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## A simple Fe<sup>3+</sup>/bisulfite system for rapid degradation of sulfamethoxazole

 Shixiang Wang, Guangsheng Wang, Yongsheng Fu, Hongbin Wang and Yiqing Liu \*

Sulfate radical (SO<sub>4</sub><sup>•-</sup>) based oxidation technologies have been widely used in the remediation of antibiotic-containing wastewater. Activated persulfates are efficient reagents for achieving SO<sub>4</sub><sup>•-</sup>, but the storage and transportation of concentrated persulfates present associated safety issues. In this study, bisulfite (BS) was used as an alternative precursor for replacing persulfates, and a simple advanced oxidation system (Fe<sup>3+</sup>/BS) for generating SO<sub>4</sub><sup>•-</sup> and hydroxyl radical (HO<sup>•</sup>) was formulated and evaluated for removing sulfamethoxazole (SMX) from contaminated water. The initial pH, dosages of Fe<sup>3+</sup> and BS, as well as the water matrix were investigated to improve the SMX degradation. The results indicated that 1 μmol L<sup>-1</sup> SMX was completely removed within 5 min at optimum initial pH of 4.0, Fe<sup>3+</sup> dosage of 10 μmol L<sup>-1</sup>, BS dosage of 100 μmol L<sup>-1</sup> and temperature of 25 °C. The presence of HCO<sub>3</sub><sup>-</sup> and natural organic matter (NOM) showed obviously negative effects on SMX degradation, while Cu<sup>2+</sup> could slightly promote the degradation of SMX if its concentration was in an appropriate range (~1 μmol L<sup>-1</sup>). Scavenger quenching experiments confirmed the presence of SO<sub>4</sub><sup>•-</sup> and HO<sup>•</sup>, which resulted in efficient SMX degradation in the Fe<sup>3+</sup>/BS system. During the radical chain reactions, Fe<sup>2+</sup> and Fe<sup>3+</sup> could be converted into each other to form self-circulation in this system. The degradation pathway of SMX by Fe<sup>3+</sup>/BS was proposed including hydroxylation and bond cleavage.

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### 1 Introduction

Advanced oxidation processes (AOPs), a method mainly based on the reactive species generated from the decomposition of precursors such as hydrogen peroxide, peracetic acid and persulfate (S<sub>2</sub>O<sub>8</sub><sup>2-</sup>),<sup>1</sup> have been widely used in wastewater remediation due to their applicability to a wide range of contaminants, high efficiency and cost effectiveness.<sup>2</sup> Among all commonly used AOPs, sulfate radical (SO<sub>4</sub><sup>•-</sup>) based oxidation technologies have been paid more attention due to its high redox potential ( $E_0 = 2.6\text{--}3.1$  V) and strong selectivity.<sup>3</sup> Even though SO<sub>4</sub><sup>•-</sup> can be effectively generated through the heat, UV and alkaline pH activation of persulfate, Fe(II) or Fe(III) based activation is a viable method for practical application due to its high radical yield and additional coagulation function for contaminant coprecipitation.<sup>4</sup>

Nowadays, some novel systems using bisulfite (BS) as an alternative precursor for replacing persulfate to generate SO<sub>4</sub><sup>•-</sup> have been developed to overcome the safety risks from transportation and storage processes of persulfate due to its chemical instability.<sup>5</sup> Furthermore, several metal ions, including Fe<sup>2+</sup>, Fe<sup>3+</sup>, Co<sup>2+</sup> and Cr<sup>6+</sup>, have been proved to be effective for catalyzing BS to generate SO<sub>4</sub><sup>•-</sup>.<sup>6</sup> Among these catalysts, Fe<sup>3+</sup>

may be extensively used because it is more environmentally friendly than Co<sup>2+</sup> or Cr<sup>6+</sup> and more chemically stable than Fe<sup>2+</sup>. Fe<sup>3+</sup> activated BS may have a lot of similarity to Fe<sup>2+</sup>/persulfate system. Once SO<sub>4</sub><sup>•-</sup> is generated, it can propagate a series of reactions involving the formation of other reactive species, particularly the hydroxyl radical (HO<sup>•</sup>). The possible chain reactions in the presence of oxygen during above process are shown in eqn (1)–(15) and (Table 1).<sup>7–14</sup> However, few works focused on the application of such system in the oxidation of organic or inorganic contaminants.

Sulfamethoxazole (SMX), a synthetic antimicrobial that is extensively used in both human and veterinary medicine, has been frequently detected in many water bodies and effluents from wastewater treatment plants due to its incomplete removal during conventional wastewater treatment,<sup>15</sup> which leads to an increase of antibiotic resistance in humans. Fe<sup>3+</sup>/BS based advanced oxidation process may be a suitable method for the removal of SMX from wastewater due to the generation of oxysulfur radicals. However, little is known about the mechanism of SMX oxidation by Fe<sup>3+</sup>/BS and the primary reactive species involved, although this system with or without light irradiation was widely used in the treatment of wastewater containing dyes or heavy metal ions.<sup>13,16,17</sup> Furthermore, few works focused on the Fe(II)/Fe(III) self-circulation during the degradation process of contaminants in Fe<sup>3+</sup>/BS system.

Faculty of Geosciences and Environmental Engineering, Southwest Jiaotong University, Chengdu 611756, China. E-mail: liuyq@swjtu.edu.cn



Table 1 Possible reactions involved in the Fe<sup>3+</sup>/BS system

Reactions	$k$ (M <sup>-1</sup> s <sup>-1</sup> )
(1) Fe(III) + $n$ HSO <sub>3</sub> <sup>-</sup> → Fe <sup>III</sup> (HSO <sub>3</sub> <sup>-</sup> ) <sub><math>n</math></sub> ( $n = 1, 2, 3$ )	
(2) Fe <sup>III</sup> (HSO <sub>3</sub> <sup>-</sup> ) <sub><math>n</math></sub> → Fe(II) + ( $n - 1$ )HSO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> + SO <sub>3</sub> <sup>-</sup>	
(3) Fe(III) + SO <sub>3</sub> <sup>-</sup> + H <sub>2</sub> O → Fe(II) + HSO <sub>4</sub> <sup>-</sup> + H <sup>+</sup>	
(4) SO <sub>3</sub> <sup>-</sup> + O <sub>2</sub> → SO <sub>5</sub> <sup>-</sup>	$k = (1.1-2.5) \times 10^9$
(5) SO <sub>5</sub> <sup>-</sup> + HSO <sub>3</sub> <sup>-</sup> → SO <sub>4</sub> <sup>-</sup> + SO <sub>4</sub> <sup>2-</sup> + H <sup>+</sup>	$k = 1.2 \times 10^4$
(6) SO <sub>4</sub> <sup>-</sup> + HSO <sub>3</sub> <sup>-</sup> → SO <sub>3</sub> <sup>-</sup> + SO <sub>4</sub> <sup>2-</sup> + H <sup>+</sup>	$k = 1.3 \times 10^8 - 2.5 \times 10^9$
(7) 2SO <sub>5</sub> <sup>-</sup> → 2SO <sub>4</sub> <sup>-</sup> + O <sub>2</sub>	$k = 10^4 - 10^8$
(8) 2SO <sub>5</sub> <sup>-</sup> → S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> + O <sub>2</sub>	$k = 10^7 - 10^8$
(9) Fe(II) + SO <sub>4</sub> <sup>-</sup> → Fe(III) + SO <sub>4</sub> <sup>2-</sup>	$k = 4.6 \times 10^9$
(10) Fe(II) + SO <sub>5</sub> <sup>-</sup> + H <sup>+</sup> → Fe(III) + HSO <sub>5</sub> <sup>-</sup>	$k = 2.0 \times 10^8$
(11) Fe(II) + HSO <sub>5</sub> <sup>-</sup> → Fe(III) + SO <sub>4</sub> <sup>-</sup> + OH <sup>-</sup>	$k = 3.0 \times 10^4$
(12) SO <sub>4</sub> <sup>-</sup> + OH <sup>-</sup> → SO <sub>4</sub> <sup>2-</sup> + HO <sup>•</sup>	$k = (1.4-6.5) \times 10^7$
(13) SO <sub>4</sub> <sup>-</sup> + H <sub>2</sub> O → SO <sub>4</sub> <sup>2-</sup> + HO <sup>•</sup> + H <sup>+</sup>	$k = 1.1 \times 10^1$
(14) HO <sup>•</sup> + HSO <sub>3</sub> <sup>-</sup> → SO <sub>3</sub> <sup>-</sup> + H <sub>2</sub> O	$k = 4.5 \times 10^9$
(15) Fe(II) + HO <sup>•</sup> → Fe(III) + OH <sup>-</sup>	$k = 4.3 \times 10^8$

Thus, the aim of this work was to propose the *in situ* simultaneous activation of BS by Fe<sup>3+</sup> and degradation of SMX by radicals generated from Fe<sup>3+</sup>/BS. The effects of operational factors, such as the initial pH, Fe<sup>3+</sup> and BS dosages, as well as the common water quality constituents including natural organic matter (NOM), inorganic anions and cations on the degradation of SMX were discussed. Besides, the dominant reactive species and Fe(II)/Fe(III) cycle in this system were investigated. Finally, the possible degradation pathways of SMX were tentatively proposed based on the detected reaction products.

## 2 Materials and methods

### 2.1 Materials

SMX, *tert*-butyl alcohol (TBA) and fulvic acid were produced by Aladdin Reagent Company, China. Ferric sulfate and sodium bisulfite were obtained from Sinopharm Chemical Reagent Corporation Ltd., China. Methanol and isopropanol (IPA) were the products of Fisher corporation. H<sub>2</sub>SO<sub>4</sub>, NaOH, NaCl, NaNO<sub>3</sub>, NaHCO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, CuSO<sub>4</sub>, Mg(NO<sub>3</sub>)<sub>2</sub>, Ca(NO<sub>3</sub>)<sub>2</sub> were all of analytical grade and purchased from Chengdu Kelong Chemical Reagent Co., Ltd, China. Deionized water was used in all experiments.

### 2.2 Experimental procedure

The SMX degradation experiments were carried out in a 250 mL glass beaker containing 100 mL SMX solution (1 μmol L<sup>-1</sup>) at 298 K. In each experiment, BS was added and the mixture was rotated for 10 min at 400 rpm. During this process, NaOH (0.5 M) and H<sub>2</sub>SO<sub>4</sub> (0.5 M) were used to adjust the initial pH of solution. When the Fe<sup>3+</sup> with specific amount was put into the SMX solution, the reaction between Fe<sup>3+</sup> and BS resulted in the degradation of SMX. Samples (1.0 mL) were extracted at pre-determined time intervals and filtered by 0.2 μm filter membrane, which were then rapidly quenched with 0.1 mol L<sup>-1</sup>

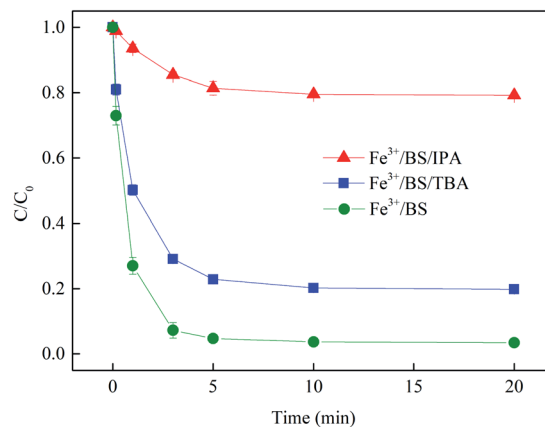


Fig. 1 Effect of radical scavenger on SMX removal. Experimental conditions: [BS]<sub>0</sub> = 100 μmol L<sup>-1</sup>, [Fe<sup>3+</sup>]<sub>0</sub> = 10 μmol L<sup>-1</sup>, [SMX]<sub>0</sub> = 1 μmol L<sup>-1</sup>, [IPA]<sub>0</sub> = [TBA]<sub>0</sub> = 1000 μmol L<sup>-1</sup>, pH<sub>0</sub> = 4.0, T = 25 °C.

Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. In the radical scavenging experiment, TBA and IPA were added into the pure SMX solution before BS addition.

### 2.3 Analysis

The SMX concentration was measured using Thermo' HPLC apparatus (Ultimate 3000) at 270 nm. The mobile phase was a mixture of methanol and 0.1% acetic acid (v/v = 60/40) at a flow rate of 0.8 mL min<sup>-1</sup>. The column temperature was set at 30 °C and the injection volume was 50 μL. The products during SMX degradation were analyzed by UPLC-Q-TOF-MS (ACQUITY UPLC, Quattro Premier XE, Waters, America) with a C18 reversed-phase column (100 × 2.1 mm, 1.7 μm). The mobile phase contained 0.1% formic acid water solution (A) and acetonitrile (B) at a flow rate of 0.5 mL min<sup>-1</sup>. The gradient was 90% A for 0.2 min, decreasing to 5% for 4.8 min, maintaining for 0.5 min, and then increasing back to 90% for 2 min. The solution pH was monitored by a pH meter (PHS-3C+, Leici). Phenanthroline colorimetric method was used for Fe<sup>2+</sup>/Fe<sup>3+</sup> concentration measurement.

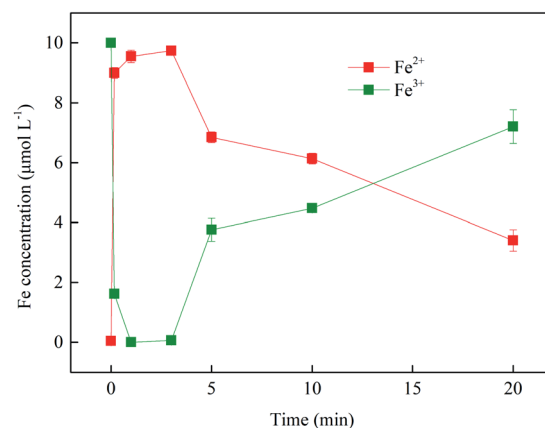
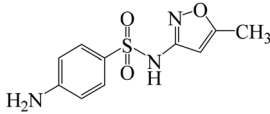
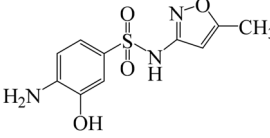
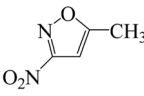
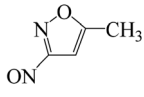
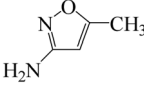


Fig. 2 Variation in concentrations of Fe<sup>2+</sup> and Fe<sup>3+</sup> during SMX removal. Experimental conditions: [BS]<sub>0</sub> = 100 μmol L<sup>-1</sup>, [Fe<sup>3+</sup>]<sub>0</sub> = 10 μmol L<sup>-1</sup>, [SMX]<sub>0</sub> = 1 μmol L<sup>-1</sup>, pH<sub>0</sub> = 4.0, T = 25 °C.

Table 2 Degradation products of SMX in Fe<sup>3+</sup>/BS system

Serial number	Mass to charge ratio ( <i>m/z</i> )	Formular	Proposed structure
SMX	254	C <sub>10</sub> H <sub>11</sub> N <sub>3</sub> O <sub>3</sub> S	
1	270	C <sub>10</sub> H <sub>11</sub> N <sub>3</sub> O <sub>4</sub> S	
2	129	C <sub>4</sub> H <sub>4</sub> N <sub>2</sub> O <sub>3</sub>	
3	113	C <sub>4</sub> H <sub>4</sub> N <sub>2</sub> O <sub>2</sub>	
4	99	C <sub>4</sub> H <sub>6</sub> N <sub>2</sub> O	

### 3 Results and discussion

#### 3.1 Degradation mechanism of SMX by Fe<sup>3+</sup>/BS

##### 3.1.1 Identification of reactive species in Fe<sup>3+</sup>/BS system.

Fig. 1 displayed the complete removal of SMX by Fe<sup>3+</sup>/BS under

proper conditions, and its degradation could be described by pseudo first-order kinetic model with the rate constant of 0.85 min<sup>-1</sup>. This result demonstrated that Fe<sup>3+</sup>/BS was an efficient system for SMX degradation and the radicals generated from Fe<sup>3+</sup>/BS might play an important role during this process. It is widely accepted that HO<sup>•</sup> and SO<sub>4</sub><sup>•-</sup> can be generated *via* the reaction of Fe(II) with peroxymonosulfate or persulfate and the transformation of reactive oxygen species,<sup>18</sup> which might also occur in a Fe(III)/S(IV) system. Thus, the radical scavenging experiments were carried out to explore the dominant active radicals which were responsible for the removal of SMX by Fe<sup>3+</sup>/BS. TBA was selected as a strong HO<sup>•</sup> scavenger with the second-order rate constant of 3.8–7.6 × 10<sup>8</sup> M<sup>-1</sup> s<sup>-1</sup>,<sup>17</sup> while IPA was used as a nonselective scavenger for both HO<sup>•</sup> and SO<sub>4</sub><sup>•-</sup>, with the second-order rate constants of 1.9 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup> and 8.2 × 10<sup>7</sup> M<sup>-1</sup> s<sup>-1</sup>, respectively.<sup>19</sup> As shown in Fig. 1, the SMX degradation rate constant in the system without TBA/IPA addition was much higher than those in Fe<sup>3+</sup>/BS/TBA (0.39 min<sup>-1</sup>) and Fe<sup>3+</sup>/BS/IPA systems (0.051 min<sup>-1</sup>). This result proved the participation of both HO<sup>•</sup> and SO<sub>4</sub><sup>•-</sup> in the SMX degradation process. Meanwhile, the SMX degradation rate in Fe<sup>3+</sup>/BS/TBA system was 7.6-fold faster than that in Fe<sup>3+</sup>/BS/IPA system, demonstrating that SO<sub>4</sub><sup>•-</sup> was the dominant radical in Fe<sup>3+</sup>/BS system under current conditions.

**3.1.2 Variation in concentrations of Fe<sup>2+</sup> and Fe<sup>3+</sup> during SMX degradation.** To clarify if Fe<sup>2+</sup> and Fe<sup>3+</sup> could be converted into each other in this system (as shown in eqn (1)–(3) and (9)–(11)), the concentration variation of Fe<sup>2+</sup> and Fe<sup>3+</sup> during SMX degradation was investigated. As shown in Fig. 2, the concentration of total Fe was maintained at about 10 μmol L<sup>-1</sup> during the whole reaction. A decrease of Fe<sup>3+</sup> concentration from 10 to

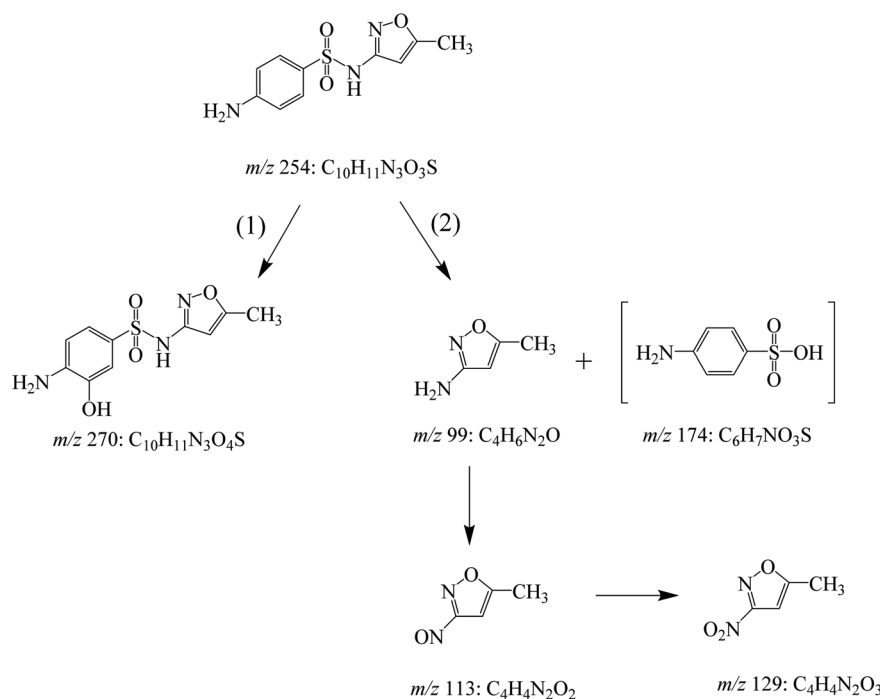


Fig. 3 Possible removal pathways of SMX by Fe<sup>3+</sup>/BS: (1) hydroxylation and (2) bond cleavage.

0.06  $\mu\text{mol L}^{-1}$  was obviously observed in the initial 3 min, while  $\text{Fe}^{2+}$  concentration increased from 0 to 9.7  $\mu\text{mol L}^{-1}$  correspondingly. However, 65.1% of  $\text{Fe}^{2+}$  was inversely transformed to  $\text{Fe}^{3+}$  after 20 min reaction, indicating that the oxidation of  $\text{Fe}^{2+}$  was occurred based on the eqn (9)–(11) and (15). This result proved the occurrence of  $\text{Fe}(\text{II})/\text{Fe}(\text{III})$  self-circulation in the  $\text{Fe}^{3+}/\text{BS}$  system. For this reason, the radicals could be continuously generated during chain reactions between precursors and regenerated  $\text{Fe}(\text{II})/\text{Fe}(\text{III})$  species.

**3.1.3 Degradation pathways of SMX by  $\text{Fe}^{3+}/\text{BS}$ .** The main degradation products of SMX in  $\text{Fe}^{3+}/\text{BS}$  system were detected and identified by UPLC-Q-TOF-MS. Except SMX itself, there were four substances identified in the reaction, and their formula and structures are shown in Table 2. Based on these products, the possible reaction pathway of SMX by  $\text{Fe}^{3+}/\text{BS}$  was proposed in Fig. 3, including hydroxylation and bond cleavage.

(1) Hydroxylation (pathway (1)) was considered as one of the classical degradation pathways of SMX, which resulted in the electrophilic replacement on the aromatic chain of SMX and the generation of  $m/z$  270 due to the electron-rich nature of aniline group in SMX structure.<sup>20</sup>

(2) Bond cleavage (pathway (2)) was resulted from the radical attack at S–N bond in the acidic medium,<sup>21</sup> which led to the formation of 3-amino-5-methylisoxazole ( $m/z$  99). The amino group of  $m/z$  99 could be further oxidized, forming  $m/z$  113 and 129. It was worth noting that the 4-amino benzene sulfonic acid ( $m/z$  174) might also be generated in this pathway. We could not exclude its formation, although this intermediate was not detected.

## 3.2 Factors influencing SMX degradation by $\text{Fe}^{3+}/\text{BS}$

**3.2.1 Effect of initial pH.** Free iron ions can activate BS to generate a series of oxysulfur radicals (e.g.,  $\text{SO}_3^{\cdot-}$ ,  $\text{SO}_4^{\cdot-}$  and  $\text{SO}_5^{\cdot-}$ ), and the pH plays an important role in this process. To determine the optimum initial pH for SMX degradation in  $\text{Fe}^{3+}/\text{BS}$  system, experiments at initial pH values between 3.0 and 8.5 were conducted. As shown in Fig. 4, the fastest and complete SMX removal was obtained at pH 4.0 and most of SMX was

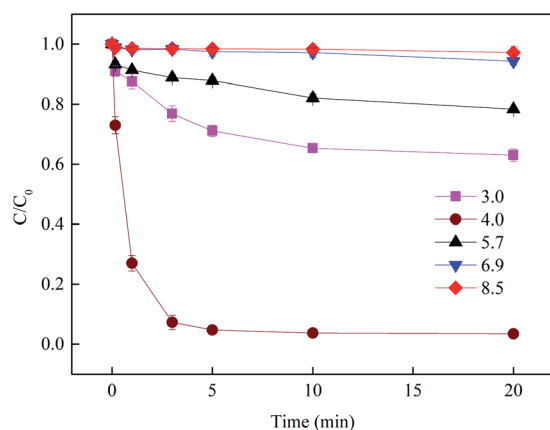


Fig. 4 Effect of initial pH on SMX removal. Experimental conditions:  $[\text{Fe}^{3+}]_0 = 10 \mu\text{mol L}^{-1}$ ,  $[\text{BS}]_0 = 100 \mu\text{mol L}^{-1}$ ,  $[\text{SMX}]_0 = 1 \mu\text{mol L}^{-1}$ ,  $T = 25 \text{ }^\circ\text{C}$ .

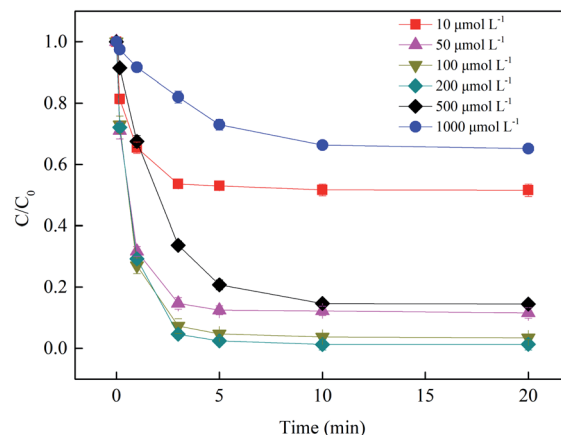


Fig. 5 Effect of BS dosage on SMX removal. Experimental conditions:  $[\text{SMX}]_0 = 1 \mu\text{mol L}^{-1}$ ,  $[\text{Fe}^{3+}]_0 = 10 \mu\text{mol L}^{-1}$ ,  $\text{pH}_0 = 4.0$ ,  $T = 25 \text{ }^\circ\text{C}$ .

efficiently removed in the first 3 min. When the pH decreased to 3.0 or increased to 8.5, the SMX removal after 20 min reaction decreased to 37.0% and 2.9%, respectively. Speciation under the aforementioned conditions might primarily account for the increase in SMX degradation at pH 4.0. As reported by Wang *et al.*,<sup>6</sup> the predominant S(IV) species at pH 4.0 is BS, and thus facilitating the formation of  $\text{Fe}^{\text{III}}(\text{HSO}_3^-)_n$  and the consequent reactions shown in eqn (1)–(15). Increasing pH might accelerate both the ionization of BS to form  $\text{SO}_3^{2-}$  or  $\text{S}_2\text{O}_6^{2-}$  and the hydrolyzation of  $\text{Fe}(\text{III})$ , which inhibited the speciation of the system. pH 3.0 (or a lower pH value) had a negative effect on both radical generation and SMX removal, because part of S(IV) was volatilized at  $\text{pH} < 3.0$ . Consequently, 4.0 was deemed as the optimal pH and was used in subsequent experiments.

**3.2.2 Effect of BS dosage.** Since BS was the only precursor of active radicals in a homogeneous  $\text{Fe}^{3+}/\text{BS}$  system under acidic conditions, the dose of BS had a significant effect on the formation of reactive species and SMX degradation. As shown in Fig. 5, the SMX removal efficiency significantly increased with the increasing BS dosage from 10 to 100  $\mu\text{mol L}^{-1}$ , owing to the

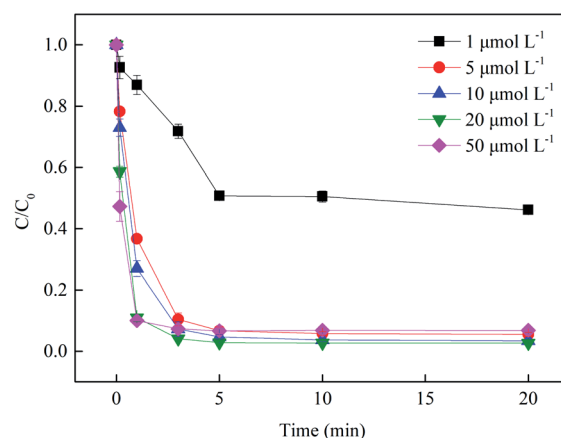


Fig. 6 Effect of  $\text{Fe}^{3+}$  dosage on SMX removal. Experimental conditions:  $[\text{BS}]_0 = 100 \mu\text{mol L}^{-1}$ ,  $[\text{SMX}]_0 = 1 \mu\text{mol L}^{-1}$ ,  $\text{pH}_0 = 4.0$ ,  $T = 25 \text{ }^\circ\text{C}$ .

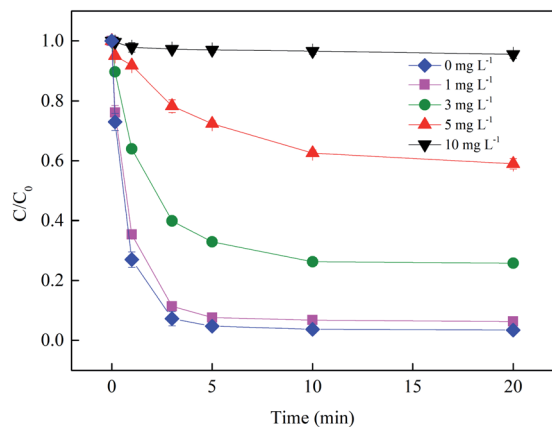


Fig. 7 Effect of NOM on SMX removal. Experimental conditions:  $[BS]_0 = 100 \mu\text{mol L}^{-1}$ ,  $[\text{Fe}^{3+}]_0 = 10 \mu\text{mol L}^{-1}$ ,  $[\text{SMX}]_0 = 1 \mu\text{mol L}^{-1}$ ,  $\text{pH}_0 = 4.0$ ,  $T = 25^\circ\text{C}$ .

increasing generation rate and accumulation of  $\text{Fe}^{\text{III}}(\text{HSO}_3^-)_n$  and the subsequent radicals with the increasing BS concentration. However, excessively high BS concentration (such as  $>500 \mu\text{mol L}^{-1}$ ) could retard SMX degradation in the system because of the competitive reactions of excess BS with the active radicals

according to eqn (5), (6) and (14). Hence, the balance between the reducing nature of BS and its activity to form radicals is critical. Considering the factors above and economic efficiency,  $100 \mu\text{mol L}^{-1}$  was used as the optimum BS concentration for this system.

**3.2.3 Effect of  $\text{Fe}^{3+}$  dosage.** Besides the solution pH and BS concentration, speciation of  $\text{Fe}(\text{III})$  under the aforementioned conditions might primarily account for the increase in chain reaction rate, which was crucially influenced by initial  $\text{Fe}^{3+}$  dosage in the system. As shown in Fig. 6, a conspicuous enhancement in the SMX removal was observed when the  $\text{Fe}^{3+}$  dosage increased from 1 to  $10 \mu\text{mol L}^{-1}$ . Nevertheless, further increasing  $\text{Fe}^{3+}$  concentration only resulted in the acceleration of SMX degradation in the first 1 min, which indicated that  $10 \mu\text{mol L}^{-1}$   $\text{Fe}^{3+}$  was enough for activating  $100 \mu\text{mol L}^{-1}$  BS. Therefore,  $10 \mu\text{mol L}^{-1}$  of  $\text{Fe}^{3+}$  was chosen as the optimum condition in this study.

**3.2.4 Effect of NOM.** Natural organic matter can be both a source and a sink of radicals, the influence mechanism of which depends on the concentration and characteristics of dissolved organic compound.<sup>22</sup> Carboxylate ligands are known to accelerate the advanced oxidation process by forming complex with  $\text{Fe}(\text{III})$  which reacts faster with  $\text{H}_2\text{O}_2/\text{HO}_2^{\cdot}/\text{O}_2^{\cdot-}$  than hydrate in the Fenton process, although they are always

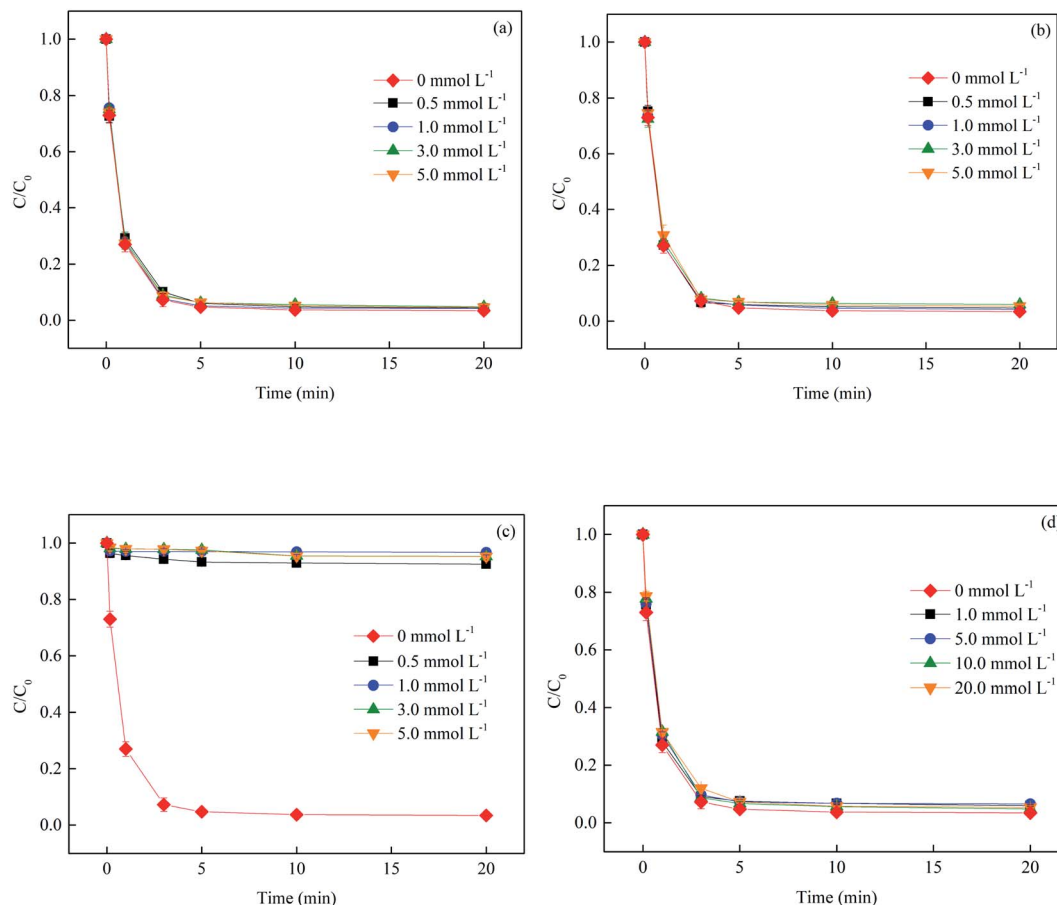
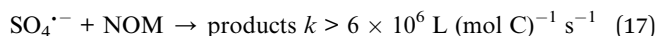
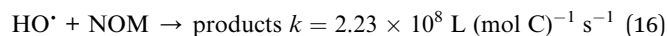


Fig. 8 Effect of  $\text{SO}_4^{2-}$  (a),  $\text{NO}_3^-$  (b),  $\text{HCO}_3^-$  (c) and  $\text{Cl}^-$  (d) on SMX removal. Experimental conditions:  $[BS]_0 = 100 \mu\text{mol L}^{-1}$ ,  $[\text{Fe}^{3+}]_0 = 10 \mu\text{mol L}^{-1}$ ,  $[\text{SMX}]_0 = 1 \mu\text{mol L}^{-1}$ ,  $\text{pH}_0 = 4.0$ ,  $T = 25^\circ\text{C}$ .

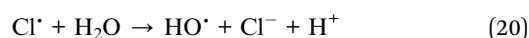
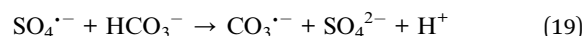
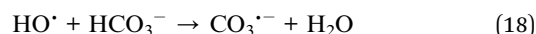


assumed as the scavengers for radicals, as shown in eqn (16) and (17).<sup>23</sup> In order to investigate the effect of NOM on the Fe(III)/S(IV) system, fulvic acid (FA), a naturally existing macromolecular carboxyl-containing substance, was added in the system. As shown in Fig. 7, the SMX removal in 20 min decreased from 100% to 4.5% with the FA concentration increasing from 0 to 10 mg L<sup>-1</sup>, which indicated that the degradation of SMX was inhibited significantly in the presence of NOM and the radical scavenging effect of NOM surpassed its promoting effect on radical generation.



**3.2.5 Effect of inorganic anions.** SMX-contaminated waters usually contain not only SMX but also substantial concentrations of other inorganic ions (*e.g.*, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, HCO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup>), which may affect the overall efficiency of Fe<sup>3+</sup>/BS system. In this study, these four typical background anions were selected for examination. As presented in Fig. 8, the presence of SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> both had little effect on SMX degradation, because they could hardly participate in the radical chain reactions. The HCO<sub>3</sub><sup>-</sup> ion exerted an obvious inhibition effect

on SMX degradation. After 20 min reaction, the removal of SMX in the presence of 0.5 mmol L<sup>-1</sup> HCO<sub>3</sub><sup>-</sup> fell to 7.5%. Possible explanations for this result include: (1) HCO<sub>3</sub><sup>-</sup> could react with HO<sup>•</sup> and SO<sub>4</sub><sup>•-</sup> with the second-order rate constants of 3.9 × 10<sup>8</sup> M<sup>-1</sup> s<sup>-1</sup> and 9.1 × 10<sup>6</sup> M<sup>-1</sup> s<sup>-1</sup>, respectively (as shown in eqn (18) and (19)), which was inefficient for SMX oxidation;<sup>23</sup> and (2) the addition of HCO<sub>3</sub><sup>-</sup> resulted in the increase of solution pH to alkaline range, which was unfavourable for the radical generation due to the formation of Fe(III) precipitate. For Cl<sup>-</sup>, as reported by Lutze *et al.*,<sup>24</sup> SO<sub>4</sub><sup>•-</sup> can react with Cl<sup>-</sup> and the oxidation product Cl<sup>•</sup> is favoured at weakly acidic pHs. No obvious difference on SMX removal was observed between the Fe<sup>3+</sup>/BS system and Fe<sup>3+</sup>/BS/Cl<sup>-</sup> system, because the oxidation of SMX by Cl<sup>•</sup> and its derivate HO<sup>•</sup> (eqn (20)) might occur synchronously.



**3.2.6 Effect of metal cations.** The cations in the solution might have different impacts on SMX removal by binding with it

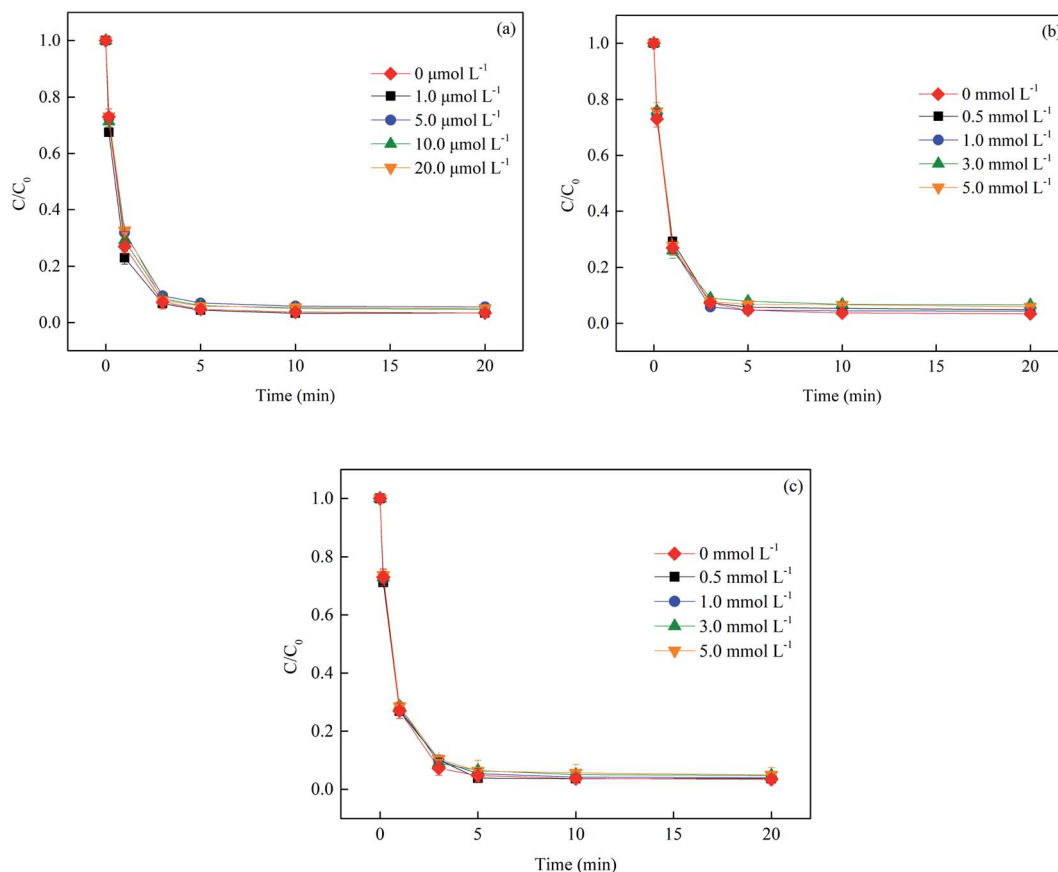
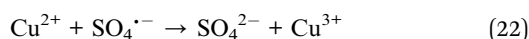
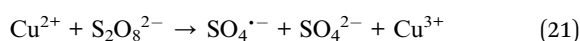


Fig. 9 Effect of Cu<sup>2+</sup> (a), Ca<sup>2+</sup> (b), and Mg<sup>2+</sup> (c) on SMX removal. Experimental conditions: [BS]<sub>0</sub> = 100 μmol L<sup>-1</sup>, [Fe<sup>3+</sup>]<sub>0</sub> = 10 μmol L<sup>-1</sup>, [SMX]<sub>0</sub> = 1 μmol L<sup>-1</sup>, pH<sub>0</sub> = 4.0, T = 25 °C.

to change its chemical properties or reacting with precursor of radicals directly.<sup>25</sup> In this study, the influence of three common cations (*i.e.*, Cu<sup>2+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>) on SMX degradation was evaluated. As shown in Fig. 9, the degradation of SMX was slightly promoted with the increase of Cu<sup>2+</sup> concentration from 0 to 1 μmol L<sup>-1</sup>. 73.1% SMX was degraded in 1 min reaction without Cu<sup>2+</sup> addition, while 76.9% SMX was removed when the Cu<sup>2+</sup> concentration was 1 μmol L<sup>-1</sup>. A reasonable explanation for this result was that SO<sub>4</sub><sup>•-</sup> could be formed extra from chemically catalyzed decomposition of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> (generated from eqn (8)) by Cu<sup>2+</sup>, as described in eqn (21), which had been reported by many researches.<sup>26</sup> However, Cu<sup>2+</sup> was also a scavenger for SO<sub>4</sub><sup>•-</sup> (eqn (22)), and thus excessive Cu<sup>2+</sup> in the system was disadvantageous for SMX degradation. The presence of Ca<sup>2+</sup> and Mg<sup>2+</sup> could hardly affect SMX removal even at high concentrations, indicating that Ca<sup>2+</sup> and Mg<sup>2+</sup> were stable so as not to participate in the radical reactions and the sensitivity of SMX after complexation with Ca<sup>2+</sup>/Mg<sup>2+</sup> was unchanged toward active radicals.



## 4 Conclusion

Fe<sup>3+</sup>/BS, a simple homogeneous advanced oxidation system that efficiently generates multiple radicals was developed. The influence of operational parameters on SMX oxidation by Fe<sup>3+</sup>/BS, the dominating reactive species contributing to SMX degradation and the reaction pathways were investigated. Under the conditions of pH of 4.0, Fe<sup>3+</sup> dosage of 10 μmol L<sup>-1</sup>, BS dosage of 100 μmol L<sup>-1</sup>, initial SMX concentration of 1 μmol L<sup>-1</sup> and temperature of 25 °C, the removal of SMX was about 100% in 5 min reaction. The presence of SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> showed little influence on SMX removal, while obviously negative effects of HCO<sub>3</sub><sup>-</sup> and NOM were observed. Cu<sup>2+</sup> could slightly promote the destruction of SMX if its concentration was in an appropriate range (~1 μmol L<sup>-1</sup>). It has to be mentioned that both HO<sup>•</sup> and SO<sub>4</sub><sup>•-</sup> were the contributing reactive species for SMX degradation. Fe<sup>2+</sup> and Fe<sup>3+</sup> could be converted into each other to form a self-circulation in this system. According to the identified products, two degradation pathways of SMX including hydroxylation and bond cleavage were proposed.

## Conflicts of interest

There are no conflicts to declare.

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