Enhanced oxidation of erythromycin by persulfate activated iron powder–H₂O₂ system: Role of the surface Fe species and synergistic effect of hydroxyl and sulfate radicals

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HIGHLIGHTS

- The peroxide-persulfate combined system activated by ZVI powder was investigated.
- Erythromycin removal was enhanced by adding persulfate into ZVI–H₂O₂ system.
- The Fe species generated by persulfate on ZVI surface triggered the HO₂ formation.
- The Cl[−] exhibited dual effects (favorable or adverse) on erythromycin removal.
- An degradation pathway of erythromycin was proposed in the oxidation system.

GRAPHICAL ABSTRACT

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ABSTRACT

Erythromycin (ERY) is one of macrolide antibiotics which are hardly removed by conventional water treatment process. In this study, the degradation of ERY using a H₂O₂ and persulfate combined process was assessed. Neutral and acidic conditions are superior to alkaline condition in the results of ERY degradation. The Cl[−] exhibited dual effects (favorable or adverse) distinctively on ERY degradation, while HCO₃[−], CO₃^{2−} and humic acid significantly inhibited ERY degradation. The results showed that with the persulfate/H₂O₂ molar ratio improved from 0:10 to 1:9 (total oxidants dosage was 0.1 mM), the ERY degradation efficiency increased from 6.5% to 90.0%. Effective oxidation of ERY only occurred after adding persulfate with the formation of surface-associated Fe(II) on the ZVI surface facilitating rapid and extensive decomposition of H₂O₂. Undetectable concentration of dissolve Fe²⁺ suggested that the generation of HO₂ was mainly from the surface-located Fe(II)-initiated heterogeneous Fenton process. The intermediate products during oxidation were identified, and the degradation pathways of ERY were tentatively proposed.

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1. Introduction

Antibiotics have been widely used in clinical treatment and diseases prevention which could induce antibiotic resistance genes

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(ARG) and pose threats to human health and safety. Recently, many kinds of antibiotics have been detected in the surface water [1] whilst lots of researches have pointed out that pharmaceuticals cannot be completely removed by conventional water treatment process. It has been found that the advanced oxidation processes (AOPs) are one of effective treatments to remove antibiotic contaminants in water, due to the generated strong oxidizing radicals such as hydroxyl radicals ($\text{HO}\cdot$) and sulfate radicals ($\text{SO}_4\cdot^-$).

Both $\text{HO}\cdot$ and $\text{SO}_4\cdot^-$ have high oxidative capabilities ($E_{0(\text{HO}\cdot)} = 2.7 \text{ V}$; $E_{0(\text{SO}_4\cdot^-)} = 2.6 \text{ V}$) [2]. However, the oxidation mechanisms of organics with these two radicals are slightly different. $\text{HO}\cdot$ reacts with organics through two possible approaches, i) electron-transfer process and ii) hydrogen-atom abstraction, while $\text{SO}_4\cdot^-$ only undergoes electron transfer [3]. Moreover, $\text{SO}_4\cdot^-$ maintains strong oxidizing under all pH conditions and has a much longer lifetime (30–40 μs) than $\text{HO}\cdot$ (20 ns). But there are still some shortages of $\text{SO}_4\cdot^-$ need to be pointed out. $\text{SO}_4\cdot^-$ will convert into SO_4^{2-} after being reduced, which is restricted under a concentration of 250 mg/L in WHO, EC, USEPA and China's drinking water standards to avoid unpleasant taste, diarrhea and corrosion problems [4]. $\text{SO}_4\cdot^-$ reacts with chemicals generally slower than $\text{HO}\cdot$, when it comes to real wastewaters which contain multiple pollutants, $\text{HO}\cdot$ exhibits higher universality than $\text{SO}_4\cdot^-$ [5]. Considering the advantages and disadvantages of these two radicals, a system combine $\text{HO}\cdot$ and $\text{SO}_4\cdot^-$ may provide a new way for contaminants removal.

Persulfate (PS) and peroxymonosulfate (PMS) are the most common sources for $\text{SO}_4\cdot^-$ and H_2O_2 is the main sources of $\text{HO}\cdot$. Activation methods for $\text{SO}_4\cdot^-$ and $\text{HO}\cdot$ involving UV, microwave, and transition metal ions like Fe^{2+} have been studied in H_2O_2 and PS combined system [5–8]. While the performance and mechanism for heterogeneous system was seldom studied. Yan et al. found that siderite could degrade trichloroethylene (TCE) and dichloroethylene (DCE) activated PS and H_2O_2 oxidation, however the initial decomposition rate of the oxidants was limited by the slow dissolution rate of ferrous ions [2].

Zero valent iron (ZVI) is one of available heterogeneous catalyst, which serve as a releasing source of Fe^{2+} through Eqs. (1) and (2) under acid condition. The ZVI can also react with PS and H_2O_2 directly (Eqs. (3) and (4)). However, the reactions of Eqs. (1) and (4) are much slower than the reactions of Eqs. (2) and (3) especially when using micrometric ZVI powder [9]. Thus, for ZVI- H_2O_2 system (designated as HR system), most of the studies are conducted under acid condition [10], using nano-ZVI [11,12] or enhanced by ultrasound and heat [13–15] to accelerate the electron transfer.

In the H_2O_2 and PS combined system, the reaction rate between H_2O_2 and ZVI powder is slow, but ZVI powder exhibits fast reaction with PS. The generation of $\text{SO}_4\cdot^-$ and ferrous species between ZVI and PS may be used to trigger a fast $\text{HO}\cdot$ formation in the $\text{Fe}(\text{II})$ - H_2O_2 reaction and enhance the degradation performance of organic pollutants. However the role of PS and the H_2O_2 catalytic mechanisms with ZVI in the combined system haven't been verified yet.

In this study, Erythromycin (ERY) was chosen as a target contaminant. ERY is toxic to aquatic photosynthetic organisms (e.g. cyan bacterium, green alga, etc.) at $\mu\text{g/L}$ concentration levels (22–350 $\mu\text{g L}^{-1}$) [16]. The occurrence of ERY in wastewater effluents [17,18] and surface water [19,20] has been reported in num-

bers of studies. Low concentrations of ERY (470–810 ng/L) with lower removal efficiency (9–19%) were observed in water treatment plants in Hong Kong and Shenzhen, China [21].

The current study focused on the ZVI reaction kinetics and catalytic mechanisms in the H_2O_2 and PS combined system. The factors that affect the ERY degradation efficiency in PS oxidation system (designated as SR system) and combined oxidation system (designated as HSR system) were investigated, including oxidant and ZVI dose, the ratio of H_2O_2 and PS, initial pH and aqueous matrices. Subsequently, the reactive species were identified, including the contribution of $\text{SO}_4\cdot^-$ and $\text{HO}\cdot$ radicals. To provide the insight into the interface mechanism between H_2O_2 and PS over ZVI, the surface structural transformation of ZVI was investigated as well as surface $\text{Fe}(\text{II})$ generating amount. Finally, the oxidation intermediates of ERY were identified, and the pathways of ERY degradation were proposed.

2. Materials and methods

2.1. Chemicals

All chemicals used in this study were at least analytical grade, and all solvents were high performance liquid chromatography (HPLC) grade. ERY was purchased from Tokyo Chemical Industry Co., Ltd. Methanol (MeOH) and acetonitrile were obtained from Fisher Scientific. Humic acid was purchased from Sigma Aldrich and prepared as a stock solution of 1 g L^{-1} keeping in 4 °C. Other reagents including commercial reductive iron powder, H_2O_2 (30%, w/w), PS, NaCl, NaHCO_3 , NaCO_3 , NaSO_4 , H_2SO_4 , ethanol (EtOH), Na_2EDTA , *tert*-butyl alcohol (TBA), and *n*-butyl alcohol (NBA) were obtained from Sinopharm Chemical Reagent Co., Ltd. The ZVI particles were approximately 20–80 μm in diameter, and BET surface area was 4.6715 $\text{m}^2 \text{g}^{-1}$. 150 U/mg horseradish peroxidase reagent (HRP), *N,N*-diethyl-*p*-phenylenediamine (DPD) and 2,2'-bipyridine for H_2O_2 determination were purchased from Sigma Aldrich and stored at 4 °C when not in use. Ultrapure water (Millipore, 18.2 M Ω) was used throughout the experimental procedure and analyses.

2.2. Experimental procedures

All degradation experiments were conducted in 250 mL glass conical flasks with 150 mL of simulated ERY-contaminated solution. The flasks were placed in incubator shakers at temperature of 25 ± 2 °C and a speed of 150 rpm to maintain the solution well mixed. Magnetic stirrer wasn't be used for its uncertain influence of low-intensity magnetic field [22]. The ERY solutions (1 mg L^{-1}) and different concentration of PS and H_2O_2 solution were added to each reactor, without controlling the initial pH. All reactions were initiated by adding a certain dosage of ZVI powder. In the study of pH effects, the solutions were adjusted initial pH by adding 0.1 M NaOH or H_2SO_4 . The aqueous matrices were simulated by adding desired level of inorganic salt and humic acid. At designated time intervals, 1.5 mL sample was transferred to a 2-milliliter tapered plastic centrifuge tube with 0.2 mL EtOH to quench the reaction. High speed centrifugation (14,000 rpm and 10 min) was needed to separate precipitation of iron hydroxides before HPLC-MS analysis. The sampling procedure for dissolved Fe^{2+} and H_2O_2 analysis were similar to those in the degradation experiments. The non-dissolved ZVI powders were collected at the end of the experiment, then rinsed with N_2 -sparged ultrapure water and ethanol for several times and dried in a vacuum freeze dryer to avoid the changing of the ZVI surface oxidation layers during drying.

2.3. Analytical methods

HPLC-MS (Alliance 2695/ZQ 4000, Waters, USA) was used to measure the ERY concentration during the degradation process. The system was equipped with electrospray ionization (ESI) and XBridge® C18 column (3.5 μm , 2.1×100 mm, Waters). Mobile phase was a mixture of 0.1% formic acid solution and acetonitrile (v/v = 60:40) at a flow rate of 0.2 mL min^{-1} . The injection volume was $5 \mu\text{L}$ and run time was 3 min. The MS was operated in positive ion (ES+) mode and cone voltage was 25 V.

Transformation products were measured by ACQUITY UPLC/ Xevo G2 QTOF-MS (Waters, USA) using a relatively high amount of ERY (20 mg L^{-1}). Data acquisition was performed in multiple reaction monitoring mode (MRM) from 100 Da to 800 Da, and cone voltage was 40 V. Mobile phase consisting of water +0.1% formic acid (eluent A) and methanol (eluent B). The elution gradient: 0–1.5 min (95% A + 5% B), 1.5–2 min (70% A + 30% B), 2–3 min (50% A + 50% B), 3–5 min (95% A + 5% B), 5–7 min (10% A + 90% B), 7–9 min (95% A + 5% B). MS data was processed using the software package MassLynx V4.1.

H_2O_2 concentration was measured using the HRP-DPD method modified to minimize the interference of Fe(II) and Fe(III) [23,24]. Primarily, 2.7 mL samples were added to 0.3 mL phosphate buffer solution (pH = 6), and mixed in a 1 cm quartz cuvette with $50 \mu\text{L}$ 100 kU L^{-1} HRP stock solution and $50 \mu\text{L}$ 0.1 g mL^{-1} DPD solution. 2,2'-Bipyridine and Na_2EDTA were added to eliminated influences of metal ions. DPD was oxidized by H_2O_2 in the presence of HRP and led to an absorbance at 551 nm and H_2O_2 concentration was spectrophotometrically determined. Electron spin-resonance spectroscopy (ESR) was used to identify $\text{HO}\cdot$, using 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as the spin trap. The DMPO-OH has unique peak height ratio of 1:2:2:1, $\alpha_N = \alpha_H = 15.0 \text{ G}$. The ZVI surface composition was studied by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS).

3. Results and discussion

3.1. Degradation of ERY in SR system

Kinetic experiments were carried out to investigate the effect of PS concentration and initial ZVI dosage on ERY degradation (Fig. 1a and b). As shown in Fig. 1a, when the initial concentration

of ERY was kept constant (1 mg L^{-1}) and the dosage of PS increased from 0.05 mM to 0.4 mM, the degradation efficiency of ERY increased significantly. Within 240 min, 69.5% and 91.2% of ERY were removed at PS dosage of 0.05 mM and 0.1 mM, respectively. While around 100% of ERY degradation achieved within 90 min at PS concentration higher than 0.2 mM. When PS dosage exceeded 0.2 mM, increasing PS concentration had no greater impact on ERY degradation. Thus, 0.1 mM was chosen as the optimum PS dosage and used in subsequent experiments based on the consideration of cost and adverse impact of residual SO_4^{2-} concentration on water body.

The results in Fig. 1b clearly demonstrated that the degradation of ERY increased with the ZVI dosage ranging from 2.8 mg L^{-1} to 22.4 mg L^{-1} . Within 240 min, the ERY removal efficiencies were 72.9%, 82.2%, 90.7%, 93.9%, and 94.5% at ZVI/PS molar ratio 0.5, 1, 2, 3 and 4, respectively. The surface adsorption effects of ZVI on the ERY removal would be negligible (data not shown). ZVI powder served as a source of Fe^{2+} (Eqs. (1), (2) and (3)) under both aerobic and anaerobic conditions through corrosion and direct reaction with PS.

The degradation of ERY by $\text{SO}_4^{\cdot-}$ was typically described as a second-order reaction:

$$\frac{d[\text{ERY}]}{dt} = -k[\text{ERY}][\text{SO}_4^{\cdot-}] \quad (5)$$

By assuming that $\text{SO}_4^{\cdot-}$ concentration was constant, the kinetics of degradation of ERY in water could be described according to the pseudo-first-order equation as given below:

$$[\text{ERY}]_t = [\text{ERY}]_0 \exp(-k_{\text{obs}}t) \quad (6)$$

Where reaction rate constant (k_{obs}) was the pseudo-first-order apparent rate constant (min^{-1}). The k_{obs} constants were obtained from the slopes of the straight lines by plotting $-\ln(C_t/C_0)$ as a function of time t , through regression. As shown in Table 1, the k_{obs} value increased with initial PS and ZVI dosage. Therefore, it could be deduced that ZVI provided surface sites for homogeneous and/or heterogeneous reaction which contribute to the decomposition of ERY.

3.2. Degradation of ERY in HSR system

The present used ZVI powder can barely initiate the catalytic decomposition of H_2O_2 and lead to an insignificant ERY removal

Fig. 1. (a) Effect of PS concentration on the degradation of ERY in SR system. Experimental conditions: $[\text{ZVI}] = 22.4 \text{ mg L}^{-1}$, $[\text{PS}] = 0.05 \text{ mM} - 0.4 \text{ mM}$; $[\text{ERY}]_0 = 1 \text{ mg L}^{-1}$; $T = 25 \pm 2^\circ\text{C}$; (b) Effect of ZVI dosage on the degradation of ERY in SR system. Experimental conditions: $[\text{PS}] = 0.1 \text{ mM}$, $n_{\text{ZVI}}/n_{\text{PS}} = 0.5, 1, 2, 3 \text{ and } 4$; $[\text{ERY}]_0 = 1 \text{ mg L}^{-1}$; $T = 25 \pm 2^\circ\text{C}$.

Table 1
Pseudo-first-order rate constant for oxidation of ERY in SR system.

[ZVI] ₀ (mg L ⁻¹)	[PS] ₀ (mM)	<i>k</i> _{obs} (min ⁻¹)	R ²
22.4	0.05	0.005	0.983
22.4	0.1	0.014	0.997
22.4	0.2	0.032	0.982
22.4	0.3	0.044	0.930
22.4	0.4	0.049	0.903
2.8	0.1	0.004	0.925
5.6	0.1	0.006	0.947
11.2	0.1	0.009	0.959
16.8	0.1	0.011	0.945
22.4	0.1	0.011	0.950

(<10%) under pH ≈ 6 within 240 min (data not shown). However, by adding a very small amount of PS, ERY degradation was extremely enhanced. Thus, the role of PS in removal of ERY by ZVI-H₂O₂ was investigated by adjusting the molar ratio of H₂O₂ and PS. The total dosage of oxidants (H₂O₂ and PS) was kept constant (0.1 mM), and the proportion of PS was 10%, 30%, 50%, 70% and 90%. The pseudo-first-order rate constants *k*_{obs} from ERY degradation curves are plotted in Fig. 2.

The ERY degradation efficiency was increased from 6.5% to 90.0% after 240 min of reaction by addition of 0.01 mM PS and 0.09 mM H₂O₂ (data not shown) instead of 0.1 mM H₂O₂ alone. The corresponding *k*_{obs} increased from 3 × 10⁻⁴ min⁻¹ to 9.7 × 10⁻³ min⁻¹ (Fig. 2), which was higher than that of using 0.05 mM PS alone as oxidant and close to 0.1 mM PS initiated ERY removal rate. When PS concentration rose from 0.01 mM to 0.07 mM, the ERY removal efficiency increased from 90.0% to 98.4%, and the corresponding *k*_{obs} increased from 9.7 × 10⁻³ min⁻¹ to 1.8 × 10⁻² min⁻¹, which was even higher than using 0.1 mM PS alone. While further increase of the PS proportion led to a worse ERY removal performance.

This phenomenon suggested that in addition to the SO₄^{•-}, HO₂ was also involved in the ERY degradation and showed a strong synergistic effect. The degradation rate was governed by two factors: the type of radicals and the generation rate of radicals. The reaction between ZVI and PS (Eq. (3)) supplied SO₄^{•-} and ferrous species, which will then account for the decomposition of H₂O₂ and generation of HO₂. Thus, increasing PS ratio can produce more ferrous

species and enhance the HO₂ generation rate. HO₂ exhibits higher universality and reaction rate than SO₄^{•-}, and increasing H₂O₂ ratio can provide precursor materials of HO₂ but may also slow down the generation of HO₂. Hence, holding the PS and H₂O₂ mole ratio in 7:3 achieved the optimum result. (Detailed discussion seen in Section 3.5.)

3.3. Effects of pH, inorganic ions and natural organic matter

3.3.1. Effect of initial pH

The ERY removal efficiencies with different initial pH and final pH in SR and HSR systems were shown in Fig. 3. The inherent pH of the ERY solutions (1 mg L⁻¹) was 5.8 ± 0.2. Here it is worthy to note that the ERY is unstable in acidic and extremely alkaline solutions [25]. So the experiments were carried out at pH levels in the range of 5–11 in which the structure of ERY was relatively stable.

As shown in Fig. 3, the ERY removal was more favorable under acidic and neutral condition than alkaline condition in both systems, similar as reported in previous studies for ZVI-PS reaction [26,27]. The ERY removal efficiency reached 97.6% for SR system and 94.8% for HSR system at pH₀ 5 (initial pH 5), and reduced to 87.2% for SR system and 42.4% for HSR system respectively at pH₀ 9. Apparently, the SR system showed a wider tolerance for initial pH increasing than HSR system. For the SR system, the pH dropped to around pH 4 for solution with pH₀ 5–9. However, for the HSR system, the solution pH changed mildly especially in the initial pH range of 5–7. The significant reduce of pH was mainly caused by the hydrolysis of SO₄^{•-}. In addition, the hydrolysis of iron ions will also cause pH decreasing. Therefore, the higher concentration of SO₄^{•-} in the SR system resulted in a more significant pH decline than in the HSR system. The corrosion of ZVI was accelerated at low pH, which was capable to produce SO₄^{•-} and HO₂. Hence higher removal efficiency occurred at lower initial pH.

3.3.2. Effect of inorganic ions

The effect of inorganic ions on ERY removal in the SR and HSR system was examined to further understand the reaction mechanisms and evaluate the performance under complex water matrix conditions (Fig. 4). Cl⁻, SO₄²⁻, HCO₃⁻, CO₃²⁻ are the most common anions in water and were chosen as probe ions. As shown in Fig. 4, SR and HSR were both sensitive to the inorganic ions. In particular, the Cl⁻ exhibited dual effects (favorable or adverse)

Fig. 2. The pseudo-first-order reaction rate constant (*k*_{obs}) under different ratios of H₂O₂ and PS. Experimental conditions: [ERY]₀ = 1 mg L⁻¹; [PS] + [H₂O₂] = 0.1 mM; [ZVI] = 22.4 mg L⁻¹; T = 25 ± 2 °C.

Fig. 3. ERY degradation efficiency in SR and HSR system under various initial pH (columns) and the final pH values after 240 min reaction (scatters). Experimental conditions: [ERY]₀ = 1 mg L⁻¹; [ZVI] = 22.4 mg L⁻¹; [PS]_{SR} = 0.1 mM; [PS]_{HSR} = 0.01 mM; [H₂O₂]_{HSR} = 0.09 mM; T = 25 ± 2 °C.

Fig. 4. The effect of co-existing inorganic ions on ERY degradation performance in (a) SR system and (b) HSR system. Experimental conditions: $[ERY]_0 = 1 \text{ mg L}^{-1}$; $[ZVI] = 22.4 \text{ mg L}^{-1}$; $T = 25 \pm 2^\circ \text{C}$.

distinctively on ERY degradation in SR and HSR systems. In SR system (Fig. 4a), under all levels of Cl^- concentration (0.1, 1 and 10 mM), the ERY degradation k_{obs} was much higher than that of without chlorine. At the highest concentration Cl^- (10 mM), the degradation seemed to be depressed but still better than that of without chlorine. While, in the HSR system, the Cl^- enhanced the ERY removal only at 0.1 mM but inhibited at 1 mM and 10 mM.

Two facts could contribute to these phenomena. Firstly, it has been reported that Cl^- can be oxidized by $SO_4^{\bullet-}$ and $HO\cdot$ to less reactive chlorine species (Eqs. (7)–(9)) and Cl^- would mostly act as $SO_4^{\bullet-}$ and $HO\cdot$ scavenger and reduce the degradation efficiency of ERY. Secondly, the chlorine radicals would also react with ERY, and reduce the concentration of ERY. Thus, if chlorine radicals participated in the degradation of ERY, their oxidation of organics may offset efficiency losses due to $SO_4^{\bullet-}$ and $HO\cdot$ scavenging. According to the experimental results, the scavenging of $SO_4^{\bullet-}$ and $HO\cdot$ played a dominant role at a high concentration of Cl^- . Meanwhile the adverse effect of Cl^- was more obvious in HSR system. As in Fig. 4b, the addition of high concentration of Cl^- (1 and 10 mM) inhibited the degradation of ERY. A possible explanation is that the reaction between $HO\cdot$ and Cl^- (Eq. (8); $k = 4.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) was easier to take place kinetically than $SO_4^{\bullet-}$ and Cl^- (Eq. (7); $k = 2.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) [28], implying that $HO\cdot$ play an important role in the HSR system.

The HCO_3^- and CO_3^{2-} showed a similar inhibitory effect on ERY degradation in both systems. This result was attributed to two factors: the competition with ERY for $SO_4^{\bullet-}$ and $HO\cdot$ (Eqs. (11)–(14)), and the precipitation with Fe^{2+}/Fe^{3+} which decrease the available dissolving Fe^{2+} for PS and H_2O_2 activation. While the SO_4^{2-} showed a negligible influence on ERY removal, only a light inhibition was observed under relatively high concentration.

3.3.3. Effect of natural organic matter

Humic acid was chosen to simulate the natural organic matter (NOM) in raw water. ERY, as a polar macrolide antimicrobial, its interaction with humic acid (HA) was mainly governed by hydrophobic interaction and hydrogen bonding [29]. HA showed significant inhibitory effect on ERY degradation and the experimental pseudo-first-order rate constants of ERY were decreased with increasing dosages of co-existing HA (Fig. 5). The size exclusion chromatography analysis showed that the molecular weight distribution of HA was slightly altered (Fig. S1). Therefore, HA acted as a radical scavenger and competed with organic pollutants which lower the degradation rates [30].

Moreover, the k_{obs} of ERY degradation in HSR system was decreased sharply at low dosages of HA, and showed a much faster decreasing speed than that of SR system. This difference can be explained by the reaction rate constant of NOM reacting with $HO\cdot$ and $SO_4^{\bullet-}$. The reaction rate constant between NOM and $HO\cdot$ ($3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) is over 10 times higher than that between NOM and $SO_4^{\bullet-}$ ($2.35 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$) [31]. Besides, the HA created a hydrophobic layer on the surface of ZVI inhibiting the corrosion of ZVI [32], and the HSR system was dependent on the amount

Fig. 5. The effect of humic acid on ERY degradation performance in SR and HSR system. Experimental conditions: $[ERY]_0 = 1 \text{ mg L}^{-1}$; $[ZVI] = 22.4 \text{ mg L}^{-1}$; $[HA] = 0\text{--}10 \text{ mg L}^{-1}$; $T = 25 \pm 2^\circ \text{C}$.

of available Fe(II) for H_2O_2 decomposing. These factors lead to a more significant decreasing in the pseudo-first-rate constant for HO $\cdot$ reaction than that for $\text{SO}_4^{\cdot-}$.

3.4. Identification of the reactive species

Radical scavengers, n-butyl alcohol (NBA) and *tert*-butyl alcohol (TBA), were used to identify the reactive species. NBA was considered as an active reactant with both radicals according to the reaction rate constants. However, the reaction of TBA with HO $\cdot$ was much rapid than with $\text{SO}_4^{\cdot-}$. The reaction rate constant of NBA with HO $\cdot$ is approximately 51 times higher than with $\text{SO}_4^{\cdot-}$. In contrast, the reaction rate constant of TBA with HO $\cdot$ is about 835 times higher than with $\text{SO}_4^{\cdot-}$ (Table 2). Literature information suggests that alcohols without α -hydrogen, such *tert*-butyl alcohol, are effective quenching agents for HO $\cdot$, but they react much slower with $\text{SO}_4^{\cdot-}$. On the basis of these properties, the experiments with NBA and TBA would have allowed us to identify the contribution of $\text{SO}_4^{\cdot-}$ and HO $\cdot$ in SR and HSR system [33,34].

A 500:1 M ratio of NBA (or TBA) and oxidants was added in the reaction solution in order to sufficiently quench the generated radicals. Fig. 6a and b illustrates the influence of radical scavengers on the degradation of ERY in both systems. For HSR system, the degradation of ERY was significantly and equivalently inhibited by the presence of NBA and TBA, reflecting that most of the reactive oxygen species reacted with NBA or TBA rather than ERY. However, for the SR system, NBA showed a serious inhibition on ERY degradation while TBA only showed a mildly inhabitation. This result clearly indicated that both $\text{SO}_4^{\cdot-}$ and HO $\cdot$ were major oxidizing species in the SR system, but HO $\cdot$ played a dominate role in the HSR system.

3.5. Possible mechanism of radical generation and ZVI powder characterization

To get a better understanding of the reaction mechanism, the residual H_2O_2 concentration was measured during the reaction. As can be seen in Fig. 7a and b, H_2O_2 was barely decomposed in the absence of PS and barely no DMPO-OH signal was detected. However, the decomposition was accelerated with the presence of PS and produced a strong DMPO-OH signal. The decomposition of H_2O_2 could be contributed to the Fenton reaction (Eqs. (15) and (16)) with both released Fe ions and surface-associated Fe sites that generated by the reaction between PS and ZVI.

To investigate the contribution of homogeneous reaction and heterogeneous reaction, the concentrations of dissolved ferrous ions and total Fe(II), namely the sum of surface-associate Fe sites and dissolved ferrous ions, were quantified by addition of phenanthroline into the filtrated supernatant or reaction solution directly (Fig. 8). It can be clearly observed that in the HSR system, the surface-associated Fe(II) ($\text{Fe}_{n-1}^0 - \text{Fe}^{\text{II}}$) accounted for the majority of total Fe(II) generated by ZVI powder in the present of PS. In the HSR system, the aqueous phase Fe(II) was very low (less than

Table 2
Rate constant between alcohol and radicals.

	Rate constant ($\text{M}^{-1} \text{S}^{-1}$)	
	With HO $\cdot$	With $\text{SO}_4^{\cdot-}$
n-Butyl alcohol	4.2×10^9	8.1×10^7
<i>tert</i> -Butyl alcohol	7.6×10^8	9.1×10^5

Fig. 6. The effect of TBA and NBA on ERY degradation performance in (a) SR system and (b) HSR system. Experimental conditions: $[\text{ERY}]_0 = 1 \text{ mg L}^{-1}$; $[\text{ZVI}] = 22.4 \text{ mg L}^{-1}$; $T = 25 \pm 2^\circ \text{C}$.

0.02 mg L^{-1}) and the contribution of homogeneous Fenton reaction was limited [35]. This phenomenon indicated that the H_2O_2 was not decomposed via homogeneous Fenton process but heterogeneous reaction (Eq. (16)), at least under the condition used in the present study. These findings consist with previous research which found that the surface-associated Fe(II) species on ZVI exposed in oxygenated water would participate in Fenton reaction [36]. In the absence of PS, surface-located Fe(II) wasn't detected either, implying that the generation of surface-located Fe(II) was mainly attributed to the reaction of ZVI with PS (Eq. (3)).

The solid ZVI powder was collected from PS, PS + H_2O_2 and H_2O_2 solutions after exposure. The surface morphology was measured by SEM (Fig. S2) and SEM-mapping (Fig. S3). The SEM picture showed that a kind of assemblages grew out of the ZVI powder and changed the surface roughness. The grade of corrosion was (from high to low): PS, PS + H_2O_2 , and H_2O_2 . And the elemental mapping revealed the matchable oxygen distribution (Figs. S3a–c) was clearly observed following $\text{PS} > \text{PS} + \text{H}_2\text{O}_2 > \text{H}_2\text{O}_2$, further confirming the important role of PS in Fe oxides layer generation. Fig. S4 shows the XPS spectrum of ZVI powder reacted with PS in a short time (named p-ZVI) and ZVI powder reacted with PS and H_2O after 4 h (named h-ZVI). The photoelectron peaks in the Fe 2p region at 711, 719, and 725 eV represent the binding energies of $2p_{3/2}$, shake-up satellite $2p_{3/2}$, and $2p_{1/2}$, respectively (Fig. S4a). These features indicated that the particle surface was enclosed with a layer of iron oxides containing Fe(III) and a small

Fig. 7. (a) The concentration of H_2O_2 along with reaction time in HR and HSR system. Experimental conditions: $[ERY]_0 = 1 \text{ mg L}^{-1}$; $[ZVI] = 22.4 \text{ mg L}^{-1}$; $[H_2O_2]_{\text{HSR}} = 90 \text{ }\mu\text{M}$; $[H_2O_2]_{\text{HR}} = 100 \text{ }\mu\text{M}$; $T = 25 \pm 2 \text{ }^\circ\text{C}$. (b) ESR spectra obtained from DMPO experiments in HR and HSR system. I: $[H_2O_2] = 2 \text{ mM}$, $[ZVI] = 0.45 \text{ g L}^{-1}$; II: $[H_2O_2] = 2 \text{ mM}$, $[p\text{-ZVI}] = 0.45 \text{ g L}^{-1}$; III: $[H_2O_2] = 1.8 \text{ mM}$, $[PS] = 0.2 \text{ mM}$, $[ZVI] = 0.45 \text{ g L}^{-1}$.

amount of $Fe(II)$. O 1 s survey scans were further conducted to delineate the surface oxygen states (Fig. S4b). The O 1 s region can be decomposed into three peaks around 530.5, 532, and 533.5 eV, corresponding to the O in O^{2-} , OH, and adsorbed water, respectively [37]. In reaction process, the ratio of OH to O^{2-} on the ZVI surface was approximately 1 and then O^{2-} increased with reaction time lasting, suggesting that the oxidized iron was likely in the state of $FeOOH$ first and changed to Fe_2O_3 [38]. The $FeOOH$ could also enhance the decomposition of H_2O_2 and generate $HO\cdot$ [36], and a $DMPO\text{-OH}$ signal was detected in the present of H_2O_2 and p-ZVI (Fig. 7b).

3.6. Investigation of byproducts

The major intermediate products were identified in the two systems and illustrated in Figs. 9 and S5. The results revealed that intermediates formed during ERY degradation in SR (Fig. S5a) and HSR (Fig. S5b) system were similar. The ERY is a 14-membered saturated organic compound divided into three parts: lactone ring, desosamine sugar and cladinose sugar. Erythromycin A (a) in aqueous solutions is likely to establish an equilibrium with erythromycin A 6,9-hemiketal (b), but it is difficult to separate the two peaks by the used HPLC method [39]. In acidic conditions, the erythromycin A 6,9-hemiketal (b) converts to hydroerythromycin

Fig. 8. The concentration of (a) dissolved $Fe(II)$ and (b) total $Fe(II)$. Experimental conditions: $[ERY]_0 = 1 \text{ mg L}^{-1}$; $[ZVI] = 22.4 \text{ mg L}^{-1}$; $T = 25 \pm 2 \text{ }^\circ\text{C}$.

A (d) easily through an internal dehydration reaction and on the other hand reversibly transfers to erythromycin A enol ether (c).

The ERY has one functional group with a lone valence electron pair on the tertiary amine. A possible generated mechanism of demethylation products (f) and (h) was the direct attack of $OH\cdot$ on tertiary amines as proposed by Lange et al. [40]. Similar products were also found in OH. oxidation by Luiz et al. [41]. The formation of (e) and (g) can be explained by the substitution reaction of methoxy group ($-OCH_3$) by the $OH\cdot$, which is consistent with Michael-Kordatou et al. [30]. Because of the high reaction rate and non-selective of $HO\cdot$ and $SO_4^{\cdot-}$, less low molecular weight degradation products can be observed in our examinations. The possible pathway for ERY degradation was sequentially losing of two sugar moieties on C-3 and C-5 and forming (i) and (j). A ring open product reported by Luiz et al. [41] in ozone oxidation was also found in the present work because of the unstable vicinal diol structure between C-11 and C-12.

4. Conclusions

A method of ZVI- H_2O_2 -PS oxidation system was carried out to remove ERY. A small amount of PS can significantly accelerate the decomposition of H_2O_2 as well as the degradation of ERY. Particular advantages of this process are the practical application value due to the use of air-stable ZVI materials rather than nano-ZVI and avoiding bringing unnecessary $SO_4^{\cdot-}$ into water. In the

Fig. 9. Major intermediate products and possible degradation pathway of ERY. Experimental conditions: $[ERY]_0 = 20 \text{ mg L}^{-1}$; $[ZVI] = 0.45 \text{ g L}^{-1}$; $T = 25 \pm 2^\circ \text{C}$.

HSR system, the corrosion of the metal iron generated in situ by PS give rise to a potent heterogeneous Fenton reaction. The H_2O_2 was decomposed through a heterogeneous reaction process by the surface-associate Fe(II) rather than a homogeneous process with dissolved Fe^{2+} . Faster degradations for both SR and HSR system were found in acidic condition. The Cl^- exhibited favorable effect at low concentration level but adverse effect at high concentration, while the HSR system was inhibited much more significantly than SR system by other co-existence of scavengers including bicarbonate and NOM. Scavenging tests suggested that $\text{HO}^\cdot$ played a dominate role in HSR system but also contributed in the SR system. Several intermediates were identified and a possible pathway of ERY degradation was proposed.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2016.12.126>.

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