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Sorption behavior of tetracyclines on suspended organic matters originating from swine wastewater

Yaoyin Lou[1,2], Zhi-Long Ye[1,*], Shaohua Chen[1], Xin Ye[1], Yujun Deng[1,2], Jianqiao Zhang[1,2]

1. Key Laboratory of Urban Pollutant Conversion, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China
2. University of Chinese Academy of Sciences, Beijing 100049, China

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A B S T R A C T

Tetracyclines (TCs) discharged from livestock wastewater have aroused public concerns due to their pharmacological threats to ecosystems and human health. As an important medium in the wastewater, suspended organic matters (SOMs) play vital roles in antibiotics transport and degradation. However, limited information has been reported in the relevant literature. This study investigated TCs sorption behavior on SOM, withdrawn from swine wastewater. High TCs sorption capacities were detected, with the maximum values ranging from 0.337 to 0.679 mg/g. Increasing pH and temperature led to the decline of sorption capacity. Results from three-dimensional excitation–emission matrix fluorescence spectroscopy and Fourier transform infrared spectrometry revealed that amide and carboxyl groups were the main functional groups for TCs adsorption. The interactions between SOM and TCs were clarified as predominated by hydrogen-bonding and cation-exchange in acid conditions, and electrostatic repulsion in neutral or alkaline conditions. Adsorption kinetics modeling was conducted, and a satisfactory fitting was achieved with the Freundlich equation. These results indicated that the adsorption process was a rather complex process, involving a combination of cation-exchange and hydrogen-bonding. The results will provide a better understanding of the capability of SOM for TCs transport and abatement in the wastewater treatment process.

Introduction

Due to rapid urban expansion and economic growth, livestock wastewater pollution is becoming a serious concern worldwide, especially for the developing countries. For instance, there is over 14 million tons of nitrogen (N) and 3 million tons of phosphorus (P) discharged *via* swine wastewater into the environment each year in China (Ye et al., 2011). However, not only the conventional pollutants, such as N and P, but also the veterinary antibiotics (VAs), a new type of emergent pollutants, pose pollution threats to the ecosystem and human health (Zhu et al., 2013). Generally, VAs are used extensively as food additives in animal breeding to prevent disease spread and to improve the efficiency of feed uptake (Liu et al., 2015; Visschers et al., 2014). As for China, over 97,000 tons VAs are used in pig production annually (Ben et al., 2013). According to the literature, 30%–90% VAs are not easily absorbed by animal digestive systems (Tan et al., 2015; Xie et al., 2012) and are excreted into the environment. Antibiotic residues in the environment can affect aquatic and terrestrial organisms, altering microbial community compositions (Hu et al., 2010). Long-term exposure to antibiotics may exert selective pressure on the microorganism community, and trigger the increase of resistant bacteria into the

* *Corresponding author*. E-mail: zlye@iue.ac.cn (Zhi-Long Ye).

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environment, which poses threats to ecological health (Zhu et al., 2013).

Among the VAs, tetracyclines (TCs) are most widely used in livestock farming (Liu et al., 2015). High concentrations of TCs of up to μg/L have been frequently found in livestock wastewater. For instance, Pan et al. (2011) surveyed TC concentrations in swine wastewater withdrawn from different pig farms located in different areas in China, including Beijing, Shanghai and Shandong province, and they found that oxytetracycline (OTC) and chlortetracycline (CTC) have high residues, with concentrations at 3.5–387.1 and 3.0–138.8 μg/L, respectively. The wastewater containing such high TC contents could cause a pollution threat to the surrounding waters and soils. Jiang et al. (2011) reported that TCs had high residues in the Huangpu River, with concentrations ranging from 5.6–147.1 ng/L, above the European standard of 10 ng/L, which has aroused ecological risks. Pereira et al. (2015) found TC residues in water bodies located in the north of Portugal ranging from 3 to 75.1 ng/L. Topal and Arslan (2015) reported that TC residue in surface water at Elazığ City (Turkey) exceeded 4.0 μg/L, which poses a threat to the local ecology.

It has been reported that organic matters, such as humic acid (Gu et al., 2007; Vaz et al., 2015), soils organics (Vaz et al., 2015) and extracellular polymeric substances (EPS) (Song et al., 2014), have high affinities for TCs. As for livestock wastewater, it contains a high concentration of suspended organic matters (SOMs), even levels above 2000 mg/L (Peng et al., 2016). Many studies have revealed that TCs are prone to complex with SOM. Ben et al. (2013) found that more than 30% of TCs in swine wastewater were partitioned in the SOM phase. Le-Minh et al. (2010) reported that suspended solids have a high affinity for TCs, with sorption constants K_d (L/kg) at 3.9–4.3. Other researchers found that TCs interacted strongly with clay and SOM by cation-exchange, surface complexation/cation, bridging hydrophobic partitioning and cation-exchange interactions (Zhou et al., 2013; Ben et al., 2013). Accordingly, it is clear that SOM may play important roles in TCs transport and abatement in the wastewater treatment process. However, little information is available regarding the interaction between SOM and TCs in swine wastewater. Disregarding this interaction may lead to neglect of possible transport or transformation pathways for antibiotics. Hence, the objective of this work was to investigate the adsorptive behaviors of TCs on SOM. Batch experiments were conducted under strict operational conditions, and the effects of pH, SOM concentration, and initial TCs concentration were evaluated. In addition, the adsorption equilibration and kinetics were investigated. FT-IR (Fourier transform infrared spectrometry) and 3DEEM (three-dimensional excitation–emission matrix fluorescence spectroscopy) analyses were applied to identify the organic characteristics of SOM, which was necessary to elucidate the mechanism of adsorption.

1. Materials and methods

1.1. SOMs

Swine wastewater was obtained from the digested effluent of a biogas tank in a pig farm located in Xiamen City, China. SOM was isolated by centrifuging the swine wastewater for 10 min at 10000 r/min, as described by Guo et al. (2012). After discarding the supernatant, SOMs were withdrawn, frozen by liquid nitrogen and stored at −18°C for further experiments.

1.2. Standard solution

TC standards, including TC, OTC, CTC and doxycycline (DXC), were obtained from the Laboratory of Dr. Ehrenstorfer (Augsburg, Germany). An internal standard (IS), TC-d6 (80%) was purchased from Toronto Research Chemicals Inc. (North York, Canada). Oasis HLB cartridges (200 mg, 6 mL) was Q6 purchased from Waters (Milford, MA, USA). TC stock standard solutions were set at 100 mg/L and prepared with methanol as the solvent.

1.3. Experimental procedure

The experiments concerning adsorption kinetics were conducted using 50 mL glass centrifuge tubes. Thirty milligrams SOM was added into each tube, followed by adding 25 mL Milli-Q water. NaCl was added to sustain the ionic strength at 0.01 mol/L. All the tubes were shaken at 250 r/min in a shaker (TENSUC, China). Sampling times were set at 0, 0.17, 0.5, 1, 2, 4, 6, 8, 10, 12, 16 and 20 hr, respectively. After sampling, the solution was immediately filtered through a 0.45 μm-glass-fiber filter, and the filtrate was stored at −18°C for further analyses. Blank experiments following the same process were also carried out without SOM addition.

For investigation of the adsorption isotherm, experiments were conducted with 30 mg SOM. Initial TC concentrations were set at 0.05, 0.10, 0.20, 0.40, 0.60, 0.80, 1.00, 1.50, and 2.00 mg/L, respectively. NaCl was added to sustain ionic strength at 0.01 mol/L.

It has been reported that pH and temperature are crucial parameters for adsorption behavior (Zhao et al., 2011; Xu and Li, 2010; Bansal, 2012). Experiments concerning the influence of pH were conducted by setting pH levels at 3.0, 6.5, 7.0, 7.5, 8.0, 8.5, 9.0, 9.5, 10.0, and 10.5, while the investigation on temperature was conducted at 10, 20 and 30°C, respectively.

1.4. Analytical methods

1.4.1. Organic matters

The basic characteristics of SOM were first analyzed using an elemental analyzer (Vario Macro CHNS-O-CL, Germany). SOM approximately contained 22.8% C, 5.7% N, 32.9% H, 31.2% O, 0.5% S, and 7.0% ash.

3DEEM was adopted to analyze the extractable organic matters (EOMs) of SOM. The extraction process of EOM was Q7 referenced to the method of Sassman and Lee (2005). The detailed extraction process was as follows: the mixed liquor of 10-mL portions of 0.5 mol/L NaCl/0.25 mol/L oxalic acid/ethyl alcohol (25/25/50, V/V/V) (extraction solution) and 30 mg SOM was mixed vigorously for 1 min using a vortex mixer, following ultrasonic extraction for 30 min at 60°C. After solid–liquid separation (7000 rpm, 10 min), the supernatant was collected in a beaker. The combined supernatant was analyzed by a fluorescence spectrofluorometer (F-4600, Hitachi, Japan).

The 3DEEM spectrogram was further evaluated by fluorescence region indexing (FRI), a quantitative method adopted to

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