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Kinetic and mechanistic investigations of the degradation of sulfachloropyridazine in heat-activated persulfate oxidation process

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A B S T R A C T

Sulfachloropyridazine (SCP) has significant threat to natural environment and human health worldwide. Efforts have been made to remove SCP using traditional water treatment technologies but the outputs achieved are limited. In this study, we focused on heat-activated persulfate oxidation of SCP. Various factors have been investigated, such as PS concentration, initial pH, temperature and natural water constituent effects. The results showed that the SCP removal rate constants ($k_{obs}$) followed a quadratic relationship with initial persulfate concentrations ($k_{obs} = -1.526 \times 10^{-6} [PS]_0^2 + 5.621 \times 10^{-4} [PS]_0 + 0.01158, R^2 = 0.923, [PS]_0 = 17.5 \sim 280 \mu M$) and excellent fitting with the

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Arrhenius equation \( \ln (k_{\text{obs}}) = -19487.9 / T + 59.63, R^2 = 0.967, T = 303.15 \sim 323.15 \text{ K} \). The pH tests were applied at a wide range of 3.0 \sim 10.0, the quickest degradation rate observed at pH 3.0. The consumption rate of PS was strengthened at elevated temperatures, and 40 \( \Box \) was determined to be an optimal condition. The presence of chloride (Cl\(^-\)), bicarbonate (HCO\(_3\)\(^-\)) and humic acid all showed inhibitory effects. The radical scavenging experiments revealed that HO\(^-\) and SO\(_4\)\(^{2-}\) were predominant oxidizing species responsible for SCP removal. These oxidizing species were further verified by EPR tests. LC-MS/MS analysis confirmed seven kinds of byproducts during the removal process which are mainly deriving from SO\(_2\) extrusion/Smiley-type rearrangement and S-N bond cleavage. Efficiencies of the antibiotics removal were over 85\% when 50 g PS L\(^{-1}\) was added to piggery anaerobic fermentation slurry. This remediation technology may appear as a promising way for the removal of highly antibiotics-contaminated water in a small scale.

**Keywords**: Sulfachloropyridazine; Heat-activated persulfate; Influencing factor; Rate constant; Degradation mechanism.

1 Introduction

Sulfonamides have become one of the most extensively consumed antibiotics in farming (pigs, cattle, and agriculture) as well as medicine for human disease treatment all over the world due to their low production cost and broad-spectrum antimicrobial activity [1]. These sulfonamides emitted from several sources, for instance, domestic and medical wastewater, fertilizer livestock manure, incomplete digestion and metabolism of disposed of pharmaceutical
products [2, 3], are directly discharged into aquatic environments. Therefore, the presence of these hazards has been verified not only in surface and groundwater but also quantified in drinking water [4]. The continuous exposure of these sulfonamides to water resources can cause the appearance of antibiotic-resistant microorganism as well as impart harmful effects on aquatic organisms and human health [1, 5-7]. Previous report proved that conventional water treatment technologies such as coagulation and sedimentation had a very poor removal efficiency for sulfonamides unfortunately [8]. Thus, it is essential to develop a cost-effective and environmentally-friendly treatment for the removal of aqueous sulfonamides.

There are many treatment techniques but sulfate radical (SO\(^{-}\)), \(E_0 \sim 2.60\) V based in situ chemical advanced oxidation (ISCO) treatment [9], has become one of the most promising technologies due to its high reactivity. SO\(^{-}\), an electrophilic reagent, reacts with organic compounds via an electron transfer mechanism [10] with second-order rate constants ranging from \(10^6\) to \(10^9\) M\(^{-1}\) s\(^{-1}\) [10]. Additionally, persulfate anions could last more than five months in the contaminated system [11] by maintaining its steady-state concentration, indicating that this oxidant is more effective than other oxidant candidates such as H\(_2\)O\(_2\) and KMnO\(_4\) [11] used in ISCO. Persulfate can be readily activated in aqueous solutions when encountered with heat [12, 13], UV light [14, 15], transition metals [16, 17], base [18, 19], ultrasonic irradiation [20, 21], semiconductors [22, 23], carbon-based catalysts [24, 25] and electro-chemistry [26, 27]. Recently, many researchers have focused on application of heterogeneous catalysts [28-31] for PS activation. However, there are three drawbacks restricting their practical application including catalysts dispersion, recovery and deactivation by fouling [28]. Homogeneous dispersion in the wastewater
enables the catalysts to degrade pollutants efficiently, which is detrimental to their recovery. And deactivation might occur due to the complex pollutants in practical water, greatly reducing their efficiency. Amongst multifarious activation methods, heat-assisted activation is widely adopted to remove contaminants and investigate the degradation mechanisms owing to its simple system and high efficiency [32]. Homolytic cleavage of the peroxide bond occurs in PS during heat activation, generating \( \text{SO}_4^- \). Previous studies have documented that heat activation of PS was used for the oxidation of herbicides [33, 34], ibuprofen [35] and methyltert-butyl ether [36].

Sulfachloropyridazine (SCP) is a typical representative of sulfonamides and its removal has been vastly examined by different methods. Kang et al. [3] investigated carbocatalytic activation of persulfate for the removal of SCP and found complete removal of SCP in 150 min. Haidar et al. [37] and Dirany et al. [38] conducted electrochemical treatment of the SCP with generated hydroxyl radicals and discovered that most of SCP was mineralized after 8 ~ 10 h. But toxicity evolution during the electro-oxidation of SCP solutions disclosed the formation of byproducts that could be more toxic than or close to the SCP. Ji et al. and Fan et al. [33, 39, 40] studied the heat-activated persulfate oxidation of sulfonamides including SCP and reported that the degradation products were obtained by hydroxylation, sulfonamide S-N bond cleavage, aniline oxidation, coupling and dissociation reactions. Anyhow, it is crucial to distinguish the optimal operational parameters for successful oxidation of contaminants at a low operational cost [14, 39]. For instance, high temperatures and low pH could increase the rate of radical generation in the reaction system at the same time a synergy effect might contribute to radical-to-radical reactions instead of radical-to-contaminant reactions [14]. As a result, the decrease of reaction temperatures
could enhance the removal efficiency at a relatively low pH condition. However, the parameters of SCP degradation by heat-activated along with related degradation mechanisms of SCP were rarely reported in literature so it needs to be investigated and confirmed. Moreover, efforts should be extended for the identification of oxidizing species that are vital to understand the oxidation mechanism.

In this study, we sought to evaluate the technical feasibility of SCP removal by heat activated persulfate in aqueous solution. The influences of various factors on the degradation were explored to determine the optimized degradation parameters, including PS concentration, initial pH, activation temperature and chloride, bicarbonate and humic acid, etc. Radical scavengers and EPR were used to identify the oxidizing species. And potential degradation mechanisms of SCP by PS oxidation were further probed. In addition, this technology was applied to remove the antibiotics from piggery anaerobic fermentation slurry.

2 Materials and methods

2.1 Reagents and materials

SCP ($C_{10}H_9ClN_4O_2S$, 99%) and sodium persulfate ($Na_2S_2O_8$, 98%) were purchased from Aladdin Chemistry Co and Sinopharm Chemical Reagent Co., respectively. Chromatographic grade methanol (MeOH), acetone (CP) and acetonitrile (ACN) were both purchased from MACKLIN. Other chemicals used in the experiment were all analytically pure at least. The SCP stock solution ($1 \text{ g L}^{-1}$) was prepared by dissolving 0.1 g target compound in 100 mL acetone and stored under 4$^\circ$C. All solutions were prepared in deionized water.
2.2 Experimental setup

Batch kinetic tests (with 3.51 µM SCP) were conducted in a 250 mL flask at predetermined PS concentration (i.e., 0 ~ 280 µM) and temperature (i.e., 303.15 ~ 313.15 K) at about 195 rpm controlled by a lucifugal oscillator. Solution pH was adjusted by 1.0 M H$_2$SO$_4$ or NaOH to a desired value. No buffer was introduced to avoid any reactions between these additives and SO$_4$$. The effects of chlorine (i.e., Cl$$^-$, 0 ~ 280 µM) and bicarbonate (i.e., HCO$_3$-, 0 ~ 70 µM) as typical natural water constituents were estimated. The supernatant (1 ml) was sampled at a given interval and chilled in an ice bath for 10 min to stop the reaction. Then the mixture of supernatant/methanol (3:7, V$_{supernatant}$/V$_{methanol}$) was filtrated through a 0.25 µm filter (SCAA-114, ANPEL, China) for further analyses. All the experiments were carried out in duplicates and the average values were reported.

2.3 Analytical methods

The SCP and reaction products were analyzed by a high performance liquid chromatograph (A Symmetry$^\text{®}$ C$_{18}$ column 2.1 mm × 50 mm × 5 µm-Waters, MA) equipped with MS/MS (ZMD triple quadrupole MS-Waters, USA). Quantification of SCP was based on a multipoint standard calibration using a multiple reaction monitoring (MRM) mode. MS Scan mode as well as Daughter Scan mode was implemented to determine the major transformation products and elucidate the possible degradation pathway. The detailed setting parameters were presented in Text S1, S2 and Table S1 in Supplementary Material.
28 target antibiotics of six classes (sulfonamides, Amphenicols, Quinolones, Macrolides, Penicillins, Tetracyclines) were investigated, and detailed information about the analytical method was shown in Supplementary Material (Text S3). In brief, the wastewater samples were centrifuged at 4000 r min$^{-1}$ for 10 min and filtered through glass fiber filters with 0.47 µm pore diameter (Whatman GF/F), and then the filtered samples were extracted by solid phase extraction method with Oasis HLB cartridges (6 mL, 200 mg, Waters). The samples were extracted adopting the method described in Supplementary Material (Text S4) [41], and the clean-up procedure was performed adopting the method presented in Supplementary Material (Text S4) [41]. The target antibiotics were determined by LC-MS/MS above.

The free radicals were confirmed by Electron Paramagnetic Resonance (EPR) (EMX-8/2.7C, Bruker, Germany) using 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) as a trapping compound. Supernatant (1.0 mL) was sampled at the desired time intervals and mixed thoroughly with 1.0 mL DMPO solution (88.4 mM) for 1 min. Then the mixture was injected to a capillary tube with a microinjector for EPR analysis. All spectra were obtained under the following conditions: Field sweep width: 200 G; Microwave frequency: 9.874 GHz; Microwave power: 6.381 mW; Modulation amplitude: 1 G; Conversion time: 40.96 ms; Time constant: 163.84 ms; Receiver gain: $7.96 \times 10^4$.

3 Results and discussion

3.1 Reaction kinetics

3.1.1 Effects of PS concentration on the SCP removal
Increasing the PS concentration could critically facilitate the formation of SO$_4$$^{•-}$ radicals, further influencing SCP oxidation [39]. Experimental results showed that SCP removal efficiency was accelerated noticeably with increase in persulfate dosage (Fig. 1a). It could be observed that half-life time of SCP decreased from 38.9 to 11.7 min as PS concentration increased from 17.5 to 140 µM. However, the half-life time nearly became consistent as the PS concentration increased from 140 to 280 µM. The reason might be that the oxidizing species produced was more than the system needed and the surplus oxidizing species would react with each other [12, 42], which lowered the utilization rate of PS. The destruction of SCP could be fitted with the pseudo-first-order kinetics model, as described in Eqs. (1) and (2).

\[
\ln \left( \frac{c_{t,SCP}}{c_{0,SCP}} \right) = k_{obs} \cdot t
\]  
(1)

\[
k_{obs} = k'_{SO_4^{•-}} [SO_4^{•-}] + k'_{OH^•} [OH^•] + k'_{S_2O_8^{2•}} [S_2O_8^{2•}]
\]  
(2)

Noticeably, $k_{obs}$ is the pseudo-first-order rate constant that represents the overall SCP degradation which could be ascribed to the reactions with various oxidizing species such as SO$_4^{•-}$, OH$^•$ and S$_2$O$_8^{2•}$ generated in the solution [33]. $c_{0,SCP}$ is the initial concentration (µM) of SCP, $c_{t,SCP}$ is the concentration (µM) of SCP at the time $t$. $k'$ represents the second-order rate constant for the reaction between SCP and each oxidizing species. [43].

Fig. 1b showed that the removal of SCP well fitted with the pseudo-first-order kinetic model ($R^2 > 0.96$). The calculated rate constants were 0.0495, 0.0594, 0.0333 and 0.178 min$^{-1}$, respectively. In addition, as demonstrated in the inset image of Fig. 1b, the $k_{obs}$ showed a good quadratic relationship with initial PS concentrations ($k_{obs} = -1.526\times10^{-6} [PS]_0^2 + 5.621\times10^{-4} [PS]_0 + 0.01158$, $R^2 = 0.923$, $[PS]_0 = 17.5–280$ µM). This formula indicated that the SCP removal ratio
would not definitely increase with the addition of PS dosage. Furthermore, the optimal PS dosage calculated by this formula was approximately equal to 140 µM, so for further experiments the initial PS concentration of 140 µM was adopted.

3.1.2 Effects of initial pH on the SCP removal

Solution pH is one of the most important parameters during thermally activated PS oxidation of contaminants since it could influence the predominant oxidizing species (Eqs. (3) - (13)) [44-46] and speciation of amphoteric organic compounds (for SCP, pK$_{a1}$ = 1.87 ± 0.3 and pK$_{a2}$ = 5.45 ± 0.06) [39, 47]. The effect of solution pH (3 ~ 10) on the degradation of SCP ([SCP]$_0$ = 3.51 µM, [PS]$_0$ = 140 µM and T = 40 °C) was investigated, and obtained results are depicted in Fig. 2. The experiments results confirmed that the SCP degradation rates followed pseudo-first-order kinetics at all pH and the degradation rate was highly pH dependent. Acidic regime was more propitious than neutral and alkaline regimes. The best SCP degradation appeared at pH 3 and its corresponding degradation rate constant was 0.0594 min$^{-1}$. However, Ji et al. [48] investigated the effect of pH on sulfamethoxazole (SMX) oxidation at 60 °C and observed k$_{obs}$ increased monotonically with increasing pH from 4.0 to 10.1. Fan et al. [39] also found that pH value of 9 at 50 °C was the most conductive to sulfamethazine (SMZ) degradation. Therefore, it can be assumed that different characteristics of the contaminants and reaction conditions might be responsible for these different results. The reaction conditions of SMX and SMZ were comparatively analysed in Table 1, the conditions used for SCP degradation generated less oxidizing species, which meant it was the amount of oxidizing species not the speciation of SCP really affected the removal rate.
Kolthoff and Miller [49] assumed that there were two simultaneous reactions involving persulfate decomposition. In acidic conditions, PS could be further catalyzed by the reaction described in Eq. 3 and 4 [50] and produce more SO$_4^{2-}$, which might accelerate the SCP degradation. The acid-catalyzation decreased with increase in the pH, leading to the reduction of degradation rate. When pH was 7 more than pK$_{a2}$, deprotonated SCP had more reactivity with SO$_4^{2-}$/OH', so the $k_{obs}$ at pH 7 nearly equaled to the $k_{obs}$ at pH 5. As pH continued to increase, most of the SO$_4^{2-}$ converted to OH' in basic conditions [51]. Unfortunately, OH' had relatively shorter lifetime in aqueous solutions than SO$_4^{2-}$ and simultaneously they were unable to oxidize SCP because they could not get close to the SCP molecules [52]. Therefore, the removal rates retarded at pH 9 and 10. Final pH values were also measured and approached initial pH values, indicating that PS consumption was tiny.

$$S_2O_8^{2-} + heat \rightarrow SO_4^{2-} + SO_4^{2-}$$ \hspace{1cm} (3)

$$SO_4^{2-} + H_2O \rightarrow OH' + SO_3^{2-} + H^+, k[H_2O] < 3 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$$ \hspace{1cm} (4)

$$SO_4^{2-} + OH' \rightarrow OH' + SO_3^{2-}, k = (6.5 \pm 1.0) \times 10^7 \text{ M}^{-1}\text{s}^{-1}$$ \hspace{1cm} (5)

$$S_2O_8^{2-} + OH' \rightarrow SO_4^{2-} + HSO_4^{-} + 1/2O_2, k = 1.2 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$$ \hspace{1cm} (6)

$$SO_4^{2-} + OH' \rightarrow HSO_4^{-} + 1/2O_2, k = 1.0 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$$ \hspace{1cm} (7)

$$S_2O_8^{2-} + SO_4^{2-} \rightarrow SO_4^{2-} + 2SO_6^{2-}, k = 6.1 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$$ \hspace{1cm} (8)

$$SO_4^{2-} + SO_4^{2-} \rightarrow S_2O_8^{2-}, k = 4.0 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$$ \hspace{1cm} (9)

$$S_2O_8^{2-} + 2H_2O \rightarrow 2SO_4^{2-} + HO_2^{-} + 3H^+$$ \hspace{1cm} (10)

$$2S_2O_8^{2-} + 2H_2O \rightarrow 3SO_4^{2-} + SO_4^{2-} + O_2^{-} + 4H^+$$ \hspace{1cm} (11)

$$2S_2O_8^{2-} + HO_2^{-} \rightarrow SO_4^{2-} + SO_4^{2-} + O_2^{-} + H^+$$ \hspace{1cm} (12)
\[ S_2O_8^{2-} + O_2^- \rightarrow SO_4^{2-} + SO_4^{2-} + O_2 \quad (13) \]
\[ S_2O_8^{2-} + H^+ \rightarrow HS_2O_6^- \quad (14) \]
\[ HS_2O_6^- \rightarrow SO_4^{2-} + SO_4^{2-} + H^+ \quad (15) \]

3.1.3 Effects of temperature on the SCP removal

To better understand the effects of temperature, a great deal of experiments were carried out at pH 3.0, initial PS and SCP concentration of 140 and 3.51 µM respectively at various temperature range (30 ~ 50 °C). Fig. 3a distinctively demonstrated that the SCP removal was highly dependent on activation temperature and SCP degraded faster with increase in the reactor temperature. The degradation process followed pseudo-first order kinetics and the \( k_{\text{obs}} \) values of SCP ranged from 0.425 to 0.0100 min\(^{-1}\). The \( k_{\text{obs}} \) values of SCP removal were similar as reported in previous literature (Table 2). Cui et al. [53] studied the UV-activated PMS to remove SCP from drinking water and found the \( k_{\text{obs}} \) was about 0.134 min\(^{-1}\) under the optimum conditions. Kang et al. [3] examined carbocatalyst activated PS to degrade SCP and discovered that the \( k_{\text{obs}} \) could be about 0.4 min\(^{-1}\) under the reaction conditions below. Additionally, temperature dependency of \( k_{\text{obs}} \) showed excellent fitting with the Arrhenius equation (\( R^2=0.974, \text{Eq. (16)} \)), where \( A \) is the pre-exponential factor, \( E_a \) is the apparent activation energy, \( R \) is the universal gas constant (8.314 kJ mol\(^{-1}\) K) and \( T \) is the absolute temperature (K). It could be seen from the inset image of Fig. 3a, the calculated apparent activation energy \( E_a \) was 155 ± 15 kJ mol\(^{-1}\). This value was close to that of some contaminants previously reported due to some similarities of their chemical structure, e.g., 155.03 ± 26.4 kJ mol\(^{-1}\) for naproxen [54], 141 kJ mol\(^{-1}\) for atrazine [33] and 144 ± 5 kJ mol\(^{-1}\) for...
diuron [34], but it was much higher than that of bisoprolol (119.8 ± 10.8 kJ mol\(^{-1}\)) [55], indicating that the SCP molecule was recalcitrant to either sulfate radicals or hydroxyl radicals.

\[
\ln k_{obs} = \ln A - \frac{E_a}{RT}
\]

(16)

To calculate the reaction stoichiometric efficiency (RSE) defined as the amount of SCP degradation against the amount of PS consumption [56], the PS concentration was determined using N,N-diethyl-p-phenylenediamine as a colorimetric reagent [57]. Fig. 3b indicated that the PS concentration moderately decreased in regard to reaction time and the rate of persulfate consumption increased owing to the enhanced activation of PS at such elevated temperatures. As shown in Fig. 3c, the RSE% values for the degradation process declined with reaction time extension. The RSE was much lower at 50 \(\square\) compared to that at 40 or 45 \(\square\) probably due to the self-quenching reaction among excessive free radicals. Baalbaki et al. [58] reported that the existence of chloride species reacting with sulfate radicals might reduce the RSE value.

3.1.4 Effects of natural water constituents on the SCP removal

Due to the extensive existence of chloride (Cl\(^-\)), bicarbonate (HCO\(_3\)^-) and natural organic matter (NOM) such as humic acid in natural water environments, the effects of various ionic species like Cl\(^-\), HCO\(_3\)^- and humic acid on the SCP degradation have to be explored.

*Effect of Chloride.* Cl\(^-\) usually plays a detrimental role in SO\(_4\)^-\(-\)-based oxidation organic pollutants [33, 59]. The Fig. 4a showed that the SCP removal well followed a pseudo-first-order kinetics model, and the rate constants were 0.0594 min\(^{-1}\) (\(R^2 = 0.989\)), 0.0487 min\(^{-1}\) (\(R^2 = 0.994\)), 0.0283 min\(^{-1}\) (\(R^2 = 0.993\)) and 0.0144 min\(^{-1}\) (\(R^2 = 0.985\)) at the molar ratios ([Cl\(^-\)]/[PS]\(_0\)) of 0:1, 1:1, 2:1 and 4:1, respectively.
0.1:1, 0.5:1 and 2:1, respectively. The reason for this tendency might be that $\text{SO}_4^{2-}$ would react with $\text{Cl}^-$ and produced $\text{Cl}'$ that was less reactive than $\text{SO}_4^{2-}$ at a low chloride level [60] (Eq. (17)). It can be observed that as the chloride level raised, more $\text{Cl}'$ would react with $\text{Cl}^-$ to generate much less reactive chloride species such as $\text{Cl}_2^-$, $\text{Cl}_2$ and HOCl [61] (Eqs. (18) - (23)). The redox potentials of all containing chloride oxidants were much lower than $\text{SO}_4^{2-}$ radicals (2.6 V). Therefore, the decline of SCP removal efficiency was discovered.

\[
\text{SO}_4^{2-} + \text{Cl}^- \leftrightarrow \text{SO}_4^2^- + \text{Cl}' \quad (2.6 \text{V})
\]

\[
\text{Cl}' + \text{Cl}^- \leftrightarrow \text{SO}_4^2^- + \text{Cl}_2^- \quad (2.41 \text{V})
\]

\[
\text{Cl}_2^- + \text{Cl}_2^- \leftrightarrow \text{Cl}_2 + 2\text{Cl}^- \quad (1.36 \text{V})
\]

\[
\text{Cl}^- + \text{Cl}^- \leftrightarrow \text{Cl}_2 \quad (1.36 \text{V})
\]

\[
\text{Cl}_2(aq) + \text{H}_2\text{O} \leftrightarrow \text{HOCl} + \text{H}^+ + \text{Cl}^- \quad (1.48 \text{V})
\]

\[
\text{Cl}_2^- + \text{R}^\cdot \leftrightarrow \text{R} - \text{Cl}^- + \text{Cl}^-
\]

\[
\text{R} - \text{Cl}^- + \text{HOCl} \leftrightarrow \text{H}_2\text{O} + \text{R} - \text{Cl}
\]

*Effect of bicarbonate.* The Fig. 4b illustrated that bicarbonate had higher inhibitory influence on the SCP degradation than chloride ions under the same dose. As the molar ratios of $\text{HCO}_3^-$ to PS increased from 0.1:1 to 0.5:1, the degradation constants dropped accordingly from 0.0594 min$^{-1}$ ($R^2 = 0.989$) to 0.0105 min$^{-1}$ ($R^2 = 0.940$). The changes of pH were little after addition of $\text{HCO}_3^-$, so the inhibitory effect of bicarbonate probably reflected the competition between SCP and bicarbonate for $\text{SO}_4^{2-}$ (Eqs. (24)-(28)). Once $\text{HCO}_3^-$ added into the system, part of $\text{HCO}_3^-$ would change to $\text{CO}_3^{2-}$ and these carbonate species would react with $\text{SO}_4^{2-}$, then generating much less reactive species such as $\text{HCO}_3^-$ and $\text{CO}_3^{2-}$ [62]. The reaction rates of $\text{HCO}_3^-$/$\text{CO}_3^{2-}$ with organic
compounds were normally 2–3 orders of magnitude lower than that of SO$_4$$^-$$^-$ [63], so the inhibitory effect of HCO$_3^-$ on the SCP degradation was clearly observed.

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$$ \hspace{1cm} (24)

$$OH^* + HCO_3^- \leftrightarrow H_2O + CO_3^{2-} \text{ (k = } 8.5 \times 10^6 \text{ } M^{-1}s^{-1})\hspace{1cm} (25)$$

$$OH^* + CO_3^{2-} \leftrightarrow OH^- + CO_3^{2-} \text{ (k = } 3.9 \times 10^8 \text{ } M^{-1}s^{-1}) \hspace{1cm} (26)$$

$$SO_4^{2-} + HCO_3^- \leftrightarrow HC O_3^- + SO_4^{2-} \text{ (k = } 1.6 \times 10^6 \text{ } M^{-1}s^{-1}) \hspace{1cm} (27)$$

$$SO_4^{2-} + CO_3^{2-} \leftrightarrow CO_3^{2-} + SO_4^{2-} \text{ (k = } 6.1 \times 10^6 \text{ } M^{-1}s^{-1}) \hspace{1cm} (28)$$

**Effect of NOM.** Fig. 4 (a) shows SCP degradation was suppressed observably with humic acid concentration increasing. NOM is known to be the radical sink because they are electron-rich and can easily react with the free radicals (e.g. OH$^*$ and SO$_4$$^-$$^-$) [64, 65]. Hence, inhibitory effect on SCP oxidation could be interpreted partly due to the radical quenching effect of NOM. SO$_4$$^-$$^-$ would react with NOM due to H-bonded reaction (Eq. (29)), supported by density functional theory (DFT) calculations [65]. NOM can quench SO$_4$$^-$$^-$ by serving as a radical quencher as presented in Eq. (30) [66]. Moreover, NOM may also inhibit the oxidation of sulfonamides by serving as antioxidants [67, 68] (Eqs. (31) ~ (32)).

$$SO_4^{2-} + NOM \rightarrow SO_4^{2-}(NOM) \hspace{1cm} (29)$$

$$SO_4^{2-} + NOM \rightarrow SO_4^{2-} + NOM^{**} \hspace{1cm} (30)$$

$$SO_4^{2-} + SCP \rightarrow SO_4^{2-} + SCP^{**} \hspace{1cm} (31)$$

$$SCP^{**} + NOM \rightarrow SCP + NOM^{**} \hspace{1cm} (32)$$

3.2 Identification of oxidizing species
In order to elucidate the degradation mechanism and clarify the role of radical species in the oxidation of SCP, excessive doses of EtOH or TBA as radical scavenger was applied to the reaction system. Normally, EtOH with \( \alpha \)-H reacts with HO• and SO\(_4\)\(^{2-}\) quickly, while TBA without \( \alpha \)-H reacts with HO• more rapidly than SO\(_4\)\(^{2-}\) (Eqs. (33) ~ (36)) [69, 70]. The different reactivity of HO• and SO\(_4\)\(^{2-}\) in alcohol can be used to distinguish the dominant radical species in a reaction system. Fig. 5a showed that the removal rate of SCP after 70 min reaction declined from 100% to 50% and 30% in the existence of 1.4 mM and 56 mM EtOH, respectively, as compared to no scavenger controls, suggesting radicals (SO\(_4\)\(^{2-}\) and HO•) played an important role in the SCP destruction. The addition of 1.4 mM TBA exhibited flimsy inhibitory effects, indicating that HO• played a less important role. These results manifested that SO\(_4\)\(^{2-}\) took a leading position at pH 3.

\[
\text{SO}_4^{2-} + \text{EtOH} \rightarrow \text{intermediates}, \quad k = (1.6 - 7.7) \times 10^7 \text{ M}^{-1}\text{s}^{-1} \quad (33)
\]

\[
\text{SO}_4^{2-} + \text{TBA} \rightarrow \text{intermediates}, \quad k = (4 - 9.1) \times 10^5 \text{ M}^{-1}\text{s}^{-1} \quad (34)
\]

\[
\text{OH}^\cdot + \text{EtOH} \rightarrow \text{intermediates}, \quad k = (3.8 - 7.6) \times 10^8 \text{ M}^{-1}\text{s}^{-1} \quad (35)
\]

\[
\text{OH}^\cdot + \text{TBA} \rightarrow \text{intermediates}, \quad k = (1.6 - 7.7) \times 10^7 \text{ M}^{-1}\text{s}^{-1} \quad (36)
\]

Moreover, to further confirm the identity of the above deduction, the Electron Paramagnetic Resonance (EPR) was employed and DMPO was selected as a trapping reagent to identify the generated OH\(^\cdot\) and SO\(_4\)\(^{2-}\) in the thermally activated PS system. The Fig. 5b displayed a four-line signal (\( a_H = a_N = 14.8 \) Gauss) and a six-line signal (\( a_N = 13.8 \) Gauss, \( a_H = 9.1 \) Gauss, \( a_H = 1.44 \) Gauss, \( a_H = 0.79 \) Gauss) evidently, which were the typical spectra of DMPO-OH and DMPO-SO\(_4\)\(^{2-}\), respectively, indicating the generation of HO• and SO\(_4\)\(^{2-}\) [71, 72]. Tan et al. explored the antipyrine degradation by heat activated persulfate and induced that O\(_2\)\(^{2-}\) might be generated under a basic
condition [73] (Eqs. (11) ~ (12)). However, O$_2^-$ was hardly detected by EPR due to its low concentration and fast conversion (Eq. (13)).

3.3 Reaction products and transformation pathways

The transformation pathways of SCP were proposed based on the intermediates identification by LC-MS/MS under a MS Scan mode (Fig. S1) and a Daughter Scan mode (Fig. S2 ~ S8). Fig. S1 shows the ESI (+) MS spectrums of SCP after 8-minute degradation, in which a series of potential products were found as well as the parent SCP (m/z 285). By referring to previous reports on SCP and other sulfonamides transformation in oxidation processes [37-40, 48, 74], seven intermediate products were proposed and further identified by their fragment ions. Typically, the sulfonamides in the sulfate radical-based oxidation system mainly underwent two ways: SO$_2$ extrusion/Smile-type rearrangement and S-N bond cleavage [75, 76]. The similar degradation pathways were observed in this study as well (Fig. 6).

SO$_2$ extrusion/Smile-type rearrangement. Ji et al. studied sulfonamides based on SO$_4^{2-}$ oxidation and concluded that the aniliny radical cations formed as SO$_4^{2-}$ attacked the aniline moiety via an electro-transfer mechanism and then cations went through intermolecular Smiles-type rearrangement to produce SO$_2$ extrusion products (SEPs) [40] (Scheme 1). In the present study, the formation of SEPs-(4-(3-chloro-6-iminopyridazine-1(6H)-yl)aniline) represented as A was detected by LC-MS/MS and the Daughter Scan (Fig. S2) of m/z 221 confirmed the existence of A. Under the attack of OH$^-$ or SO$_4^{2-}$, the A would transform into the (4-(6-iminopyridazine-1(6H)-yl)aniline (B) with Cl$^-$ release [74] and then C emerged after
hydroxylation. Fragmentation pattern of B and C were interpreted in Fig. S3-S4. Note that, the hydroxylation was more likely to occur at aromatic ring or amine-N due to their higher election density instead of the pyridine ring [77, 78]. The characteristic fragments of m/z 201.5 such as m/z 95, 109 indicated that the hydroxylation did happen at the aromatic ring (Fig. S4). Furthermore, hydroxylation perhaps happened at the ortho position of the amino group due to the orientation effect amino group and steric hindrance of sulfonamide chain [40, 79].

*S-N bond cleavage.* S-N bond cleavage of SCP led to the formation of m/z 130, which was identified as 3-amino-6-chloropyridazine (D) (Fig. S5) [38]. However, sulfanilic acid as another part originating from S-N bond cleavage was not detected, most probably due to its good water-solubility [40]. Furthermore, direct attack of HO• or SO₄•⁻ on the D could also contribute to the formation of 3-amino-4-hydroxyl-6-chloropyridazine (E) without Cl⁻ release (Fig. S6) or 3-amino-6-hydroxylpyridazine (G) with Cl⁻ release. These results were also reported in a previous study on electro-Fenton treatment of SCP in water [38]. Dihydroxylation of the D, 3-amino-4,5-dyhydroxyl-6-chloropyridazine (F) was also observed in the MS spectrum (Fig. S8). A similar discovery was reported in the heat activated PS of sulfamethoxazole [48]. But unfortunately, the G wasn’t observed in this study. The reason may be that most of the G was quickly transformed into 3-nitro-6-hydroxylpyridazine (H) after oxidation (Fig. S7).

### 3.4 Removal of antibiotics from piggery anaerobic fermentation slurry

The heat-activated PS ability to remove antibiotics from real water was also tested. PS was added to anaerobic fermentation slurry from a piggery farm as a representative sample. The pH
value of the water was 8.5 and the TOC was about 1134 mg L\(^{-1}\). We selected 50 g L\(^{-1}\) as a PS dosage. Among the 28 target antibiotics, 17 antibiotics of different categories were detected in the piggery wastewater (Fig. 7). The degradation experiments implemented at the pH value of 3 and 8.5 were aimed to find out the ideal reaction pH, keeping other parameters such as reaction temperature (40 °C) and time (70 min) the same as the parameters of SCP degradation (Fig. 7). As a whole, the removal efficiencies of 17 antibiotics ranged from 40% to 99%, and the total removal efficiencies of each category of antibiotics were over 85% at pH 8.5. It seemed that a weak alkaline environment more contributed to the antibiotics degradation compared with an acidic environment. Arslanalaton et al. [80], Andreozzi et al. [81] and Akmehtet al. [82] studied the ozonation of antibiotics wastewater, and reported that the removal efficiencies added with the solution pH increasing. Ghauch et al. [15] explored the UV-activated PS treatment system to purify the CAP-spiked wastewater and river water, and concluded that the presence of particulate matter and ammonia weakened the removal efficiency of CAP. Moreover, the turbidity, total suspended solids and toxicity of waste water were markedly reduced after the UV-PS remedy.

4 Conclusions

In the present study, the heat-activated persulfate oxidation of aqueous SCP was systematically scrutinized. The SCP decomposition was notably affected by PS concentration, operating temperature, initial pH, chloride and bicarbonate, following the pseudo-first-order reaction kinetics model. The increase of temperature and initial oxidant levels considerably boosted the removal rate of SCP. The relationship between rate constants (\(k_{\text{obs}}\)) and initial
persulfate concentrations could be well described by a quadratic curving ($k_{obs} = 5.621 \times 10^{-4} [\text{PS}]_0^2 - 1.526 \times 10^{-6} [\text{PS}]_0 + 0.01158$, $R^2 = 0.923$, $[\text{PS}]_0 = 17.5 - 280 \, \mu\text{M}$). The SCP removal rate was effected by solution pH (3.0 ~ 10.0), a lower pH accelerating the SCP removal rate and the best degradation rate occurring at pH 3.0. Cl$^-$ and HCO$_3^-$ greatly restrained the degradation rate of SCP. Radical scavenger tests and EPR spectrum validated that SO$_4^{2-}$ and HO$^-$ were the predominant oxidizing species. The degradation pathways could mainly be divided into two ways: SO$_2$ extrusion/Smile-type rearrangement and S-N bond cleavage, accompanied by dechlorination, hydroxylation and oxidation. The application in piggery anaerobic fermentation slurry confirmed the feasibility of heat-activated PS for removing antibiotics from wastewater with high TOC. The results showed that heat-activated persulfate oxidation could be an effective method for the antibiotics removal, but it was more appropriate for the small-scale wastewater.

Acknowledgements

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Table captions:

**Table 1** Reaction conditions of sulfonamides degraded by heat-activated persulfate.

**Table 2** Degradation rates of SCP removal in similar treatment methods.
Table 1 Reaction conditions of sulfonamides degraded by heat-activated persulfate.

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>[PS]₀/[Contaminant]₀ (µM / µM)</th>
<th>Activation temperature (°C)</th>
<th>Best pH</th>
<th>Reference</th>
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<tr>
<td>SMX</td>
<td>66.67/1</td>
<td>60</td>
<td>10.1</td>
<td>[48]</td>
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<tr>
<td>SMZ</td>
<td>66.67/1</td>
<td>50</td>
<td>9</td>
<td>[39]</td>
</tr>
<tr>
<td>SCP</td>
<td>39.86/1</td>
<td>40</td>
<td>3</td>
<td>This study</td>
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Table 2 Degradation rates of SCP removal in similar treatment methods.

<table>
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<tr>
<th>Treatment methods</th>
<th>pH</th>
<th>Temperature</th>
<th>[SCP]₀</th>
<th>[Oxidants]</th>
<th>k&lt;sub&gt;obs&lt;/sub&gt;</th>
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<tbody>
<tr>
<td>UV-activated PMS</td>
<td>7.5</td>
<td>25</td>
<td>0.2</td>
<td>1.0</td>
<td>0.134</td>
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<tr>
<td>Carbocatalyst activated PS</td>
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<td>25</td>
<td>20000</td>
<td>2000</td>
<td>0.4</td>
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<tr>
<td>Heat activated PS</td>
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<td>50</td>
<td>1000</td>
<td>33.3</td>
<td>0.425</td>
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</table>
Figure captions:

**Fig. 1.** Effect of initial PS concentration on SCP oxidation performance (a) and pseudo-first-order rate constants under different PS concentrations (b). Experimental conditions: T = 40 °C, [SCP]₀ = 3.51 µM, pH = 3, t = 180 min.

**Fig. 2.** Effect of initial pH on SCP oxidation performance (a) and pseudo-first-order rate constants under different pH (b). Experimental conditions: T = 40 °C, [SCP]₀ = 3.51 µM, [PS]₀ = 140 µM, t = 300 min.

**Fig. 3.** Effect of temperature on SCP oxidation performance (a), PS concentration (b) and the calculated RSE (c) in aqueous solution at different temperatures. Experimental conditions: pH = 3, [SCP]₀ = 3.51 µM, [PS]₀ = 140 µM, T = 303.15 ~ 323.15 K, t = 0 ~ 300 min.

**Fig. 4.** Effect of natural water constituents on SCP oxidation performance: Cl⁻ (a) and HCO₃⁻ (b) on the pseudo-first-order rate constants of SCP oxidation. Experimental conditions: T = 40 °C, [SCP]₀ = 3.51 µM, [PS]₀ = 140 µM, pH = 3, t = 70 min.

**Fig. 5.** (a) Identification of predominant radical species in the heat-activated PS system. Experimental conditions: T = 40 °C, [SCP]₀ = 3.51 µM, [PS]₀ = 140 µM, pH = 3, t = 70 min, [Scavenger]₀/[PS]₀ = 10/1; (b) EPR spectra obtained from DMPO experiments after 10 min. Experimental conditions: T = 50 °C, [SCP]₀ = 35.1 µM, [PS]₀ = 2800 µM, pH = 3, t = 10 min, [DMPO]₀ = 44.2 µM.

**Fig. 6.** Proposed transformation pathways of SCP in the heat-activated PS system.

**Fig. 7.** Removal rates (%) of detected antibiotics (a) Sulfonamides, including SCP, Sulfamonomethoxine (SMX), Sulfafurazole (SFZ), Sulfadimidine (SDD) and total
sulfonamides (ΣSAs); (b) Amphenicols, including Thiamphenicol (THI), Florfenicol thiamphenicol (FF), Chloramphenicol (CAP) and total Amphenicols (ΣAPs); (c) Quinolones, including Ciprofloxacin (CIP), Fleroxacin (FLE) and total Quinolones; (d) Macrolides, including Clarithromycin (CLR), Erythromycin (SPI), Spiramycin (ERY), Tilmicosin (TIL) and total Macrolides (ΣMAs); (e) Penicillins, including Amoxicillin (AML), Penicillin (P) and total Penicillins (PCs); (f) Tetracyclines, including Oxytetracycline (OXY), Chlorotetracycline (CTE) and total Tetracyclines (TCs) from piggery anaerobic fermentation slurry using heat-activated PS. Reaction conditions: pH = 3.0 and 8.5, T = 40 °C, [PS]₀ = 50 g L⁻¹, t = 70 min.

**Scheme 1.** Proposed mechanism for SEPs-(4-(3-chloro-6-iminopyridazine-1(6H)-yl)aniline) (m/z 221) generation by Similes-type rearrangement followed by SO₂ extrusion during heat-activated persulfate oxidation of SCP.
Fig. 1. Effect of initial PS concentration on SCP oxidation performance (a) and pseudo-first-order rate constants under different PS concentrations (b). Experimental conditions: T = 40 °C, [SCP]₀ = 3.51 µM, [PS]₀ = 0 ~ 280 µM, pH = 3, t = 180 min. The error bars of the $k_{obs}$ were calculated by LINEST from Excel.
Fig. 2. Effect of initial pH on SCP oxidation performance (a) and pseudo-first-order rate constants under different pH (b). Experimental conditions: T = 40 °C, [SCP]₀ = 3.51 µM, [PS]₀ = 140 µM, pH = 3 ~ 10, t = 300 min. The error bars of the $k_{obs}$ were calculated by LINEST from Excel.
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Highlights

(1) The parameters of heat-activated PS for degrading SCP were optimized.

(2) The SCP degradation mechanisms by heat-activated PS were proposed.

(3) The treatment for anaerobic fermentation slurry provided guidance for practical applications.
Graphical Abstract