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Adsorption behavior of tetracyclines by struvite particles in the process of phosphorus recovery from synthetic swine wastewater

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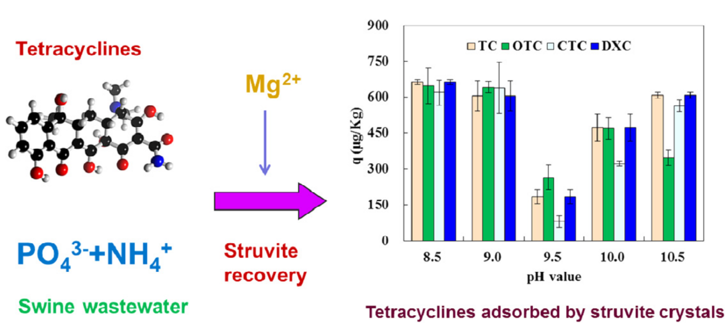
HIGHLIGHTS

- Antibiotics in wastewater pose pharmacological threats to phosphorous recovery.
- Struvite crystals possessed a notable adsorption capability on tetracyclines.
- pH and Mg played different roles on tetracyclines adsorption.
- Tetracyclines adsorption onto struvite crystals evolved different stages.

GRAPHICAL ABSTRACT



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ABSTRACT

Due to the residues of tetracyclines (TCs) in swine wastewater, recovering phosphate as struvite (slow-release fertilizer) from swine wastewater may pose TCs-pharmacological threats to the agricultural planting and human health. However, limited information has been reported on the relevant works. In this study, the transport of TCs in the process of struvite crystallization was examined, and the influencing parameters, including pH value, Mg/P molar ratio and initial TCs concentration, were investigated. Results revealed that the maximum TCs adsorption capacities onto struvite crystals ranged from 1494.7 μg/L to 2160.0 μg/L. The mechanism of TCs adsorption onto struvite crystals was electrostatic adherence. The presence of Mg^{2+} interfered TCs adsorption through complexing with TCs, which was also determined by pH variation. TCs adsorption onto struvite crystals evolved three phases, including quick increase phase, fluctuation phase and steady phase, which were dominant by electrostatic adherence, dissociation and equilibrium, respectively. Furthermore, the simulated equilibrium data exhibited a Freundlich adsorption isotherm, indicating that TCs adsorption took place on the heterogeneous surface of struvite crystals.

1. Introduction

Rapid economic growth and urban expansion in the developing countries have led to enormous demand on animal products, with the emergence of lots of intensive livestock and poultry farms. Consequently, dramatic increases of phosphorus and ammonium discharge from livestock wastewater into the environment have become one of the major issues that many countries have to face. For instance, the annual amount of nitrogen and phosphorus discharged from swine wastewater in China are more than 14 and 3 million tons, respectively [1]. However, from another perspective, such numerous discharge of nitrogen and phosphorus from swine wastewater poses great potential for nutrient recovery, especially for struvite ($MgNH_4PO_4{\cdot}6H_2O$, a slow-release fertilizer) recovery,

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which has been regarded as an important mean of relieving the scarcity of phosphorus rock resources worldwide [1,2].

Veterinary antibiotics are used worldwide to treat disease and protect animal health. They are also used as additives into animal feed to improve growth rate and feed efficiency. It has been estimated that annual antibiotics production in China was more than 210 million kg, and 46.1% were used in livestock industries [3]. Since antibiotics are poorly adsorbed by the animal guts, the majority is excreted unchanged in feces and urine. This indicates that large amounts of veterinary antibiotics are discharged into the environment and pose potent pollution danger to environment consequently [3–5]. The occurrence of antibiotics in the environment can affect microorganisms in the aquatic and terrestrial environment, and alter microbial activity and community composition [5,6]. Besides, Long-term exposure of antibiotics will generate bacterial resistance to the antibiotics, and may pose a threat to human and animal health [7,8].

Tetracyclines (TCs), as a family of broad-spectrum antibiotics, are the most widely used in the livestock industry due to the cost effect and desirable antimicrobial activity [9]. According to the literature, TCs were found at high residue in swine wastewater, with relative maximum concentrations ranging from 23.8 μg/L to 685 μg/L [10,11]. Therefore, swine wastewater is a major source of TCs pollution. TCs are amphoteric molecules having multiple ionized groups, such as hydroxyl, amino and ketone, and thereby are expected to interact with cations and matters that are polar or charged. TCs adsorption by various adsorbents has been extensively investigated, and several specific interaction, including surface complexation, cation exchange, bridging hydrophobic partitioning, and electro donor-acceptor interactions, have been proposed as the major mechanisms [9,12,13].

As for struvite recovery from swine wastewater, the occurrence of TCs with high concentrations may transport from aqueous phase to struvite crystals, which undoubtedly pose potential threat to agricultural planting and human health. However, litter literature has been reported on the relative works by now, and the relevant mechanisms governing TCs transportation need to be understood. In this study, the transport of TCs in the process of struvite crystallization was examined. The influencing factors, including pH value, Mg/P molar ratio, contact time and initial TCs concentration, were investigated. In addition, the adsorption isotherms were also evaluated.

2. Materials and methods

2.1. Chemicals and standards

Four TCs standards, including tetracycline (TC), oxytetracycline (OTC), chlortetracycline (CTC) and doxycycline (DXC), were obtained from Ehrenstorfer GmbH, Germany. The standard purity was above 99%. Internal tetracycline-D_6 (TC-D_6) was obtained from Toronto Research Chemicals Inc., Canada.

The stock solutions of antibiotics were prepared by dissolving each compound in methanol at 500 mg/L. They were stored at −20 °C in the refrigerator before use.

2.2. Experimental design and setup

For struvite precipitation, stock solution containing NH_4^+, PO_4^{3-} and Mg^{2+} were prepared by dissolving $(NH_4)_2HPO_4$ and $MgCl_2{\cdot}6H_2O$ into deionized water, respectively. In case stock solution was dosed into the standard beaker (1 L working volume) by controlling molar ratio of Mg:N:P at desired levels, the liquor was mixed rapidly at 200 r/min. Subsequently, pH value was increased to 8.5–10.5 for struvite reaction and kept stable by dosing 2 mol/L NaOH. After 4 h stirring, the mixture was centrifugated at 3000 rpm for 10 min, and aqueous and solid samples were withdrawn prior to analyses.

A series of experimental factors including solution pH, Mg/P ratio, contact time and initial antibiotics concentration were investigated to understand the adsorption process. According to the literature, the suitable pH range for struvite recovery in wastewater was 8.5–10.5 [1]. Hence, all the experiments in the present study were conducted at pH 8.5–10.5. The initial phosphate concentration and the levels of Mg:P molar ratio applied in the study were referred on the basis of the previous studies, where initial phosphate in swine wastewater was 3–6 mmol/L and the optimal Mg:P molar ratios for struvite crystallization were at 0.8–2.4 [1,14,15]. Referencing antibiotic concentrations detected in biogas slurry in pig farm [4,5], TCs ranging from 50 μg/L to 750 μg/L were added into the standard beaker before/after struvite crystallization.

2.2.1. Influence of solution pH

In order to clarify the adsorption characteristics of struvite crystals and their adsorption capacities under struvite crystallization, two sets of experiments were conducted by adding antibiotics into the solution after (Set A) or before (Set B) struvite reaction, respectively. Molar ratio of Mg:N:P in both sets was set at 1.2:2:1, with initial phosphate concentration at 4 mmol/L. For Set A, crystalline precipitates after struvite reaction were collected and rinsed by deionized water for 3 times to screen Mg^{2+}, NH_4^+-N and PO_4^{3-}-P interference. Subsequently, pH value of the liquor was adjusted to 8.5, 9.0, 9.5, 10.0 and 10.5, respectively. After that, TCs were dosed into the liquor immediately to reach 250 μg/L, and the mixture was agitated for 4 h. With regard to Set B, 250 μg/L TCs were firstly dosed into the stock solution, and subsequent struvite reaction was conducted by setting pH value at 8.5, 9.0, 9.5, 10.0 and 10.5, respectively. The aqueous and solid samples in both Set A and Set B were withdrawn for antibiotic analyses.

2.2.2. Influence of Mg/P ratio

Influence of Mg/P ratio on TCs adsorption was conducted by setting the initial phosphate at 4 mmol/L and Mg/P ratios at 0.8, 1.0, 1.4, 1.8 and 2.2, respectively. TCs was dosed before struvite reaction and set initial concentration at 200 μg/L, and pH value was kept 9.2 to perform struvite crystallization. After adsorption equilibrium time had elapsed, as determined from contact time, samples were withdrawn for TCs, Mg and P determination.

2.2.3. Influence of contact time

Contact time was investigated to determine the adsorption equilibrium. Initial P concentration, Mg:N:P molar ratio and TCs concentration were set at 3 mmol/L, 1.2:2:1 and 500 μg/L, respectively. Struvite crystallization was conducted at pH 9.5, so that the spontaneous crystallization occurred rapidly [16]. Considering that struvite crystal formation might pass through two stages, including nucleation and crystal growth, which take 10–45 min [17], the sampling time interval was set at 60, 90, 120, 180 and 240 min, respectively. In each sampling, 5 mL solution was taken out for further analyses.

2.2.4. Adsorption isotherm

In order to investigate the adsorption equilibrium characteristics of TCs onto struvite, experiments were carried out at pH 9.3 and TCs concentrations ranged from 50 μg/L to 750 μg/L. The two most common adsorption models, i.e. Langmuir and Freundlich, were used to describe the adsorption process [12]. The Langmuir equation assumes that the adsorbate covers homogeneously on the surface of adsorbent, and the adsorbate molecules do not interact, which is describe by the following equation: