Sorption of Atrazine in Tropical Soil by Biochar Prepared from Cassava Waste

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Biochar (BC) is a carbonaceous and porous product generated from the incomplete combustion of biomass and has been recognized as an efficient adsorbent. This study evaluated the ability of BC to sorb atrazine pesticide in tropical soil, and explored potential environmental values of BC on mitigating organic micro-pollutants. BC was produced from cassava waste *via* pyrolyzation under oxygen-limiting conditions at 350, 550, and 750 °C (MS350, MS550, and MS750, respectively). Three biochars were characterized and investigated as sorbents for the removal atrazine from tropical soil. BC pyrolyzed at higher temperatures more quickly reached equilibrium. The pseudo-second-order model perfectly simulated the sorption kinetics for atrazine with the coefficients R^2 above 0.996, and the sorption amount at equilibrium (q_e) was 0.016 mg/g for MS350, 0.025 mg/g for MS550 and 0.050 mg/g for MS750. The isotherms of MS350 displayed relatively linear behavior, whereas the sorption of atrazine on MS550 and MS750 followed a nonlinear isotherm. The sorption data were well described by the Freundlich model with $\log K_F$ of 0.476 for MS350, 0.771 for MS550, 1.865 for MS750. A thermodynamic study indicated that the sorption of atrazine in BC-added soil was a spontaneous and endothermic process and was primarily controlled by physisorption. In addition, lower pH was conducive to the sorption of atrazine in BC-added soil.

Keywords: Sorption; Biochars; Cassava wastes; Atrazine; Paddy soil

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INTRODUCTION

Atrazine (AT), 2-chloro-4-ethylamino-6-isopropylamino-s-triazine, is one of the most widely applied pesticides for the control of annual grasses and broadleaf weeds in cereals, orchards, and plantations; it is effective because it inhibits photosynthesis (Mudhoo and Garg 2011). Because of its widespread application, AT and its metabolites have been frequently detected in the environment beyond safe concentrations (Jin and Ke 2002; Sun *et al*. 2010; Lima *et al*. 2011; Lin and Chu 2011). Recently, it has been recognized as an endocrine disruptor and a possible carcinogen by the EPA (Lin and Chu 2011), as it has adverse effects on the central nervous, endocrine, and immune systems of mammals and aquatic life (Hayes *et al*. 2002; 2006; 2010). Therefore, widespread occurrence of AT and its adverse health effects have led to extensive environmental studies. Sorption is one of the major processes for the removal of AT. Several studies have evaluated the removal efficiency of AT in soils and water bodies by adding different sorbents, such as organic matter fractions, humics, carbonate soil, activated carbon, and minerals (Salvestrini *et al*. 2010; Shi *et al*. 2010; Sun *et al*. 2010; Guzman-Perez *et al*. 2011; Jamil *et al.* 2011; Kovaios *et al.* 2011; Kasozi *et al.* 2012).

At present, a number of waste materials from agricultural products have been exploited as alternatives to activated carbon to remove hazardous chemicals (Mittal *et al*. 2005; Gupta *et al*. 2011). Biochar (BC) has attracted much attention in environmental and agricultural applications as an efficient, versatile, and environment-friendly material. It is also of interest for its potential for *in situ* environmental remediation of organic pollutants due to its specific properties (Cao *et al.* 2009). BC is a carbon-rich material generated from oxygen-limited pyrolysis of biomass and has high aromaticity. Its sources, such as plant pruning (Zheng *et al*. 2010), straw (Nag *et al*. 2011), woodchips, livestock, and sludge, are widely available. BC plays a crucial role in controlling the environmental effects of pollutants and risks to the ecosystem with a porous structure and special physicochemical properties. Studies dealing with the sorption of pollutants, such as heavy metals (Chen *et al*. 2011), antibiotics (Teixido *et al*. 2011), and pesticides (Mesa and Spokas 2011), on BC suggest that BC may be an effective material for pre-concentration and removal of contaminants. The sorption of AT on BC from aqueous solution has been reported by Zheng *et al.* (2010), Zhang *et al*. (2011), Zhang *et al*. (2013), and Zhao *et al*. (2013). They found that BC demonstrated high efficiency in improving the sorption affinity for AT. However, little is known concerning the sorption of AT in BC-added soil, especially in tropical areas. Understanding of sorption kinetics and thermodynamics is also critical for AT removal from the environment.

Cassava is a common food crop in tropical area and is mainly used to produce starch and alcohol. However, cassava processing results in a large amount of waste. It is reported that the output is more than 15 million tons per year, with an annual growth rate of over 30% in China (Wang *et al*. 2012). In this study, cassava waste was chosen as the source to produce BC, which is valuable for waste resource utilizations and BC application to agriculture.

The objective of the study was to obtain a wide and deep understanding of the influence of BC on pesticides. Three BC samples were generated from cassava waste at different pyrolysis temperatures, and their characteristics were compared. Atrazine was selected as the model agricultural chemical. The sorption behavior of AT was investigated in tropical soil with BC amendment, and the sorption mechanism was determined.

EXPERIMENT

Materials

Chemicals

Atrazine (99.9% purity) was purchased from Dr. Ehrenstofer company (German). Atrazine is a weakly basic pesticide with a p*K*a value of 1.7, and its solubility in water is 28 mg/L (20 °C) with a logk_{ow} of 2.74 (Chen *et al.* 2009). Methanol was supplied by Sinopharm Chemical Reagent Co. Ltd. (China). Calcium chloride and sodium azide were of analytical grade. Deionized water (18.25 MΩ) was obtained from a Spring-S60i+PALL system (Research Scientific Instruments Co. Ltd. China).

Properties of soil

Paddy soils (0 to 20 cm) used for sorption experiments were collected from Qiongzhong in Hainan Province, China. Posthole diggers washed with deionized water between samples were used to collect the soils, which were air-dried slowly under sheets of paper at room temperature until the moisture content reached about 3%. The soil samples were then sifted through a 40-mesh sieve for the analysis of their chemical and physical properties and a 1-mm sieve for sorption experiments. Characteristics of the soils were determined according to routine methods (Institute of Soil Science 1978) and are listed in Table 1.

Table 1. Physicochemical Properties of Soil

Sample	pH	Organic	CEC[a]	Texture (%)		
	1:20[b]	%	cmol/kg	Sand grain	Clay grain	Silt grain
Paddy soil	5.21	4.19	7.16	42.09	33.99	23.92

[a] cation exchange capacity.
[b] adding soil to deionized water in a mass ratio of 1:20.

Methods

Production and characterization of biochar

Cassava waste was collected from Danzhou City, Hainan Province, China. The waste was air dried, cut into small pieces, and mashed into powder with a crusher. The powder was stacked in porcelain crucibles with lids and placed in a muffle furnace under O_2-limited conditions at 200 °C for 2 h, then subsequently heated at 350/550/750 °C for 3 h to carbonize. The BC was ground to pass through 0.3-mm (60-mesh) sieves and stored in hermetic bags. Based on the temperature at which they were carbonized, the BC was denoted as MS350, MS550, and MS750.

The physical and chemical properties of the BC were investigated. Yields of BC were calculated by mass difference between source material and BC. Ash content was measured by combusting the BC at 750 °C for 4 h. The pH value of the BC was measured by adding the BC to deionized water in a mass ratio of 1:20. The cation exchange capacity of the samples was analyzed according to the $BaCl_2$-H_2SO_4 forcing exchange method (Zhang *et al*. 2014). The abundance of elemental C, H, N, and S was determined using a Vario EL analyzer (German). The O content was estimated by mass difference (100%-C, H, N, and ash %). Scanning electron microscopy (SEM) analysis of the samples was performed on a Zeiss EVO18 operating at an accelerating voltage of 20 kV. The Brunauer-Emmett-Teller (BET) surface area and the pore volume of the samples were measured using a JW-BK224 surface area analyzer (JWGB Sci. & Tech. Co. Ltd., China) and calculated from the BET equation. The functional groups of the samples were detected using Fourier transform infrared (FTIR) spectroscopy (Nicolet iS10, Thermo Fisher Scientific), recording the spectral region from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}.

Sorption experiments

Sorption experiments were conducted using a batch equilibration method. Briefly, 10 mL of AT solution that contained 0.01 M $CaCl_2$ to maintain a constant ionic strength and 0.2 g/L of NaN_3 to inhibit microbial activities and an appropriate amount of sample (BC/(soil + BC), w/w: 1%) was placed in centrifuge tubes. The samples were designated as CK (without BC), MS350, MS550, and MS750 based on their types. All tubes were agitated in the dark at 200 rpm at 25 °C. Preliminary experiments confirmed that 24 h was suitable to reach equilibrium. After equilibrium, the samples were centrifuged for 5 min at 4000 rpm, and supernatants were filtered through a 0.45-μm membrane using a syringe. To determine the desorption behavior, the remaining supernatant was replaced by fresh background solution without AT.

To analyze the sorption kinetics, sampling times were set at 35, 180, 360, 540, 1290, 1440, and 2880 min. AT initial concentration was 5 mg/L. To evaluate the impact of the solution temperature on the isothermal sorption and compare the sorption capacities of AT on the four sorbents, sorption equilibrium experiments were carried out at 15, 25, and 35 °C, at initial concentrations of 0.5, 1, 5, 10, and 20 mg/L. The effect of solution pH on AT sorption was investigated using 0.1 M HCl and 0.1 M NaOH to adjust the pH of the suspensions to values of 3, 5, 7, and 9. During the experimental process, the solution pH was checked frequently to verify that it remained unchanged. All experiments were carried out in triplicate. Preliminary experiments showed that loss during the tests was negligible, and no interference was found. Origin 8.0 software was used to analyze kinetics and isotherms.

The filtrates were analyzed using a Waters 2695 Separations Module HPLC (U.S.A.) equipped with a 2487 UV detector. Solutes were separated using a Gemini C18 analytical column (150 mm × 4.0 mm; ID, 5 μm) at a set temperature of 35 °C. The mobile phase consisted of methanol/water (70:30, v/v), the flow rate was 1.0 mL/min, and the detector wavelength was 220 nm. The retention time of AT was 4.8 min.

RESULTS AND DISCUSSION

Characterization of Biochar

The physicochemical properties of the BC are presented in Table 2. With increasing pyrolysis temperature, the BC yields decreased from 29.81% for MS350 to 18.79% for MS750. The total number of basic groups was increasing due to pyrolysis of biomass, and the pH values were in the order of MS750 > MS550 > MS350. Chen *et al.* (2011) indicated that alkali salts begin to separate from the organic matrix during biomass pyrolysis, resulting in an increase of the pH of the BC. The high pH of the BC suggested that it can have potential for tropical soil remediation. Ash is known to be an important factor to influence the sorption behavior of hydrophobic organic contaminants (HOCs). Some organic sorption sites in BC can be blocked by ash or become difficult to access due to their interactions with inorganic moieties (Zhang *et al.* 2013). As the charring temperature increased, the ash content of BC also increased, *e.g.*, 5.03% for cassava waste and 30.56% for MS750.

With increasing pyrolysis temperature, the C content increased, while the H and N contents decreased. Chen *et al.* (2008) demonstrated that the C content increased with increasing charring temperature. However, the C content of MS750 (62.38%) was lower than that of MS550 (68.93%), which indicated that some amorphous carbon was decomposed into CO_2 at 750 °C; the ash content also increased. The elemental ratio of H/C was used to evaluate the carbonization degree of the BC. Thus, an H/C ratio of 0.024 for MS750 suggested its high degree of carbonization. The decrease in the O/C and

(N+O)/C ratios indicated an increase in aromaticity and a reduction in polarity. Hydrophobic carbon can provide more sorption domains for HOCs, and aromaticity and pore-filling are positively correlated with aromatic carbon contents (Teixido *et al*. 2011; Yang *et al*. 2011).

Scanning electron microscopy (SEM) was used to examine the specific surface area changes of BC and to determine the elemental composition of the surface (Fig. 1). The surface structure of cassava waste was complete and smooth before heating. However, after pyrolysis, its structure became rough, and multiple holes were formed, which increased the surface area of the BC. The surface properties of the biochars are given in Table 3. The specific surface area (SSA) of the BC increased as the charring temperature increased, from 48.19 m^2/g for MS350 to 430.37 m^2/g for MS750, and some micropores could be detected in MS750 (0.144 cm^3/g). Total pore volume (TPV) and micropore volume mostly depend on the charring temperature (Cao and Harris 2010). Increasing pyrolysis temperature contributed to the increase in aromatic C content by the progressive destruction of -OH, ester C=O, aliphatic CH_2, and C-O groups.

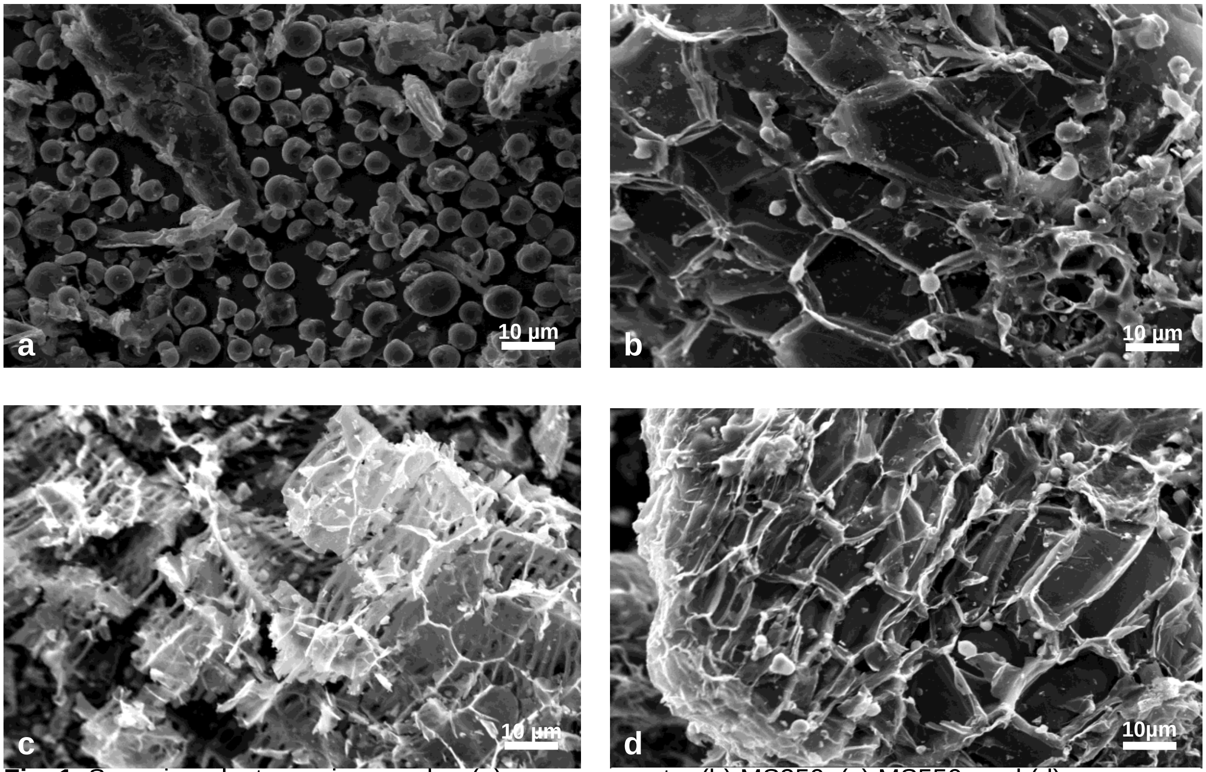

Fig. 1. Scanning electron micrographs: (a) cassava waste, (b) MS350, (c) MS550, and (d) MS7500

The FTIR spectra of the three BCs were similar for most of the wavenumbers (Fig. 2). As pyrolysis temperature increased, the band intensities at 3400 cm^{-1}, the stretching vibration of hydroxyl groups (Chen *et al*. 2011), declined, suggesting that cellulose and lignin were transformed into aromatic carbon. The disappearance of the bands at 2940 and 2904 cm^{-1}, the $-CH_2$ and $-CH_3$ groups of long-chain aliphatic carbons, respectively (Das *et al*. 2009), implied the destruction of the original lignin structure at 350 °C. The bands near 1730 cm^{-1} and at 1650 cm^{-1} were appointed to the stretching vibrations of ester carbonyl groups and C=O stretching vibrations of amides, respectively (Das *et al*. 2009).

Table 2. Properties of Biochar and Cassava Waste

Sample	Yields	pH	CEC	Ash	Elemental analysis							
	%	1:20	cmol/kg	%	C (%)	N (%)	H (%)	S (%)	O[a] (%)	H/C	O/C	(N+O)/C
Cassava	0	-[b]	-	5.03	38.06	0.90	7.00	0.17	49.01	0.18	1.29	1.31
MS350	29.81	6.08	23.2	12.79	58.52	1.50	3.57	0.15	23.62	0.06	0.40	0.43
MS550	23.61	7.41	77.3	17.12	68.93	1.26	2.46	0.13	10.23	0.04	0.15	0.17
MS750	18.79	9.55	213.2	30.56	62.38	1.23	1.52	0.15	4.31	0.02	0.07	0.09

[a] estimated by mass difference (100%-C, H, N, and ash %)
[b] presents “not been analyzed”

Table 3. Specific Surface Areas and Pore Structure Parameters of Biochar

Biochar	SSA (m^2/g)	TPV (cm^3/g)	Micropore volume (cm^3/g)	Average pore size (nm)
MS350	48.19	0.080	0.011	6.605
MS550	167.55	0.183	0.036	4.361
MS750	430.37	0.169	0.144	15.681

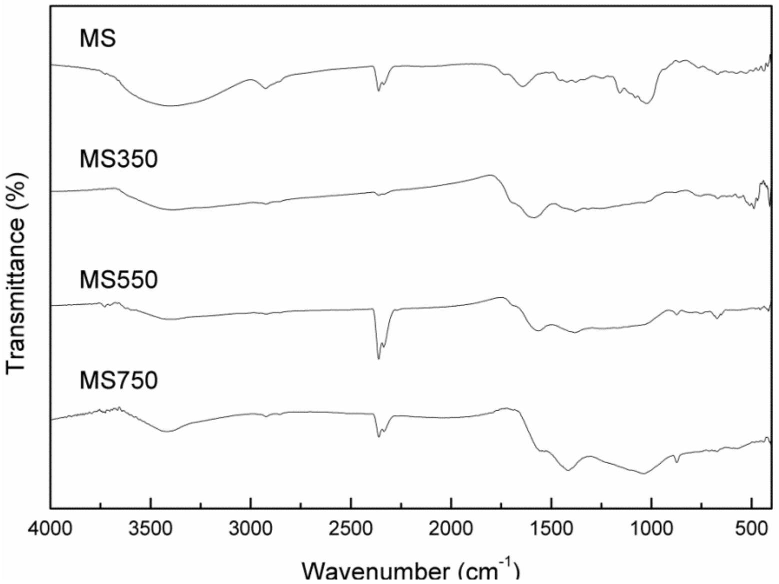

Fig. 2. FTIR spectra of cassava waste biochar

Sorption Kinetics

Sorption kinetics is an important factor affecting pollutants sorption behavior. Pseudo-second-order kinetics (Eq. 1) and the Elovich model (Eq. 2) were used to study the sorption kinetics of AT in soil with amended BC. The equations can be expressed as,

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{1}$$

$$q_t = a + bt \tag{2}$$

where q_t (mg/g) and q_e (mg/g) are the amounts of AT adsorbed at time t and at equilibrium, respectively; k_2 (g/mg/min) is a second-order kinetics sorption rate constant; a is an initial sorption rate constant; and b is a sorption activation energy constant.

Biochar amendment into soil not only could increase the amount of AT sorption but also change the physicochemical properties of paddy soil, for instance, increasing pH values and CEC of soil, promoting soil water-holding ability. According to Fig. 3, the kinetics of AT in BC-added soil was completed in two steps: a fast step and a slow step. At the early stage, the sorption rate of AT increased quickly, and 80 to 90% of the ultimate sorption occurred in the first 180 min. Once BC was added to the soil solution, approximate AT amounts of 17.2%, 21.54%, 35.12%, and 86.64% were removed by CK, MS350, MS550, and MS750, respectively, in 180 min. With increasing contact time, the sorption rate gradually decreased until the maximum sorption of the BC was reached. Atrazine was absorbed first at the readily accessible sites around the pores; it then diffused to the interior of the BC. The time at which AT reached equilibrium may be related to the carbonization temperature of the BC; MS750 was found to require less time to achieve equilibrium than other sorbents.

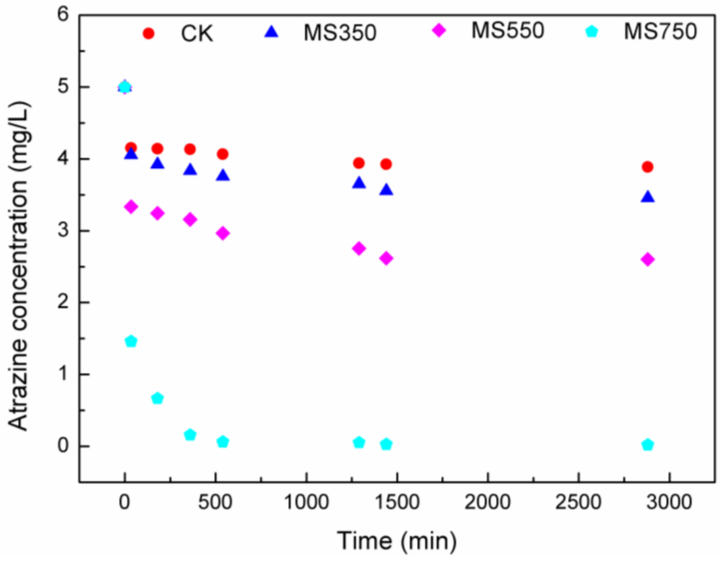

Fig. 3. Sorption kinetics of AT by adding biochar into soil. The initial concentration of AT was 5 mg/L, the amount of biochar was 1%, and the volume of pesticide solution was 10 mL

The highly hydrophobic surface and special functional groups of BC may be conducive to the initial rapid removal of AT. The surface areas of BC at low temperatures were too small to accommodate higher amounts of AT. Generally speaking, the sorption behavior of HOCs is primarily driven by hydrophobic interactions (Zhou *et al*. 2010). However, once coming into contact with water, the structure and composition of the BC would be altered by hydration (Chun *et al*. 2004), so the sorption of AT was a gradual process and controlled by intra-particle diffusion mechanisms before approaching equilibrium (Pan *et al*. 2008; Valderrama *et al*. 2008).

Pseudo-second-order and Elovich models were employed to study the AT sorption mechanism (Table 4). The R^2 value for the pseudo-second-order model was near 1, higher than that of the Elovich equation (0.801~0.954), which indicated that the pseudo-second-order model provided a good fit to the kinetics of AT.

Table 4. Kinetics Constants for AT Sorption in BC-amended Soil

Sample	Pseudo-second-order model			Elovich equation		
	q_e (mg/g)	k_2 (g/(mg/min))	$R^{2\,a}$	*a*	*b*	R^2
CK	0.006	2.370	**0.999**	-5.040	2330	0.801
MS350	0.016	0.597	**0.996**	-2.522	697	0.954
MS550	0.025	0.519	**0.998**	-3.280	463	0.883
MS750	0.050	1.274	**1.000**	-5.564	253	0.843

[a] Bold letters represent the highest R^2 values

Sorption Isotherm

To examine the AT sorption intensity and understand its mechanism, the Langmuir (Eq. 3) (Langmuir 1918), Freundlich (Eq. 4) (Freundlich 1906), and Tekmin (Eq. 5) (Yang 2014) models were used to fit the experimental data,

$$\frac{1}{q_e}=\frac{1}{q_{\max}}+\left(\frac{1}{\mathrm{K}_L q_{\max}}\right)\left(\frac{1}{c_e}\right) \tag{3}$$

$$\log q_e=\log K_F+\left(\frac{1}{n}\right)\log c_e \tag{4}$$

$$q_e=A+B\log c_e \tag{5}$$

where c_e (mg/L) is the equilibrium concentration of AT; q_{max} (mg/g) is the maximum sorption amount of adsorbent; n is the unitless Freundlich exponent; K_L and K_F are Langmuir and Freundlich coefficients, respectively; and A and B are the coefficients of the Tekmin model.

Sorption isotherms were used to describe the partitioning of AT between the soil solution and solid surface and to help in understanding the nature of interactions between AT and the soil matrix (Kasozi *et al.* 2012). The BC comprised carbonized and non-carbonized fractions, which demonstrated that BC was heterogeneous (Chen *et al*. 2008; Cao *et al*. 2009). The sorption for AT by BC had two principal types of sorption domains; one was a soft carbon domain analogous to rubbery polymers and characterized by a partition mechanism exhibiting a linear sorption behavior, and the other was a hard carbon domain analogous to glassy polymers and characterized by a pore-filling mechanism; its sorption behavior was nonlinear (Xia and Pignatello 2001). Sorption isotherms of AT in BC-added soil were linear/nonlinear (Fig. 4). The isotherms of CK and MS350 displayed relatively linear behavior, and partition was a dominant mechanism. By contrast, because of presence of the glassy domain, the sorption of AT with added MS550 and MS750 followed a pore-filling mechanism, which can be described by nonlinear isotherms. Pore-filling was the primary mechanism for AT sorption in MS750 and contributed more at low solute concentrations. According to the H/C, O/C, and (O+N)/C ratios, the aromaticity increased in the order of MS750 > MS550 > MS350, so the affinity of the BC for AT should increase strongly and nonlinearity should be higher in the same order. This suggested that the organic carbon of BC produced at different temperatures had different sorption capacities.

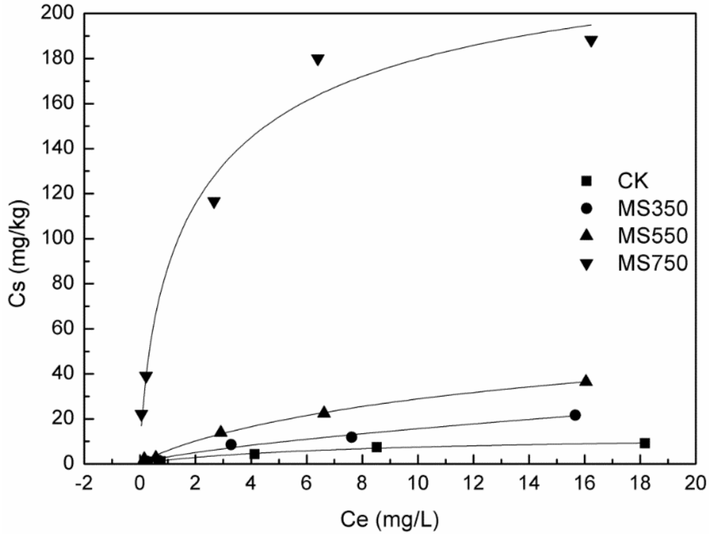

Fig. 4. Sorption isotherms of AT in BC-amended soil. The initial concentrations of AT were 0.5, 1.0, 5.0, 10.0, and 20.0 mg/L. The volume of AT solution was 10 mL, and the amount of biochar was 1% in soil

Isotherm parameters of the three AT models are listed in Table 5. The Freundlich fitting was found to give relatively higher values of coefficients of determination (0.944 to 0.984) than the Langmuir (0.770 to 0.933) and Tekmin (0.872 to 0.958) equations, which suggested that the surface of the BC was heterogeneous and supplied indeterminate sorption sites. Higher surface areas and aromaticity of MS750 led to a linearly decreasing adsorption heat as the adsorption quantity decreased. The sorption capacity of AT had a positive correlation with the charring temperature of the BC, which was illustrated by the values of q_{max}, $1/n$, and log K_F. For instance, the maximal sorption value on MS750 was approximately 13.5 times larger than that of MS350. Based on these results, the nonlinearity coefficient $1/n$ value decreased from 0.715 for MS350 to 0.400 for MS750, indicating that the isotherms changed from linear to strongly nonlinear. Compared with CK ($1/n > 1$), $1/n$ of adding BC was lower, since BC had more condensed sorption domain to enhance affinity for AT.

Table 5. Isotherms Parameters for AT Sorption in BC-Amended Soil[a]

Sample	Freundlich model			Langmuir model			Temkin model		
	log K_F	$1/n$	R^2 [b]	K_L	q_{max}/(mg/kg)	R^2	A	B	R^2
CK	0.268	0.581	**0.976**	0.694	5.58	0.848	-0.493	0.198	0.937
MS350	0.476	0.715	**0.969**	0.600	9.32	0.835	-0.387	0.083	0.872
MS550	0.771	0.604	**0.944**	1.282	12.44	0.770	-0.676	0.071	0.935
MS750	1.865	0.400	**0.984**	3.810	125.0	0.933	-1.326	0.013	0.958

[a] The initial concentrations of AT were 0.5,1.0,5.0,10.0, and 20.0 mg/L. The volume of AT solution was 10 mL, and the amount of biochar in soil was 1%

[b] Bold letters represent the highest R^2 values

The mechanism of sorption of AT as a result of adding BC into soil is complicated because many factors can influence the sorption behavior, such as polarity, aromaticity, surface area, and pore size. In this study, MS350 contained more amorphous carbons and lacked micropores, leading to a weak interaction mechanism. Biochar pyrolyzed at high temperatures contained crystalline carbons with specific interactions, which could provide sorption sites. The HOCs on micro-porous and meso-porous BC usually undergo specific interactions, including hydrophobic effects, pore-filling, and electron donor-acceptor interaction (Zhang *et al*. 2011). Atrazine not only is an H-bonding donor for N atoms of heterocyclic rings but also is an acceptor of H atoms of amino groups (Sun *et al.* 2010); thus, charge-transfer interactions could occur between aromatic C, an electron acceptor on the BC surface, and the AT ring electron donor (Zhang *et al*. 2011; Zhao *et al.* 2013). In addition, the hydrophobic effects, dispersion, weak dipolar forces, and micropore diffusion could greatly influence the sorption reaction (Chen *et al*. 2009). Therefore, specific interactions between AT molecules and the BC surfaces could contribute to high sorption affinity.

Sorption Thermodynamics

Thermodynamic parameters were determined using the following equations,

$$K_d = q_e / c_e \tag{6}$$

$$\Delta G^\circ = -RT\ln K_d \tag{7}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{8}$$

where T (K) is the absolute temperature, R is the universal gas constant (8.314 J/molK), and K_d is the distribution constant. It is assumed here that n= 1, K_d can be calculated as K_d=K_F (Zhang *et al*. 2008; Liu 2009); and the parameter $\triangle G^o$ (kJ/mol) is the standard free energy change. The values of enthalpy ($\triangle H^o$) and entropy change ($\triangle S^o$) can be obtained from the slope and intercept of a plot of $\triangle G^o$ *versus* T.

The thermodynamic parameters ($\triangle G^o$, $\triangle H^o$, $\triangle S^o$) for the sorption process are given in Table 6. All of the $\triangle G^o$ values were negative, suggesting that the process was spontaneous and thermodynamically favorable. The absolute values of $\triangle G^o$ increased with increasing sorption temperature, *i.e.*, $\triangle G^o$ 308 K >$\triangle G^o$ 298 K >$\triangle G^o$ 288 K. Higher temperatures can provide more energy to overcome the diffuse double layer and adsorb into the interior structure of the BC (Liu and Zhang 2009). In addition, adding BC to soil was beneficial to AT sorption under the same experimental conditions. In general, the $\triangle G^o$ value for physical sorption is in the range of 0 to -20 kJ/mol, and that for chemisorption is between -80 and -400 kJ/mol (Zhang *et al.* 2014). In this study, the values of $\triangle G^o$ were in the range of -0.4 to -11.3 kJ/mol, which suggested that the sorption process may be mainly controlled by physisorption.

Table 6. Thermodynamic Parameters for the AT Sorption Process[a]

Sample	Temperature (K)	$\Delta G°$ (kJ/mol)	$\Delta S°$ (kJ/(mol.K))	$\Delta H°$ (kJ/mol)
CK	288	-0.831	0.080	22.348
	298	-1.531		
	308	-2.439		
MS350	288	-0.446	0.162	45.836
	298	-2.712		
	308	-3.675		
MS550	288	-2.251	0.139	37.54
	298	-4.397		
	308	-5.031		
MS750	288	-8.570	0.139	31.158
	298	-10.641		
	308	-11.345		

[a] The initial concentrations of AT were 0.5, 1.0, 5.0,10.0, and 20.0 mg/L. The volume of AT solution was 10 mL, and the amount of biochar was 1% in soil. The sorption equilibrium experiments were carried out at 15, 25, and 35 °C

A negative $\triangle H^o$ value suggests the sorption process is exothermic. Based on the results, all of the $\triangle H^o$ values were positive, which indicated that the sorption process was endothermic and that increasing temperature could be mostly favorable for sorption. In addition, the absolute value of $\triangle H^o$ was lower than 40 kJ/mol, which indicated that physisorption was mainly adsorption mechanism (Feng *et al*. 2013). In this work, the $\triangle H^o$ values were between 20 and 50 kJ/mol, confirming that AT sorption was primarily physisorption. According to the sorption energy of different forces (Table 7) (von Oepen *et al*. 1991), the sorption mechanism of AT on CK may be an H-bonding and dipole bond force, and that on MS350, MS550, and MS750 may involve H-bonding and ion exchange. Atrazine is a weak base, and its pK_a value is 1.7. At the pH in the experiment, AT existed as neutral molecules and formed weak H-bonds with clay surfaces and carboxyl groups because of their heterocyclic nitrogen atoms (Zhang *et al*. 2013).

The $\triangle S^o$ values were all positive, indicating that the entropy increased because of the increase in molecule randomness in the soil solutions.

Table 7. Energy of Sorption by Different Forces (kJ/mol)

Van der Waals force	Hydrophobic interaction	H-bonding	Charge-transfer	Ion-exchange	Dipole bond force	Chemical bond
4~10	≈5	2~40	Not available	≈40	2~29	>60

Effect of pH

The pH value is an important factor for AT sorption-desorption and determines the sorption capacity of BC. Figure 5 shows that the effect of pH value on the sorption of AT exhibited a similar tendency in the studied pH range (3 to 9) for all samples. The sorbed amount of AT decreased with an increase in the pH value, indicating that the sorption of AT was favored by a lower pH. For example, the sorption capacities of CK were 11.97, 8.24, 7.38, and 6.81 mg/kg at pH 3, 5, 7, and 9, respectively. In addition, the sorption ability of different sorbates was different and the sorption level for pesticides was in the order of MS750 > MS550 > MS350 > CK, which showed that BC addition could improve the removal of AT in paddy soil.

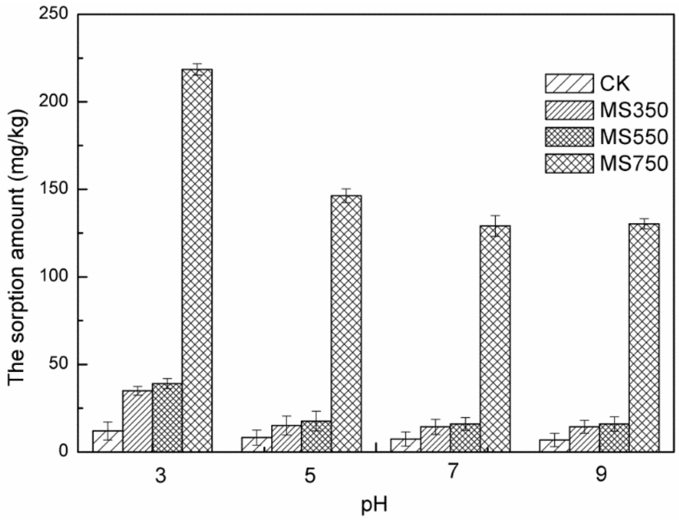

Fig. 5. Effect of pH on AT sorption in biochar-amended soil. The initial concentration of AT was 5 mg/L, the amount of biochar was 1%, and the volume of AT solution was 10 mL. Error bars represent standard deviation of triplicate samples

The results were primarily caused by the interaction between BC and AT through charge forces in aqueous environments (Zhao *et al*. 2013). The pK_a of AT is 1.7, indicating a weakly basic pesticide. Biochar exists mostly in protonated form in acidic media and in deprotonated form in alkaline media (Oliveira *et al*. 2001). Low pH solutions would be favorable for the formation of AT cations, which would combine with the negatively charged surfaces of BC through electrostatic attraction in acidic media to improve the sorption affinity of BC for AT. At higher pH values, AT would combine with the negatively charged BC surface with a weak electronic interaction.

The effects of pH on desorption are displayed in Fig. 6. Higher pH values were more conducive to enhancing desorption for AT, *i.e.*, pH 9 > pH 7 > pH 5 > pH 3. For MS750, the desorption rate at pH 9 was approximately 2.65 times higher than at pH 3. Atrazine desorbed more, but less from absorbed soil with increasing BC pyrolysis temperature. For instance, the desorption rate of MS750 was 20.01 times less than that of

CK at pH 3, which showed that BC addition could reduce the mobility of AT in paddy soil.

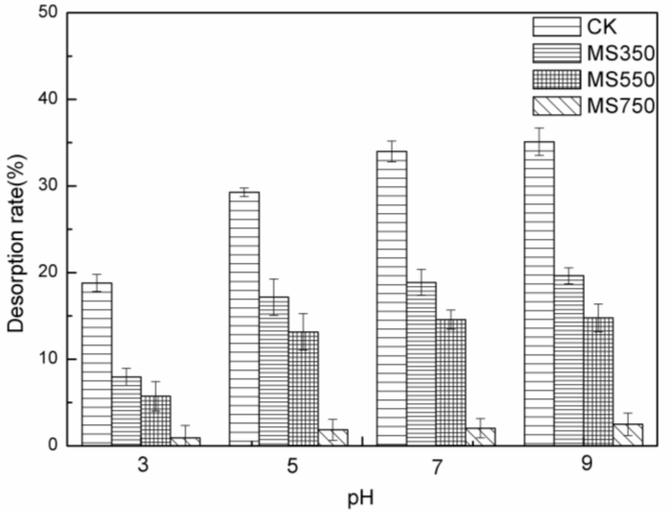

Fig. 6. Effect of solution pH on the desorption capacity of amended biochars for AT. The initial concentration of AT was 5 mg/L, the amount of biochar was 1%, and the volume of AT solution was 10 mL. Error bars represent standard deviation of triplicate samples

CONCLUSIONS

1. The sorption kinetics showed that the removal rate of atrazine (AT) depends on the carbonization temperatures of biochar. Biochar carbonized at high temperatures may reach equilibrium in shorter amounts of time. The pseudo-second-order model gives the best fit to the sorption kinetics of AT.
2. The isotherms of CK and MS350 displayed relatively linear behavior, and partitioning was the dominant mechanism, whereas the sorption of AT by MS550 and MS750 occurred *via* a pore-filling mechanism, which can be described by nonlinear isotherms. The Freundlich model can be used to describe the sorption isotherm of AT in biochar-amended soil.
3. A thermodynamic study indicated that the sorption of AT in biochar-added soil is a spontaneous endothermic process.
4. Acidic solutions are more conducive to the sorption of AT in biochar-added soil.

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