Influence of chloride ions on organic contaminants decolorization through the Fe$^{0}$-activated persulfate oxidation process: efficiency and intermediates

Feng Ding, Yong Xie, Tengyan Wu and Na Liu

ABSTRACT

This study was conducted to evaluate the influence of chloride ions (Cl$^{-}$) on organic contaminants decolorization by the Fe$^{0}$-activated persulfate process (PS/Fe$^{0}$), as well as the generation of transformation products. Orange II (OII) was chosen as the target pollution. The results indicated that Cl$^{-}$/CO$^{2-}$ influenced the OII decolorization by PS/Fe$^{0}$ system, resulting in the generation of chlorine-containing by-products. OII containing Cl$^{-}$/CO$^{2-}$ solution can be efficiently decolorized by PS/Fe$^{0}$ process, and the decolorization efficiencies changed depending on Cl$^{-}$/CO$^{2-}$ concentration due to the reaction between Cl$^{-}$/CO$^{2-}$ and sulfate radicals (SO$_4$$^{2-}$). The operating cost for 94% color and 64% COD removal of the OII dye was estimated at 0.73 USD/m$^{3}$. The chlorine-containing by-products, such as chlorobenzene, 3,5-dichloro-benzene-1,2-diol, and 2,3-dichloro-2,3-dihydro-1,4-naphthoquinone, were generated during the reaction. The results further indicated that increasing both PS concentration and temperature enhanced OII decolorization and reduced the generation of chlorine-containing intermediates. The addition of ultrasound can further decrease the generation of chlorine-containing intermediates under high-temperature conditions. The proposed pathways of decolorization of OII containing Cl$^{-}$/CO$^{2-}$ also indicated that SO$_4$$^{2-}$ dominated the OII degradation, while the presence of Cl$^{-}$ led to the generation of chlorine-containing intermediates.

Key words | chloride ions, decolorization, intermediate products, organic contaminant, PS/Fe$^{0}$ process

INTRODUCTION

Currently, chemical oxidation methods, especially advanced oxidation processes (AOPs), provide an alternative way to degrade pollutants with high concentration and toxicity that cannot be treated by conventional biological treatment (Outsiou et al. 2017; Hussain et al. 2018; Liu et al. 2018a; Wu et al. 2018a, 2018b). As one of the AOPs, the persulfate (Na$_2$S$_2$O$_8$) activated by Fe$^{0}$ aggregates (PS/Fe$^{0}$) process has been widely used in treating recalcitrant organic pollutants and has received an increasing amount of attention in studies (Li et al. 2017; Rayaroth et al. 2017; Liu et al. 2018b). Compared with other methods, the PS/Fe$^{0}$ process has certain advantages with respect to the degradation and mineralization of refractory contaminants. PS was recently identified as a promising source of sulfate radicals due to its moderate cost, high stability, and aqueous solubility, in addition to the fact that it is a solid at ambient temperature, which facilitates its transport and storage (Choi et al. 2018; Lin et al. 2019). Sulfate radicals (SO$_4$$^{2-}$) can be generated during the PS/Fe$^{0}$ process (Equation (1)) by breaking the O-O bond of PS in which the bond length corresponds to 1.497 Å, and they have a strong oxidation potential (E$_{0}^{0}$ = 2.6 V), longer half-life, as well as higher reactivity over a relatively wide pH range (Hussain et al. 2017). In addition, as an electron donor in the PS/Fe$^{0}$ system, Fe$^{0}$ aggregates are relatively stable, easily separable, and reusable during the reaction, which also provides a longer-term supply of Fe$^{2+}$ for persulfate activation (Equations (2) and (3)) (Kambhu et al. 2017).

\[
\begin{align*}
\text{Fe}^{0} + \text{S}_2\text{O}_8^{2-} & \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} \quad (1) \\
\text{Fe}^{2+} + \text{S}_2\text{O}_8^{2-} & \rightarrow \text{Fe}^{3+} + \text{SO}_4^{2-} + \text{SO}_4^{2-} \quad (2) \\
\text{Fe}^{0} + \text{S}_2\text{O}_8^{2-} & \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} \quad (3)
\end{align*}
\]

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Key words | chloride ions, decolorization, intermediate products, organic contaminant, PS/Fe$^{0}$ process
Chloride ions (Cl\(^{-}\)) are widespread in the aqueous environment, and are also the common inorganic anions in industrial organic wastewater. NaCl is a type of inorganic salt that is usually used in the printing and dyeing process, and its presence can improve the dye uptake and evenness. Therefore, the chloride ions are usually present in industrial wastewater of printing and dyeing industries. When the persulfate, Fenton and Fenton-like oxidation processes were used to treat organic wastewater, the presence of chloride ions may have influenced the oxidation efficiency (Monteagudo et al. 2015; Sizykh & Batoeva 2016; Lin & Tsai 2019). From a thermodynamic point of view, the sulfate radical can oxidize chloride ions to activate chlorine radicals. Chloride ions may be involved in the PS decomposition reaction via sulfate radical-based pathways (Equations (4)–(9)).

\[
\begin{align*}
SO_4^{2-} + Cl^- & \rightarrow Cl^- + SO_2^- \\
Cl^- + Cl^- & \rightarrow Cl_2^- \\
Cl_2^- + H_2O & \rightarrow ClOH^- + H^+ + Cl^- \\
ClOH^- + H^+ & \rightarrow Cl^- + H_2O \\
ClOH^- + H_2O & \rightarrow OH^- + Cl^- \\
\end{align*}
\]

The influence of chloride ions on the decomposition of perfluorooctanoic acid (PFOA) by microwave-activated persulfate was studied by Lee et al. (2011). Cl\(^{-}\) was believed to be an efficient scavenger for SO\(_4^{2-}\) in PFOA oxidation, and the degradation rate of PFOA was thought to be significantly inhibited with an increase in the background chloride concentration under a higher temperature. Liao et al. (2001) investigated the hydroxyl radical scavenging role of chloride ions in the H\(_2\)O\(_2\)/UV process, and results revealed that when the Cl\(^{-}\) concentration was lower than 1,250 mM, the increase of chloride concentration led to a significant decrease in the OH\(^{-}\) concentration. However, the OH\(^{-}\) concentration remained virtually unchanged for Cl\(^{-}\) concentrations ≥1,250 mM. Lu et al. (2005) also examined the mechanism of chloride ions specifically affecting aniline oxidation by Fenton’s reagent. In that study, the Fenton reaction was found to be extremely sensitive to chloride ions that remained in solution. Low chloride ion concentrations influenced aniline oxidation, which could reportedly be overcome by extending the reaction time. High concentrations of chloride ion also inhibited the oxidation of aniline, and actually halted it due to the complexation of Fe-Cl. Yang et al. (2009) investigated the influence of high Cl\(^{-}\) concentrations (0.10 and 0.50 mol/L) on the decolorization of acid Orange 7 by microwave-activated persulfate oxidation, and found that the presence of Cl\(^{-}\) delayed the complete decolorization time for about 1–2 min.

Current studies are focused on the influence of Cl\(^{-}\) on the decolorization efficiency of organic compounds by PS oxidation methods and Fenton oxidation processes. However, very limited information is available on the decomposition of azo dyes containing chloride ions, especially using the PS/Fe\(^0\) process. Furthermore, the influence of chloride ions on the generation of intermediate products of organic contaminants decolorization by the PS/Fe\(^0\) process has not been reported.

In this study, the influence of chloride ions on the degradation efficiency and decomposition products of organic contaminants through the PS/Fe\(^0\) process was studied, and azo dye Orange II (OII) was selected as the target contaminant. Moreover, the degradation by-products of OII were examined under different conditions (chloride ions concentration, PS concentration, temperature, and ultrasonic addition). The UV-visible spectra, chemical oxygen demand (COD), American Dye Manufactures Institute (ADMI) value, and potential pathways were also investigated.

**MATERIALS AND METHODS**

**Materials**

Orange II (C\(_{18}\)H\(_{11}\)N\(_2\)NaO\(_4\)S, CAS No. 633-96-5) (Figure S1) was obtained from Sinopharm Chemical Reagent Co., Ltd (China). Fe\(^0\) aggregates were obtained from Connelly-GPM Inc. (USA) with particle size 0.297–2.380 nm and specific weight 2,240–2,560 kg/m\(^3\). Ethyl acetate and dichloromethane were chromatographically pure, and were purchased from Thermo Fisher Scientific (USA). Sodium persulfate (Na\(_2\)S\(_2\)O\(_8\)) and sodium chloride (NaCl) were purchased from Sinopharm Chemical Reagent Co., Ltd (China). All other reagents were analytical grade.

**Persulfate oxidation procedure**

Experiments were conducted at ambient temperature (25 ± 2 °C), except where stated otherwise; 1 L fresh dye solution was mixed with 1 \( \times \) 10\(^{-2}\) M sodium chloride. Unless otherwise stated, the experimental procedures were as follows: (1) 0.5 g/L Fe\(^0\) aggregates and 2 \( \times \) 10\(^{-3}\) M PS were added to solution at the start of the experiment. (2) The solution
was immediately agitated with a mechanical stirrer (Shin-Kwang, Taiwan) at 800 rpm for 30 min. (3) 10 mL of solution was taken from the reactor at predetermined times and filtered immediately through a 0.45-μm membrane filter (Tianjin Jinteng Experiment Equipment Co., Ltd, China). (4) The residual OII concentration and ADMI value in the filtrates were determined. (5) After 30 min, 200 mL reaction solution was extracted with ethyl acetate and dichloromethane; then the intermediate products were measured.

The influence of chloride ions concentration on OII decolorization was conducted by mixing 1 L fresh dye solution with 1 L methane; then the intermediate products were measured. (7) After 30 min, 200 mL reaction solution was extracted with ethyl acetate and dichloromethane; then the intermediate products were measured.

The influence of temperature on PS/Fe⁰ process decolorization was investigated under the initial temperature conditions at 10, 25, 40, and 55 °C using an electric stove, and the other operating parameters were OII 25 mg/L, Fe⁰ 0.5 g/L, PS 2 × 10⁻³ M, and sodium chloride 1 × 10⁻² M.

In experiments using PS coupled with ultrasound (US), dye solutions were sonicated using an ultrasonic generator (S-450A, Branson, USA) equipped with a titanium horn transducer. The sonication was administered in pulses (S-450A, Branson, USA) equipped with a titanium horn transducer. The sonication was administered in pulses (S-450A, Branson, USA) equipped with a titanium horn transducer. The sonication was administered in pulses (S-450A, Branson, USA) equipped with a titanium horn transducer.

### Analytical methods

The OII concentration was analyzed using a spectrophotometer (Hach DR/3900, USA) at 478 nm. COD was determined by the Hach 8000 reactor digestion method with the Hach spectrophotometer. This method was approved by the United States Environmental Protection Agency for wastewater analyses (Standard Method 5220D) (APHA et al. 2012).

The potential intermediate products of OII were identified using gas chromatography mass spectrometry (GC/MS) (Agilent 6890A/5973C) equipped with a capillary column (30.0 m × 250 μm × 0.25 μm, HP 19091s-433) and the following conditions were used: inlet temperature, 200 °C; injection volume, 1 μL; splitless; flow rate, 1 mL/min; carrier gas, He; the oven temperature program, 206 °C/min to 250 °C, hold for 2 min, 20 °C/min to 280 °C, hold for 20 min; ionization energy, 70 eV; ion source temperature, 230 °C; mass range, 35–350 amu in the full-scan acquisition mode. Each compound was identified by comparing mass spectra with NIST98 library data.

The tristimulus filter method from ADMI was used for true color analysis of the solution. The ADMI value was determined under three preset wavelengths (438, 540, and 590 nm). Decolorization efficiency (η) was calculated according to Equation (10):

\[
\eta (%) = \frac{(A_0 - A)}{A_0} \times 100%
\]

where \(A_0\) and \(A\) were the ADMI or OII concentration of the sample at time 0 and \(t\), respectively.

### RESULTS AND DISCUSSION

#### Effect of chloride ions concentration on the decolorization efficiency and intermediate products of OII by PS/Fe⁰ process

NaCl was chosen as the only source of chloride ions, and the influence of chloride ions concentration on the decolorization efficiency and intermediate products of OII in the PS/Fe⁰ process were evaluated (Figure 1 and Table 1). As shown in Figure 1, in the absence of chloride ions (0 M), OII was degraded gradually in the PS/Fe⁰ system, and the decolorization efficiency was 97% within 30 min. OII decolorization efficiencies changed with different chloride ions concentration present in solution. When the NaCl concentration was 5 × 10⁻³ M, the presence of chloride ions accelerated the OII decolorization. The decolorization efficiency was nearly unchanged when the NaCl concentration was 1 × 10⁻² M compared with 0 M. The presence of 5 × 10⁻² and 1 × 10⁻¹ M NaCl had significantly inhibited OII decolorization, and the decolorization efficiency was 92% and 91% within 30 min, respectively. The existence of chloride ions can affect the degradation of organic contaminants in the PS/Fe⁰ process. The presence of 5 × 10⁻³ M NaCl resulting in the acceleration of the OII decolorization can be explained by the modicum of chloride ions reacting with SO⁴²⁻ to generate Cl⁻ (Equation (4)). The reaction would consume a small part of SO⁴²⁻ and facilitate the radical-chain reactions (Equation (1)) leading to the additional formation of SO⁴²⁻ radicals. Therefore, the total number of free radicals increased, and the OII decolorization rate was accelerated (Khan & Adewuyi 2010).

The presence of 1 × 10⁻² M NaCl had no significant influence on the OII decolorization efficiency because the generation and consumption of SO⁴²⁻ by Cl⁻ can be
offset, whereas higher NaCl concentrations ($5 \times 10^{-2}$ and $1 \times 10^{-1}$ M) enhanced the possibility of Cl$^-$ participating in the direct reaction, and SO$_4^{2-}$ was consumed in large quantities by generating Cl$^-$. The oxidative activity of Cl$^-$ ($E^{0}$ = 2.4 V) was much less than SO$_4^{2-}$, which led to a decrease in the decolorization efficiency of OII. These

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**Figure 1** | Effect of NaCl concentration on the decolorization of OII by PS/Fe$^0$ process. Conditions: PS $2 \times 10^{-3}$ M, Fe$^0$ 0.5 g/L, natural pH, 25°C.

**Table 1** | By-products of OII under different NaCl concentration. Conditions: PS $2 \times 10^{-3}$ M, Fe$^0$ 0.5 g/L, natural pH, 25°C

<table>
<thead>
<tr>
<th>NaCl concentration</th>
<th>Intermediates</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 M</td>
<td>Crotonic acid, Naphthalene, Phthalic anhydride, 1,2-Benzene dicarboxylic acid</td>
</tr>
<tr>
<td>$1 \times 10^{-2}$ M</td>
<td>Acetic acid, Benzene, chloro-, Naphthalene, Phthalic anhydride, 1,2-Benzenedicarboxylic acid</td>
</tr>
<tr>
<td></td>
<td>4,5-Dichloro-benzene-1,2-diol, 1,2-Naphthalenedione, 1,2-Dihydroxynaphthalene</td>
</tr>
<tr>
<td></td>
<td>2-Nitro-1-naphthol, 1,4-Naphthalenedione, 2-chloro-3-hydroxy</td>
</tr>
</tbody>
</table>
results were similar to those in the study on the influence of chloride concentrations on the oxidation of methyl orange with persulfate activated by high-frequency ultrasound (Sizykh & Batoeva 2016).

SO₄²⁻ generated from the PS/Fe⁰ process will destroy the molecular structure of contaminants when the PS/Fe⁰ process is used to degrade contaminants. Thus, the pollutants can be degraded and removed. The presence of Cl⁻ can react with SO₄²⁻, generating Cl₂, which displays reactive activity and may participate in the pollutant’s oxidative degradation. Therefore, the degradation products of contaminants might contain chlorinated intermediates (Yuan et al. 2011; Liu et al. 2016). The influence of Cl⁻ on the OII intermediate products in the PS/Fe⁰ process was identified through GC/MS analysis (Table 1). When the concentration of NaCl was 0 M, four OII by-products were identified, and no chlorine-containing intermediates were generated. When NaCl (1×10⁻² M) was added to the OII solution, the chlorine-containing by-products such as chlorobenzene, 3,5-dichloro-benzene-1,2-diol, chloranilic acid, and 2,3-dichloro-2,3-dihydro-1,4-naphthoquinone were generated. Results indicated that Cl⁻ radicals participated in OII degradation and led to the production of chlorine-containing intermediates. The toxicity of chlorine-containing by-products was much higher than other intermediate products; thus, the production of chlorine-containing intermediates must be reduced.

**Effect of PS concentration on the decolorization and by-products of OII**

As the only source of SO₄²⁻, the concentration of persulfate was the decisive factor in the OII degradation efficiency. The influence of different PS concentrations on the degradation efficiency and intermediate products of OII was studied in this experiment. The other operating parameters remained unchanged (Fe⁰ 0.5 g/L, 25 °C, and NaCl 1×10⁻² M), and the results are shown in Figure 2 and Table S1. The decolorization efficiency of OII containing 1×10⁻² M NaCl was 58% within 30 min with 5×10⁻⁴ M persulfate. Increasing the PS concentration led to the enhancement of OII decolorization efficiency. When the persulfate concentration was 1×10⁻³ M, the decolorization efficiency reached 92% in the same period of time, whereas it took just 20 min to reach 92% decolorization efficiency by increasing the PS concentration to 2×10⁻³ M. OII decolorization efficiency of 99% was achieved in the presence of 5×10⁻³ M persulfate within 30 min. When the PS concentration was increased to 1×10⁻² M, virtually 100% decolorization efficiency was achieved. However,
this additional increase was insignificant when compared with $5 \times 10^{-3}$ M persulfate. This phenomenon was due to excess PS concentration leading to the reaction between $S_2O_8^{2-}$ and $SO_4^{2-}$, which would consume a part of $SO_4^{2-}$ via the following reactions (Wang et al. 2014):

$$S_2O_8^{2-} + SO_4^{2-} \rightarrow S_2O_8^{2-} + 2SO_4^{2-} \quad (11)$$

$$SO_4^{2-} + SO_4^{2-} \rightarrow S_2O_8^{2-} \quad (12)$$

The degradation by-products of OII associated with different PS concentrations were also studied, and the results are shown in Table S1. When the PS concentration was $5 \times 10^{-4}$ M (low PS concentration), a small quantity of $SO_4^{2-}$ radicals was generated, and was used to degrade OII. Thus, the production of chlorine radicals generated from the PS and Cl$^-$ reaction was also relatively small, and the amount of chlorine-containing by-products in the solution was also relatively lower. When the PS concentration was increased to $5 \times 10^{-3}$ and $1 \times 10^{-2}$ M, some small molecular intermediates, such as propanoic acid and dichloroacetic acid, were detected by GC/MS in solution. OII was degraded more completely than for low PS concentration. Therefore, the PS/Fe$^0$ process can decolorize OII effectively, and increased PS concentrations can efficiently degrade chlorine-containing intermediate products.

### Influence of temperature on OII decolorization and intermediate products

The dyeing and printing processes are often operated at high temperature to ensure the dye uptake and certain dyeing effects. As such, dyeing and printing effluents are often produced at relatively high temperatures. Temperature is also an important factor for the practical application of the PS/Fe$^0$ process. Studies have shown that high temperatures could enhance the degradation efficiency of contaminants treated by Fenton and Fenton-like methods (Soares et al. 2013; Weng & Tsai 2016). In this study, the experiments were conducted with different temperatures (10, 25, 40, and 55°C) to investigate the influence of temperature on the decolorization efficiency and intermediate products of OII containing NaCl in the PS/Fe$^0$ system. Results are presented in Figure 3 and Table S2. An increase in temperature favored the decolorization of OII containing chloride ions in the PS/Fe$^0$ process. The decolorization efficiency of OII containing Cl$^-$ was 91% within 30 min when the temperature was 10°C. The decolorization efficiency enhanced with temperature increasing. When the temperature was 40°C, only 7.5 min was needed to achieve 91% decolorization efficiency, and 98% decolorization efficiency of OII can be reached within 30 min. Increasing the temperature to
55 °C, OII decolorization efficiency was further improved: almost 100% decolorization efficiency was achieved within 30 min.

Since the content of chloride ions in solution was known, the influence of Cl− on the OII degradation was uniform at different temperature. However, heat can also catalyze PS to generate SO4− radicals, so the quantity of SO4− radicals was significantly higher at 55 °C than 10 °C. Therefore, the decolorization efficiency of OII containing chloride ions in the PS/Fe0 process at high temperature was also much better than the efficiency at low temperatures.

Temperature would also have an influence on the degradation by-products of OII because it affects SO4− radicals generation. As shown in Table S2, the number of small molecular intermediates increased gradually with increasing temperature. High temperatures can catalyze persulfate to produce much more SO4− based on the persulfate activated by Fe0, which can also be used to degrade OII intermediates and the chlorine-containing intermediate products. Therefore, high temperatures can not only improve the degradation efficiency of OII containing chloride ions in the PS/Fe0 process, but also reduce the generation of chlorine-containing intermediate products in solution.

**Effect of ultrasound on decolorization efficiency and by-products under different temperature**

US irradiation with a power density of 120 W/L was applied to the solution at 25 and 55 °C, respectively, to investigate the influence of ultrasound on the decolorization of OII by the PS/Fe0 process. As shown in Figure 4, the decolorization efficiency of the PS/Fe0/US system was higher than that of the PS/Fe0 system at 25 °C when 5 min of US irradiance was applied. Decolorization efficiency was 94% within 30 min in the PS/Fe0 system, while the PS/Fe0/US system achieved 96% decolorization efficiency in the same treatment period. When the temperature of the reaction system was 55 °C, the degradations of OII by PS/Fe0 and PS/Fe0/US system were both 99% within 30 min.

The PS/Fe0 process can effectively degrade OII mainly because Fe0 can catalyze PS to produce sulfate radicals. Ultrasound can also catalyze PS to generate SO4− after applying ultrasound in the PS/Fe0 process. The cavitation effect would be produced during the ultrasound reaction, which resulted in the enhancement of mass transport of the reactants and products between the liquid phase and the catalyst surface. In addition, the production and collapse of the cavitation bubble produced by ultrasound would have a cleaning effect on the Fe0 surface such that the passivation films on the Fe0 surface would be removed and destroyed. Thus, more Fe0 could be used to catalyze PS to produce sulfate radicals. These effects can explain why the decolorization rate increased with the addition of ultrasound. High temperature (55 °C) improved OII degradation compared with 25 °C, which indicated that the acceleration of OII degradation by ultrasound was not obvious at high temperatures.

In this part of the experiment, the intermediate products of OII by the PS/Fe0 and PS/Fe0/US processes under 25 and 55 °C were analyzed, respectively. Results are shown in Table S3. The presence of chloride ions eventually led to the generation of chlorine-containing by-products. Increasing the temperature not only speeded up the reaction rate, but also reduced the production of chlorine-containing intermediates. The addition of US also accelerated the by-products degradation. When US was used in combination with the PS/Fe0 system at 25 °C, p-benzoquinone, 1,4-benzenediol and parachlorophenol were detected by GC/MS, which can be degraded by chlorobenzene and 3,5-dichlorobenzene-1,2-diol. When US was added to the solution at 55 °C, it was also revealed that US can accelerate the degradation of intermediate products. In addition, there were fewer types of chlorine-containing intermediate products generated by the PS/Fe0/US system compared with the PS/Fe0 process. Results indicated that US had a certain influence on the degradation of the chlorine-containing intermediate products.
Decolorization mechanisms of OII decolorizing by PS/Fe⁰ system

To relate the changes in chemical structure of OII and color depletion during PS/Fe⁰ treatment, UV-vis spectra, ADMI, and COD were measured as a function of reaction time. A concentration of $1 \times 10^{-2}$ M NaCl was chosen as representative to investigate the influence of chloride ions on UV-vis spectroscopic characteristics and mineralization of OII (Figure 5). The spectrum of OII was characterized by one main band in the visible region with an absorbance peak at approximately 478 nm, which was associated with the chromosphere-containing azo linkage of the OII molecule. Two other bands in the ultraviolet region with absorbance peaks at 310 nm and 265 nm were also characterized, and the peaks were related to the naphthalene nucleus and benzene rings bonding to the $\equiv N \equiv N \equiv$ groups, respectively. Results showed that the characteristic peak at 478 nm decreased gradually after the reaction and was reduced to its minimum after 15 min. The conjugate structure of OII was destroyed by SO₄⁻ and the color disappeared rapidly. The absorbance peak at 265 nm increased during the initial 15 min, the intermediate products containing benzene rings were generated and the OII molecular structure was destroyed. After 15 min, the peak at 265 nm decreased as the reaction proceeded, which illustrated the intermediate products containing benzene rings can also be degraded by the PS/Fe⁰ process.

The inset graph in Figure 5 shows that the OII solution containing NaCl can be decolorized effectively by the PS/Fe⁰ system, and the ADMI value of OII was decreased from 9,115 to 520 (94%) within 30 min. The COD of OII solution containing NaCl decreased from 22 to 8 mg/L, which indicated that the PS/Fe⁰ process could destroy the OII molecular structure and mineralize the OII solution efficiently. The photo in Figure 5 demonstrates that the color of solution changed from orange to primrose yellow after 15 min of treatment, and then gradually became transparent. The color change indicated that the PS/Fe⁰ process could decolorize the OII solution containing chloride ions efficiently.

Degradation products and proposed pathways

Twenty-nine intermediates, including 1,2-naphthalenedione, 1,2-dihydroxynaphthalene, 1-nitro-2-naphthol, 5-amino-2-naphthalenol, phthalic anhydride, naphthalene, 1,2-benzenedicarboxylic, p-benzoquinone, 1,4-naphthalenedione, 1,6-dihydroxynaphthalene, propandioic acid, propanoic acid, crotonic acid, acetic acid, chloro-benzene, 1,2,3,4-tetrachloro-benzene, parachlorophenol, 4,6-dichloro-1,3-benzenediol, 3,5-dichloro-benzene-1,2-diol, 3,4-dichloro-benzene-1,2-diol, 4,5-dichloro-benzene-1,2-diol, 2-chloro-2-methylindan-1,3-dione, 3,4-dichloroisocoumarin, chloranilic acid, 2,3-dichloro-2,3-dihydro-1,4-naphthoquinone, dichloro-acetic acid, 2-chloro-3-hydroxy-1,4-naphthalenedione, and 4-chloro-1,2-benzenedicarboxylic acid, were identified through GC/MS analysis. The generation of powerful SO₄⁻ radicals is essential and plays an
important role in Fe\(^0\)-activated persulfate oxidative systems. SO\(_4\)\(^{-}\) radicals are electrophilic, and preferably remove electrons from an organic molecule. Thus, based on our major intermediates, a substitution reaction mechanism is proposed for the PS/Fe\(^0\) system. A tentative pathway for the degradation of OII containing NaCl during the treatment of PS/Fe\(^0\) is proposed (Figure 6). When the PS/Fe\(^0\) system degraded OII, SO\(_4\)\(^{-}\) radicals were added to the \(\sim N = N\sim\) structure of OII. With the help of SO\(_4\)\(^{-}\) radicals, the \(\sim N = N\sim\) structure was potentially cleaved to form sodium p-aminobenzenesulfonate (S2) and 1-naphthalenamine (S3). Compound S2 could be oxidized by SO\(_4\)\(^{-}\) radicals to form S4 (phenol) and S5 (o-aminophenol), which could be further oxidized by SO\(_4\)\(^{-}\) to form S8 (pyrocatechol) and D6 (1,4-benzenediol). Then, S8 and D6 were further oxidized to form p-benzoquinone. Thereafter, the benzene ring was cleaved to form maleic acid and finally formed carboxylic acids, such as propanedioic acid, crotonic acid, propanoic acid, acetic acid, CO\(_2\), and H\(_2\)O.

Under the presence of SO\(_4\)\(^{-}\), state S3 was then transformed into compounds S6, S7, D1, and D2. A small quantity of naphthalene (D1) was identified by GC/MS analysis. However, naphthalene can be further degraded by PS/Fe\(^0\) system because SO\(_4\)\(^{-}\) radicals are electrophilic radicals which attack the naphthalene ring (Weng et al. 2015). S6, S7, and D2 can be further oxidized to D3, D4, and D5, which would then be transformed into compounds S9, S10, and D7. D9 (phthalic anhydride) and D10 (2-hydroxy-1,4-naphthalenedione) were generated under the presence of SO\(_4\)\(^{-}\) radicals oxidation. D10 could also be oxidized to transformed D9, which was further oxidized to D11 (1,2-benzenedicarboxylic) by SO\(_4\)\(^{-}\) radical oxidation. Then, the benzene ring in 1,2-benzenedicarboxylic was cleaved to form maleic acid (D8), and finally carboxylic acids, CO\(_2\), and H\(_2\)O were formed.

In the presence of chloride ions, the chlorine radicals such as Cl\(^-\), Cl\(_2\)\(^-\), and ClOH\(^-\) were generated by the reaction between SO\(_4\)\(^-\) radical and Cl\(^-\) ion. These chlorine radicals are generally less reactive than SO\(_4\)\(^-\) radical, leading to slower degradation of OII dye. Cl\(^-\)/Cl\(_2\)\(^-\) may react with dye and its intermediates by one-electron oxidation, H-abstraction, and addition to unsaturated C-C bonds (Grebel et al. 2015), and result in the production of chlorine-containing intermediates. Compound S2 could be oxidized by Cl\(^-\)/Cl\(_2\)\(^-\) radical to form chloro-benzene (D16) and 1,2,3,4-tetrachloro-benzene (D17). Parachlorophenol (D18) can also be produced from S4 and S5 under the presence of Cl\(^-\) radical. S8 and D6 can also be oxidized to D20, D21, D22, and D23 by Cl\(^-\) radicals, and the D26 (chloranilic acid) generation can also occur in solution in the presence of Cl\(^-\)/Cl\(_2\)\(^-\) radicals and D8 (p-benzoquinone). For compound S3, Cl\(^-\)/Cl\(_2\)\(^-\) radicals can also oxidize the by-products to generate chlorine-containing intermediates. D19 (2,3-dichloro-2,3-dihydro-1,4-naphthoquinone) was identified by GC/MS, and was generated from D3, D4, or D5. Then, the other chlorine-containing intermediates, such as D24, D25, D27, and D28, were formed in OII solution in the

![Figure 6](https://iwaponline.com/wst/article-pdf/doi/10.2166/wst.2019.303/603911/wst2019303.pdf)
presence of Cl/Cl\textsuperscript{−} radicals. Finally, OII was oxidized to carboxylic acids, CO\textsubscript{2}, and H\textsubscript{2}O, and the chlorine-containing by-products were also degraded to organic acids, such as D\textsubscript{29} (dichloro-acetic acid), CO\textsubscript{2}, and H\textsubscript{2}O. The products and proposed pathways of OII containing NaCl indicated that SO\textsubscript{4}\textsuperscript{−} radicals were the primary oxidizing species in the OII degradation process, and may react with the dye molecule via addition to the aromatic ring followed by hydrolysis. In contrast, Cl\textsuperscript{−} ions would have influence on the generation of the OII intermediates by forming chlorine radicals, which just took effect on the intermediates by one-electron oxidation, H-abstraction and addition to unsaturated C-C bonds. Results also indicated that the oxidizability of SO\textsubscript{4}\textsuperscript{−} radicals was much higher than that of chlorine radicals.

**Preliminary cost analysis of PS/Fe\textsuperscript{0}**

The consumption of chemicals are the major concern in the PS/Fe\textsuperscript{0} process practical application; therefore, an evaluation of the operating cost of the PS/Fe\textsuperscript{0} process is essential. Using a price of 500 USD/ton for Fe\textsuperscript{0}, the cost for 0.5 g/L Fe\textsuperscript{0} aggregates is 0.25 USD/m\textsuperscript{3}. The cost of 2 × 10\textsuperscript{−3} M Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8} is 0.48 USD/m\textsuperscript{3} on the basis of 1,000 USD/ton for Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8}. Therefore, the total operating cost of this process with 94% color and 64% COD removal for OII within 30 min is estimated to be 0.73 USD/m\textsuperscript{3}.

Table 2 presents a comparison of treatment performances and operating cost between AOPs commonly used for the treatment of dyeing and printing wastewaters. Chemicals and electricity constitute the majority costs of the AOPs. In the PS/Fe\textsuperscript{0}/US process, the addition of ultrasound can effectively enhance both color and COD degradation of synthetic wastewater, but the operating cost is also relatively higher. Although the use of photo-Fenton processes in both synthetic and real textile wastewater can obtain satisfactory color degradation, the processes have low COD removal efficiency and require long treatment duration. The operating costs for photo-Fenton, Fenton, and electro-Fenton processes range between 3.85 and 22.3 USD/m\textsuperscript{3}. Costs for processes such as PMS/ZVI (peroxymonosulfate/zero-valent iron) and H\textsubscript{2}O\textsubscript{2}/ZVI are even higher due to the use of high-priced catalysts or excessive energy consumptions. In this respect, PS/Fe\textsuperscript{0} stands out as a low cost decolorization process that is highly effective in removing color and COD from dyeing and printing wastewaters containing chloride ions.

**CONCLUSIONS**

The presence of chloride ions would have influence on the decolorization efficiency of OII, and lead to the generation of chloride-containing intermediates. Enhancing PS concentrations and temperature can not only accelerate the decolorization efficiency of OII, but also reduce the amount of chloride-containing intermediates. The addition

<table>
<thead>
<tr>
<th>Process</th>
<th>Sample</th>
<th>Initial concentration</th>
<th>Removal efficiency (time)</th>
<th>Cost (USD/m\textsuperscript{3})</th>
<th>Cost accounting</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS/Fe\textsuperscript{0}</td>
<td>Synthetic wastewater</td>
<td>25 mg/L OII, ADMI 9113</td>
<td>94% color, 64% COD (30 min)</td>
<td>0.73</td>
<td>Chemicals</td>
<td>This study</td>
</tr>
<tr>
<td>PS/Fe\textsuperscript{0}/US</td>
<td>Synthetic wastewater</td>
<td>25 mg/LSRF3B, ADMI 8046</td>
<td>100% color, 100% COD (10 min)</td>
<td>2.79</td>
<td>Energy and chemicals</td>
<td>Liu et al. (2016)</td>
</tr>
<tr>
<td>PMS/ZVI</td>
<td>Textile wastewater</td>
<td>ADMI 3080, COD 1,550 mg/L</td>
<td>100% color, 100% COD (150 min)</td>
<td>1,340</td>
<td>Chemicals</td>
<td>Ghanbari et al. (2014)</td>
</tr>
<tr>
<td>Photo-Fenton (solar)</td>
<td>Synthetic wastewater</td>
<td>Cotton: COD 350 mg/L</td>
<td>98-99% color, 30.1% COD (2 hr)</td>
<td>3.85</td>
<td>Chemicals</td>
<td>Módenes et al. (2012)</td>
</tr>
<tr>
<td>H\textsubscript{2}O\textsubscript{2}/ZVI</td>
<td>Textile wastewater</td>
<td>ADMI 3080, COD 1,550 mg/L</td>
<td>100% color 100%, COD (150 min)</td>
<td>280</td>
<td>Chemicals</td>
<td>Ghanbari et al. (2014)</td>
</tr>
<tr>
<td>Photo-Fenton (solar)</td>
<td>Synthetic wastewater</td>
<td>Acrylic: COD 517.9 mg/L</td>
<td>98-99% color, 72% COD (2 hr)</td>
<td>6.38</td>
<td>Chemicals</td>
<td>Módenes et al. (2012)</td>
</tr>
<tr>
<td>Fenton (H\textsubscript{2}O\textsubscript{2}/Fe\textsuperscript{2+})</td>
<td>Textile wastewater</td>
<td>ADMI 1080</td>
<td>52.3% color (1 hr)</td>
<td>7.93</td>
<td>Chemicals</td>
<td>Eslami et al. (2015)</td>
</tr>
<tr>
<td>Electro-Fenton</td>
<td>Textile wastewater</td>
<td>ADMI 1080</td>
<td>72.9% color (1 hr)</td>
<td>22.32</td>
<td>Energy and chemicals</td>
<td>Eslami et al. (2015)</td>
</tr>
</tbody>
</table>
of ultrasound can reduce the generation of chlorine-containing intermediates on the basis of high temperature, so as to make OII degrade more thoroughly. Degradation products and proposed pathways demonstrated that SO₄²⁻ radicals were the primary oxidizing species in the OII degradation, while the presence of chloride ions would result in the production of chlorine-containing intermediates. The increase of PS concentration and temperature and the addition of ultrasound can reduce the generation of chlorine-containing organics effectively, while improving treatment efficiency. The operating costs of PS/Fe⁰ system were relative low comparing with other processes, whereas the efficiency is greatly higher. The findings demonstrate that PS/Fe⁰ is a viable technology for the removal of OII dye from chloride-containing wastewaters.

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REFERENCES


Kambhu, A., Goren, M., Tang, W., Comfort, S. & Harris, C. E. 2017 Remediating 1,4-dioxane-contaminated water with slow-release persulfate and zerovalent iron. Chemosphere 175, 170–177.


