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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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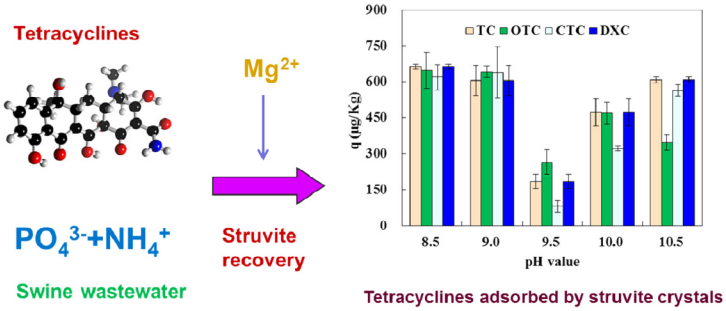
HIGHLIGHTS

- 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:

$$q = q_m \frac{K_L C_e}{1 + K_L C_e} \quad (1)$$

where q (μg/kg) is the equilibrium adsorption capacity, q_m (μg/kg) the theoretical maximum adsorption capacity, K_L the Langmuir constant (L/mg), C_e (μg/L) the equilibrium concentration of TCs, K_L the Langmuir constant. The separation factor (R_L), which is used to evaluate the affinity between the adsorbate and the adsorbent, is described by Zhang et al. [9] as follows:

$$R_L = \frac{1}{1 + K_L C_0} \quad (2)$$

R_L value presents the isotherm process to be either irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$).

The Freundlich isotherm is based on the assumption that adsorption occurs on a heterogeneous surface, in which the energy varies as a function of the surface coverage. The model can described as the following equation:

$$q = K_f C_e^n \quad (3)$$

herein, K_f ($mg^{1-n} \cdot L^n/kg$) is the empirical constant, n the adsorption intensity. $n > 1$ indicates the unfavorable adsorption, while the preferential adsorption occurs in case of $n < 1$.

2.3. Analytical methods

All the water samples collected were adjusted to pH 3.0 using HCl, followed by adding 5% (v/v) methanol to inhibit microbial activity. Solid samples were collected and firstly air-dried at 35–40 °C, subsequently dosing 10% (v/v) HCl to dissolve the solids and keep pH at 3.0. 20% (v/v) methanol was also added into the dissolved solution to restrain microbial growth.

2.3.1. Antibiotics assay

Solid-phase extraction method was employed to concentrate TCs from the aqueous samples by using Oasis HLB cartridge (200 mg/6 mL, Waters, Milford, USA). After that, the concentrates were subjected to liquid chromatography/tandem mass spectrometry (LC-MS/MS) (ABI3200 QTRAP, USA) in combination with a Phenomenex Kinetex Symmetry C18 column (4.6 mm × 100 mm) for antibiotics identification and quantitation. The mass spectrometry system equipped with electrospray ionization (ESI) source was operated in the positive mode with desolvation temperature at 300 °C and capillary voltage 5.5 kV.

TCs detected with the LC–MS/MS was evaluated for linearity and recovery rate, and detection limits and the quantification for the instrument were determined by using calibration curves containing several concentration levels as reported in the previous literature [18].

2.3.2. Other analytical methods

Ammonium (NH_4^+-N) and phosphorus (PO_4^{3-}-P) were determined according to the standards methods [19]. pH was measured by PHS-3C probe. Magnesium ion was determined by inductively coupled plasma optical emission spectroscopy (Optima 7000DV, PerkinElmer, USA).

Visual Minteq, as chemical equilibrium software originally developed by the US EPA, was extensively applied to determine speciation, solubility and equilibrium of solid and dissolved phases of minerals in aqueous solutions [20,21]. In this study, Visual Minteq 3.0 was adopted to predict the variation of Mg^{2+} speciation under different experimental conditions.

3. Results and discussion

3.1. Influence of pH value

To investigate pH influence on TCs adsorption capacity under recovering struvite condition, pH values were adjusted ranging from 8.5 to 10.5. Fig. 1 demonstrated the TCs adsorption capacities of struvite crystals in pure water (Set A). A profile of drastic decline at pH 9.5 and following steady increase were observed, with the minimum values (TC 184.27 μg/kg, OTC 264.00 μg/kg, CTC 80.13 μg/kg and DXC 184.27 μg/kg) at pH 9.5 and the maximum values (TC 663.01 μg/kg, OTC 648.01 μg/kg, CTC 618.36 μg/kg and DXC 663.01 μg/kg) at pH 8.5, respectively. However, difference profiles of TCs adsorption were observed under struvite crystallization (Set B) as shown in Fig. 2, where TCs adsorption capacities declined gradually to certain extents despite pH increasing from 8.5 to 10.0. In case pH was enhanced to 10.5, drastic increases of TCs were performed with TC 571.33 μg/kg, OTC 570.67 μg/kg, CTC 189.13 μg/kg and DXC 628.67 μg/kg, respectively.

TCs are regarded as hydrophilic compounds since their molecules contain three dissociated groups, i.e. tricarbonyl group (TCs_1, pK_{a1}), phenolic diketone moiety (TCs_2, pK_{a2}) and dimethylamino group (TCs_3, pK_{a3}) (Fig. S1). The molecular structures of TCs bring about different adsorption mechanisms, including electrostatic interaction, hydrogen bonding formation, electron donor-acceptor and π-π dispersion interaction [22], which also directly correlate to pH variation and the surface charge of adsorbent. Take the functional groups of TC as an example, the dissociation constants (pK_a) of TC_1, TC_2 and TC_3 are 3.3z0, 7.68 and 9.68, respectively [12], indicating that the TC molecular conformation could be positive charged ($pH < 3.30$, TCH^{3+}), neutral ($3.30 < pH < 7.68$, $TCH^{2\pm}$), negative ($7.68 < pH < 9.68$, TCH^-), or much more negative ($pH > 9.68$, TC^{2-}). Accordingly, TCs adsorption mechanisms of hydrogen bonding, electron donor-acceptor and π-π dispersion interaction were predominant in acidic conditions, whereas electrostatic repulsion was predominant in alkaline conditions and might cause the decrease of TCs adsorption capacity onto the adsorbents due to the TCs molecule negatively charged [9]. A further pH growth resulted in a decline of adsorption efficiency [6,23]. However, experimental results showed that struvite crystals adsorbing TCs displayed behavior inconsistent with the previous studies. A profile of drastic decline at pH 9.5 and following steady increase were detected, as presented in Fig. 1. Such results were thought to closely associate with the electrostatic

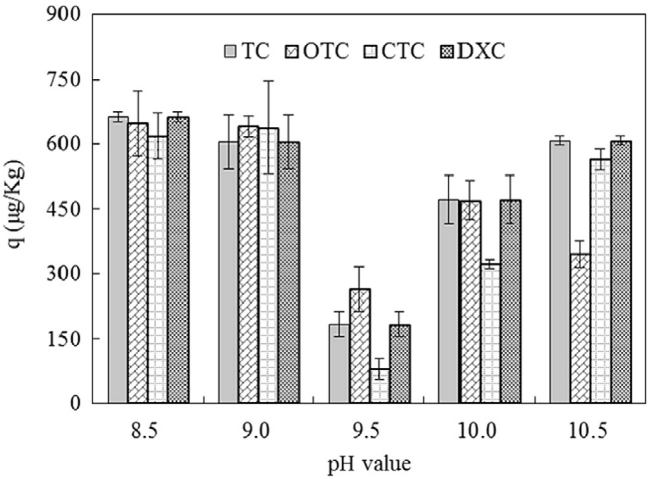

Fig. 1. Effect of pH on TCs adsorption by struvite crystals.

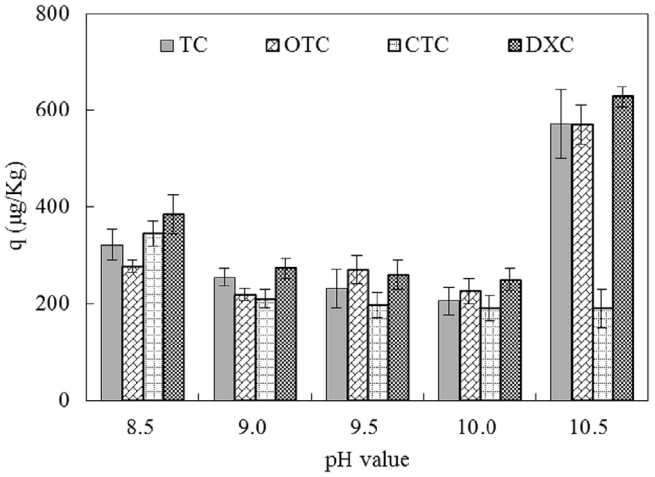

Fig. 2. Effect of pH on TCs adsorption capacities under struvite crystallization.

charge of struvite crystals and the protonation or deprotonation of TCs. It has been known that the struvite crystal structure consists of PO_4^{3-} and NH_4^+ tetrahedral and $Mg[H_2O]_6^{2+}$ octahedral, and the rectangular *ac* or *bc* crystallite facets were rich in $Mg[H_2O]_6^{2+}$ or positive charge [16,24]. Considering that TCs were deprotonated at alkaline solutions (from pK_a values in Table S1), struvite crystallite facets in $Mg[H_2O]_6^{2+}$ were prone to adsorb TCs, and therefore relatively high adsorption capacities were achieved at pH 8.5, 9.0, 10.0 and 10.5 (Fig. 1). As to pH 9.5, the depression of TCs adsorption capacity was observed. This was because the majority of TCs changed to zwitterion forms (pK_{a3} values in Table S1), and the electrostatic attraction was weakened in great extent.

Compared to the profiles in Fig. 1, TCs adsorption capacity in Fig. 2 displayed distinct profiles despite pH similarly enhancing from 8.5 to 10.5. Such results revealed that in addition to electrostatic interaction, other mechanisms might be predominant in TCs adsorption in the process of struvite crystallization. After analyzing the experimental conditions between Set A and Set B, it could be conclusive that the presence of Mg^{2+} in the solution played an important role on TCs dissociation from struvite crystals. Previous researches have indicated that Mg^{2+} was prone to react with TCs via surface complexation [23,25]. In the present study, the interaction between Mg^{2+} and TCs was investigated. As illustrated in Fig. 3, when Mg^{2+} was dosed into the TCs solution, the adsorbance intensities were amplified and the peaks were translated. The characteristic adsorbance peaks of TC were translated from 290 and 355 nm to 289 and 374 nm, OTC from 288 and 352 nm to 287 and 371 nm, CTC from 289 and 366 nm to 288 and 371 nm, and DXC from 289 and 345 nm to 286 and 371 nm, respectively. Such peak alternation confirmed that Mg^{2+} could connect the negatively charged part of TCs to form the complexes of antibiotics-metal ion, which was also reported by Chang et al. [26]. Consequently, TCs deprotonation was inhibited and a low interaction between TCs and struvite crystals at pH 8.5–10.0 was observed, as shown in Fig. 2.

Drastic increment of adsorption capacities was observed at pH 10.5 (Fig. 2). This was because the complexation between TCs and Mg^{2+} was also influenced by the species of magnesium ion. According to the calculation of Visual Minteq, the possible existence of magnesium ions under different pH values were Mg^{2+}, $MgHPO_{4(aq)}$, $MgOH^+$, $MgPO_4^-$ and $Mg(NH_3)_2^{2+}$, respectively. It has been reported that active Mg^{2+} remarkably reduce in highly alkaline conditions to form brucite ($Mg(OH)_2$) [27], which was also predicted in the present study as $MgOH^+$ precursor increasing significantly at pH above 10.5 (Fig. 4). Hence, TCs adsorption was significantly promoted by electrostatic interaction originated from struvite crystals (Fig. 2).

3.2. Influence of Mg/P molar ratio

Mg/P molar ratio is an important parameter to insure struvite recovery efficiency. The investigation of Mg/P molar ratio was conducted by setting pH at 9.2, so as to achieved relatively high struvite recovery efficiency. As displayed in Fig. 5, relatively low TCs adsorption was detected in case of Mg/P molar ratio less than 1.4, while significant increase of adsorption capacities was observed in case of Mg/P molar ratio above 1.8. In addition, struvite crystals possessed low CTC adsorption capacities in the experiment runs, on comparison to other TCs.

As a divalent cation, Mg^{2+} had competitive effect with the positive-charged struvite molecule and might lead to a reduction of TCs adsorption capacity. Theoretically, the cations (Na^+, K^+, Mg^{2+}, Ca^{2+}) with higher concentrations have stronger inhibition effects on TCs adsorption [9]. However, experimental results presented different adsorption mode, as presented in Fig. 5. At neutral and alkalescent conditions, TCs are mainly present as mono- and dianions, indicating that three species (free TCs, together with

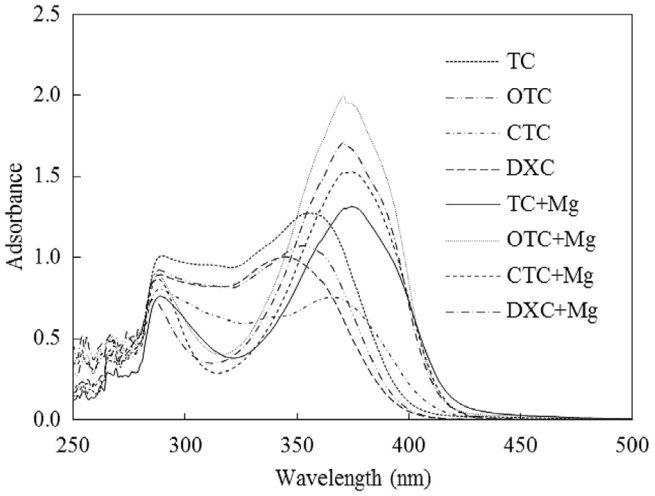

Fig. 3. UV–VIS spectrum of TCs combining with Mg ions.

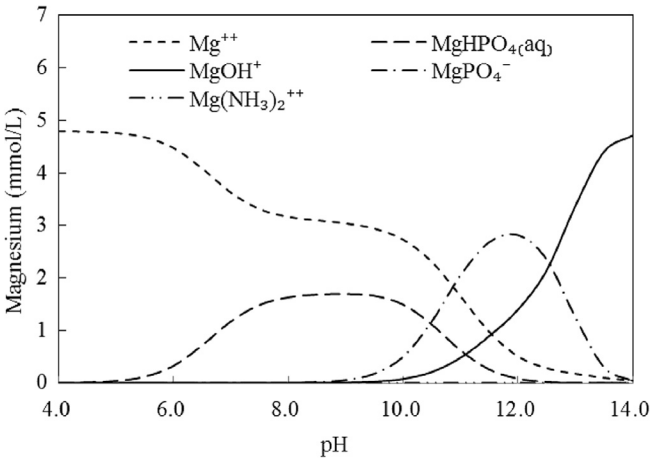

Fig. 4. Variation of magnesium speciation under different pH conditions.

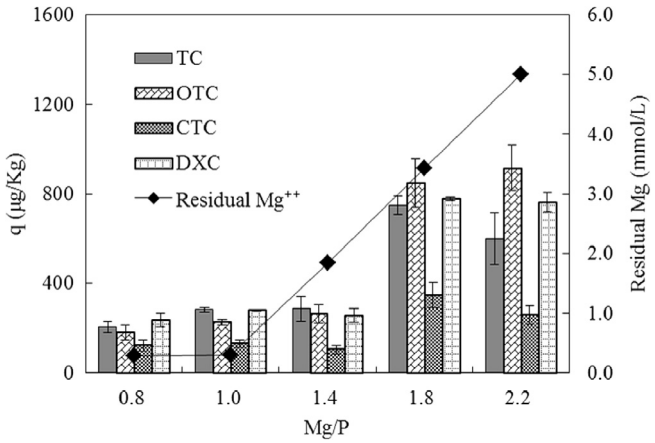

Fig. 5. Effect of Mg/P molar ratio on TCs adsorption.

1:1 and 1:2 TCs-Mg complexes) of TCs exist in the solution. For alkaline conditions, the free TCs is only predominant at extremely low Mg^{2+} concentration, while 1:1 and 1:2 TCs-Mg complexes becomes more important once Mg^{2+} concentration increase [25,28]. Mg^{2+} ion can easily combine with the phenolic diketone moiety group of the TCs molecules and form 1:1 TCs-Mg complexes. In case the chelation between Mg^{2+} and phenolic diketone moiety is saturated, excess Mg^{2+} will be prone to chelate with negative-charged dimethylamino group to form the 1:2 TCs-Mg complexes [28]. The more Mg^{2+} chelated with TCs, the more hydrophobic TCs molecules has [13,25]. Consequently, the hydrophobic TCs molecules with negatively charged were easily adsorbed by struvite crystals.

As to CTC adsorption (Fig. 5), low adsorption capacities could be ascribed to the fact the majority of CTC might transform to zwitterion states (pK_{a3} = 9.33, Table S1) since the experimental pH set at 9.20. Therefore, the electrostatic attraction of negatively charged CTC to positively charged struvite crystals and Mg^{2+} was distinctly weakened.

3.3. Effect of contact time

The evolution of TCs adsorption versus time onto struvite crystals was illustrated in Fig. 6. All the curves appeared to have a similar form. The overall adsorption process could be divided into three phases, i.e., quick increase phase, where struvite evolved from nucleation to crystal growth coupling with significant increase of TCs adsorption to a significant extent, fluctuation phase, where TCs dissociated from the crystals significantly to certain ranges, and steady phase, where TCs adsorption capacities did not significantly fluctuate to the end of experiments. The profiles suggested that TCs adsorption onto struvite crystals was dominated by electrostatic adherence and dissociation in first two phases, respectively. Afterwards, equilibrium was reached. It has been known that struvite crystallization consists of nucleation and crystal growth stages [16,17], where ions combine to form struvite embryos and crystal embryos subsequently increase in size until they form detectable crystals. In the process of crystal growth, struvite crystallites underwent particle size enlargement through colliding and adhering with each other, revealing that the specific surface area of struvite crystals reduced continuously to a certain extent. Consequently, TCs dissociation was observed in the second phase.

3.4. Adsorption isotherm

Adsorption isotherm is normally applied to analyze how adsorbate molecules distribute between adsorbent and solution after the system equilibrium is reached. To evaluate the adsorption isotherm, initial TCs concentrations ranging from 50 μg/L to 750 μg/L were applied to the experiments. As demonstrated in Fig. 7, stepwise enhancement of adsorption capacities was obtained. The maximum adsorption capacities in this study were obtained with the values of OTC 1367.5 μg/L, TC 1348.2 μg/L, CTC 1684.3 μg/L and DXC 1476.7 μg/L, respectively.

The isotherm models of Langmuir and Freundlich were implemented to evaluate the adsorption process. The Langmuir equation assumes that the adsorbate covers homogeneously on the surface of adsorbent, and the adsorbate molecules do not interact. As for Freundlich equation, it assumes that adsorption occurs on a heterogeneous surface, in which the energy varies as a function of the surface coverage. The experimental data were subjected to equation regression, and the parameter values were listed in Table 1. Assessment on Langmuir modeling showed determination coefficient (R^2) of 0.394–0.750, indicating that this model was not appropriate to describe the adsorption process. Freundlich modeling presented R^2 of 0.925–0.953 and n values were 0.613–0.753, evidencing that the physical adsorption was favorable. This result suggested that TCs adsorption took place on heterogeneous surface of struvite crystals.

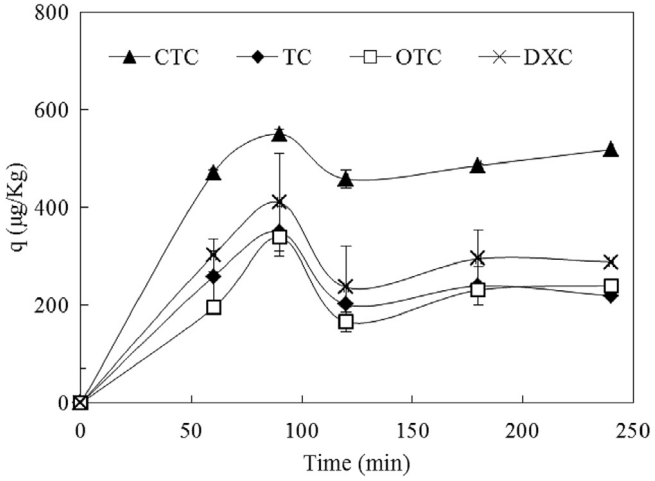

Fig. 6. TCs adsorption onto struvite crystals as a function of time.

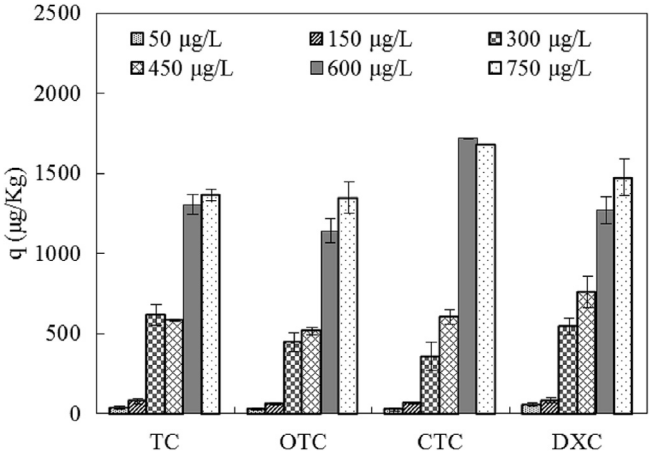

Fig. 7. TCs adsorption under different initial concentrations.

Table 1
The fitting parameters of adsorption isotherms for TCs adsorption.

TCs	Langmuir model				Freundlich model		
	q_m (μg/kg)	K_L (L/μg)	R_L	R^2	K_f ($mg^{1-n}·L^n$/kg)	n	R^2
OTC	454.5	0.00112	0.543–0.947	0.604	0.063	0.665	0.946
TC	625.0	0.00106	0.557–0.950	0.527	0.114	0.699	0.935
CTC	400.0	0.00123	0.520–0.942	0.750	0.034	0.613	0.953
DXC	833.3	0.00095	0.584–0.955	0.394	0.225	0.753	0.925

4. Conclusion

This study gave information about TCs adsorption onto struvite crystals in the process of struvite recovery from wastewater, which is of great practical interest because TCs exert pharmacological action in recovered struvite utilization. The maximum TCs adsorption capacities in this study was, OTC 1494.7 μg/kg, TC 2094.0 μg/kg, CTC 1771.0 μg/kg and DXC 2160 μg/kg, respectively. Despite stepwise pH enhancement in alkaline conditions, struvite crystals adsorbing TCs displayed a profile of drastic decline and steady increase with the minimum adsorption capacities exhibited at pH 9.5. Similar to pH variation, TCs adsorption in the process of struvite crystallization displayed different behavior, with the profile of gradual decline to pH 10.0 and following sharp increase. The presence of Mg^{2+} posed different mechanisms for the interaction between TCs and struvite crystals. In case of Mg/P molar ratio less than 1.4, relatively low TCs adsorption was detected. Once Mg/P molar ratio was above 1.8, drastic increment of adsorption capacities was observed. It has been found that TCs adsorption evolved three phases, including quick increase phase, fluctuation phase and steady phase, where were dominant by complexation, dissociation and equilibrium, respectively. Furthermore, the simulated equilibrium data exhibited a Freundlich adsorption isotherm, indicating that TCs adsorption was taking place on heterogeneous surface of struvite crystals. Further experiments will be expanded to struvite recovery in the real swine wastewater, and the effects of other parameters, such as organic matters, on antibiotics adsorption behavior will be investigated.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2016.11.062.

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