependence of K_D values on pH for biochars produced at 700 °C; the K_D values for SMT sorption was the highest at pH 3, and decreased with increasing pH.

3.3. Possible mechanisms for SMT sorption

The physical changes including surface area and pore volume occurred in steam treated biochars increase SMT diffusion into these pores, thereby enhancing the sorption efficiency, would likely be one of the mechanisms involved in the increased SMT sorption by the steam activated biochar produced under high temperature (Yang et al., 2011a). As shown in Fig. 1, steam activated TWBC consisted of a large number of micropores (0–2 nm) with high pore volumes as compared to other TWBCs studied. In addition, TWBC-700S exhibited high meso- (2–50 nm) and macropores (>50 nm). The SMT molecular size is reported to be 1.050 nm × 0.672 nm (Braschi et al., 2010). Therefore, SMT may diffuse into micro-, meso- and macropores. The TWBC-700S and TWBC-700N had high micropore volumes, which likely contributed to the high SMT retention. The occupied areas per sorbed SMT molecule (A_m) were calculated to be 2403.40 (TWBC-700), 727.53 (TWBC-700N) and 860.16 Å^2 (TWBC-700S). The A_m values for TWBC-700N and TWBC-700S were less than TWBC-700, resulting from a much more compact molecular arrangement on the surface (Yang et al., 2011a). This demonstrates that the strength of interac-

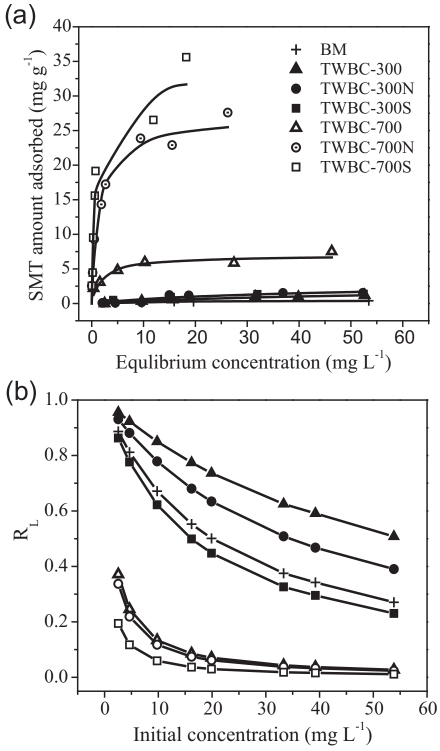

Fig. 2. (a) Langmuir adsorption isotherms of SMT and (b) separation factor (R_L) obtained from Langmuir isotherms at pH 5 by tea waste biomass (BM), biochars produced at 300 °C (TWBC-300) and at 700 °C (TWBC-700) under various conditions. Lines represent the model predicted data fittings. “S” represents steam activated biochars, whereas “N” represents biochars produced under N_2 flow.

Table 2
Nonlinear Freundlich and Langmuir isotherm constants for sulfamethazine (SMT) adsorption on to biochars (BCs) and biomass (BM). "S" represents steam activated biochars, whereas "N" represents biochars produced under N_2 flow.

Adsorbent	Langmuir				Freundlich		
	pH	k (L mg^{-1})	q_{max} (mg g^{-1})	r^2	K_F (mg^{1-n} L^n g^{-1})	n	r^2
TWBC-700	3	0.464	7.12	0.82	2.67	0.275	0.94
TWBC-700N	3	1.227	30.06	0.91	15.47	0.234	0.91
TWBC-700S	3	2.454	33.81	0.90	19.59	0.219	0.87
BM	5	0.050	0.537	0.91	0.06	0.497	0.89
TWBC-300	5	0.018	2.43	0.98	0.07	0.723	0.96
TWBC-300N	5	0.029	2.79	0.83	0.13	0.654	0.79
TWBC-300S	5	0.062	1.88	0.94	0.21	0.507	0.89
TWBC-700	5	0.661	6.58	0.83	3.02	0.229	0.92
TWBC-700N	5	0.767	26.76	0.96	11.66	0.272	0.95
TWBC-700S	5	1.619	30.95	0.92	15.08	0.270	0.91
TWBC-700	7	1.080	8.25	0.93	1.316	0.435	0.83
TWBC-700N	7	0.494	26.49	0.95	10.37	0.285	0.89
TWBC-700S	7	1.250	27.47	0.96	13.30	0.250	0.92
TWBC-700	9	0.761	2.70	0.60	1.37	0.191	0.91
TWBC-700N	9	0.235	16.72	0.90	4.70	0.346	0.91
TWBC-700S	9	0.494	24.62	0.93	9.82	0.278	0.89

K_F is a constant indicative of the relative adsorption capacity of the adsorbent (mg g^{-1}) and n is a constant indicative of the intensity of the adsorption, k is the Langmuir affinity parameter (L mg^{-1}), q_{max} is the Langmuir capacity parameter (mg g^{-1}).

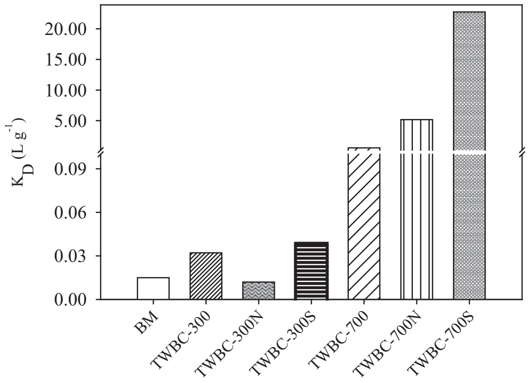

Fig. 3. Distribution coefficients (K_D) at pH 5 of biomass (BM) and biochars (BCs) produced from tea waste (TW) under different conditions at low equilibrium concentrations. "S" represents steam activated biochars, whereas "N" represents biochars produced under N_2 flow.

tions on TWBC-700N and TWBC-700S was more intense than that on TWBC-700, indicating the different contribution of sorption interactions (Yang et al., 2011a). The calculated values for surface coverage by SMT were high for TWBC-700 (10.02 m^2 g^{-1}), TWBC-700N (40.74 m^2 g^{-1}) and TWBC-700S (47.12 m^2 g^{-1}) compared to other biochars (<5 m^2 g^{-1}). It should be noted that the surface area covered by one SMT molecule depends on the orientation of the SMT molecule, i.e., the angle between the longest axis of the SMT and the surface plane. The volume occupied by SMT molecules was the highest for TWBC-700S (0.02 cm^3 g^{-1}), which is in agreement with the highest adsorption capacities of this biochar. Furthermore, biochars produced at 700 °C had fewer O containing functional groups which reduce the surface interaction with water molecules. Oxygen containing functional groups compete with organic compounds for sorption and show steric hindrance to some pore networks (Zhu et al., 2005).

A possible mechanism for SMT sorption on biochar at low pHs can be explained by π^+–π electron donor–acceptor (EDA) (which includes the cation–π bonding) interactions between the protonated amino groups on the ring (Fig. S1) and electron rich graphene surfaces, which may be expanded to that of biochar, rather than the normal cationic exchange reactions (Ji et al., 2009; Teixidó et al., 2011). Cation exchange reactions have been highlighted specially for SA drugs with clay containing materials and natural soils (Kahle and Stamm, 2007) and it can also be valid for biochars. The distribution coefficient data obtained are in agreement with the study of Teixidó et al. (2011). The proposed mechanisms are supported by the pH effect on sorption. At pH 3, SMT$^+$ sorption exhibits strong cation–π bonding, as indicated by high K_D values (Fig. S4), whereas under neutral conditions (at pH 7) the distribution coefficients decreased, indicating a partial cation exchange and zwitterionic interactions as the main mechanisms for the sorption of SMT onto biochar (Teixidó et al., 2011). In the alkali region at pH 9, as anionic SMT species prevail in the aqueous phase, low K_D values were observed, which may be due to electrostatic repulsions between negatively charged SMT molecules and the biochar surface, and the negative charge assisted H-bonding was believed to be the predominant sorption mechanism (Teixidó et al., 2011). SMT sorption on all the biochars was lower in alkaline than in acidic pH conditions. Overall, the sorption capacity of TWBC-700S was higher than that of TWBC-700N and TWBC-700. Therefore, TWBC-700S would be the best biochar, among those tested in this study, to be used for SMT removal over a broad pH range, which can provide a distinct advantage in environmental remediation processes.

4. Conclusions

Steam activated biochar produced at 700 °C (TWBC-700S) showed the highest SMT sorption among all biochars studied due to its largest surface area and pore volume. Sorption of SMT on biochars was pH dependent, higher sorption was recorded under low pH conditions. We conclude that the steam activated biochars produced under high temperatures is effective for SMT removal under broad environmental pH conditions. Giving the significant implication of producing designer biochars for improved efficiencies of contaminant removal, further research should be conducted to field-test the application of such biochars for the remediation of SMT contaminated water or soils.

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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.biortech.2014.05.029.

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