Enhanced oxidation of erythromycin by persulfate activated iron powder–H$_2$O$_2$ system: Role of the surface Fe species and synergistic effect of hydroxyl and sulfate radicals

Meng Li$^{a,c}$, Xiaofang Yang$^{a,*}$, DongSheng Wang$^a$, Jin Yuan$^b$

$^a$Key Laboratory of Drinking Water Science and Technology, Research Centre for Eco-Environmental Sciences, Chinese Academy Sciences, 18#, Shuangqing Rd., Haidian District, Beijing 100085, China
$^b$Hangzhou Xiaoshan Environmental Investment Development Co., Ltd., 1068 Jincheng Rd., Xiaoshan District, Hangzhou 311200, China
$^c$University of Chinese Academy of Sciences, Beijing 100049, China

**Highlights**
- The peroxide-persulfate combined system activated by ZVI powder was investigated.
- Erythromycin removal was enhanced by adding persulfate into ZVI–H$_2$O$_2$ system.
- The Fe species generated by persulfate on ZVI surface triggered the HO\(_\cdot\) formation.
- The Cl$^-$ exhibited dual effects (favorable or adverse) on erythromycin removal.
- An degradation pathway of erythromycin was proposed in the oxidation system.

**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 H$_2$O$_2$ 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 HCO$_3^-$, CO$_3^{2-}$ and humic acid significantly inhibited ERY degradation. The results showed that with the persulfate/H$_2$O$_2$ 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 H$_2$O$_2$. Undetectable concentration of dissolve Fe$^{2+}$ suggested that the generation of HO\(_\cdot\) 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.

© 2017 Elsevier B.V. All rights reserved.

**1. Introduction**
Antibiotics have been widely used in clinical treatment and diseases prevention which could induce antibiotic resistance genes...
SO₄

which serve as a releasing source of Fe²⁺ through Eqs. (1) and (2) with PS. The generation of SO₄²⁻ from Fe₀ 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-H₂O₂ 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.

Zero valent iron (ZVI) is one of available heterogeneous catalysts, which serve as a releasing source of Fe²⁺ through Eqs. (1) and (2) under acid condition. The ZVI can also react with PS and H₂O₂ 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-H₂O₂ 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.

(ERG) 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 (HO·) and sulfate radicals (SO₄²⁻). The generation of SO₄²⁻ has been reported in numbers 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 H₂O₂ 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 H₂O₂ and PS, initial pH and aqueous matrices. Subsequently, the reactive species were identified, including the contribution of SO₄²⁻ and HO· radicals. To provide the insights into the interface mechanism between H₂O₂ and PS over ZVI, the surface structural transformation of ZVI was investigated as well as surface Fe(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, H₂O₂ (30%, w/w), PS, NaCl, NaHCO₃, NaCO₃, NaSO₄, H₂SO₄, ethanol (EtOH), Na₂EDTA, 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 m² g⁻¹. 150 U/mg horseradish peroxidase reagent (HRP), N,N-diethyl-p-phenylenediamine (DPD) and 2,2′-bipyridine for H₂O₂ determination were purchased from Sigma Aldrich and stored at 4 °C when not in use. Ultrapure water (Millipore, 18.2 MΩ) 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 used for its uncertain influence of low-intensity magnetic field [22]. The ERY solutions (1 mg L⁻¹) and different concentration of PS and H₂O₂ 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 H₂SO₄. 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 (14000 rpm and 10 min) was needed to separate precipitation of iron hydroxides before HPLC-MS analysis. The sampling procedure for dissolved Fe²⁺ and H₂O₂ 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 N₂-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.

In the H₂O₂ and PS combined system, the reaction rate between H₂O₂ and ZVI powder is slow, but ZVI powder exhibits fast reaction with PS. The generation of SO₄²⁻ and ferrous species between ZVI and PS may be used to trigger a fast HO· formation in the Fe(II)-H₂O₂ reaction and enhance the degradation performance of organic pollutants. However the role of PS and the H₂O₂ 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 μg/L concentration levels (22–350 μg L⁻¹) [16]. The occurrence of ERY in wastewater effluents [17,18] and surface water [19,20] has been reported in...
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 μL and run time was 3 min. The MS was operated in positive (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.

H₂O₂ 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 modified to minimize the interference of Fe(II) and Fe(III) [23,24]. 2,2′-Bipyridine and Na₂EDTA were added to eliminated influences of metal ions. DPD was oxidized by H₂O₂ in the presence of HRP and leaded to an absorbance at 551 nm and H₂O₂ concentration was spectrophotometrically determined. Electron spin-resonance spectroscopy (ESR) was used to identify HO·. Using 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as the spin trap. The DMPO-OH has a unique peak height ratio of 1:2:2:1, using 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as the spin trap. The DMPO-OH has a unique peak height ratio of 1:2:2:1.

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 SO₄²⁻ 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 Fe²⁺ (Eqs. (1), (2) and (3)) under both aerobic and anaerobic conditions through corrosion and direct reaction with PS.

The degradation of ERY by SO₄⁻ was typically described as a second-order reaction:

\[
\frac{d[ERY]}{dt} = -k_{erb}[SO_4^-]
\]

By assuming that SO₄⁻ concentration was constant, the kinetics of degradation of ERY in water could be described according to the pseudo-first-order equation as given below:

\[
[ERY]_t = [ERY]_0 \exp(-k_{erb}t)
\]

Where reaction rate constant \(k_{erb}\) was the pseudo-first-order apparent rate constant (min⁻¹). The \(k_{erb}\) constants were obtained from the slopes of the straight lines by plotting \(-\ln([C/Co])\) as a function of \(t\), through regression. As shown in Table 1, the \(k_{erb}\) 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 H₂O₂ and lead to an insignificant ERY removal.
(<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-H$_2$O$_2$ was investigated by adjusting the molar ratio of H$_2$O$_2$ and PS. The total dosage of oxidants (H$_2$O$_2$ 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 $k_{obs}$ (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 H$_2$O$_2$ (data not shown) instead of 0.1 mM H$_2$O$_2$ alone. The corresponding $k_{obs}$ increased from $3 \times 10^{-4}$ min$^{-1}$ to $9.7 \times 10^{-3}$ 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 1.8(C2)$_{10}$ 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 SO$_4^{2-}$, HO. 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 SO$_4^{2-}$ and ferrous species, which would then account for the decomposition of H$_2$O$_2$ and generation of HO$. Thus, increasing PS ratio can produce more ferrous species and enhance the HO. generation rate. HO. exhibits higher universality and reaction rate than SO$_4^{2-}$, and increasing H$_2$O$_2$ ratio can provide precursor materials of HO, but may also slow down the generation of HO$. Hence, holding the PS and H$_2$O$_2$ 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 pH$_{0.5}$ (initial pH 5), and reduced to 87.2% for SR system and 42.4% for HSR system respectively at pH$_{9}$. 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 pH$_{0.5}$ 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 SO$_4^{2-}$. In addition, the hydrolysis of iron ions will also cause pH decreasing. Therefore, the higher concentration of SO$_4^{2-}$ 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 SO$_4^{2-}$ and HO$. rapidly. 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$^-$, SO$_4^{2-}$, HCO$_3^-$, CO$_3^{2-}$ 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 H$_2$O$_2$ and PS. Experimental conditions: [ERY]$_0$ = 1 mg L$^{-1}$; [PS] = 0.1 mM; [ZVI] = 22.4 mg L$^{-1}$; T = 25 ± 2 °C.](image)

![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]$_{0.01}$ = 0.1 mM; [PS]$_{0.01}$ = 0.01 mM; [H$_2$O$_2$]$_{0.05}$ = 0.09 mM; T = 25 ± 2 °C.](image)

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

| [ZVI]$_0$ (mg L$^{-1}$) | [PS]$_0$ (mM) | $k_{obs}$ (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 |
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 SO4− and HO− to less reactive chlorine species (Eqs. (7)–(9)) and Cl− would mostly act as SO4− and HO− 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 SO4− and HO− scavenging. According to the experimental results, the scavenging of SO4− and HO− 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− and Cl− (Eq. (8); \( k = 4.3 \times 10^8 \text{M}^{-1} \text{s}^{-1} \)) was easier to take place kinetically than SO4− and Cl− (Eq. (7); \( k = 2.7 \times 10^8 \text{M}^{-1} \text{s}^{-1} \)) [28], implying that HO− play an important role in the HSR system.

\[
\text{SO}_4^{2-} + \text{Cl}^- \rightarrow \text{SO}_4^{2-} + \text{Cl}^- \quad (7)
\]

\[
\text{HO}^- + \text{H}_2\text{O} \rightarrow \text{HO}_2^- + \text{H}_2\text{O} \quad (8)
\]

\[
\text{Cl}_2 + \text{Cl}^- \rightarrow \text{Cl}_2^- \quad (9)
\]

\[
\text{Cl}_2^- + \text{H}_2\text{O} \rightarrow \text{Cl}^- + \text{H}_2\text{O} \quad (10)
\]

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− and SO4−. The reaction rate constant between NOM and HO− (3 \times 10^8 \text{M}^{-1} \text{s}^{-1}) is over 10 times higher than that between NOM and SO4− (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. 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 mg L⁻¹; [ZVI] = 22.4 mg L⁻¹; T = 25 ± 2 °C.](image)

![Fig. 5. The effect of humic acid on ERY degradation performance in SR and HSR system. Experimental conditions: [ERY]₀ = 1 mg L⁻¹; [ZVI] = 22.4 mg L⁻¹; [HA] = 0–10 mg L⁻¹; T = 25 ± 2 °C.](image)
of available Fe(II) for H₂O₂ decomposing. These factors lead to a more significant decreasing in the pseudo-first-rate constant for HO₂ reaction than that for SO₄⁻⁻.

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 HO₂ was much rapid than with SO₄⁻⁻. The reaction rate constant of NBA with HO₂ is approximately 51 times higher than with SO₄⁻⁻. In contrast, the reaction rate constant of TBA with HO₂ is about 835 times higher than with SO₄⁻⁻ (Table 2). Literature information suggests that alcohols without a-hydrogen, such tert-butyl alcohol, are effective quenching agents for HO₂, but they react much slower with SO₄⁻⁻. On the basis of these properties, the experiments with NBA and TBA would have allowed us to identify the contribution of SO₄⁻⁻ and HO₂ 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 SO₄⁻⁻ and HO₂ were major oxidizing species in the SR system, but HO₂ 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 H₂O₂ concentration was measured during the reaction. As can be seen in Fig. 7a and b, H₂O₂ 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 H₂O₂ could be contributed to the Fenton reaction (Eqs. (15) and (16)) with both released Fe ions and surface-associated Fe sites generated by the reaction between PS and ZVI.

\[
\text{H}_2\text{O}_2 + \text{Fe}^{3+} \rightarrow \text{OH}^- + \text{OH}^- + \text{Fe}^{3+}
\]  \hspace{1cm} (15)

\[
\text{H}_2\text{O}_2 + \text{Fe}^{0}_{\text{m}-1} - \text{Fe}^{3+} \rightarrow \text{OH}^- + \text{OH}^- + \text{Fe}^{0}_{\text{m}-1} - \text{Fe}^{3+}
\]  \hspace{1cm} (16)

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-assocate 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) (Fe^{0}_{\text{m}} - Fe^{3+}) 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 0.02 mg L⁻¹) and the contribution of homogeneous Fenton reaction was limited [35]. This phenomenon indicated that the H₂O₂ 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 + H₂O₂ and H₂O₂ 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 + H₂O₂, and H₂O₂. And the elemental mapping revealed the matchable oxygen distribution (Figs. S3a-c) was clearly observed following PS > PS + H₂O₂ > H₂O₂, 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 H₂O 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 2p₃/₂, shake-up satellite 2p₅/₂, and 2p₇/₂, respectively (Fig. S4a). These features indicated that the particle surface was enclosed with a layer of iron oxides containing Fe(III) and a small amount of available Fe(II) for H₂O₂ decomposing. These factors lead to a more significant decreasing in the pseudo-first-rate constant for HO₂ reaction than that for SO₄⁻⁻.

Table 2

| Alcohol          | Rate constant (M⁻¹S⁻¹) |
|------------------|------------------------|
|                  | With HO₂ | With SO₄⁻⁻ |
| n-Butyl alcohol  | 4.2 × 10⁹ | 8.1 × 10⁹ |
| tert-Butyl alcohol| 7.6 × 10⁹ | 9.1 × 10⁹ |

Fig. 6. The effect of TBA and NBA on ERY degradation performance in (a) SR system and (b) HSR system. Experimental conditions: [ERY]₀ = 1 mg L⁻¹; [ZVI] = 22.4 mg L⁻¹; T = 25 ± 2 °C.
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 2O3 [38]. The FeOOH
could also enhance the decomposition of H 2O2 and generate HO
[36], and a DMPO-OH signal was detected in the present of H 2O2
and p-ZVI (Fig. 7b).

3.6. Investigation of byproducts

The major intermediate products were identified in the two sys-
tems 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
erthyromycin A 6,9-hemiketal (b), but it is difficult to separate the
two peaks by the used HPLC method [39]. In acidic conditions, the
erthyromycin A 6,9-hemiketal (b) converts to hydroerythromycin
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
[35] on tertiary amines as proposed by Lange et al. [40]. Similar prod-
ucts were also found in OH [35] oxidation by Luiz et al. [41]. The forma-
tion of (e) and (g) can be explained by the substitution reaction of
methoxy group (–OCH 3) by the OH [35], which is consistent with
Michael-Kordatou et al. [30]. Because of the high reaction rate
and non-selective of HO [35] and SO 4 [35], 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 2O2-PS oxidation system was carried out to
remove ERY. A small amount of PS can significantly accelerate
the decomposition of H 2O2 as well as the degradation of ERY. Partic-
ular 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 into water. In the
HSR system, the corrosion of the metal iron generated in situ by PS give rise to a potent heterogeneous Fenton reaction. The $\text{H}_2\text{O}_2$ was decomposed through a heterogeneous reaction process by the surface-associate $\text{Fe(II)}$ rather than a homogeneous process with dissolved $\text{Fe}^{2+}$. Faster degradations for both SR and HSR system were found in acidic condition. The $\text{Cl}^-$ 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 HO$^-$ 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.

Acknowledgments

We thank the financial support from the National Natural Science Foundation of China (Grant No. 21577160, 51290282, and 51338010).

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.

References

[1] S.J. Harris, M. Cormican, E. Cummins, Antimicrobial residues and antimicrobial-resistant bacteria: impact on the microbial environment and risk to human health – a review, Hum. Ecol. Risk Assess. 18 (2012) 767–809.
[2] N. Yan, F. Liu, W. Huang, Interaction of oxidants in siderite catalyzed hydrogen peroxide and persulfate system using trichloroethylene as a target contaminant, Chem. Eng. J. 219 (2013) 149–154.
[3] J.M. Monteguido, A. Durán, J. Latorre, A.J. Expósito, Application of activated persulfate for removal of intermediates from antipyrine wastewater degradation refractory towards hydroxyl radical, J. Hazard. Mater. 306 (2015).
[4] A.M. Dietrich, G.A. Burlingame, Critical review and rethinking of USEPA secondary standards for maintaining organoleptic quality of drinking water, Environ. Sci. Technol. 49 (2015).
[5] D. Zhou, H. Zhang, L. Chen, Sulfur-replaced Fenton systems: can sulfite radical substitute hydroxyl radical for advanced oxidation technologies?, J. Chem. Technol. Biotechnol. 90 (2014) 775–779.
[6] C. Tan, N. Gao, Y. Deng, Y. Zhang, M. Sui, J. Deng, S. Zhou, Degradation of antipyrine by UV, UV/$\text{H}_2\text{O}_2$, and UV/PS, J. Hazard. Mater. 260C (2013) 1008–1016.
[7] K.F. Chen, C.M. Kao, L.C. Wu, R.Y. Surampalli, S.H. Liang, Methyl tert-butyl ether (MTBE) degradation by ferrous ion-activated persulfate oxidation: feasibility and kinetics studies, Water Environ. Res. A Res. Publ. Water Environ. Federat. 81 (2009) 687–694.
[8] G. Asgari, A. Seidmohammadi, A. Chavoshani, Pentachlorophenol removal from aqueous solutions by microwave/persulfate and microwave/$\text{H}_2\text{O}_2$: a comparative kinetic study, J. Environ. Health. Sci. Eng 12 (2014) 1–7.
[9] L. Xu, J. Wang, A heterogeneous Fenton-like system with nanoparticulate zero-valent iron for removal of 4-chloro-3-methyl phenol, J. Hazard. Mater. 186 (2011) 256–264.
[10] D.H. Bremner, A.E. Burgess, D. Houllemare, K.C. Namkung, Phenol degradation using hydroxyl radicals generated from zero-valent iron and hydrogen peroxide, Appl. Catal. B Environ. 63 (2006) 15–19.
[11] W. Wang, M. Zhou, Q. Mao, J. Yue, X. Wang, Novel NaY zeolite-supported nanoscale zero-valent iron as an efficient heterogeneous Fenton catalyst, Catal. Commun. 11 (2010) 937–941.
[12] K. Choi, W. Lee, Enhanced degradation of trichloroethylene in nano-scale zero-valent iron Fenton system with Cu(II), J. Hazard. Mater. 211–212 (2012) 146–153.
[13] C.H. Weng, V. Huang, Application of Fe 0 aggregate in ultrasound enhanced advanced Fenton process for decolorization of methylene blue, J. Ind. Eng. Chem. 28 (2015) 153–160.
[14] C.H. Weng, Y.T. Lin, N. Liu, H.Y. Yang, Enhancement of the advanced Fenton process by ultrasound for decolorisation of real textile wastewater, Color. Technol. 130 (2014) 133–139.
[15] C.H. Weng, K.L. Tsai, Ultrasound and heat enhanced persulfate oxidation activated with Fe(0) aggregate for the decolorization of C.I. Direct Red 23, Ultrasan. Sonochem. 29 (2016) 11–18.
[16] M. González-Pleiter, S. Gonzalo, I. Rodea-Palomares, F. Leganés, R. Rosal, K. Boltes, E. Marco, F. Fernández-Piñas, Toxicity of five antibiotics and their mixtures towards photosynthetic aquatic organisms: implications for environmental risk assessment, Water Res. 47 (2013) 2050–2064.
[17] D.K. Sang, J. Cho, I.S. Kim, B.J. Vanderford, S.A. Snyder, Occurrence and removal of pharmaceuticals and endocrine disrupting agents in South Korean surface, drinking, and waste waters, Water Res. 41 (2007) 1013–1021.
D.B. Luiz, A.K. Genena, E. Virmond, H.J. José, R.F. Moreira, W. Gebhardt, H.F. Y.H. Kim, T.M. Heinze, R. Beger, J.V. Pothuluri, C.E. Cerniglia, A. A kinetic study on D. He, J.X. Ma, R.N. Collins, T.D. Waite, Effect of structural transformation of G.D. Fang, D.D. Dionysiou, W. Yu, S.R. Al-Abed, D.M. Zhou, Sulfate radical-based S. Yuankui, G. Xiaohong, W. Jianmin, M. Xiaoguang, X. Chunhua, Z. Gongming, C. Wu, X. Huang, J.D. Witter, A.L. Spongberg, K. Wang, D. Wang, J. Liu, M.J. Hilton, K.V. Thomas, Determination of selected human pharmaceutical X. Wei, N. Gao, C. Li, Y. Deng, S. Zhou, L. Li, Zero-valent iron (ZVI) activation of B.M. Voelker, B. Sulzberger, Effects of fulvic acid on Fe(II) oxidation by I. Michael-Kordatou, M. Iacovou, Z. Frontistis, E. Hapeshi, D.D. Dionysiou, D. G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, Critical Review of rate /C0 H. Li, J. Wan, Y. Ma, M. Huang, W. Yan, Y. Chen, New insights into the role of Y. Wang, D. Zhou, Y. Wang, X. Zhu, S. Jin, Humic acid and metal ions accelerating the dechlorination of 4-chlorobiphenyl by nanoscale zero-valent iron, J. Environ. Sci. 23 (2011) 1286–1292. G.V. Buxton, C.L. Greenstock, W.F. Helman, A.B. Ross, Critical Review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (OH/OH) in Aqueous Solution, J. Phys. Chem. Ref. Data 17 (1988) 513–886. G.P.A. And, D.D. Dionysiou, Radical generation by the interaction of transition metals with common oxidants, Environ. Sci. Technol. 38 (2004) 3705–3712, X. Xue, K. Hanna, M. Abdelmoula, N. Deng, Adsorption and oxidation of PCP on the surface of magnetic: kinetic experiments and spectroscopic investigations, Appl. Catal. B Environ. 89 (2009) 432–440, D. He, J.X. Ma, R.N. Collins, T.D. Waite, Effect of structural transformation of nanoparticulate zero-valent iron on generation of reactive oxygen species, Environ. Sci. Technol. 3820–3828 (2016). H. Li, J. Wan, Y. Ma, M. Huang, W. Yan, Y. Chen, New insights into the role of zero-valent iron surface oxidation layers in persulfate oxidation of dibutyl phthalate solutions, Chem. Eng. J. 250 (2014) 137–147, X.L. And, W. Zhang, Iron nanoparticles: the core–shell structure and unique properties for Ni(II) sequestration, Langmuir 22 (2006) 4638–4642. S.Y. Liu, J.W. Zhu, A kinetic study on the degradation of erythromycin A in acetone solution with chemical technology, Adv. Mater. Res. 577 (2012) 73–76, F. Lange, S. Cornelissen, D. Kubac, M.M. Sein, J.V. Sonntag, C.B. Hannich, A. Golloch, H.J. Heipieper, M. Möder, C.V. Sonntag, Degradation of macrolide antibiotics by ozone: a mechanistic case study with clarithromycin, Chemosphere 65 (2006) 17–23, D.B. Luiz, A.K. Genena, E. Virmond, H.J. José, R.F. Moreira, W. Gebhardt, H.F. Schröder, Identification of degradation products of erythromycin A arising from ozone and advanced oxidation process treatment, Water Environ. Res. 82 (2010) 797–805, \[18\] E. Zuccato, C. Chiabrando, S. Castiglioni, D. Calamari, R. Bagnati, S. Schiarea, R. Fanelli, Cocaine in surface waters: a new evidence-based tool to monitor community drug abuse, Environ. Health 4 (2005) 1–7, \[19\] M.J. Hilton, K.V. Thomas, Determination of selected human pharmaceutical compounds in effluent and surface water samples by high-performance liquid chromatography-electrospray tandem mass spectrometry, J. Chromatogr. A 1015 (2003) 129–141, \[20\] C. Wu, X. Huang, J.D. Witter, A.L. Spongberg, K. Wang, D. Wang, J. Liu, Occurrence of pharmaceuticals and personal care products and associated environmental risks in the central and lower Yangtze river, China, Ecotoxicol. Environ. Safe 108C (2014) 19–26, \[21\] A. Gulkowska, H.W. Leung, M.K. So, S. Taniyasu, N. Yamashita, L.W.Y. Yeung, B. J. Richardson, A.P. Lei, J.P. Giery, P.K.S. Lam, Removal of antibiotics from wastewater by sewage treatment facilities in Hong Kong and Shenzhen, China, Water Res. 42 (2008) 395–403, \[22\] S. Yuankui, G. Xiaohong, W. Jianmin, M. Xiaoguang, X. Chunhua, Z. Gongming, Effect of weak magnetic field on arsenate and arsenite removal from water by zero-valent iron: an XAFS investigation, Environ. Sci. Technol. 48 (2014) 6850–6858, \[23\] B.M. Voelker, B. Sulzberger, Effects of fulvic acid on Fe(II) oxidation by hydrogen peroxide, Environ. Sci. Technol. 30 (1996) 1106–1114, \[24\] H. Bader, V. Sturzenegger, J. Hoigné, Photometric method for the determination of low concentrations of hydrogen peroxide by the peroxidase catalyzed oxidation of N,N-diethyl-p-phenylenediamine (DPD), Water Res. 22 (1988) 1109–1115, \[25\] Y.H. Kim, T.M. Heinze, R. Beger, J.V. Pothuluri, C.E. Cerniglia, A kinetic study on the degradation of erythromycin A in aqueous solution, Int. J. Pharm. 271 (2004) 63–76, \[26\] X. Wei, N. Gao, C. Li, Y. Deng, S. Zhou, L. Li, Zero-valent iron (ZVI) activation of persulfate (PS) for oxidation of bentazon in water, Chem. Eng. J. 285 (2015), \[27\] I. Hussain, Y. Zhang, S. Huang, X. Du, Degradation of p-chloroaniline under UV-C irradiation, Water Res. 85 (2015) 346–358, \[28\] I. Michael-Kordatou, M. Iacovou, Z. Frontistis, E. Hapeshi, D.D. Dionysiou, D. Fatta-Kassinos, Erythromycin oxidation and ERY-resistant Escherichia coli inactivation in urban wastewater by sulfate radical-based oxidation process under UV-C irradiation, Water Res. 83 (2015) 346–358, \[29\] P. Xie, J. Ma, L. Wei, Z. Jing, S. Yue, X. Li, M.R. Wiesner, J. Fang, Removal of 2-MIB and geosmin using UV/persulfate: Contributions of hydroxyl and sulfate radicals, Water Res. 69 (2015) 223–233, \[30\] Y. Wang, D. Zhou, Y. Wang, X. Zhu, S. Jin, Humic acid and metal ions accelerating the dechlorination of 4-chlorobiphenyl by nanoscale zero-valent iron, J. Environ. Sci. 23 (2011) 1286–1292, \[31\] G.V. Buxton, C.L. Greenstock, W.F. Helman, A.B. Ross, Critical Review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (OH/OH) in Aqueous Solution, J. Phys. Chem. Ref. Data 17 (1988) 513–886, \[32\] G.P.A. And, D.D. Dionysiou, Radical generation by the interaction of transition metals with common oxidants, Environ. Sci. Technol. 38 (2004) 3705–3712, \[33\] X. Xue, K. Hanna, M. Abdelmoula, N. Deng, Adsorption and oxidation of PCP on the surface of magnetic: kinetic experiments and spectroscopic investigations, Appl. Catal. B Environ. 89 (2009) 432–440, \[34\] D. He, J.X. Ma, R.N. Collins, T.D. Waite, Effect of structural transformation of nanoparticulate zero-valent iron on generation of reactive oxygen species, Environ. Sci. Technol. 3820–3828 (2016), \[35\] H. Li, J. Wan, Y. Ma, M. Huang, W. Yan, Y. Chen, New insights into the role of zero-valent iron surface oxidation layers in persulfate oxidation of dibutyl phthalate solutions, Chem. Eng. J. 250 (2014) 137–147, \[36\] X.L. And, W. Zhang, Iron nanoparticles: the core–shell structure and unique properties for Ni(II) sequestration, Langmuir 22 (2006) 4638–4642, \[37\] S.Y. Liu, J.W. Zhu, A kinetic study on the degradation of erythromycin A in acetone solution with chemical technology, Adv. Mater. Res. 577 (2012) 73–76, \[38\] F. Lange, S. Cornelissen, D. Kubac, M.M. Sein, J.V. Sonntag, C.B. Hannich, A. Golloch, H.J. Heipieper, M. Möder, C.V. Sonntag, Degradation of macrolide antibiotics by ozone: a mechanistic case study with clarithromycin, Chemosphere 65 (2006) 17–23, \[39\] D.B. Luiz, A.K. Genena, E. Virmond, H.J. José, R.F. Moreira, W. Gebhardt, H.F. Schröder, Identification of degradation products of erythromycin A arising from ozone and advanced oxidation process treatment, Water Environ. Res. 82 (2010) 797–805, \[40\] J. Richardson, A.P. Lei, J.P. Giesy, P.K.S. Lam, Removal of antibiotics from wastewater by sewage treatment facilities in Hong Kong and Shenzhen, China, Water Res. 22 (1988) 1109–1115, \[41\] M. Li et al. / Chemical Engineering Journal 317 (2017) 103–111.