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Sorption of tetracycline on H_3PO_4 modified biochar derived from rice straw and swine manure

Tingwei Chen[a,1], Ling Luo[a,1,*], Shihuai Deng[a,*], Guozhong Shi[b,*], Shirong Zhang[a], Yanzong Zhang[a], Ouping Deng[c], Lilin Wang[a], Jing Zhang[a], Luoyu Wei[b]

[a] College of Environmental Sciences, Sichuan Agricultural University, Chengdu 611130, People's Republic of China
[b] Biogas Institute of Ministry of Agriculture, Chengdu 610041, People's Republic of China
[c] College of Resources, Sichuan Agricultural University, Chengdu 611130, People's Republic of China

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ABSTRACT

Currently, the information about the sorption of tetracycline (TC) on animal manure derived biochar was rare although plant residue derived biochar showed high sorption of TC). Therefore, this study explored the sorption of TC on swine manure derived biochar, and compared with rice straw derived biochar simultaneously. Also, H_3PO_4 was adopted to modify both types of biochar. The sorption kinetic and isotherm data showed H_3PO_4 modification enhanced the sorption of TC on both types of biochar (especially swine-manure-biochar), and indicated the chemisorptions including H-bonding and π-π electron donor acceptor interaction might be the primary mechanism. Moreover, the strengthened electrostatic attraction between TC and biochars might largely explain the enhanced sorption capacity of TC along with pH increasing from 5.0 to 9.0. At the same conditions, swine manure derived biochar demonstrated lower sorption capacity of TC than rice straw biochar, but still could be good material for the sorption of TC.

1. Introduction

Recent years, antibiotics have gained significant attention due to the extensive usage of antibiotics and the resulting environmental pollution (Chen et al., 2017). Usually, antibiotics are extensively used in human and animal healthcare and are also used as an animal growth promoter in the farming industry (Bao et al., 2010). Antibiotics are not easily biodegraded, therefore, they are frequently detected in soils, sediments, aquatic environment, and so on (Jing et al., 2014). When used widely, antibiotics can cause the proliferation of antibiotic resistance genes (ARGs) in the environment, which might pose potential hazards to human health and ecology (Chen et al., 2017).

Tetracyclines (TCs) are one of the most frequently used antibiotics for human healthcare and feed additives of animals. According to statistics, the consumption of TCs was ranked second in the world, but first in China (Bao et al., 2010). Approximate 70–90% TCs can't be metabolized by body, and then released in the environment as unchanged form (Xu and Li, 2010). The concentrations of TCs in the environment reported in literatures were ranging from ng kg^{-1} to mg kg^{-1} (e.g., 500 mg kg^{-1} in hospital and pharmaceutical manufacturing wastewater) (Jing et al., 2014). TCs may be carcinogenic on chronic exposure, hence, the removal of TCs should be paid significant attention (Peiris et al., 2017). Until now, several technologies have been tired to remove TCs from wastewater, such as ozone oxidation, anaerobic biodegradation, photocatalytic degradation, and so on (Chen and Zhang, 2013; Lucas et al., 2016; Sousa et al., 2017). These technologies can remove TCs effectively, but the cost is relatively expensive and the operation is often complex or unstable. Compared with these technologies, sorptive removal of TCs by biochar has received numerous research focus because biochar showed the great benefit of adsorption properties, cost effectiveness and easy operation (Peiris et al., 2017; Zhu et al., 2014).

Biochar, biomass-derived carbonaceous material, gained enormous attention due to its role in sequestering carbon (Luo and Gu, 2016), improving soil fertility (Ding et al., 2016) and removing environmental pollutants such as heavy metals (Li et al., 2017a), hydrophobic organic contaminants (HOCs) (Wang et al., 2016), ionic and nonionic organic pollutants (Kim and Hyun, 2018), and so on. In general, biochar is produced from oxygen-limited pyrolysis of biomass, including plant residues, sewage sludge, and animal manures (Jang et al., 2018; Xu et al., 2014; Wang et al., 2016). Plant residues were the most widely used feedstock than animal manures and sewage sludge to produce

* Corresponding authors.
E-mail addresses: luoling@sicau.edu.cn (L. Luo), shdeng8888@163.com (S. Deng), brtc666@163.com (G. Shi).
[1] These authors contributed equally.

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biochar, especially rice straw (Luo et al., 2011; Wang et al., 2017). Also, there is an increasing interest in biochar derived from animal manures. For example, several studies reported swine manure derived biochar showed good potential to adsorb HOCs (Wang et al., 2016), heavy metals (Meng et al., 2014) and pesticides (Zhang et al., 2013). Relative to rice straw, swine manures were less used to produce biochar and the related research literatures were also quite limited. Currently, rice straw and swine manure are two of the most abundant agricultural wastes in China (Meng et al., 2018). Considering the annual production of rice straw (approximate 0.12 billion tonnes) and swine manure (approximate 3.8 billion tonnes), swine manure may be a promising potential feedstock for biochar production.

It is reported that the animal manure derived biochar usually contains high ash content that might interact with pollutants (Zhang et al., 2013; Wang et al., 2016). Besides, animal manure derived bicohar may have higher pH and O/C ratio as well as lower surface area and carbon content than plant residue derived biochar (Zhao et al., 2016). Therefore, it is assumed that the sorption of TCs on animal manure derived biochar may be different with plant residue derived one.

To date, there are several studies about the sorption of TCs on biochar, and most of them are related to plant residue derived biochar (Meng et al., 2013; Tsai et al., 2012; Wang et al., 2016). The studies about animal residue derived biochar are less, and the mechanism of TC on animal derived biochar is not clear. Moreover, the comparison of sorption properties between animal manure and plant residue derived biochar is less explored. For better utilization of animal manure derived biochar in adsorbing TCs, it is necessary to understand the mechanism of TCs on animal manure derived biochar, and compare the sorption properties of animal manure derived biochar to plant residue derived biochar.

In this study, rice straw and swine manure were chosen as feedstocks of biochar due to their abundance in agricultural wastes and the difference of their physicochemical properties. In order to enhance sorption capacity of TC, H_3PO_4 was applied to modify biochars. The aim of this study was 1) to compare the characteristics of rice straw-derived biochar with swine manure-derived biochar; 2) to investigate the performance and mechanism of rice straw-derived and swine manure-derived biochars as sorbents for TC removal. Furthermore, the effect of pH on the sorption capacity of TC was explored to further understand the mechanism of TC on both biochars.

2. Materials and methods

2.1. Materials

Tetracycline hydrochloride (TC) (purity ≥ 95%) was purchased from Sigma. Chemicals used in this study were all analytical grade. Rice straw was collected from Chongzhou experimental base of Sichuan Agricultural University, Chengdu, China, while swine manure was obtained from the experimental farm of Sichuan Agricultural University, Ya'an, China. Both rice straw and swine manure were air-dried and ground to pass through a 2 mm sieve before producing biochars.

2.2. Biochars

As previously described (Zhang et al., 2013), the biomass was packed into 30 mL ceramic pot covered with lid to limit oxygen supply and then heated at 700 °C in a preheated muffle furnace for 2 h. The produced biochars were ground and passed through a 100 mesh sieve (0.15 mm). H_3PO_4 solution was applied to modify the biochars for enhancing the sorption capacity for adsorption of TC since H_3PO_4 is nonpolluting and easily washed away by water (Peng et al., 2017). Briefly, 20 g biochars were immersed in 40 mL 14% H_3PO_4 solution for 24 h at 25 °C. After that, the H_3PO_4 modified biochars were washed by distilled water until the pH of supernatants was stable. Subsequently, the supernatants were discarded and the biochars were oven-dried overnight at 105 °C (Luo et al., 2011; Peng et al., 2017). The H_3PO_4 modified biochar derived from rice straw and swine manure were recorded as RCA and SCA, respectively. For understanding the role of H_3PO_4 modification in enhancing sorption capacity of TC, rice straw derived biochar and swine manure biochar were only washed by distilled water with the similar procedures, and labeled as RC and SC.

2.3. Characteristics of biochars

The structure and morphology of biochars were characterized using a scanning electron microscopy equipped with an energy dispersive spectrometer (SEM -EDS, Zeiss Sigma300, Germany). Fourier Transform Infrared Spectroscopy (FTIR, PerkinElmer Frontier, America) of biochars was recorded with 4 cm^{-1} resolution between wavenumbers of 4000 cm^{-1} and 400 cm^{-1}. The results of SEM-EDS and FTIR were presented in Supporting Information. The elemental compositions of biochars were determined by an element analyzer (YX-CHN5000, China). Moreover, Brunauer-Emmett-Teller (BET, ASAP2460, Micromeritics, America) was applied to determine the surface area, porosity and pore volume of biochars. The pH of zero point charges (pH_{PZC}) of SC, SCA, RC and RCA were measured according to the methods reported in the previous research (Jang et al., 2018). The measurement of pH_{PZC} was presented in Supporting Information.

2.4. Sorption experiments

2.4.1. Sorption kinetics

Sorption kinetics experiments were performed to evaluate the equilibrium time for the subsequent sorption isotherm experiments.10 mg of RCA and SCA and 20 mg of RC and SC were added to 50 mL centrifuge glass tubes containing 30 mL TC solution with concentration of 120 mg L^{-1}, respectively. All tubes were put in a table concentrator shaker and shaken at 200 rpm at 25 °C from 0.5 h to 216 h. Each treatment was conducted in triplicates, and also the tubes containing only 30 mL TC solution of the same concentration was used for observing the loss of TC during this procedure. At predetermined times, the tubes were taken out and centrifuged at 3000 rpm for 20 min and then filtered by millipore membranes (0.45 μm). Thereafter, the filtrate was determined by a V-5000 spectrophotometer at wavelength of 360 nm (Zhu et al., 2014).

2.4.2. Batch sorption experiments

Sorption isotherms of TC to modified biochars were studied. Sorption isotherms for each biochar were determined at different initial solution concentrations of 30, 40, 50, 60, 80, 100, 150, 200 mg L^{-1}. Each concentration for each biochar had triplicate treatments. To each 50 mL centrifuge glass tube, 5–10 mg of biochar (the weighed amounts depending on the concentration of TC and also the type of biochars) and 30 mL TC solution with varying concentrations were combined and shaken at 200 rpm at 25 °C to reach apparent equilibrium based on the sorption kinetics of Section 2.4.1. Moreover, tubes adding only TC solution were used as blanks to test the loss of TC during the periods of experiments. Afterward, the following procedures such as centrifugation, filtration and measurement, were the same as Section 2.4.1.

2.4.3. Effect of pH on sorption isotherms

The pH values of TC solution with varying concentrations were adjusted to pH 5, pH 7 and pH 9 by using 0.1 mol L^{-1} HCl and NaOH solution. After that, sorption isotherms were conducted at 25 °C in the same way as described in Section 2.4.2. Equilibrium pH of solution was measured after sorption experiments.

2.5. Sorption data analysis

The experimental data of sorption kinetics were examined by the pseudo-first-order (PFO) and pseudo-second-order (PSO) (Zhou et al.,