



Degradation of Acid Orange 7 in aqueous solution by a novel electro/Fe²⁺/peroxydisulfate process

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ABSTRACT

A novel process in which electrochemistry (EC) was coupled with ferrous ion activation of peroxydisulfate (Fe²⁺/S₂O₈²⁻) was proposed for the decolorization of Acid Orange 7. In this process, the reaction between peroxydisulfate and externally added ferrous ion results in the production of sulfate free radical as well as ferric ion, and at the same time ferrous ion could be electro-regenerated at the cathode by the reduction of ferric ion. Color removal by the Fe²⁺/S₂O₈²⁻ process was significantly enhanced in the presence of applied current. The effects of some important reaction parameters such as initial pH, current density, S₂O₈²⁻ concentration and Fe²⁺ concentration on the decolorization of Acid Orange 7 by EC/Fe²⁺/S₂O₈²⁻ process were investigated. The results showed that the decolorization efficiency was not significantly affected by the initial pH value, and the decolorization efficiency increased with the increase of S₂O₈²⁻ concentration and Fe²⁺ concentration. The current densities had little effect on the decolorization of Acid Orange 7 at the beginning of the reaction, while it improved the decolorization efficiency after 60 min reaction. The GC–MS analysis was employed to identify the intermediate products and a plausible degradation pathway is proposed. The chemical oxygen demand (COD) removal efficiency was 57.6% after 60 min reaction and it reached 90.2% when the reaction time was extended to 600 min. Toxicity test with *Daphnia magna* showed that the acute toxicity of the solution increased during the first stage of the reaction, and then gradually decreased with the progress of the oxidation.

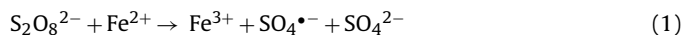
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1. Introduction

The environmental impact of synthetic dyes is a concern over the last few decades. Industries such as textile, leather, paper, plastics, pharmaceutical and food produce a great deal of wastewater contaminated with dyes annually in the world [1,2]. Among all synthetic dyes, azo dyes constitute the largest and the most important class of dyes for industrial applications [3]. The presence of dyes not only highly colors the effluent even at very low concentration, it also causes ecological and environmental problems because of their toxic or mutagenic and carcinogenic characteristics [4,5]. Therefore, the degradation of wastewater contaminated with azo dyes has aroused worldwide interest.

Among various treatment methods, advanced oxidation processes (AOPs) are considered as one of the most effective methods to degrade azo dyes, which involve the generation of powerful oxidizing species such as hydroxyl radicals (•OH) that attack the dye molecules [6–8]. In recent years, sulfate radical-based AOPs have proven to be the very promising techniques for the treatment of

refractory pollutants [9–13]. Similar to hydroxyl radicals, sulfate radicals have a high redox potential ($E^0 = 2.6\text{V}$), which can oxidize azo dyes into small molecules and carbon dioxide [14]. But compared to hydroxyl radicals, sulfate radicals have a longer half-life [10]. As a source of sulfate radicals, peroxydisulfate (PS, S₂O₈²⁻) has the advantages of high aqueous solubility and high stability at room temperature [15,16]. Generally, peroxydisulfate can be activated by heat [12,17,18], UV [12,19–21] or transition metals [22]. The transition metals include Co²⁺ [23], Ag⁺ [22,24] and Fe²⁺ [16,25]. Among these transition metals, Fe²⁺ has the advantage of inexpensive, nontoxic and effective, which has been widely applied in catalytic oxidation processes [26]. The Fe²⁺/S₂O₈²⁻ reagent is similar to the Fenton's reagent (Fe²⁺/H₂O₂). Peroxydisulfate can be activated by Fe²⁺ to produce sulfate radicals via Eq. (1) [16], while H₂O₂ can be catalyzed by Fe²⁺ to generate hydroxyl radicals through Eq. (2) [7]



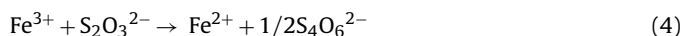
Similar to conventional Fenton process, there are some drawbacks encountered in the Fe²⁺/S₂O₈²⁻ process. On one hand, Fe²⁺ is hard to be regenerated after conversion to Fe³⁺ [27], therefore, high ferrous ion dosage is required to activate peroxydisulfate. This results in large amount of iron sludge. On the other hand, the

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excess Fe^{2+} could react with sulfate radicals (Eq. (3)), resulting in the reduced efficiency of the process.



In order to solve these problems, the reducing agent such as sodium thiosulfate was applied into the reaction system so that ferrous ion could be regenerated through Eq. (4) [28]



In addition, a chelating agent (citric acid) was used to complex with ferrous ion to maintain the available ferrous ion in solution [13]. As a kind of effective and environmentally friendly technology, electrochemical process could degrade dye wastewater by direct oxidation on the anode or indirect oxidation using electro-generated active radicals [29,30]. Moreover, the combination of electrochemical process with Fenton's reagent (known as electro-Fenton) was proposed, which could be generally divided into four categories [7,31,32]. In the first one, both ferrous ion and hydrogen peroxide are externally applied. In the second category, the ferrous ion is generated by sacrificial anode and hydrogen peroxide is externally applied. In the third category, the ferrous ion is externally applied and the hydrogen peroxide is generated at cathode. In the last category, both ferrous and hydrogen peroxide are electro-generated. It was proven that the efficiency of electro-Fenton process was higher than that of conventional Fenton process [32]. Due to the similarity between peroxydisulfate-ferrous ion reaction and hydrogen peroxide-ferrous ion reaction, it can be expected that the electrochemical process can also improve the efficiency of $\text{Fe}^{2+}/\text{S}_2\text{O}_8^{2-}$ process. Recently, Chu and Wang proposed an "Electro-Fe(II)/Oxone" process, which is similar with the second category of electro-Fenton process [33]. Oxone is a commercial name of a triple salt of potassium, which is another source of sulfate radicals, and the active ingredient of oxone is peroxymonosulfate (PMS) [22]. In this process, ferrous ions were generated from the sacrificed anode and further activated oxone to generate sulfate radicals. Meanwhile, cathodic reduction reaction could enhance the regeneration of ferrous ion [33],



As a result, the ferrous ion could be continuously regenerated and the degradation efficiency could be improved.

In our previous studies, the first category of electro-Fenton process has been successfully applied to the degradation of nitrophenol and COD from landfill leachate [31,32]. Therefore, a novel process named as "electro/ Fe^{2+} /peroxydisulfate" process by coupling electrochemical process and ferrous ion activation of peroxydisulfate was proposed in this study. The effects of some important reaction parameters such as initial pH, current density, $\text{S}_2\text{O}_8^{2-}$ concentration and Fe^{2+} concentration on the decolorization of Acid Orange 7, a model azo dye, were investigated. Gas chromatography-mass spectrometry (GC-MS) was also applied to determine the intermediates and the degradation pathway of Acid Orange 7 was proposed accordingly. The degradation of Acid Orange 7 in terms of COD removal efficiency and the variation of acute toxicity to *Daphnia magna* during this process were also investigated.

2. Materials and methods

C.I. Acid Orange 7 (4-(2-hydroxynaphthylazo)benzenesulfonic acid sodium salt) was purchased from Shanghai No. 3 Reagent Factory (China) and used without further purification. All other reagents were of analytical grade. Before each run, a fresh stock solution of Acid Orange 7 was prepared in deionised water and the initial concentration (C_0) was kept at 0.1 mM. Sodium sulfate was added as a supporting electrolyte, and the concentration was

0.1 M. Sulfuric acid or sodium hydroxide used to adjust the initial pH (pH_0) of the dye solution. The solution pH was measured with a Mettler-Toledo FE20 pH-meter (Mettler-Toledo Instruments Co., Ltd., Shanghai).

Batch experiments were performed in an electrolytic reactor (glass beaker) containing 200 mL of solution. A 5 cm \times 11.9 cm plate anode (Ti/RuO₂-IrO₂) and a plate cathode (stainless steel) of the same dimensions were arranged parallel to each other at a distance of 3.8 cm. The working surface area of the electrode was 31.5 cm². The reactor was immersed in a water bath to keep the temperature constant at 20 °C. Electrolysis was conducted under constant current conditions using a direct current (DC) power supply (Model WYK-305) from Yangzhou Jintong Source, Co., Ltd. (China). A magnetic stirrer (Model 78-1, Hangzhou Instrument Motors Factory, China) provided mixing of the solution in the reactor. When the DC power supply was initiated, the $\text{S}_2\text{O}_8^{2-}$ and Fe^{2+} solutions were applied to the electrolytic cell. At pre-selected time intervals, samples were withdrawn from the electrolytic cell. The absorbency of Acid Orange 7 was measured at $\lambda_{\text{max}} = 485$ nm using a Rayleigh UV-9100 spectrophotometer (Rayleigh Co., China). Decolorization efficiency was calculated according to Eq. (6),

$$\text{Decolorization efficiency (\%)} = \frac{A_0 - A_t}{A_0} \times 100 \quad (6)$$

where the A_0 and A_t were the absorbency of the sample at time 0 and t , respectively. The concentration of peroxydisulfate was analyzed using an iodometric titration method [34]. The Fe^{2+} concentration was analyzed using a phenanthroline spectrophotometric method based on the Standard of the People's Republic of China for Environmental Protection [35].

The intermediate products during the reaction were detected by gas chromatography-mass spectrometry (GC-MS) (Agilent 7890A/5975C). Samples for GC-MS analysis were prepared as follows: 200 mL of dye solution was extracted with 20 mL of dichloromethane ten times; the extracts were then concentrated by rotary evaporator at 40 °C to about 1 mL before being analyzed by GC-MS [36,37]. A HP-5 MS capillary column (30 m length \times 0.25 mm ID \times 0.25 μm film thickness) was employed for GC separation. The GC equipment was operated in a temperature programmed mode with an initial temperature of 40 °C held for 2 min, then ramped first to 100 °C with a 12 °C min⁻¹ rate; then ramped to 200 °C with 5 °C min⁻¹ rate, finally ramped to 270 °C with 20 °C min⁻¹ rate and held at that temperature for 10 min. Helium was used as a carrier gas. Electronimpact (EI) mass spectra were scanned from 0 to 550 m/z [38].

COD was determined using a closed reflux spectrophotometric method based on the Standard of the People's Republic of China for Environmental Protection [39]. The active toxicity was determined with *D. magna* immobilization test [40]. *D. magna* was cultured in laboratory for more than three generations. The acute toxicity experiments were repeated four times using 24-h-old *D. magna* in 100-mL-capacity test beakers. They were set in the incubator along with testing samples. The incubator was kept at 20 °C in a 16 h light-8 h dark cycle. No food was given during the acute toxic test. Surviving and mobile *D. magna* were counted after 24 h.

3. Results and discussion

3.1. Effect of initial pH

The initial pH values investigated in this study were 3, 7 and 9, respectively when initial dye concentration was 0.1 mM, Fe^{2+} concentration was 1 mM, $\text{S}_2\text{O}_8^{2-}$ concentration was 4 mM, and current density j was 16.8 mA cm⁻². As the initial pH value decreased from 9 to 3, the initial decolorization rates increased from 0.0070 to 0.0093 mM min⁻¹, while the decolorization efficiencies only

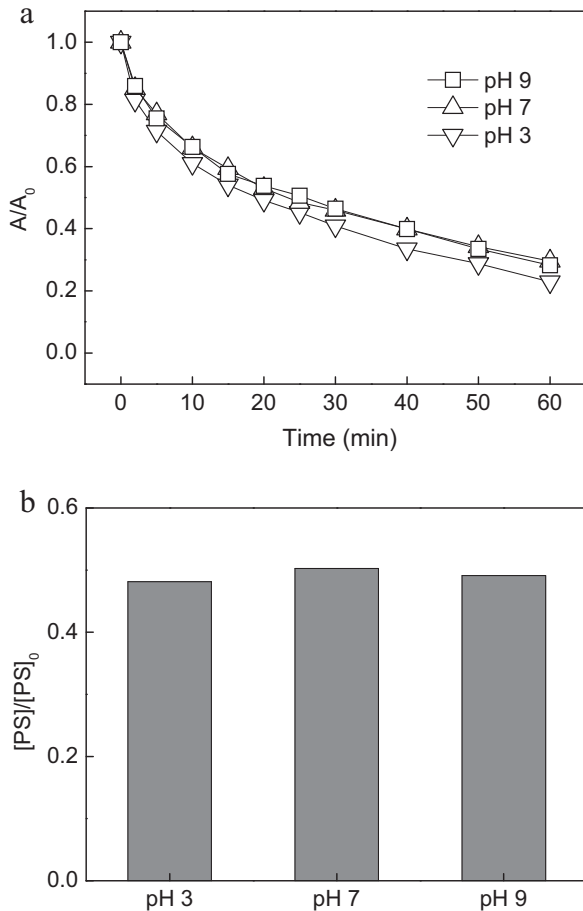


Fig. 1. Evolution of decolorization efficiency with reaction time (a) and remaining percentage of peroxydisulfate (b) at different initial pH values: (▽) pH₀ 3; (△) pH₀ 7; (□) pH₀ 9 ($C_0 = 0.1$ mM, $\text{Na}_2\text{SO}_4 = 0.1$ M, $[\text{Fe}^{2+}] = 1$ mM, $[\text{S}_2\text{O}_8^{2-}] = 4$ mM, $T = 20^\circ\text{C}$, $j = 16.8$ mA cm⁻²).

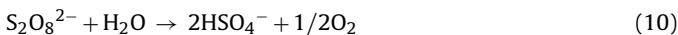
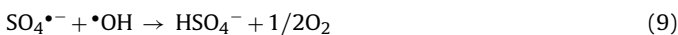
increased from 71.8% to 77.1% (Fig. 1(a)). The insignificant influence of initial pH on the decolorization efficiency may result from the overlap of absorption of intermediates with parent compound and the fact that the pH value of the dye solution would drop with the progress of the reaction and finally tend to be around 3 at initial pH higher than 3.

When sulfate radicals were generated by the ferrous iron-mediated decomposition of peroxydisulfate via Eq. (1), it could react with H₂O or OH⁻ to produce hydroxyl radical [41,42]



Based on Eqs. (7) and (8), either H⁺ would be released or OH⁻ would be consumed, which results in a reduction in pH.

Meanwhile, H⁺ would be further released by the dissociation of HSO₄⁻ [43], which was formed through the reaction of hydroxyl radical and sulfate radical (Eq. (9)) as well as the decomposition of peroxydisulfate in water (Eq. (10)) [43]



Therefore, pH would decrease to almost the same value and the decolorization of Acid Orange 7 tended to be conducted under the similar conditions as the reaction proceeded. Then the similar decolorization efficiency as well as the similar decomposition of

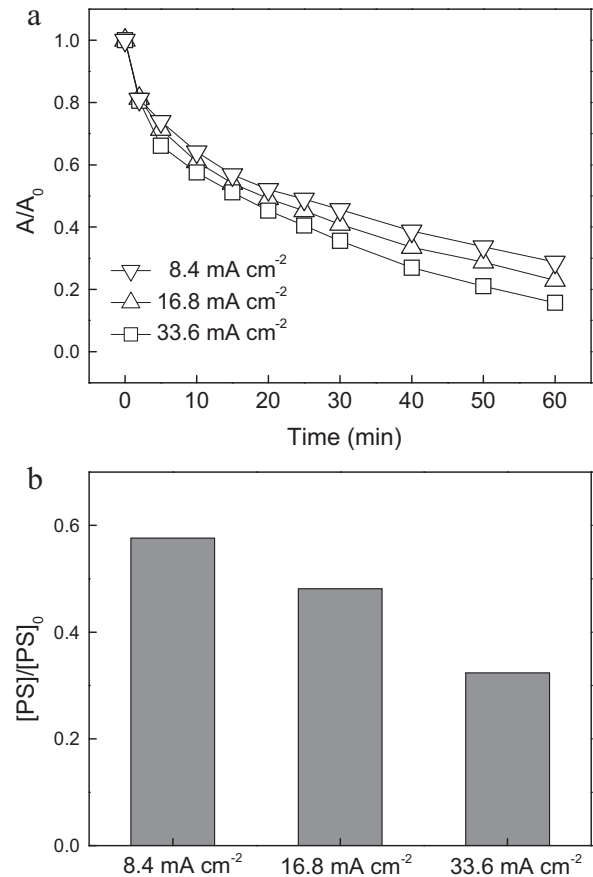


Fig. 2. Evolution of decolorization efficiency with reaction time (a) and remaining percentage of peroxydisulfate (b) at different current densities: (▽) 8.4 mA cm⁻²; (△) 16.8 mA cm⁻²; (□) 33.6 mA cm⁻² ($C_0 = 0.1$ mM, $\text{Na}_2\text{SO}_4 = 0.1$ M, $[\text{S}_2\text{O}_8^{2-}] = 4$ mM, $[\text{Fe}^{2+}] = 1$ mM, pH₀ 3, $T = 20^\circ\text{C}$).

peroxydisulfate was observed at different initial pH values, as illustrated in Fig. 1(a) and (b). This indicated that the EC/Fe²⁺/S₂O₈²⁻ process could be successfully applied at a wide range of initial pH.

3.2. Effect of current density

Fig. 2(a) illustrated the decolorization efficiency of Acid Orange 7 at different current density when initial dye concentration was 0.1 mM, Fe²⁺ concentration was 1 mM, S₂O₈²⁻ concentration was 4 mM, and initial pH value was 3. The initial decolorization rates varied from 0.0093 to 0.0097 mM min⁻¹ when the current densities ranged from 8.4 to 33.6 mA cm⁻². The results indicated that the current densities had little effect on the decolorization of Acid Orange 7 at the beginning of the reaction. However, the decolorization efficiency after 60 min reaction increased with the increase of the current density. The initial decolorization rates were nearly the same at three different current densities since the same ferrous ion concentration was added into the system. Thereafter, increasing the current density would accelerate the regeneration of ferrous ion according to Eq. (5), and then improve the decomposition of the peroxydisulfate to generate sulfate radicals (Eq. (1)). In addition, the peroxydisulfate could generate sulfate radicals via electron transfer reaction (Eq. (12)) [26]



Consequently, as the current density increased from 8.4 to 33.6 mA cm⁻², the decomposition percentages of peroxydisulfate increased from 42.4% to 67.6% (Fig. 2(b)), and the decolorization

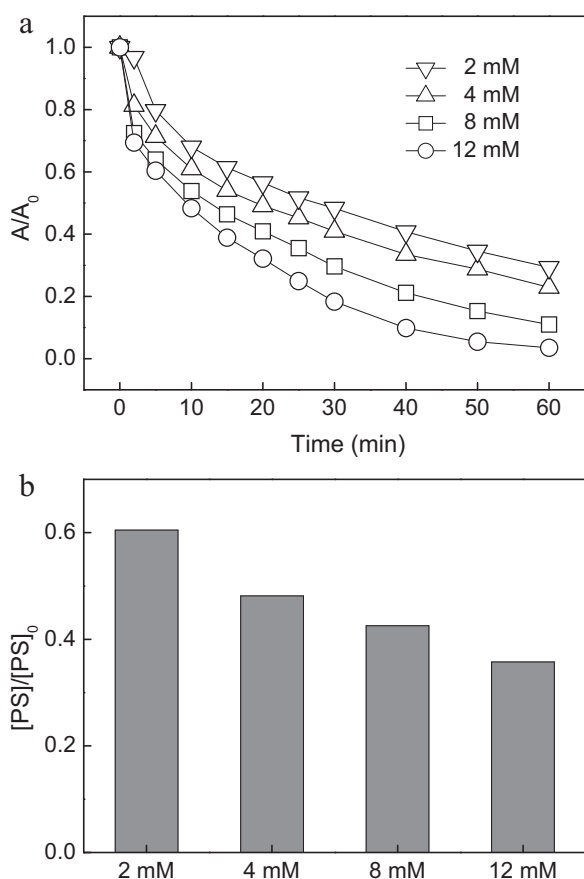
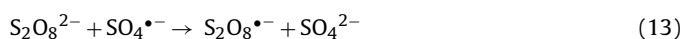


Fig. 3. Evolution of decolorization efficiency with reaction time (a) and remaining percentage of peroxydisulfate (b) at different peroxydisulfate concentrations: (∇) 2 mM; (Δ) 4 mM; (\square) 8 mM; (\circ) 12 mM ($C_0 = 0.1$ mM, $\text{Na}_2\text{SO}_4 = 0.1$ M, $[\text{Fe}^{2+}] = 1$ mM, $\text{pH}_0 = 3$, $T = 20^\circ\text{C}$, $j = 16.8$ mA cm⁻²).

efficiencies increased from 71.2% to 84.3% accordingly (Fig. 2(a)). Although the highest decolorization efficiency was achieved at 33.6 mA cm⁻² current density, the selection of current density was 16.8 mA cm⁻² in the rest of experiments considering the balance between color removal and energy consumption.

3.3. Effect of peroxydisulfate concentration

The effect of peroxydisulfate concentration on Acid Orange 7 decolorization efficiency was evaluated by conducting experiments at 2, 4, 8 and 12 mM, respectively. The initial dye concentration was fixed at 0.1 mM, Fe^{2+} concentration was 1 mM, current density was 16.8 mA cm⁻², and initial pH value was 3. When $\text{S}_2\text{O}_8^{2-}$ concentration increased from 2 to 12 mM, the initial decolorization rates and the decolorization efficiencies increased from 0.0016 to 0.0153 mM min⁻¹ and 70.7% to 96.5%, respectively (Fig. 3(a)). Peroxydisulfate is a source of sulfate radicals in the system, and more reactive radicals would be generated to degrade of Acid Orange 7 at higher $\text{S}_2\text{O}_8^{2-}$ concentration. On the other hand, the side reaction between persulfate anion and sulfate radical became more significant with the increase of $\text{S}_2\text{O}_8^{2-}$ concentration, which would consume more peroxydisulfate via Eq. (13) [42]



Therefore, the remaining percentage of peroxydisulfate decreased with the increase of the $\text{S}_2\text{O}_8^{2-}$ concentration, as observed in Fig. 3(b). According to the obtained results, 12 mM

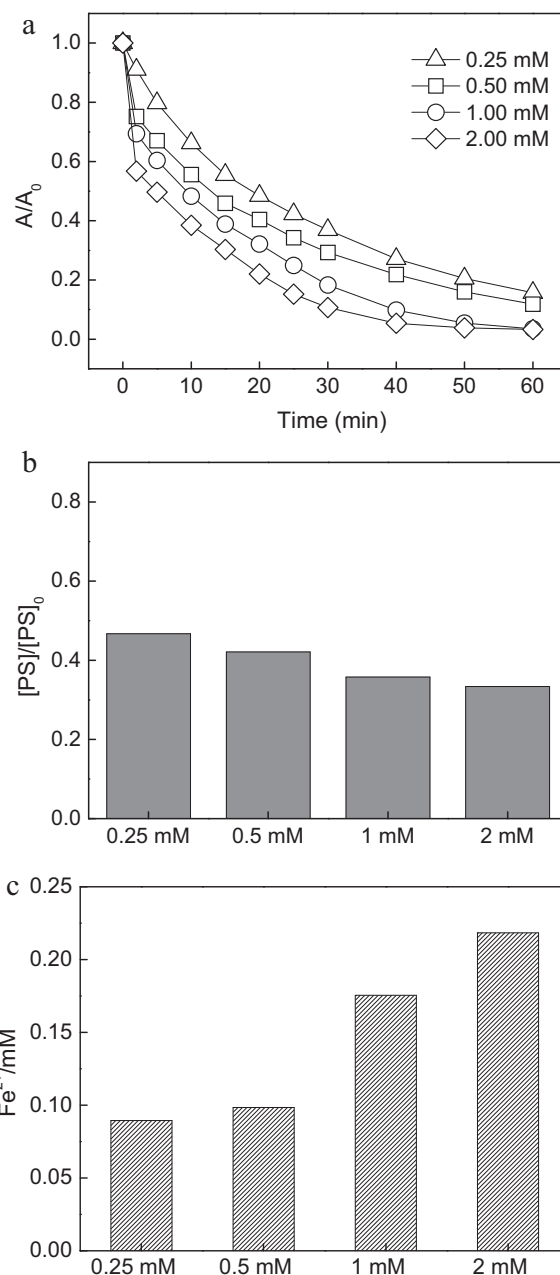


Fig. 4. Evolution of decolorization efficiency with reaction time (a) and remaining percentage of peroxydisulfate (b) and Fe^{2+} concentration (c) at different Fe^{2+} concentrations: (Δ) 0.25 mM; (\square) 0.5 mM; (\circ) 1 mM; (\diamond) 2 mM ($C_0 = 0.1$ mM, $\text{Na}_2\text{SO}_4 = 0.1$ M, $[\text{S}_2\text{O}_8^{2-}] = 12$ mM, $\text{pH}_0 = 3$, $T = 20^\circ\text{C}$, $j = 16.8$ mA cm⁻²).

was chosen as the optimal $\text{S}_2\text{O}_8^{2-}$ concentration value under these conditions and used in the following experiments.

3.4. Effect of ferrous ion concentration

The effect of Fe^{2+} concentration on the decolorization of Acid Orange 7 was investigated by conducting experiments at 0.25, 0.50, 1.00 and 2.00 mM, respectively when the initial dye concentration was 0.1 mM, $\text{S}_2\text{O}_8^{2-}$ concentration was 12 mM, current density was 16.8 mA cm⁻², and initial pH value was 3. As shown in Fig. 4(a), both the initial decolorization rate and the decolorization efficiency increased with the increase of the Fe^{2+} concentration. The ferrous ion can activate peroxydisulfate to produce sulfate radicals. Increasing ferrous ion dosage would correspond to a higher

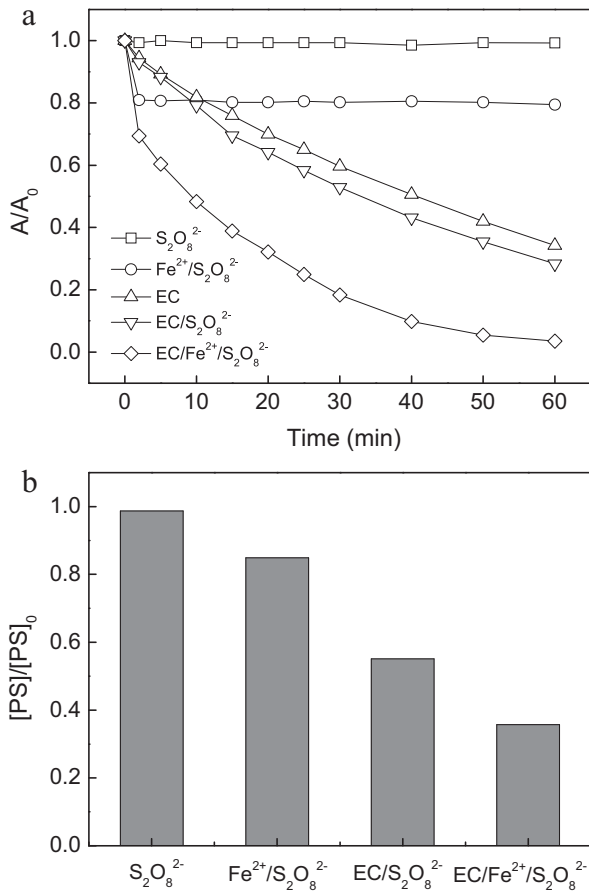


Fig. 5. Decolorization of Acid Orange 7 solution (a) and remaining percentage of peroxydisulfate (b) with 0.1 M Na₂SO₄, pH₀ 3 and 20 °C temperature in different systems: (□) S₂O₈²⁻ ([S₂O₈²⁻] = 12 mM); (○) Fe²⁺/S₂O₈²⁻ ([S₂O₈²⁻] = 12 mM, [Fe²⁺] = 1 mM); (Δ) EC (I = 1 A); (∇) EC/S₂O₈²⁻ ([S₂O₈²⁻] = 12 mM, j = 16.8 mA cm⁻²); (◇) EC/Fe²⁺/S₂O₈²⁻ ([S₂O₈²⁻] = 12 mM, [Fe²⁺] = 1 mM, j = 16.8 mA cm⁻²).

available Fe²⁺ concentration. As can be seen in Fig. 4(c), the remaining Fe²⁺ concentrations were 0.09, 0.10, 0.18 and 0.22 mM, respectively when the dosed Fe²⁺ concentrations were 0.25, 0.50, 1.00 and 2.00 mM. Higher available Fe²⁺ concentration improved the decomposition of peroxydisulfate to generate sulfate radicals. As can be seen in Fig. 4(b), the remaining percentage of peroxydisulfate decreased from 46.7% to 33.4% when the Fe²⁺ concentration increased from 0.25 to 2.00 mM. Considering that the decolorization efficiencies at 1 and 2 mM ferrous ion concentrations were nearly the same, 1 mM of ferrous ion concentration was selected as the appropriate concentration value and used in the remaining experiments.

3.5. Decolorization of Acid Orange 7 in different systems

To investigate the decolorization efficiency of different systems, various experiments were carried out using the optimal conditions but: (a) in the absence of Fe²⁺ and EC (S₂O₈²⁻ alone), (b) in the absence of EC (Fe²⁺/S₂O₈²⁻ process), (c) in the absence of Fe²⁺ and S₂O₈²⁻ (EC alone), (d) in the absence of Fe²⁺ (EC/S₂O₈²⁻ process) and (e) in the presence of all components (EC/Fe²⁺/S₂O₈²⁻ process). As can be seen in Fig. 5(a), negligible color removal was observed when Acid Orange 7 was treated by S₂O₈²⁻ alone due to the limit oxidation power of peroxydisulfate ($E^0 = 2.01$ V) [26]. The remaining percentage of peroxydisulfate in the S₂O₈²⁻ process was 98.7% (Fig. 5(b)), indicating almost no peroxydisulfate was decomposed in this case. Improved decolorization efficiency,

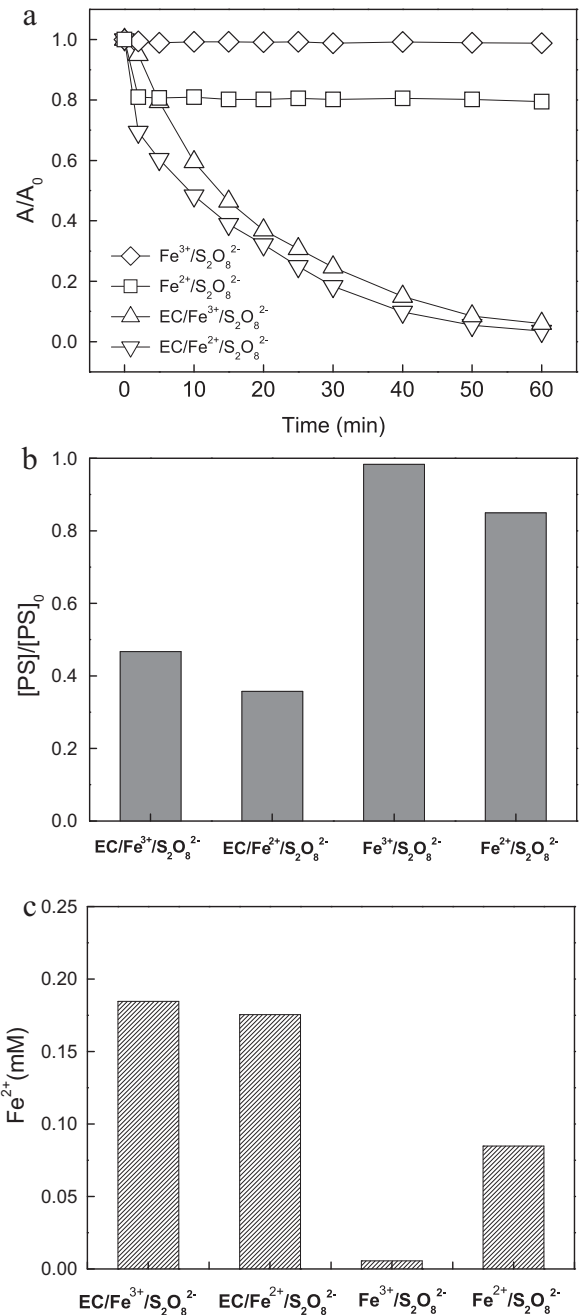


Fig. 6. Evolution of decolorization efficiency with reaction time (a) and remaining percentage of peroxydisulfate (b) and Fe²⁺ concentration (c) at different iron source: (◇) Fe³⁺/S₂O₈²⁻; (□) Fe²⁺/S₂O₈²⁻; (Δ) EC/Fe³⁺/S₂O₈²⁻; (∇) EC/Fe²⁺/S₂O₈²⁻.

reaching 20% was achieved by the ferrous ion activation of peroxydisulfate process. It indicated the ferrous ion could react with peroxydisulfate to generate sulfate radicals. However, the oxidation of Acid Orange 7 occurred only within the first few minutes in this system since the regeneration of ferrous ion is not thermodynamically favorable [22]. The anodic oxidation removed 65.8% of the initial Acid Orange 7, which was due to the electro-generation of hydroxyl radicals by the oxidation of water at the anode. But these hydroxyl radicals were insufficient to remove Acid Orange 7 completely within 60 min reaction. Addition of peroxydisulfate to the electrolytic reactor (EC/S₂O₈²⁻ process) slightly improved the decolorization efficiency (71.6%) as a result of the fact that sulfate radicals could be generated via electron transfer reaction (Eq. (12)). In this case, 44.9% of peroxydisulfate was decomposed after 60 min

reaction (Fig. 5(b)). When electrochemical process was combined with ferrous ion activated peroxydisulfate process (EC/Fe²⁺/S₂O₈²⁻ process), peroxydisulfate could be activated by the continuously regenerated ferrous ions. As can be seen in Fig. 5(c), the remaining percentage of peroxydisulfate in the EC/Fe²⁺/S₂O₈²⁻ process was lowest (35.8%), corresponding to the generation of the most reactive radicals to oxidize Acid Orange 7 among all the processes. The decolorization efficiency achieved by EC/Fe²⁺/S₂O₈²⁻ process (96.5%) was higher than the sum of the decolorization efficiencies when Acid Orange 7 was individually removed by EC (65.8%) and Fe²⁺/S₂O₈²⁻ (20.5%) process. Evidently, the synergetic effect was existed in the combination of EC and Fe²⁺/S₂O₈²⁻ process.

3.6. Comparison of different iron species

In order to investigate the effect of different iron species, ferrous and ferric ions were used as the iron source in both iron activated peroxydisulfate process and the coupled EC/iron activated peroxydisulfate process. The initial dye concentration was 0.1 mM, iron concentration was 1 mM, peroxydisulfate concentration was 12 mM, and initial pH value was 3 in the both process. The current density was 16.8 mA cm⁻² in the combined EC/iron activated peroxydisulfate process. Negligible color removal was observed in the EC/Fe³⁺ process since ferric ion would not appreciably activate peroxydisulfate to generate sulfate radicals [44]. Moreover, the ferrous ions were hard to be generated in the absence of applied current since the reduction of Fe³⁺ is not thermodynamically favorable [22]. Therefore, almost no peroxydisulfate was decomposed (Fig. 6(b)), and the ferrous ion was not detected either (Fig. 6(c)). When the Fe³⁺/S₂O₈²⁻ was coupled with electrochemistry process, the cathodic reduction of Fe³⁺ could generate Fe²⁺ to activate peroxydisulfate. As observed in Fig. 6(b), the concentrations of remaining peroxydisulfate and ferrous ion in EC/Fe³⁺/S₂O₈²⁻ process were very close to those in EC/Fe²⁺/S₂O₈²⁻ processes. It indicated that nearly the same amount of peroxydisulfate (around 60%) was decomposed by ferrous ion to generate sulfate radicals in the both processes. Therefore, EC/Fe³⁺/S₂O₈²⁻ process could achieve

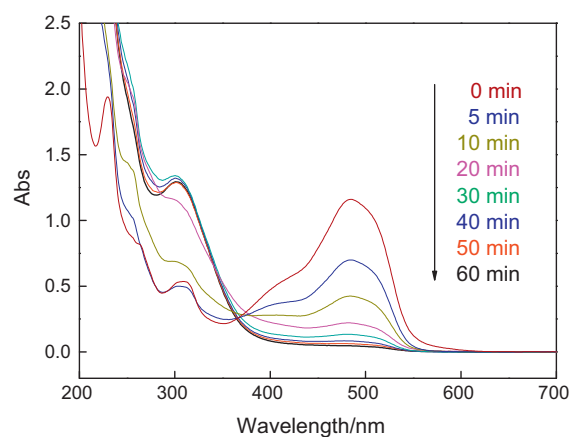


Fig. 7. UV-vis spectral changes with reaction time ($C_0 = 0.1$ mM, $\text{Na}_2\text{SO}_4 = 0.1$ M, $[\text{S}_2\text{O}_8^{2-}] = 12$ mM, $[\text{Fe}^{2+}] = 1$ mM, $\text{pH}_0 = 3$, $T = 20^\circ\text{C}$, $j = 16.8$ mA cm⁻²).

nearly the same color removal (94.1%) as EC/Fe²⁺/S₂O₈²⁻ process (96.5%) after 60 min reaction though the initial decolorization rate of EC/Fe³⁺/S₂O₈²⁻ process was lower than that of EC/Fe²⁺/S₂O₈²⁻ process.

3.7. The degradation pathway of Acid Orange 7

To investigate the degradation of Acid Orange 7 as a result of the EC/Fe²⁺/S₂O₈²⁻ process, representative UV-vis spectra changes in the solution as a function of reaction time were observed, and the corresponding spectra are shown in Fig. 7. As can be seen from the corresponding spectra, there was one main band in the visible region located at 485 nm, which was originated from an extended chromophore. This extended chromophore was comprised of both aromatic rings, which connected through the azo bone [45,46]. Meanwhile, the absorption at 310 and 228 nm in the ultraviolet region were associated with naphthalene ring and benzene ring structures in the dye molecule [47]. As the reaction proceeded, the

Table 1
GC-MS identified reaction intermediates during C.I. Acid Orange 7 degradation.

Compound	Retention time (min)	Chemical name	Chemical structure
A	22.99	1,2-Naphthalenediol	
B	13.80	2H-1-benzopyran-2-one	
C	13.83	Ninhydrin	
D	14.42	1(3H)-isobenzofuranone	

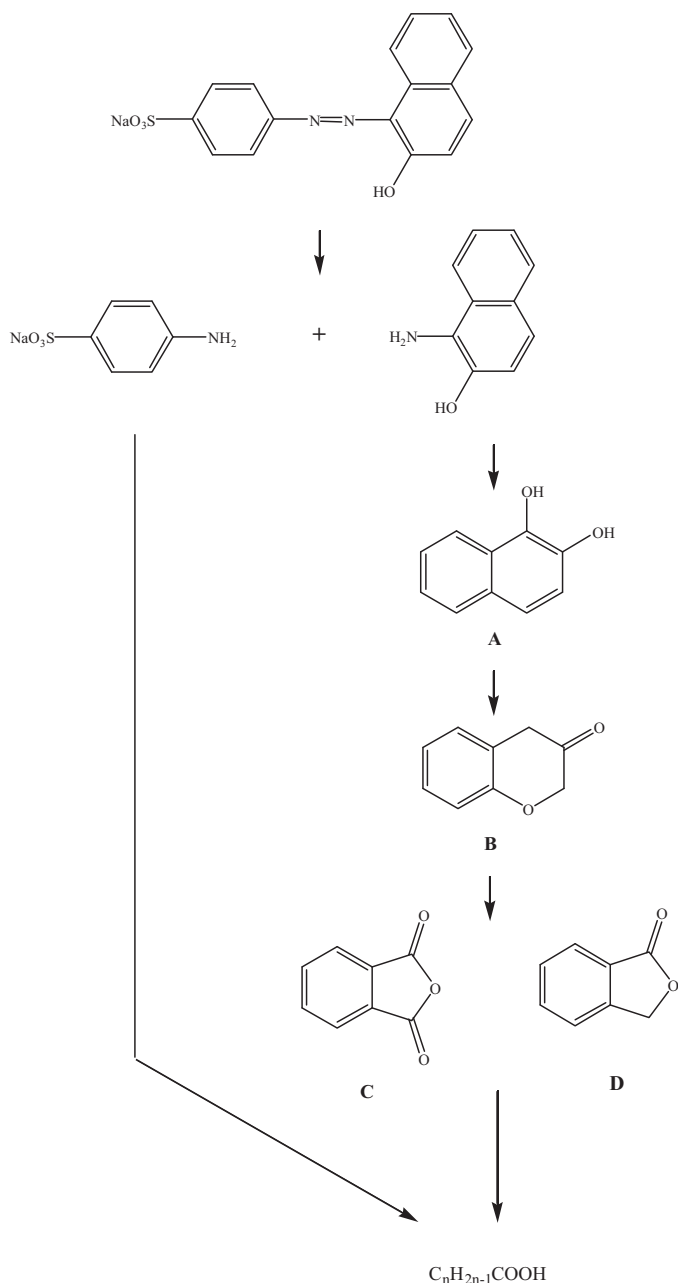


Fig. 8. Proposed pathways for degradation of Acid Orange 7 by EC/Fe²⁺/S₂O₈²⁻ process ($C_0 = 0.1$ mM, Na₂SO₄ = 0.1 M, [S₂O₈²⁻] = 12 mM, [Fe²⁺] = 1 mM, pH₀ 3, T = 20 °C, j = 16.8 mA cm⁻²).

visible band disappeared, indicating that at least the azo links were broken down by the reaction. The absorption at 310 and 228 nm were increased, showing that the azo structure was destroyed and some aromatic fragment such as naphthalene ring and benzene ring were formed.

To further identify the intermediate products, GC-MS analysis was employed and the intermediate products identified were shown in Table 1. Based on the results and previous studies [1,5,38,48–50], a plausible degradation pathway is proposed in Fig. 8. Through N–N cleavage, Acid Orange 7 was firstly decomposed to aromatic intermediates such as sodium sulfanilamide and 1-amino-2-naphthol [48]. Afterwards, 1-amino-2-naphthol was further oxidized to 1,2-naphthalenediol (A). It was subsequently oxidized to a quinone radical, resulting in the formation of 2H-1-benzopyran-2-one (B) [48]. Then 2H-1-benzopyran-2-one (B) was

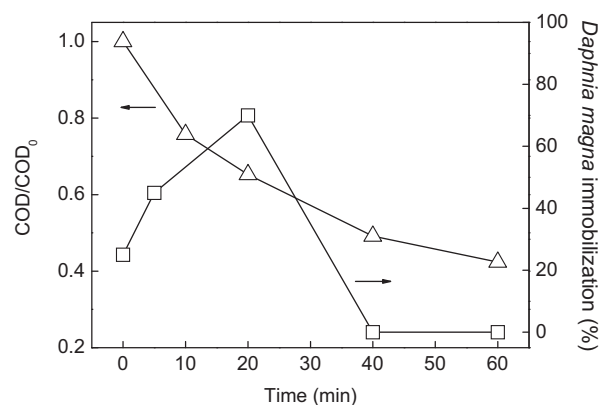


Fig. 9. The changes of (Δ) the COD degradation efficiency and (□) the *Daphnia magna* immobilization with the reaction time ($C_0 = 0.1$ mM, Na₂SO₄ = 0.1 M, [S₂O₈²⁻] = 12 mM, [Fe²⁺] = 1 mM, pH₀ 3, T = 20 °C, j = 16.8 mA cm⁻²).

degraded to generate heterocyclic compounds containing a five-atom ring, such as ninhydrin (C) and 1(3H)-isobenzofuranone (D). Further oxidation reactions by sulfate radicals lead to the degradation of these intermediates to smaller molecule compounds.

3.8. The changes of COD and toxicity with reaction time

The changes of COD removal efficiency and the acute toxicity on the *D. magna* were investigated with initial dye concentration 0.1 mM, electrolyte concentration 0.1 M, Fe²⁺ concentration 1 mM, peroxydisulfate concentration 12 mM, and current density 16.8 mA cm⁻². As shown in Fig. 9, the COD removal efficiency was 57.6% after 60 min reaction. The COD removal efficiency achieved 90.2% when the reaction time extended to 600 min. The acute toxicity of Acid Orange 7 was investigated on the freshwater crustacean *D. magna*. As shown in Fig. 9, the *D. magna* immobilization rate of the initial Acid Orange 7 was 25% after 24 h exposition. As the reaction proceeded, the acute toxicity increased compared to the initial Acid Orange 7 solution. The enhancement of toxicity during the EC/Fe²⁺/S₂O₈²⁻ process indicates the higher toxicity of the intermediates and adverse risk. After 40 min reaction, there is nearly no inhibition of *D. magna* immobilization. It indicated the acute toxicity of the Acid Orange 7 and its oxidation byproducts could be reduced by this process if enough reaction time is allowed.

4. Conclusions

This study showed that the novel EC/Fe²⁺/S₂O₈²⁻ process can decolorize the Acid Orange 7, and the decolorization efficiency could be significantly enhanced by the combination of these two processes. The decolorization efficiency increased with the increase of peroxydisulfate concentration and ferrous ion concentration, while it was nearly independent of initial pH between 3 and 9. The current densities had little effect on the decolorization of Acid Orange 7 at the beginning of the reaction. However, the decolorization efficiency as well as the decomposition percentage of peroxydisulfate increased with the increase of current densities after 60 min reaction. The COD removal efficiency reached 57.6% after 60 min reaction, and it achieved 90.2% when the reaction time extended to 600 min. The *D. magna* immobilization rate of the initial Acid Orange 7 was 25%, which reached the maximum after 20 min reaction and then decreased to zero after 40 min reaction. The main intermediates were separated and identified by GC-MS technique and a plausible degradation pathway of Acid Orange 7 was proposed. Further studies will be followed to integrate with other

technologies such as biological methods and to reduce peroxydisulfate dosage by improving its utilization efficiency.

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