Adsorption of tylosin in wastewater by iron-rich farmland soil and the effect of iron reduction and common cations

Luoying Lin, Xingbao Hu, Jianming Liang, Zhujiang Huang, Guangwei Yu and Yunxiao Chong

ABSTRACT

Livestock wastewater reused in farmland may cause tylosin to stay in farmland soil. Under the influence of some factors, such as irrigation and fertilization, tylosin may desorb and diffuse into the water environment. Batch adsorption experiments and soil column flooding experiments were set up to investigate the effects of several cations and iron reduction on the adsorption, desorption and oxidation removal of tylosin in iron-rich farmland soils (red soil). The results showed that tylosin can be adsorbed by the red soil. The coexistence of these cations significantly reduced its adsorption capacity. The order of influence was as follows: $Ca^{2+} > Mg^{2+} > K^+ > NH_4^+ > Na^+$. This means that some agricultural farming measures, such as the application of chemical fertilizers, would release the adsorbed tylosin into the farmland. Anaerobic iron reduction and massive production of ferrous ions did not affect the adsorption and desorption of tylosin in the red soil column. Moreover, the ferrous iron could activate persulfate to generate hydroxyl radicals and sulfate radicals which oxidized and removed the tylosin adsorbed in the soil column. Therefore, the iron reduction that occurred during flooding was not a factor causing tylosin release, which provided a way for tylosin in iron-rich farmland soils to be oxidized and removed.

Key words | antibiotic, cation, iron reduction, iron-rich farmland soil, tylosin

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HIGHLIGHTS

- All of Ca^{2+}, Mg^{2+}, K^+, NH_4^+ and Na^+ significantly reduced the tylosin adsorption capacity.
- The iron reduction did not affect the adsorption and desorption.
- Persulfate largely removed the tylosin adsorbed in red soil pretreated by iron reduction.
- The Fe^{2+} from iron reduction could activate persulfate to generate free radicals.
- Horizontal flow constructed wetland (HSCW) assisted by persulfate has the potential to remove antibiotics from livestock wastewater.

INTRODUCTION

As an antibiotic widely used in poultry and livestock, tylosin (TYL, $C_{46}H_{77}NO_{17}$, MW 916.10, water solubility: 5 g/L, log K_{ow}: 1.63 (McFarland *et al.* 1997), pK_a: 7.1

(Wollenberger *et al.* 2000)) exists largely in livestock manure in the form of maternal or metabolites (Halling-Sørensen *et al.* 2001; Aust *et al.* 2008; García-Sánchez *et al.* 2013). Hoese *et al.* (2009) found that tylosin could reach 0.3 mg/g in the swine manure. There was 1–30 mg/L tylosin in some manure storage tanks (Kolz *et al.* 2005). In many areas, livestock wastewater was reused for farmland

irrigation and fertilization after anaerobic treatment. However, antibiotics, such as tylosin, were rarely eliminated during anaerobic treatment (Ben *et al.* 2009) and would diffuse to farmland soil with wastewater reuse. It is reported that the adsorption distribution coefficient (K_d) of tylosin for some types of farmland soil in the United States was 24–65 L/kg (Hu & Coats 2009) and 10.4–387 L/kg in the Netherlands (Ter Laak *et al.* 2006b), indicating that farmland soil has a strong adsorption capacity for tylosin. Part of the tylosin remaining in farmland soil might be degraded (Hu & Coats 2007; Sassman *et al.* 2007), whereas some factors might cause its further diffusion to natural water environments, endangering the safety of aquatic organisms (Wollenberger *et al.* 2000).

The mineral particles in the soil, especially those containing rich Fe(III), play an important role in the adsorption of tylosin (Guo *et al.* 2013, 2016; Call *et al.* 2019). However, when the soil is flooded (wetland soil or paddy farming) and forms an anaerobic environment, dissimilatory iron reduction (DIR) reactions are likely to occur. During DIR, some bacteria can use Fe(III) in the soil as an electron acceptor, coupled to oxidation of organic matter. The energy released in iron reduction is captured by the bacteria for growth (Lovley 1991). Studies found that DIR caused the release of phosphate and heavy metals absorbed on the surface of soil mineral particles containing Fe(III) (Wang *et al.* 2016; Upreti *et al.* 2019). It is unclear whether tylosin would also be released into the soil solution due to DIR and then spread to downstream rivers with the discharge of water.

Meanwhile, as ion exchange was the main mechanism of adsorption of tylosin on iron minerals, it is easily affected by the ionic strength (Ter Laak *et al.* 2006a; Essington *et al.* 2010). Call *et al.* (2019) revealed that both Na^+ and Ca^{2+} in solution could compete with tylosin for soil surface adsorption sites. Many cations may be brought to the farmland soil by irrigation or fertilization, such as ammonium ions in chemical nitrogen fertilizers, and calcium and magnesium ions in chemical phosphate fertilizers. These cations may also be a factor leading to the release and diffusion of tylosin in farmland.

To prevent tylosin from entering farmland soil and natural water environment, the tylosin in the wastewater needs to be treated before reuse. DIR in the soil may also

provide a potential way for the oxidation and removal of tylosin. Ferrous iron generated by DIR could be adsorbed on the surface of the soil and form the Fe(II)/Fe(III) solid-phase interface. It is well known that Fe(II) and Fe(III) are the most efficient transition metals for activating hydrogen peroxide (Anipsitakis & Dionysiou 2004). Sulfate radicals ($SO_4^{\bullet-}$, $E° = 2.5$–3.1 V) produced by the persulfate (PS) have strong oxidation properties. Zhong *et al.* (2015) revealed iron filings containing Fe_3O_4 combined with persulfate can immediately generate a large number of radicals for contaminant degradation. Therefore, the Fe(II)/Fe(III) solid-phase interface of the soil may have the potential to activate persulfate for sulfate radicals, leading to the removal of tylosin.

To verify the above speculation, red soils rich in iron oxides were used to conduct the following investigations: (1) the adsorption characteristics of tylosin on iron-rich red soil and the influence of main cations existing in chemical fertilizer; (2) the effect of DIR on the adsorption of tylosin; and (3) the removal of tylosin by persulfate in red soil pretreated by DIR.

MATERIALS AND METHODS

Tylosin and iron-rich red soil

Tylosin tartrate (TYL, potency: ≥ 800 units/mg tylosin, CAS No.: 74610-55-2) was purchased from Aladdin® (Shanghai, China) and stored at $4\,°C$. The red soil was collected from farmland in the Leizhou Peninsula, Guangdong Province. It was air-dried and sieved through 0.15 mm for use. The total iron content in red soil was 53.7 g/kg, and the main iron minerals were hematite (Fe_2O_3) and magnetite (Fe_3O_4).

Effects of different cations

The batch adsorption experiments using 2.0000 ± 0.0005 g red soil and 50 mL tylosin solution were conducted in Erlenmeyer flasks. The adsorption isotherm experiments had different initial concentrations ranging from 0.5 to 100 mg/L. Common cations (Na^+, K^+, NH_4^+, Ca^{2+} and Mg^{2+}) contained in fertilizers were selected as coexisting ions, and their effects on the adsorption of tylosin were

investigated. The concentration of these ions was set at 0.01 mol/L and was, respectively, formed by adding NaCl, KCl, NH$_4$Cl, CaCl$_2$ and MgCl$_2$ to the experimental system. The initial concentration of tylosin was set at 5 mg/L.

According to the results of this experiment, the calcium ion having the greatest influence on the adsorption of tylosin was selected for the desorption experiment.

Effect of DIR

A 2.5 L glass bottle was used to build a sealed flooded soil system (Supplementary Figure S1). Because the red soil particles were tiny and the pore water in the soil column was limited, quartz sand was added to increase pore water. Preliminary experiments showed that tylosin was not adsorbed by quartz sand (Supplementary Figure S2). The glass bottle was filled with about 10 cm soil column, including 90 g red soil, 1,500 g quartz sand and 10 g paddy soil, providing iron-reducing bacteria. During the experiment, nitrogen was purged into the bottle to form the anaerobic environment. The adsorption efficiency of tylosin in the soil column system was verified by preliminary experiments (Supplementary Figure S3).

To explore the effect of DIR on the adsorption of tylosin, three experimental groups were set up. They were named as DIR pretreatment, Continuous DIR and No DIR. The soil columns were submerged with a solution with glucose concentration at 2,000 mg/L in both DIR pretreatment and Continuous DIR systems, and No DIR was treated using a solution without glucose. Except for glucose, the other components of the solutions remained the same (Supplementary Table S1). All three systems were kept in anaerobic incubation, and the ferrous ion in pore water was monitored. When ferrous ion concentration no longer increased, the incubation was terminated and the solution was discharged. Then, one solution containing 2 mg/L tylosin was added into the No DIR and the DIR pretreatment to flood the soil columns. Another solution added to the Continuous DIR included both 2 mg/L tylosin and 2,000 mg/L glucose. Subsequently, pore water in three systems was taken at 1 h, 2, 4, 6, 8 and 10 days to determine the concentrations of tylosin and ferrous ion.

Fe(II)-activated persulfate oxidation

The experimental device was the same as that described in the section 'Effect of DIR'. Four groups were set up this time. All groups were pretreated to produce ferrous ions and to allow tylosin adsorption in the soil column similar to that in DIR pretreatment in the section 'Effect of DIR'. Then, the soil column in four groups was flooded again by different concentrations (0, 3, 6 and 9 mmol/L) of sodium persulfate (Na$_2$S$_2$O$_8$) solution when the pretreatment solution was discharged. After 1 day of reaction, sodium persulfate solution was also discharged, and 0.02 mol/L calcium chloride solution was added for desorption. Before the sodium persulfate solution and calcium chloride solution were drained, pore water samples in the soil column of four groups were taken to determine the tylosin concentration.

Radical verification

To verify the types of radicals involved in the Fe(II)-activated persulfate oxidation reaction, methanol and *tert*-butyl alcohol (TBA) were used as the scavenger of $^{•}$OH and SO$_4^{•-}$. It was reported that methanol can react with both $^{•}$OH and SO$_4^{•-}$, while TBA reacts mainly with $^{•}$OH (Eibenberger *et al.* 1978; Buxton *et al.* 1988; Anipsitakis & Dionysiou 2004). When there was excessive methanol or TBA in the experiment, the radicals would first react with them, instead of the target pollutants, indicating that the radicals have participated in the reaction. The experiment was divided into three groups: the control check group, the methanol group and the TBA group. Similarly, all groups were pretreated to produce ferrous ions and to allow tylosin (with the initial concentration of 20 mg/L) to be adsorbed in the soil column. First, the soil columns in three groups after pretreatment were treated by 0.02 mol/L calcium chloride solution to desorb tylosin for 1 day. Then, 10 mL methanol and 10 mL TBA were slowly infiltrated into the soil column in the methanol group and the TBA group, respectively. After 6 h, 10 mL sodium persulfate solution with concentration at 50 g/L was infiltrated into the soil column in all groups again, reaching the concentration of persulfate in pore water of the soil column at 3 mmol/L. After 1 day of reaction, water samples were taken to determine the tylosin concentration.

Analytical methods

The concentrations of tylosin were detected by reverse-phase high-performance liquid chromatography (Agilent 1260 HPLC) with Agilent ZARBAX SB-C18 column (5 μm, 4.6 × 250 mm) and a UV detector (wavelength at 290 nm for tylosin). The mobile phase (at a flow rate of 0.5 mL/min) was a mixture of 0.01 mol/L KH_2PO_4 (65%) (pH = 2 adjusted by formic acid) and acetonitrile (35%). The injection volume was 100 μL. The column temperature was 30 °C.

The pH value was detected by a Shanghai Rex PHSJ-5 laboratory pH meter. The ferrous ion concentration in the reaction solution was detected by the phenanthroline method, and the soil samples were immediately transferred to 0.5 mol/L HCl (solid–liquid ratio of 1 : 50) to extract for 24 h (García-Balboa *et al.* 2011).

Data analysis

All experiments were in triplicate, and all data represented the average of three independent experiments with error bars representing standard errors. Microsoft® Excel was used for statistical data. One-way ANOVA in IBM SPSS 25 was used to compare the significant differences between treatments with *p*-value <0.05, suggesting a statistically significant difference. Origin 2018 was used to draw the chart.

RESULTS AND DISCUSSION

Adsorption isotherm of tylosin

The adsorption isotherm of tylosin could be well described by the Henry model and the Freundlich model (Figure 1). Compared with them, the correlation coefficient of 0.861 for Langmuir equation fitting was much lower. The Freundlich equation is an empirical formula suitable for the case where the surface of the adsorbent is uneven. The $1/n$ value characterized the degree of nonlinearity of the adsorption isotherm and the strength of the adsorption reaction. The $1/n$ value here was 0.661, indicating that the adsorption was nonlinear. It is suggested that there may be some specific interactions with functional groups of the soil in
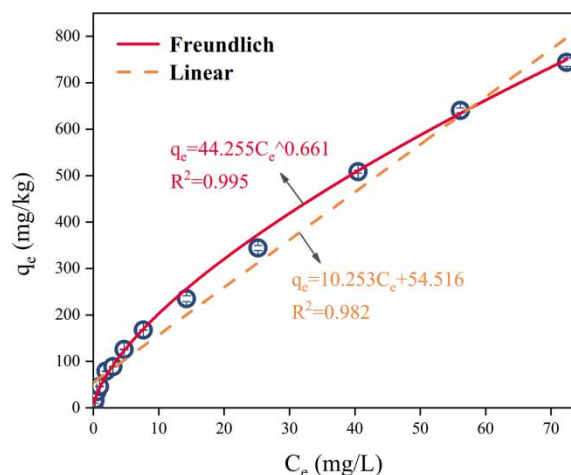

Figure 1 │ Tylosin adsorption isotherm on the red soil (initial concentration was 0.5–100 mg/L; contact time was 24 h and temperature was 25 °C).

addition to surface adsorption (Pei *et al.* 2014). For example, polar groups (phenolic and carboxylic groups) in soil organic matter could be bonded to sulfonamides via hydrogen bonds and van der Waals forces (Thiele-Bruhn & Aust 2004; Kahle & Stamm 2007). Meanwhile, when the $1/n$ value was less than 1, the adsorption ability of soil on pollutants decreased with the increase in pollutant concentration, which may be due to the pollutants occupying the high energy sites of the soil first and then being followed by lower energy sites (Guo *et al.* 2013). This is a characteristic of heterogeneous media. The adsorption distribution coefficient (K_d) for tylosin on red soil was 10.253 L/kg, which was similar to previous studies. Zhang *et al.* (2011) had reported K_d for tylosin on agricultural soils ranging from 1.7 to 12 L/kg. Ter Laak *et al.* (2006a) found that K_d of tylosin on another agricultural soil loamy sand was 8.9 L/kg. The result indicated that tylosin could retain in the red soil.

Effects of different cations

Figure 2 shows the adsorption capacity of tylosin on red soil with the coexistence of some cations. It can be clearly seen that these cations significantly decreased the adsorption of tylosin. Among them, the adsorption capacity order was as follows: $Na^+ > NH_4^+ > K^+ > Mg^{2+} > Ca^{2+}$. Tylosin is an ionizable compound with a pK_a of 7.1. It was positively charged under acidic conditions and exists in the form of TYL^+, so adsorption sites of red soil particles were easily
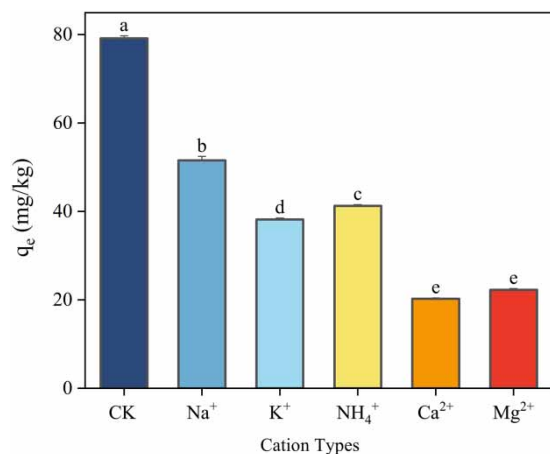
Figure 2 | Effects of different cations' coexistence on the adsorption capacity of tylosin (different letters indicate significant differences at $p < 0.05$).

Figure 3 | Ferrous ion concentration in pore water of three groups of soil columns with different pretreatment.

competed by these cations. Moreover, the influence of divalent cations appeared greater than that of monovalent cations, which may be attributed to higher charge densities of divalent cations (Kutzner *et al.* 2014).

Calcium ion was the most competitive. When Ca^{2+} coexisted, the adsorption of tylosin was reduced by 74.4%. The result of desorption experiments showed that, compared with ultrapure water, calcium chloride could release more tylosin adsorbed on red soil (Supplementary Figure S4). This means that many conventional farming measures would cause the tylosin adsorbed on soil to be desorbed and released. The greatest impact may be the treatment of soil acidification (using lime largely) and the application of chemical phosphate fertilizers (calcium phosphate as the main ingredient). Both of them would cause a large quantity of calcium ions to enter the soil. In addition, the application of liquid fertilizers containing NH_4^+, Na^+, Mg^{2+} and Ca^{2+} together, such as integrated water and fertilizer irrigation or biogas slurry (Yu *et al.* 2010), will also be a risk factor leading to the release of tylosin.

Effect of DIR on tylosin adsorption

The glucose in the pretreatment solution caused the reduction of iron oxides in both DIR pretreatment and Continuous DIR systems and a large number of ferrous ions were released into the pore water, reaching 170 and 189.7 mg/L (Figure 3), respectively. In the No DIR system,
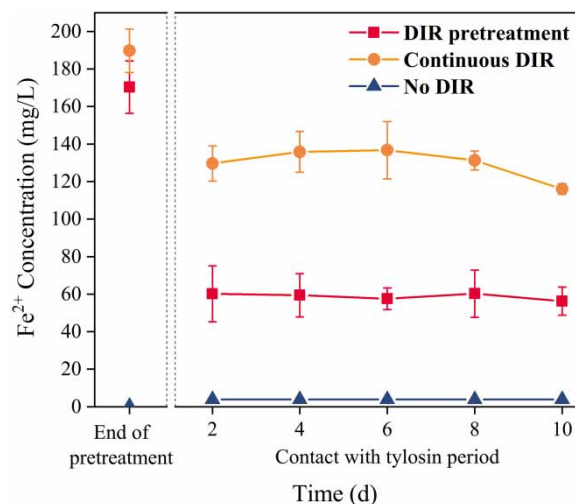
since the pretreatment liquid did not contain glucose, there were very few ferrous ions in pore water after anaerobic incubation. After adding the solution containing tylosin, the ferrous ion in pore water of the soil column in three types of systems showed significant differences (Figure 3; $p < 0.05$). It was maintained at about 60 mg/L in the DIR pretreatment, which should be caused by the desorption of ferrous ions adsorbed on the red soil particles. The Continuous DIR system had a much higher concentration than the DIR pretreatment, reaching 130 mg/L. This was because the simultaneous addition of glucose with tylosin caused the iron oxides in the red soil to continuously reduce. Ferrous ion was still very low in No DIR (Figure 3).

However, the adsorption of tylosin in the soil columns of the three types of systems did not show significant differences ($p > 0.05$), and their concentrations in pore water and the variation tendency over time were also similar. In all of the systems, the rapid adsorption of tylosin on the red soil in the soil column made it decrease to about 0.1 mg/L in the initial 1 h (Figure 4), and then a small amount of desorption occurred over time, stabilizing between 0.2 and 0.4 mg/L. This means that, within 1 h of contact with tylosin solution, the red soil column in DIR pretreatment and Continuous DIR where iron reduction had occurred still maintained the same quick adsorption capacity for tylosin as that in No DIR without iron reduction. Due to the richness of iron oxides in red soil (Ma *et al.* 2010; Yu *et al.*
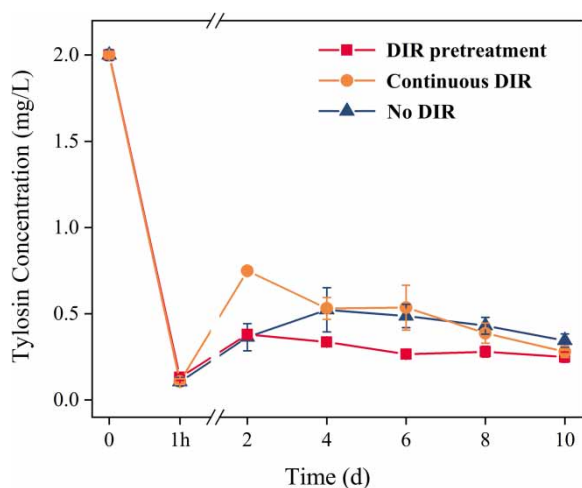
Figure 4 | Tylosin concentration changes in pore water of three groups of soil columns with different pretreatment.

2016), the proportion of reduced iron oxides was relatively small (Supplementary Table S3), so it could not affect the adsorption sites of tylosin on the red soil.

The continued reduction of iron oxides in the red soil column of Continuous DIR did not lead to an increase of tylosin in the pore water, which indicated that the adsorbed tylosin did not undergo a large amount of desorption. This further showed that the DIR, which can cause changes in the chemical form of ferric iron in red soil, had no effect on the adsorption and desorption of tylosin. It was speculated that the inhibitory effect of tylosin on iron-reducing bacteria makes iron oxides adsorbing tylosin difficult to reduce. Tylosin has a great influence on soil microbial activity and microbial community (Westergaard *et al.* 2001; Aldén Demoling & Bååth 2008). Therefore, the reduction of iron oxides may be part of the soil particles that did not adsorb tylosin. In addition, it seemed that ferrous ions did not compete for tylosin adsorption sites of red soil particles like divalent cations such as calcium and magnesium ions. The reason may be the low concentration of ferrous ion, which was lower than that of calcium and magnesium ions in the section 'Effects of different cations'. For the actual iron-rich farmland soil, although the types of organic matter that could induce iron reduction contained in most farmlands were diverse, the iron concentrations in pore water were far lower than that in this study (Garnier *et al.* 2017). This means that the

iron reduction and ferrous ions caused by flooding in the soil would be lower than the level of this study. Therefore, it can be inferred that DIR in farmland soil would not affect the adsorption and desorption of tylosin.

Removal of tylosin by the reduced red soil and persulfate

In this study, four groups of red soil columns (pretreated with iron reduction) that adsorbed tylosin were contacted with persulfate solutions of different concentrations and contacted with calcium chloride solution after the persulfate solution was discharged. The tylosin concentration in pore water of each group of soil columns is shown in Figure 5. Among them, the tylosin in the soil column contacted with a solution containing no persulfate (with a concentration of 0) reached 0.126 mg/L, and those with a persulfate concentration of 3, 6 and 9 mmol/L, respectively, were 0.034, 0.029 and 0.021 mg/L. These were significantly lower than the one without persulfate. After contact with calcium chloride solution, tylosin in these three groups of soil columns was also much lower than the first one. This indicated that after the reaction with persulfate, the tylosin adsorbed on the red soil column was largely removed, with the result that the portion of the residual ones that could be released into the pore water was also greatly
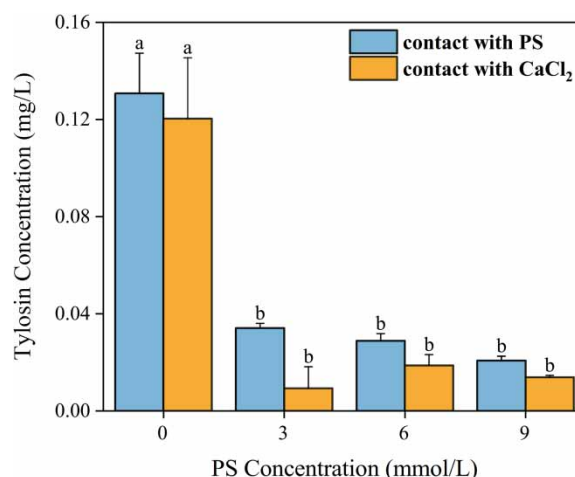

Figure 5 | The tylosin concentration in pore water of four groups of red soil columns after contacting with different persulfate (PS) solutions and calcium chloride solutions successively (different letters indicate significant differences between treatment processes at $p < 0.05$).

reduced. However, the removal of tylosin did not increase with increase of persulfate. Therefore, for the amount of tylosin adsorbed by the soil columns, 3 mmol/L persulfate could achieve the maximum removal. In addition, the variation of ferrous iron before and after reaction in the first group soil column was also much lower than those in the other three groups (Figure 6). Obviously, the ferrous iron in the soil column of the other three groups was involved in the reaction. It can be judged that the Fe(II)-activated persulfate oxidation reaction between ferrous iron and persulfate in these soil columns was likely to occur; the removal of tylosin should be the result of free radical oxidation produced by the reaction. Meanwhile, the variation of ferrous content in red soil columns increased with the increase in persulfate concentration, attributed to the reaction between excessive persulfate and ferrous iron, which was similar to a previous study (Xu & Li 2010).

Radical verification

Figure 7 shows the changes of tylosin in pore water of the soil column of different systems before and after persulfate exposure. After oxidation, the tylosin concentration in the methanol or TBA coexisting system was significantly higher than that in the control system. This means that they prevented the removal of tylosin. Methanol is usually
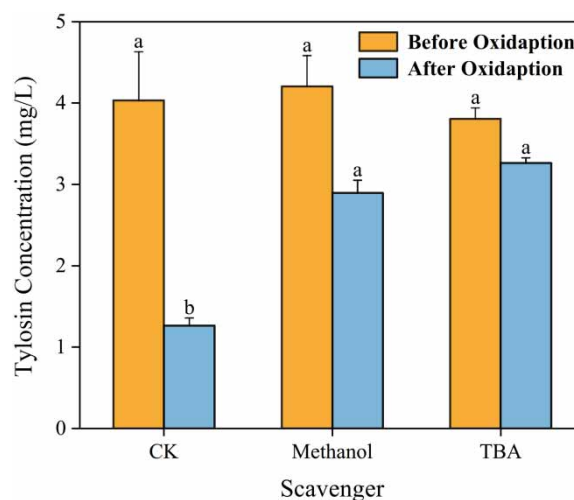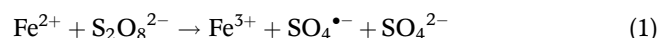

Figure 7 │ The changes of tylosin in pore water of the soil column of different systems before and after persulfate exposure (different letters indicate significant differences between the treatment groups at $p < 0.05$).

used as a scavenger for $^{\bullet}OH$ and $SO_4^{\bullet-}$, and TBA was for $SO_4^{\bullet-}$. Therefore, the result confirmed that the two radicals, $^{\bullet}OH$ and $SO_4^{\bullet-}$, participated in the reaction. This is similar to the result of ferrous-activated persulfate oxidation of 2,4-dichlorophenol (Anipsitakis & Dionysiou 2004). $SO_4^{\bullet-}$ formed from Fe(II)-activated persulfate (Equation (1)), and $^{\bullet}OH$ may be from $SO_4^{\bullet-}$ initiated other reactions (Equation (2)) (Eibenberger *et al.* 1978):

$$Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{\bullet-} + SO_4^{2-} \tag{1}$$

$$SO_4^{\bullet-} + H_2O \rightarrow {}^{\bullet}OH + HSO_4^{-} \tag{2}$$

This further confirmed that the ferrous iron formed by the anaerobic reduction of the iron-rich soil could activate the persulfate to form an Fe(II)-activated persulfate oxidation system, which in turn caused the adsorbed tylosin to be oxidized and removed. Since free radical was not selective, other organic pollutants could also be removed in this reaction system. Therefore, it is also a potential way to remove other antibiotics in livestock wastewater. The removal was achieved in the following way. Before reusing, the wastewater first entered into a horizontal flow constructed wetland (HFCW) using iron-rich soil as substrate and periodically adding persulfate during operation.
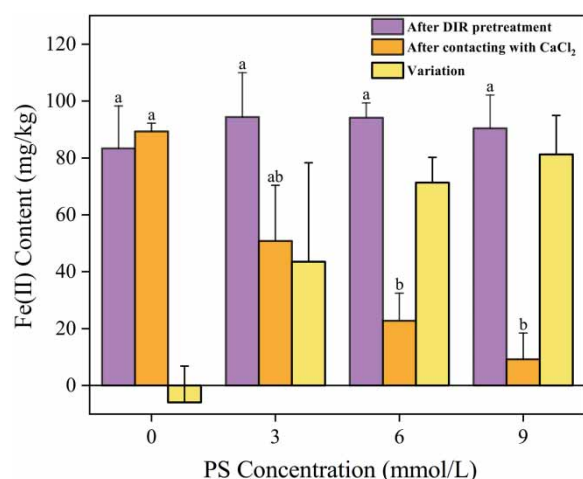

Figure 6 │ The change of ferrous content of four groups of red soil columns contacting with different persulfate solutions (different letters indicate significant differences between treatment processes at $p < 0.05$).

CONCLUSION

Tylosin was retained in the iron-rich red soil by adsorption. The adsorption isotherm was well described by the Henry model and the Freundlich model. A variety of cations contained in chemical fertilizers had an impact on the adsorption of tylosin. Divalent calcium ions and magnesium ions had the greatest impact, which could cause a large amount of adsorbed tylosin to be released. Therefore, tylosin entering the farmland soil was unstable. Anaerobic iron reduction and ferrous iron production had no significant effect on the adsorption and desorption of tylosin in the iron-rich red soil column. The ferrous iron from iron reduction could activate the persulfate to form free radicals, causing the adsorbed tylosin in the soil column to be oxidized and removed. This result can be used as a way to remove tylosin.

ACKNOWLEDGEMENT

DECLARATION OF INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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