



Simultaneous removal of cadmium and sulfamethoxazole from aqueous solution by rice straw biochar^{*}

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Received Dec. 20, 2012; Revision accepted Apr. 2, 2013; Crosschecked June 8, 2013

Abstract: The simultaneous sorption behavior and characteristics of cadmium (Cd) and sulfamethoxazole (SMX) on rice straw biochar were investigated. Isotherms of Cd and SMX were well modeled by the Langmuir equation ($R^2 > 0.95$). The calculated maximum adsorption parameter (Q) of Cd was similar in single and binary systems (34 129.69 and 35 919.54 mg/kg, respectively). However, the Q of SMX in a binary system (9 182.74 mg/kg) was much higher than that in a single system (1 827.82 mg/kg). The presence of Cd significantly promoted the sorption of SMX on rice straw biochar. When the pH ranged from 3 to 7.5, the sorption of Cd had the characteristics of a parabola pattern with maximum adsorption at pH 5, while the adsorption quantity of SMX decreased with increasing pH, with maximum adsorption at pH 3. The amount of SMX adsorbed on biochar was positively correlated with the surface area of the biochar, and the maximum adsorption occurred with d 250 biochar (biochar with a diameter of 150–250 μm). Scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) showed that the removal of Cd and SMX by rice straw biochar may be attributed to precipitation and the formation of surface complexes between Cd or SMX and carboxyl or hydroxyl groups. The results of this study indicate that rice straw biochar has the potential for simultaneous removal of Cd and SMX from co-contaminated water.

Key words: Biochar, Rice straw, Simultaneous sorption, Cadmium (Cd), Sulfamethoxazole (SMX)

doi:10.1631/jzus.B1200353

Document code: A

CLC number: X712

1 Introduction

Cadmium (Cd) is an extremely toxic metal with unknown biological functions. Excessive Cd released into the environment by mining, industrial, and agricultural activities (Kannan and Rengasamy, 2005) causes high ecological risks to ground water and soil biota, thus threatening human health through the food chain (Loganathan *et al.*, 2012). Veterinary antibiot-

ics are commonly used to treat disease or promote growth of animals. However, their abuse has caused growing concerns about antibiotic-resistant organisms which have the potential to become superbugs that are immune to antibiotics (Martinez, 2008; Allen *et al.*, 2010). Sulfamethoxazole (SMX) is a widely used sulfonamide antibiotic. Previous studies reported that it was detected in soils in higher concentrations than other antibiotics (Stoob *et al.*, 2007). A lower removal rate of SMX compared to macrolides, trimethoprim and other sulfonamides was reported in final effluents of wastewater treatment facilities (Luo *et al.*, 2011). The coexistence of heavy metals and antibiotics in the environment has recently been reported (Máthé *et al.*, 2012; Matyar, 2012). However,

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^{*} Project supported by the National Key Technology R&D Program of China (No. 2012BAC17B04) and the Fundamental Research Funds for the Central Universities, China

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techniques for the simultaneous removal of Cd and SMX from wastewater have rarely been published.

Numerous methods have been developed for the removal or in situ stabilization of pollutants, including precipitation, flotation, ion exchange, membrane-related processes, electrochemical techniques, biological processes, and adsorption (Febrianto *et al.*, 2009). Among these, adsorption of pollutants by sorbents has been proven to be an efficient technique for the stabilization of pollutants (Yadanaparthi *et al.*, 2009). However, the large-scale application of sorbents may be cost-prohibitive (Tong *et al.*, 2011). Biochar is pyrolyzed from biomass under conditions of limited oxygen, and is considered to be an alternative low-cost sorbent. Biochar has a high stability against decay and a superior ability to retain nutrients, which may be beneficial in decreasing the bioavailability of pollutants, thus mitigating their ecological toxicities (Lehmann, 2007). For example, broiler litter-derived char formed under a low pyrolysis temperature (350 °C) improved the immobilization of Cu(II), Cd(II), and Ni(II) in soils (Uchimiya *et al.*, 2010). The ability of oak bark char to remove Pb(II) and Cd(II) from water, represented by the amount of metal adsorbed per unit surface area (SA) (0.5157 mg/m² for Pb(II) and 0.213 mg/m² for Cd(II)), was much greater than that of high-priced commercial activated carbon (Mohan *et al.*, 2007).

Biochars made from agricultural wastes, including fruit peels (Chen and Chen, 2009), pine needles (Chen *et al.*, 2008), grass (Bornemann *et al.*, 2007), hardwood (Chen *et al.*, 2011), and crop straw (Chun *et al.*, 2004) have been widely investigated. According to the agricultural crop database of China, 0.2 billion tons of rice is produced in China every year (<http://www.zzys.gov.cn/nongqing.aspx>). However, most rice straw is discarded or burned inappropriately, leading to serious air pollution caused by emission of carbon monoxide (CO), non-methane hydrocarbons (NMHCs), nitrogen oxides (NO_x), particulate matter with an aerodynamic diameter of 10 μm or less (PM₁₀), and sulfur dioxide (SO₂) (Qu *et al.*, 2012), and resource losses. Previous studies reported that rice straw biochar could be applied to enhance the immobilization of organic pollutants (Nag *et al.*, 2011) or heavy metals (Chen *et al.*, 2011; Jiang *et al.*, 2012), but the potential for abatement of multiple contaminants was not fully explored.

The main purposes of this study were to investigate: (1) the simultaneous sorption behavior and characteristics of Cd and SMX on rice straw biochar; (2) the interactions between Cd and SMX in their simultaneous sorption process; (3) the effects of solution pH and biochar diameter on sorption of Cd and SMX on biochar.

2 Materials and methods

2.1 Biochar and chemicals

Rice straw biochar made at 400 °C was provided by the Institute of Urban Environment, Chinese Academy of Sciences. Biochar with different diameters was prepared according to the method of Oleszczuk *et al.* (2012) with some modification. The rice straw biochar was firstly sieved through a 150-μm sieve, then a 250-μm sieve, and finally a 425-μm sieve to obtain biochar subsamples with different diameters: <150, 150–250, and 250–425 μm. The surface parameters of biochar were determined using an SA and porosity analyzer (Micromeritics, Tristar 3020, USA), and the elemental compositions of carbon (C), hydrogen (H), and nitrogen (N) were detected using an elemental analyzer (Thermo Finnigan, Flash EA1112, USA). The content of oxygen (O) was calculated as the difference between C, H, N and ash. Fourier transform infrared spectroscopy (FTIR) spectra were collected in the range of 600–4000 cm⁻¹ using a Nicolet FTIR spectrophotometer (Thermo Fisher Scientific LLC, Nicolet 6700, USA). A scanning electron microscopy (SEM; Carl Zeiss, Ultra 55, Germany) was used to distinguish the sorption characteristics of Cd and SMX on biochar in a single Cd or SMX system and in a binary system. SMX (99.9% purity) was purchased from Sigma-Aldrich Chemical Co. Sodium salts and Cd(NO₃)₂·4H₂O were of analytical grade or better.

2.2 Batch experiments

Batch experiments were conducted to investigate the adsorption isotherms of Cd and SMX in single and binary systems. A stock solution of Cd (1000 mg/L) was prepared by dissolving Cd(NO₃)₂·4H₂O in a background solution consisting of 0.01 mol/L NaNO₃ to maintain a constant ionic strength and 200 mg/L NaN₃ to inhibit biological activity. SMX was firstly

dissolved in methanol, and then diluted with background solution to 500 mg/L as a stock solution. In single systems, the series of initial concentrations were 5, 10, 25, 50, and 100 mg/L for Cd and 5, 10, 20, 40, 80, and 200 mg/L for SMX. In binary systems, SMX was added into Cd single systems as above, and the initial concentration of SMX was 20 mg/L. Cd was mixed with SMX single systems as above, and the initial concentration of Cd was 200 mg/L. Batch experiments were performed by adding 20 ml of single (Cd/SMX) or binary (Cd+SMX) solutions to 0.05 g biochar samples in 50 ml vials equipped with teflon-lined screw caps. The vials were kept in the dark and rotated vertically on a rotator at 150 r/min for 24 h at room temperature (25 ± 2) °C and then equilibrated for another 16 h (Lertpaitoonpan *et al.*, 2009). After equilibration, the vials were centrifuged. The supernatant was filtered through a 0.45- μm filter and then stored at 4 °C prior to analyses of Cd and SMX. The biochar used in this experiment was *d* 250 (biochar with a diameter of 150–250 μm), and all treatments were performed in triplicate.

Sorption edge experiments were conducted to investigate the effects of solution pH and biochar diameter on the simultaneous removal of Cd and SMX in single and binary systems. In single systems, the initial concentration of Cd was 200 mg/L and of SMX was 20 mg/L. In the binary system, the initial concentrations of Cd and SMX were the same as in the corresponding single system. The initial pH of the solution was adjusted to 3, 4, 5, 6, or 7.5 using 0.01 mol/L HCl or NaOH. The biochar used in experiments to determine the effects of pH was *d* 250 biochar. Biochars with different diameters (<150, 150–250, and 250–425 μm) were added to both single systems and the binary system at pH 6. The remaining procedures were the same as those used in the adsorption isotherm experiments. All treatments were performed in triplicate.

2.3 Analytical methods

SMX concentrations in the supernatants were

determined using high-performance liquid chromatography (HPLC; Agilent 1200, USA) with a reversed-phase XDB-C18 column (5 μm , 4.6 mm \times 150 mm) and an ultraviolet (UV) detector at 265 nm. Chromatography was performed at 25 °C with acetonitrile/water (40/60, v/v) containing 0.1% acetic acid as the mobile phase at a flow rate of 1 ml/min. The equilibrium concentrations of Cd were determined by inductively coupled plasma mass spectrometry (ICP-MS; Agilent 7500a, USA).

2.4 Statistical analysis

All data were analyzed using SPSS 16.0, and Student's *t*-test was applied to test for significant differences between the means.

3 Results

3.1 Characterization of biochar

Surface elemental compositions (C, H, O, N), specific SA, and pore volume parameters of the rice straw biochar are shown in Table 1. The SA of the biochar was not significantly related to its diameter. The *d* 250 biochar had the largest SA (3.58 m²/g), followed by the *d* 150 (1.25 m²/g) and *d* 425 (0.25 m²/g) biochars. However, the *d* 425 biochar had the largest micropore area and volume among the three biochars.

The FTIR spectrum revealed the principle surface functionalities of rice straw biochar (Fig. 1). The spectrum of biochar was characterized by five bands at wave numbers 3374, 1587, 1378, 1090, and 791 cm⁻¹. The bands at 3374, 1090, 791, and 1587 cm⁻¹ are attributed to hydroxyl (–OH) stretching, CO–C stretching of secondary hydroxyl, aliphatic CH₂ deformation, and aromatic C=C ring or COO– group stretching, respectively (Fu *et al.*, 2009; Harvey *et al.*, 2011; Kumar *et al.*, 2012). At 1378 cm⁻¹, bands are attributed to aliphatic CH₃ deformation (Harvey *et al.*, 2011) or O–H/C–H bending of hydroxyl, acid, phenol and methyl (Fu *et al.*, 2009).

Table 1 Characteristics of rice straw biochars

Biochar	Content (%)					Surface area (m ² /g)	Micropore area (m ² /g)	Micropore volume (cm ³ /g)
	Ash	N	C	O	H			
<i>d</i> 150						1.25	8.43	0.0037
<i>d</i> 250	29.45	2.28	38.39	27.90	1.98	3.58	5.42	0.0025
<i>d</i> 425						0.25	11.61	0.0045

d 150, *d* 250, and *d* 425 represent biochars with diameters <150, 150–250, and 250–425 μm , respectively

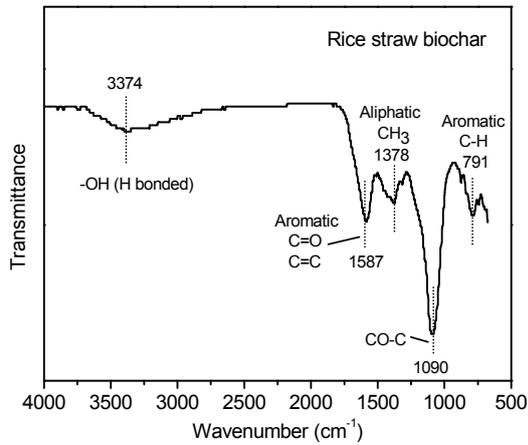


Fig. 1 FTIR image of a rice straw biochar

3.2 Adsorption isotherms of Cd

Cd adsorption capacity increased with increasing Cd concentration in the equilibrium solution (Fig. 2). The amount of Cd adsorbed on biochar was similar in solutions with or without SMX. The Langmuir and Freundlich models were used to simulate the sorption characteristics in this study. The equations of the two models are given as follows:

$$C_e/Q_e = 1/(bQ) + C_e/Q, \quad (1)$$

$$\lg Q_e = \lg K_f + (1/n)\lg C_e, \quad (2)$$

where C_e is the concentration of adsorbate in the equilibrium solution (mg/L), Q_e is the amount of the metal adsorbed per unit weight of biochar (mg/kg), Q is the maximum adsorption capacity (mg/kg), b is the bonding energy coefficient, n is a sorption intensity constant, and K_f is the Freundlich constant. The calculated parameters are listed in Table 2. The Langmuir model was more suitable for Cd adsorption ($R^2=0.96$ for Cd with SMX, and 0.99 without SMX) than the Freundlich model ($R^2=0.61$ for Cd with SMX, and 0.94 without SMX). The sorption behavior of Cd on biochar in the presence of SMX as indicated by Q and b ($Q=35919.54$ mg/kg, $b=0.370$) was not significantly different from that in the system without SMX ($Q=34129.69$ mg/kg, $b=0.360$).

3.3 Adsorption isotherms of SMX

The quantity of SMX adsorbed on biochar increased with increasing SMX concentration in the equilibrium solution (Fig. 2). The Langmuir and Freundlich models were again used to simulate the sorption characteristics (Table 2). The Langmuir model ($R^2=0.99$ for SMX with Cd, and 0.96 without Cd) fitted the data better than the Freundlich model ($R^2=0.97$ for SMX with Cd, and 0.94 without Cd). The Langmuir parameters (Q and b) indicated that the adsorption of SMX on biochar was significantly enhanced by the addition of Cd.

Table 2 Calculated Langmuir and Freundlich parameters of Cd and SMX adsorption isotherms

Treatment	Freundlich model			Langmuir model		
	K_f (L/kg)	$1/n$	R^2	Q (mg/kg)	b	R^2
Cd	8477.20	0.45	0.94	34129.69	0.360	0.99
Cd+SMX	9808.12	0.42	0.61	35919.54	0.370	0.96
SMX	62.40	0.62	0.94	1827.82	0.016	0.96
SMX+Cd	542.25	0.54	0.97	9182.74	0.026	0.99

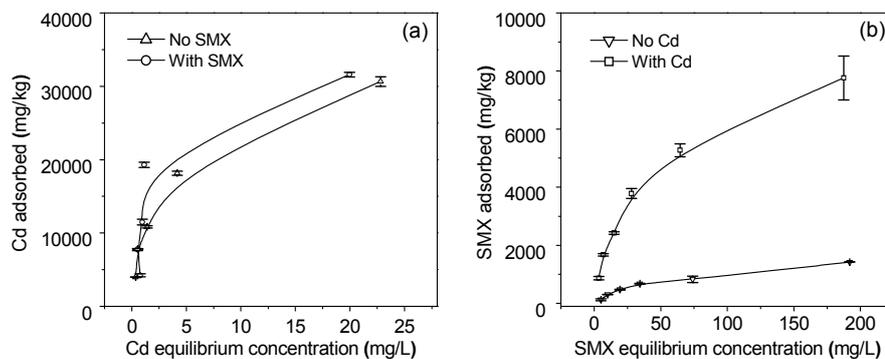


Fig. 2 Adsorption isotherms of Cd (a) and SMX (b) on rice straw biochar as affected by their concentrations in the equilibrium solution

3.4 Effect of biochar diameter

Differences in the diameter of the biochar showed no significant influence on the sorption of Cd, regardless of the presence of SMX (Fig. 3). However, *d* 250 biochar adsorbed a significantly larger amount of SMX than did the other two biochars in both the single and binary systems.

3.5 Effect of solution pH

The solution pH significantly influenced the sorption of Cd and SMX onto biochar (Fig. 4). The amount of Cd adsorbed kept on increasing with increasing pH, until the pH plateaued at pH 5, in both single and binary systems. Then, the amount of Cd adsorbed decreased with the increasing pH value. The trend of SMX sorption was negatively correlated with the pH values (Fig. 4). The highest adsorption of SMX occurred at pH 3 in both single and binary systems.

4 Discussion

4.1 Adsorption capability of rice straw biochar for Cd and SMX

A few studies have evaluated the capacity of some carbonaceous materials to adsorb Cd (Kannan and Rengasamy, 2005; Mohan *et al.*, 2007; Wang *et al.*, 2010). Adsorbents produced from different agricultural or industrial materials varied in their sorption characteristics (Yadanaparathi *et al.*, 2009). Carbon adsorbents with an initial Cd concentration of 2.25 mg/L at a dose of 5 g/L of 12–20 meshes carbon achieved an adsorption capacity of 600 mg/kg. According to the Langmuir isotherm, bamboo charcoal had a maximum Cd adsorption capacity of 12080 mg/kg under the conditions of 3.33 g/L of 200 meshes bamboo charcoal and an initial Cd concentration of 20–100 mg/L (Wang *et al.*, 2010). When the amount and particle size of carbon and the initial concentration of Cd were 10 g/L, 9 μ m, and 10–66 mg/L,

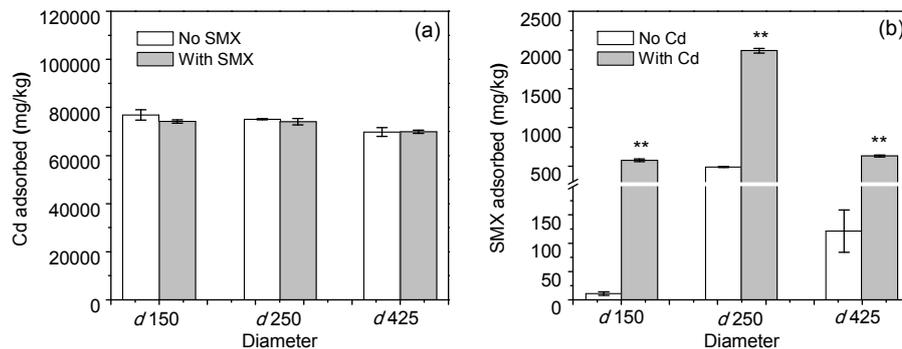


Fig. 3 Effect of biochar diameter on adsorption of Cd (a) and SMX (b) on rice straw biochar *d* 150, *d* 250, and *d* 425 represent biochars with diameters <150, 150–250, and 250–425 μ m, respectively. * $P < 0.05$, ** $P < 0.01$: significant differences between SMX solely and in combination with Cd at each diameter

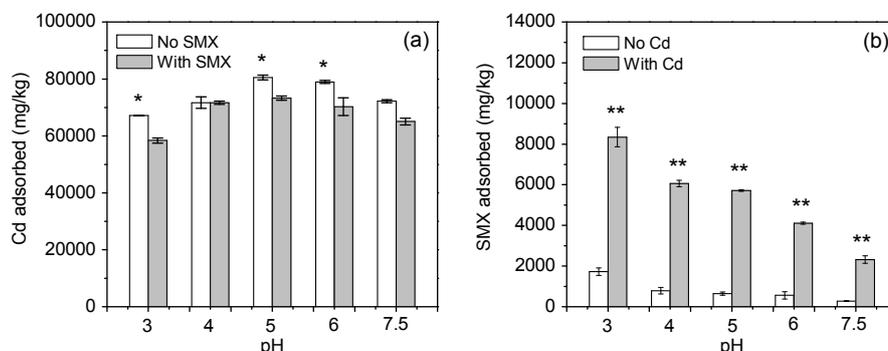


Fig. 4 Effect of pH on the adsorption of Cd (a) and SMX (b) on rice straw biochar * $P < 0.05$, ** $P < 0.01$: significant differences between SMX solely and in combination with Cd at each pH

respectively, straw-activated carbon had the greatest adsorption capacity for Cd^{2+} (4140 mg/kg) among various activated carbons based on Langmuir isotherm data (Kannan and Rengasamy, 2005). Based on the maximum adsorption capacity parameter Q of the Langmuir isotherm in this study, rice straw biochar showed a strong ability to adsorb Cd in both single (34129.69 mg/kg) and binary systems (35919.54 mg/kg), and the adsorption capacity was much higher than that of previously reported adsorbents. In conclusion, rice straw biochars are efficient in the adsorption of Cd.

Previous studies on adsorption of SMX focused mainly on carbon nanotubes (Ji *et al.*, 2009; Wu *et al.*, 2012). Carbon nanotubes are considered an effective adsorbent for removing antibiotics from aqueous solution, and the K_f value, which represents the sorption affinity of SMX in carbon nanotubes, is about 500 L/kg (Ji *et al.*, 2009; Zhang *et al.*, 2010b). Although in our study the Langmuir model gave a better data fit than the Freundlich model, previous studies used the Freundlich parameter to describe the sorption of SMX, so K_f was adopted for comparison. The K_f values of SMX were 60.40 L/kg in the single systems and 542.25 L/kg in the binary systems. This result was consistent with prediction by the Langmuir parameter Q . Apparently, the SMX adsorption capacity of rice straw biochar in solution was significantly enhanced by the addition of Cd, and was equivalent to that of carbon nanotubes. As reported, acid-treated wheat-residue-derived black carbon showed a higher capacity to adsorb SMX than did raw carbon or maize-residue derived carbon. The K_f of acid wheat carbon was 570 L/kg, higher than that of maize (200 L/kg) (Ji *et al.*, 2011), which was higher than that of the rice straw biochar in the single system, but comparable to that in the binary condition in this study. This suggests that rice straw biochar could be an effective alternative adsorbent for SMX, and further treatment of rice straw biochar may increase this ability.

4.2 Sorption mechanism of Cd on rice straw biochar

The good fit of the Langmuir adsorption isotherm was based on monolayer coverage of the adsorbate on the surface of the adsorbent, indicating that the sorption of Cd on rice straw biochar is monolayer

sorption on a fixed number of surface sites on the biochar (Wang *et al.*, 2010). Several studies have reported that a larger SA of biochar can enhance sorption of heavy metals such as As, Pb, Cu, Zn, and Cd, by providing more surface sites (Mohan *et al.*, 2007; Chen *et al.*, 2011). For example, corn straw char produced at 600 °C has a larger SA than hardwood char produced at 450 °C, leading to greater adsorption capacities of corn straw char for Cu and Zn (Chen *et al.*, 2011). However, in our study, different diameters showed no significant effect on the sorption of Cd on biochar, regardless of the presence of SMX (Fig. 3). Xu *et al.* (2012) reported that sorption would not be expected to depend on the SA if the adsorbent had a low SA (5.61 m²/g). In our study, the SA of three biochars were comparatively low (Table 1), and hence, an effect of biochar diameter on Cd sorption was not obvious. The maximum adsorption capacity of rice straw biochar for Cd calculated by the Langmuir model was similar to the result of the study by Xu *et al.* (2013), which attributed the large adsorption capacity of dairy manure-derived biochar for Cd (32036.85 mg/kg) to the formation of metal-phosphate and carbonate precipitates on the surface of biochar. Echeverría *et al.* (1998) also reported the importance of precipitation in the sorption of Cd by adsorbents. In our study, the amount of adsorption was also extraordinarily large, and the SEM images (Fig. 5) of rice straw biochar after Cd adsorption showed visible precipitates on the surface of the biochar, indicating that precipitation was involved in the process.

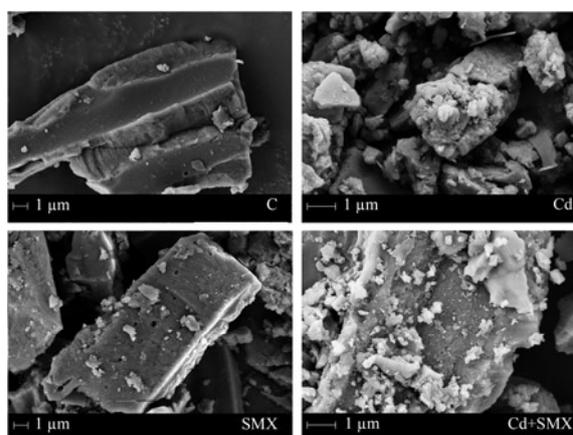


Fig. 5 SEM images of rice straw biochar before and after equilibration with solutions of Cd and SMX

Harvey *et al.* (2011) reported that Cd sorption occurred via cation-exchange on biochars produced at <350 °C, but predominantly via two distinct cation- π bonding mechanisms on biochars produced at ≥ 350 °C. In our study, the rice straw biochar was produced at 400 °C, which suggests that Cd²⁺- π bonding may have been involved. Hydrogen-bonding interaction could also contribute to the sorption of Cd because of the presence of hydroxyl (-OH) in biochar, indicated by the band at 3374 cm⁻¹ (Fig. 1) (Chen *et al.*, 2011). Besides, electrostatic interaction and ion exchange could also contribute to Cd sorption on rice straw biochar.

In this study, the amount of Cd adsorption increased with increasing pH and trended to be stable after pH 5 in both single and binary systems (Fig. 4). Similar results were reported by Chen *et al.* (2011) and Liu and Zhang (2009), regardless of the original material of the biochar. As the p*H*_{zpc} (zero point of charge) of biochar is between 2.0 and 3.5 (Mukherjee *et al.*, 2011), the surface charge of biochar in the solution was mainly negative in the pH range (3, 4, 5, 6 and 7.5) in our study. Negative charge on the surface of the biochar increased with the increase in solution pH from 3 to 5. Thus, the enhanced electrostatic attraction could promote adsorption of cationic Cd onto the negatively charged surface of the biochar. There is also competition between protons and metal cations for sorption sites on the surface of the biochar (Martins *et al.*, 2004). When the pH exceeded 5, the decreasing adsorption trend was likely caused by the formation of hydroxide complexes (Chen *et al.*, 2011).

4.3 Sorption mechanism of SMX on rice straw biochar

Although biochar diameter had no significant effect on sorption of Cd, it had a significant effect on sorption of SMX. The *d* 250 biochar with the largest SA showed the maximum amount of adsorption of SMX in both single and binary systems, which confirmed that the SA is of great importance to the sorption of organic molecules on adsorbents (Shinogi and Kanri, 2003).

Solution pH also significantly influenced the sorption of SMX on biochar. The sorption of SMX at selected pH values reflected the sorption behavior of different SMX species. SMX has two p*K*_a (acid dis-

sociation constant) values, 1.7 and 5.7 (Lucida *et al.*, 2000). The cationic, neutral, and anionic species of SMX dominate at pH values of <1.7, around 3.7, and >5.7, respectively (Zhang *et al.*, 2010a). Therefore, in this study, the majority of SMX in solution was in neutral form at pH 3. Neutral species would have decreased with increasing pH, whereas anionic species would have increased, and the electrostatic repulsion between the negatively charged biochar surface and anionic SMX species would have become stronger. This is one possible reason why the amount of SMX sorption was negatively correlated with the pH values. The solubility of SMX changed with solution pH. The minimum solubility of SMX was 281 mg/L at pH 3.22 (25 °C); however, its solubility can increase to 17900 mg/L (pH=7.5) or 560 mg/L (pH=1.7) (Dahlan *et al.*, 1987). Apparently, the amount of SMX adsorption on rice straw biochar was negatively related to solubility. When the pH increased from 3 to 7.5, the increasing amount of soluble SMX would result in less hydrophobic partitioning between SMX and the rice straw biochar, indicating that hydrophobic partitioning is an important mechanism of SMX sorption on rice straw biochar.

SMX is a strong π -acceptor compound because of amino functional groups and *N*-heteroaromatic rings (Zhang *et al.*, 2010a). The π - π electron donor-acceptor (EDA) (Zhu *et al.*, 2004) is a mechanism controlling the strong interaction between nitroaromatics and black carbon (char) (Zhu and Pignatello, 2005). In the FTIR spectrum (Fig. 1), the COO-groups (1587 cm⁻¹) in rice straw biochar may facilitate the π - π EDA interaction between SMX and biochar. The π -acceptor ability would increase with protonation, which would mean that a higher pH would lead to weaker interaction of π - π EDA between SMX and biochar in this study. In summary, the largest amount of adsorption at pH 3 was the result of various sorption mechanisms of SMX on rice straw biochar.

4.4 Effect of Cd on SMX sorption on rice straw biochar

Previous studies reported that the interaction between heavy metals and organic compounds could be either antagonistic (Wang *et al.*, 2010) or synergistic (Wu *et al.*, 2009). A notable promotion of SMX sorption by Cd was observed (Figs. 2–4) in our study.

In the co-contaminated solution, Cd^{2+} would affect the sorption of SMX by modifying the biochar surface. Cd ions could first be adsorbed on the surface of the biochar, and the negative charge on the surface of the biochar would be mitigated (Wu *et al.*, 2009). Then, the electrostatic repulsion between the biochar surface and anionic SMX could be moderated, thereby increasing the adsorption of SMX. The Cd first adsorbed on the surface of the biochar could also act as a Cd bridge, similar to those of Ca^{2+} and Mg^{2+} (Wan *et al.*, 2010), facilitating the adsorption of SMX. Cd^{2+} could decrease the competition between SMX and water for sorption sites by decreasing the hydrophobicity of the local region (Chen *et al.*, 2007). The presence of Cd not only modified the surface of the biochar, but produced a Cd-SMX complex (Wu *et al.*, 2012) with a higher sorption affinity on biochar than SMX, based on the metal complexes (Wang *et al.*, 2008). In conclusion, the increase in the amount of SMX adsorption caused by Cd could be the result of all these positive effects.

5 Conclusions

This study investigated the ability of rice straw biochar to remove Cd and SMX from aqueous solution, and described the sorption characteristics of Cd and SMX on the biochar. The following conclusions can be drawn based on the experimental results: (1) rice straw biochar had a strong ability to remove Cd and SMX from aqueous solution; (2) the presence of SMX had no significant impact on the sorption of Cd, whereas the presence of Cd significantly promoted sorption of SMX; (3) the solution pH significantly influenced the sorption of both Cd and SMX, with maximum sorption occurring at pH 5 for Cd and at pH 3 for SMX; (4) biochar diameter significantly affected the sorption of SMX, with maximum adsorption occurring with d 250. This study demonstrated that rice straw biochar is an effective sorbent for removing Cd and SMX from solution.

Compliance with ethics guidelines

Xuan HAN, Cheng-feng LIANG, Ting-qiang LI, Kai WANG, Hua-gang HUANG, and Xiao-e YANG

declare that they have no conflict of interest.

This article does not contain any studies with human or animal subjects performed by any of the authors.

References

- Allen, H.K., Donato, J., Wang, H.H., Cloud-Hansen, K.A., Davies, J., Handelsman, J., 2010. Call of the wild: antibiotic resistance genes in natural environments. *Nat. Rev. Microbiol.*, **8**(4):251-259. [doi:10.1038/nrmicro2312]
- Bornemann, L.C., Kookana, R.S., Welp, G., 2007. Differential sorption behaviour of aromatic hydrocarbons on charcoals prepared at different temperatures from grass and wood. *Chemosphere*, **67**(5):1033-1042. [doi:10.1016/j.chemosphere.2006.10.052]
- Chen, B.L., Chen, Z.M., 2009. Sorption of naphthalene and 1-naphthol by biochars of orange peels with different pyrolytic temperatures. *Chemosphere*, **76**(1):127-133. [doi:10.1016/j.chemosphere.2009.02.004]
- Chen, B.L., Zhou, D.D., Zhu, L.Z., 2008. Transitional adsorption and partition of nonpolar and polar aromatic contaminants by biochars of pine needles with different pyrolytic temperatures. *Environ. Sci. Technol.*, **42**(14):5137-5143. [doi:10.1021/es8002684]
- Chen, J.Y., Zhu, D.Q., Sun, C., 2007. Effect of heavy metals on the sorption of hydrophobic organic compounds to wood charcoal. *Environ. Sci. Technol.*, **41**(7):2536-2541. [doi:10.1021/es062113+]
- Chen, X.C., Chen, G.C., Chen, L.G., Chen, Y.X., Lehmann, J., McBride, M.B., Hay, A.G., 2011. Adsorption of copper and zinc by biochars produced from pyrolysis of hardwood and corn straw in aqueous solution. *Bioresour. Technol.*, **102**(19):8877-8884. [doi:10.1016/j.biortech.2011.06.078]
- Chun, Y., Sheng, G.Y., Chiou, C.T., Xing, B.S., 2004. Compositions and sorptive properties of crop residue-derived chars. *Environ. Sci. Technol.*, **38**(17):4649-4655. [doi:10.1021/es035034w]
- Dahlan, R., McDonald, C., Sunderland, V.B., 1987. Solubilities and intrinsic dissolution rates of sulfamethoxazole and trimethoprim. *J. Pharm. Pharmacol.*, **39**(4):246-251. [doi:10.1111/j.2042-7158.1987.tb06261.x]
- Echeverría, J.C., Morera, M.T., Mazkiarán, C., Garrido, J.J., 1998. Competitive sorption of heavy metal by soils. Isotherms and fractional factorial experiments. *Environ. Pollut.*, **101**(2):275-284. [doi:10.1016/S0269-7491(98)00038-4]
- Febrianto, J., Kosasih, A.N., Sunarso, J., Ju, Y.H., Indraswati, N., Ismadji, S., 2009. Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: a summary of recent studies. *J. Hazard. Mater.*, **162**(2-3):616-645. [doi:10.1016/j.jhazmat.2008.06.042]
- Fu, P., Hu, S., Xiang, J., Sun, L.S., Li, P.S., Zhang, J.Y., Zheng, C.G., 2009. Pyrolysis of maize stalk on the characterization of chars formed under different devolatilization conditions. *Energy Fuels*, **23**(9):4605-4611. [doi:10.1021/ef900268y]

- Harvey, O.R., Herbert, B.E., Rhue, R.D., Kuo, L.J., 2011. Metal interactions at the biochar-water interface: energetics and structure-sorption relationships elucidated by flow adsorption microcalorimetry. *Environ. Sci. Technol.*, **45**(13):5550-5556. [doi:10.1021/es104401h]
- Ji, L.L., Chen, W., Zheng, S.R., Xu, Z.Y., Zhu, D.Q., 2009. Adsorption of sulfonamide antibiotics to multiwalled carbon nanotubes. *Langmuir*, **25**(19):11608-11613. [doi:10.1021/la9015838]
- Ji, L.L., Wan, Y.Q., Zheng, S.R., Zhu, D.Q., 2011. 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**(13):5580-5586. [doi:10.1021/es200483b]
- Jiang, J., Xu, R.K., Jiang, T.Y., Li, Z., 2012. Immobilization of Cu(II), Pb(II) and Cd(II) by the addition of rice straw derived biochar to a simulated polluted ultisol. *J. Hazard. Mater.*, **229**:145-150. [doi:10.1016/j.jhazmat.2012.05.086]
- Kannan, N., Rengasamy, G., 2005. Comparison of cadmium ion adsorption on various activated carbons. *Water Air Soil Pollut.*, **163**(1-4):185-201. [doi:10.1007/s11270-005-0277-y]
- Kumar, P.S., Ramalingam, S., Sathyaselvabala, V., Kirupha, S.D., Murugesan, A., Sivanesan, S., 2012. Removal of cadmium(II) from aqueous solution by agricultural waste cashew nut shell. *Korean J. Chem. Eng.*, **29**(6):756-768. [doi:10.1007/s11814-011-0259-2]
- Lehmann, J., 2007. Bio-energy in the black. *Front. Ecol. Environ.*, **5**(7):381-387. [doi:10.1890/1540-9295(2007)5[381:BITB]2.0.CO;2]
- Lertpaitoonpan, W., Ong, S.K., Moorman, T.B., 2009. Effect of organic carbon and pH on soil sorption of sulfamethazine. *Chemosphere*, **76**(4):558-564. [doi:10.1016/j.chemosphere.2009.02.066]
- Liu, Z.G., Zhang, F.S., 2009. Removal of lead from water using biochars prepared from hydrothermal liquefaction of biomass. *J. Hazard. Mater.*, **167**(1-3):933-939. [doi:10.1016/j.jhazmat.2009.01.085]
- Loganathan, P., Vigneswaran, S., Kandasamy, J., Naidu, R., 2012. Cadmium sorption and desorption in soils: a review. *Crit. Rev. Environ. Sci. Technol.*, **42**(5):489-533. [doi:10.1080/10643389.2010.520234]
- Lucida, H., Parkin, J.E., Sunderland, V.B., 2000. Kinetic study of the reaction of sulfamethoxazole and glucose under acidic conditions—I. Effect of pH and temperature. *Int. J. Pharm.*, **202**(1-2):47-61. [doi:10.1016/S0378-5173(00)00413-0]
- Luo, Y., Xu, L., Rysz, M., Wang, Y.Q., Zhang, H., Alvarez, P.J.J., 2011. Occurrence and transport of tetracycline, sulfonamide, quinolone, and macrolide antibiotics in the Haihe River Basin, China. *Environ. Sci. Technol.*, **45**(5):1827-1833. [doi:10.1021/es104009s]
- Martinez, J.L., 2008. Antibiotics and antibiotic resistance genes in natural environments. *Science*, **321**(5887):365-367. [doi:10.1126/science.1159483]
- Martins, R.J.E., Pardo, R., Boaventura, R.A.R., 2004. Cadmium(II) and zinc(II) adsorption by the aquatic moss *Fontinalis antipyretica*: effect of temperature, pH and water hardness. *Water Res.*, **38**(3):693-699. [doi:10.1016/j.watres.2003.10.013]
- Máthé, I., Benedek, T., Táncsics, A., Palatinszky, M., Lányi, S., Márialigeti, K., 2012. Diversity, activity, antibiotic and heavy metal resistance of bacteria from petroleum hydrocarbon contaminated soils located in Harghita County (Romania). *Int. Biodeter. Biodegr.*, **73**:41-49. [doi:10.1016/j.ibiod.2012.05.018]
- Matyar, F., 2012. Antibiotic and heavy metal resistance in bacteria isolated from the Eastern Mediterranean Sea Coast. *Bull. Environ. Contam. Toxicol.*, **89**(3):551-556. [doi:10.1007/s00128-012-0726-4]
- Mohan, D., Pittman, C.U., Bricka, M., Smith, F., Yancey, B., Mohammad, J., Steele, P.H., Alexandre-Franco, M.F., Gomez-Serrano, V., Gong, H., 2007. Sorption of arsenic, cadmium, and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production. *J. Colloid Interface Sci.*, **310**(1):57-73. [doi:10.1016/j.jcis.2007.01.020]
- Mukherjee, A., Zimmerman, A.R., Harris, W., 2011. Surface chemistry variations among a series of laboratory-produced biochars. *Geoderma*, **163**(3-4):247-255. [doi:10.1016/j.geoderma.2011.04.021]
- Nag, S.K., Kookana, R., Smith, L., Krull, E., Macdonald, L.M., Gill, G., 2011. Poor efficacy of herbicides in biochar-amended soils as affected by their chemistry and mode of action. *Chemosphere*, **84**(11):1572-1577. [doi:10.1016/j.chemosphere.2011.05.052]
- Oleszczuk, P., Rycaj, M., Lehmann, J., Cornelissen, G., 2012. Influence of activated carbon and biochar on phytotoxicity of air-dried sewage sludges to *Lepidium sativum*. *Ecotoxicol. Environ. Saf.*, **80**:321-326. [doi:10.1016/j.ecoenv.2012.03.015]
- Qu, C.S., Li, B., Wu, H.S., Giesy, J.P., 2012. Controlling air pollution from straw burning in china calls for efficient recycling. *Environ. Sci. Technol.*, **46**(15):7934-7936. [doi:10.1021/es302666s]
- Shinogi, Y., Kanri, Y., 2003. Pyrolysis of plant, animal and human waste: physical and chemical characterization of the pyrolytic products. *Bioresour. Technol.*, **90**(3):241-247. [doi:10.1016/S0960-8524(03)00147-0]
- Stoob, K., Singer, H.P., Mueller, S.R., Schwarzenbach, R.P., Stamm, C.H., 2007. Dissipation and transport of veterinary sulfonamide antibiotics after manure application to grassland in a small catchment. *Environ. Sci. Technol.*, **41**(21):7349-7355. [doi:10.1021/es070840e]
- Tong, X.J., Li, J.Y., Yuan, J.H., Xu, R.K., 2011. Adsorption of Cu(II) by biochars generated from three crop straws. *Chem. Eng. J.*, **172**(2-3):828-834. [doi:10.1016/j.cej.2011.06.069]
- Uchimiya, M., Lima, I.M., Klasson, K.T., Wartelle, L.H., 2010. Contaminant immobilization and nutrient release by biochar soil amendment: roles of natural organic matter. *Chemosphere*, **80**(8):935-940. [doi:10.1016/j.chemosphere.2010.05.020]
- Wan, Y., Bao, Y.Y., Zhou, Q.X., 2010. Simultaneous adsorption and desorption of cadmium and tetracycline

- on cinnamon soil. *Chemosphere*, **80**(7):807-812. [doi:10.1016/j.chemosphere.2010.04.066]
- Wang, F.Y., Wang, H., Ma, J.W., 2010. Adsorption of cadmium(II) ions from aqueous solution by a new low-cost adsorbent-bamboo charcoal. *J. Hazard. Mater.*, **177**(1-3):300-306. [doi:10.1016/j.jhazmat.2009.12.032]
- Wang, Y.J., Jia, D.A., Sun, R.J., Zhu, H.W., Zhou, D.M., 2008. Adsorption and cosorption of tetracycline and copper(II) on montmorillonite as affected by solution pH. *Environ. Sci. Technol.*, **42**(9):3254-3259. [doi:10.1021/es702641a]
- Wu, D., Pan, B., Wu, M., Peng, H.B., Zhang, D., Xing, B.S., 2012. Coadsorption of Cu and sulfamethoxazole on hydroxylized and graphitized carbon nanotubes. *Sci. Total Environ.*, **427**:247-252. [doi:10.1016/j.scitotenv.2012.03.039]
- Wu, W.H., Wang, H.Z., Xu, J.M., Xie, Z.M., 2009. Adsorption characteristic of bensulfuron-methyl at variable added Pb^{2+} concentrations on paddy soils. *J. Environ. Sci.*, **21**(8): 1129-1134. [doi:10.1016/S1001-0742(08)62392-X]
- Xu, X., Cao, X., Zhao, L., Wang, H., Yu, H., Gao, B., 2013. Removal of Cu, Zn, and Cd from aqueous solutions by the dairy manure-derived biochar. *Environ. Sci. Pollut. Res. Int.*, **20**(1):358-368. [doi:10.1007/s11356-012-0873-5]
- Yadanaparathi, S.K., Graybill, D., von Wandruszka, R., 2009. Adsorbents for the removal of arsenic, cadmium, and lead from contaminated waters. *J. Hazard. Mater.*, **171**(1-3): 1-15. [doi:10.1016/j.jhazmat.2009.05.103]
- Zhang, D., Pan, B., Zhang, H., Ning, P., Xing, B.S., 2010a. Contribution of different sulfamethoxazole species to their overall adsorption on functionalized carbon nanotubes. *Environ. Sci. Technol.*, **44**(10):3806-3811. [doi:10.1021/es903851q]
- Zhang, X., Pan, B., Yang, K., Zhang, D., Hou, J.A., 2010b. Adsorption of sulfamethoxazole on different types of carbon nanotubes in comparison to other natural adsorbents. *J. Environ. Sci. Health A*, **45**(12):1625-1634. [doi:10.1080/10934529.2010.506127]
- Zhu, D.Q., Pignatello, J.J., 2005. Characterization of aromatic compound sorptive interactions with black carbon (charcoal) assisted by graphite as a model. *Environ. Sci. Technol.*, **39**(7):2033-2041. [doi:10.1021/es0491376]
- Zhu, D.Q., Hyun, S.H., Pignatello, J.J., Lee, L.S., 2004. Evidence for pi-pi electron donor-acceptor interactions between pi-donor aromatic compounds and pi-acceptor sites in soil organic matter through pH effects on sorption. *Environ. Sci. Technol.*, **38**(16):4361-4368. [doi:10.1021/es035379e]

Recommended paper related to this topic

Cadmium accumulation in different pakchoi cultivars and screening for pollution-safe cultivars

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doi:10.1631/jzus.B1100356

J. Zhejiang Univ.-Sci. B (Biomed. & Biotechnol.), 2012 Vol.13 No.6 P.494-502

Abstract: The selection and breeding of pollution-safe cultivars (PSCs) is a practicable and cost-effective approach to minimize the influx of heavy metal to the human food chain. In this study, both pot-culture and field experiments were conducted to identify and screen out cadmium pollution-safe cultivars (Cd-PSCs) from 50 pakchoi (*Brassica rapa* L. ssp. *chinensis*) cultivars for food safety. When treated with 1.0 or 2.5 mg/kg Cd, most of the pakchoi cultivars (>70%) showed greater or similar shoot biomass when compared with the control. This result indicates that pakchoi has a considerable tolerance to soil Cd stress. Cd concentrations in the shoot varied significantly ($P<0.05$) between cultivars: in two Cd treatments (1.0 and 2.5 mg/kg), the average values were 0.074 and 0.175 mg/kg fresh weight (FW), respectively. Cd concentrations in the shoots of 14 pakchoi cultivars were lower than 0.05 mg/kg FW. In pot-culture experiments, both enrichment factors (EFs) and translocation factors (TFs) of six pakchoi cultivars were lower than 1.0. The field studies further confirmed that the Hangzhouyoudonger, Aijiaoheiyi 333, and Zaoshenghuajing cultivars are Cd-PSCs, and are therefore suitable for growth in low Cd-contaminated soils (≤ 1.2 mg/kg) without any risk to food safety.