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Sorption of sulfamethazine to biochars as affected by dissolved organic matters of different origin

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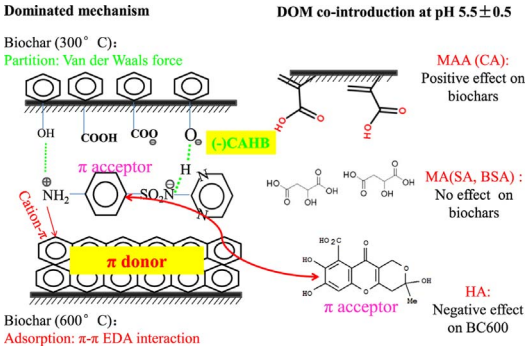
GRAPHICAL ABSTRACT



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ABSTRACT

Sorption characteristic of sulfamethazine (SMT) to straw biochars pyrolyzed at 300 °C (BC300) and 600 °C (BC600), and the effect of ubiquitous DOM were investigated. Results showed that physisorption (partition) and weak chemical binding (π-π EDA interaction) dominated the sorption of SMT to BC300 and BC600, respectively. Graphene sheets in biochar played important roles in the sorption of SMT, leading to higher sorption capacity (K_f) on BC600 (1.77 $mg^{1-n} L^n g^{-1}$) than BC300 (0.11 $mg^{1-n} L^n g^{-1}$). Sorption amount of SMT to BC300 was not affected by polysaccharide and malic acid, while it was slightly promoted by citric acid, but dramatically increased 1.25 times by methacrylic acid through decreasing solution pH and providing new sorption sites. Humic acid and bovine serum albumin restrained the sorption of SMT to BC600, but enhanced SMT^- adsorption to BC300. The chemical nature of DOM, biochar properties and antibiotic species co-determined the impact of DOM on antibiotics adsorption.

1. Introduction

Antibiotics are extensively used in both human and animals for disease control and growth promotion of animals (Sarmah et al., 2006; Hou et al., 2015). Because of the poorly metabolized feature, large proportion of the ingested antibiotics are excreted out of body via urine and feces and enter into soil, sediment and water bodies, leading to antibiotics contamination and the emergence of antimicrobial resistance genes (Zhang et al., 2015; Aust et al., 2008; Allen et al., 2010). It was reported that, the total emission of 36 frequently detected

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antibiotics in China in 2013 was 54,000 tons, and eventually 53,800 tons entered into the environment following wastewater treatment (Zhang et al., 2015). Sorption is one of the most widely applied techniques for antibiotics removal (Yu et al., 2016), in addition, sorption process controls the bioavailability of organic contaminants, influencing their fate and transport in the environment. Therefore, investigating the sorption process, mechanism(s) and environmental factors of antibiotics is of great environmental significance.

Biochar, such as rice straw biochars pyrolyzed at 400–800 °C, possessing high surface area (10.8–50.6 $m^2 g^{-1}$), micro-pore volume (0.0074–0.0343 $cm^3 g^{-1}$), and organic functional groups (−OH, C═O, C═C) (Li et al., 2017a), is recognized as a renewable and promising carbonaceous material, has been studied to adsorb metals and organic contaminants (Mohan et al., 2014), and is an increasingly attractive solution for ionizable antibiotics (Ji et al., 2011; Jia et al., 2013). However, present research is mainly focused on the modification of biochars to promote sorption efficiency (Rajapaksha et al., 2015; Ahmed et al., 2017). Less research is on the environmental factors influencing sorption of antibiotics to biochar, particularly to dissolved organic matter (DOM), which is ubiquitous in water and soil. Moreover, as the DOM has various chemical compositions and functional groups, they play an important role in the fate and transport of organic contaminants in the environment (Haham et al., 2012; Ling et al., 2015). It has been reported that the low molecular weight organic acids (LMWOAs) can enhance the desorption of PAHs and affects their degradation (Ling et al., 2015; Gao et al., 2010). In addition, humic acid (HA) with complicated composition and structure, the hydrophobicity, aromaticity and functionality properties of which let it easily been adsorbed by the solid matrix, might either compete with antibiotics for sorption sites or create new sorption sites (Lian et al., 2015). Polysaccharides and proteins, the most important components of bacteria biofilm, are another commonly detected DOM species, the functional groups (Wei et al., 2011; Binupriya et al., 2010) of which might also affect the sorption of ionizable antibiotics to biochar. However, the effect of various DOM species on the sorption of ionizable antibiotic has rarely been investigated (Lian et al., 2015; Sun et al., 2016).

It is known that, the physical and chemical property of biochar, which depends on the biomass source and pyrolysis conditions, controls the sorption process and dominated sorption mechanism of the antibiotics (Rajapaksha et al., 2014; Jia et al., 2016). Besides, antibiotic species varies with solution pH increasing. When the pH was below the pK_{a1} value of antibiotics, cation ion prevails; between pK_{a1} and pK_{a2}, zwitterion predominates; and above pK_{a2}, anion becomes dominate. The different species of antibiotics might result in different predominant driving forces and sorption mechanisms to the adsorbents (Figueroa et al., 2004). On the other hand, the functional groups of the DOM will dissociate with increasing pH. Therefore, to investigate the effect of different DOM on the sorption of antibiotics, the biochar properties, pH conditions and the predominated sorption mechanism must be considered.

To investigate the effect of DOM from different sources and types on the sorption of antibiotics to biochars, sulfamethazine (SMT), a sulfonamide antibiotic extensively used in cattle and swine feeding that is frequently detected in water bodies (Zhang et al., 2015), was used as the model antibiotic in this study. Various kinetic and isotherm sorption models, accompanied with spectra analysis and charge characteristic of biochars, were used to illustrate the predominated mechanism of SMT to biochars. Furthermore, edge sorption experiments at different concentrations and pH were conducted to investigate the interaction among various DOM, SMT and biochars, and the mechanism involved.

2. Materials and methods

2.1. Chemicals

Sulfamethazine (pK_{a1}: 2.24; pK_{a2}: 7.42) standard compound (> 98.5% purity) was bought from Dr. Ehrenstorfer GmbH company (Augsburg, Germany). The HPLC grade acetonitrile and glacial acetic were obtained from Tedia Company (Fairfield, USA). All other chemical reagents were of analytical grade. Humic acid was bought from Sigma Aldrich Chemical GmbH (Switzerland). The sodium alginate (SA, 90% purity) and bovine serum albumin (BSA, purity > 98%) were produced by Aladdin industrial corporation (Shanghai, China). All the other solvents and chemical reagents obtained from Nanjing chemical factory (Nanjing, China).

2.2. Biochar preparation and characterization

Wheat and maize straw were collected and used as the feedstock to produce biochars through pyrolysis with a patented biochar reactor (NO.: ZL2009 2 0232191.9) as previously described (Jia et al., 2013, 2016). Briefly, the straws were washed and oven-dried (DHG-9145A, Shanghai Yiheng Scientific Instruments, China), then transferred to the biochar reactor and underwent a step-wise heating procedure under limited oxygen condition to produce biochars with final temperature of 300 °C and 600 °C. The heating program was started from 200 °C, followed by consecutive increase to 250 °C, 300 °C, 400 °C, 500 °C and 600 °C and held for 1.5 h at each temperature. After cooling, the biochars were ground and sieved with a 100 mesh sieve, and recorded as WBC300, WBC600, MBC300 and MBC600, respectively for wheat and maize straw biochars pyrolyzed at final temperature of 300 and 600 °C.

The physicochemical properties of biochars have been reported in previous studies (Jia et al., 2013, 2014, 2016), such as elemental composition (C, N, H, and O) measured by a CNH analyzer (Vario MICRO, Germany elementar, Germany), contents of organic oxygen-containing functional groups measured by Boehm titration method, surface morphology images measured by SEM-EDS (Hitachi-3400N, Japan), and BET surface areas and pore distributions determined at 77 K by the N_2 adsorption method using a surface area analyzer (ASAP-2020, Micromeritics, USA). In addition, Raman spectra technique was employed to further analyze the graphite-like microstructure evolution of the biochars. Briefly, the biochar powders were transferred to the silicon chip to prepare solid film samples and Raman scattering spectroscopy was recorded at 532 nm using InVia laser Raman spectrometer (Renishaw, UK). Zeta potential values of the biochar particles were measured using ZetaPlus instrument from Brookhaven Company (New York, USA). Furthermore, FTIR spectrum of the biochars before and after isotherm sorption of SMT were recorded by FTIR (NEXUS 870 spectrophotometer, Thermo Nicolet, USA), to investigate surface functional group changes and illustrate the probable sorption mechanism of SMT to biochar.

2.3. Sorption experiments

Kinetics and isotherm sorption of SMT to biochar were conducted using batch experiments. Briefly, 0.01 mol L^{-1} $CaCl_2$ was used as the background solution to maintain ionic strength, the prepared samples were shaken on a Rolldrum shaker (WH-962, Taicang, China) end-over-end with a speed of 15 rpm at 25 ± 0.5 °C in the dark, and performed in triplicates. After shaking, 1.0 mL of the biochar suspensions was sampled and filtrated with a 0.45 μm microfiltration membrane (PES, Membrana Company, Germany) and used for HPLC analysis. The remaining suspension was used to measure pH using a benchtop pH meter (Thermo Scientific Orion 4-Star, USA).

2.3.1. Sorption kinetics

Fifty milligrams of biochar powder (WBC300, WBC600, MBC300 and MBC600) was weighed into a 20 mL brown glass tubes, then 5 mL of 0.02 mol L^{-1} $CaCl_2$ and a certain amount of 0.1 mol L^{-1} HCl were added to adjust the solution pH to around 5.0. After shaken for 24 h on a Rolldrum shaker (15 rpm) at 25 °C, the solution pH were 6.55, 6.62, 5.93 and 6.38 for WBC300, WBC600, MBC300 and MBC600,