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1 Application of a microbial siderophore Desferrioxamine B in
2 sunlight/Fe³⁺/persulfate system: from the radical formation to the
3 degradation of Atenolol at neutral pH

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14 **Abstract**

15 The present work reported a modified persulfate activation process with a microbial siderophore
16 named Desferrioxamine B (DFOB). DFOB was a natural complexing agent and could complex with
17 Fe³⁺ strongly. The photochemical reactivity of Fe(III)-DFOB was studied. Fe²⁺ and HO[•] were produced
18 from Fe(III)-DFOB photolysis. Furthermore, the degradation of Atenolol (ATL) was followed in
19 light/persulfate (PS)/Fe(III)-DFOB system. The main oxidative radicals were SO₄^{•-} in this system. The
20 results of pH effect showed that there was no obviously fluctuation on ATL degradation efficiency with
21 the pH increased from 2.5 to 8.4. Moreover, *k*<sub>SO₄^{•-},DFOB was determined by laser flash photolysis (LFP)
22 experiments. DFOB had positive effect on Fe²⁺ formation but negative effect on ATL degradation due
23 to the high react rate constant between DFOB and SO₄^{•-}. The effects of chloride and carbonate ion were
24 also investigated. The results in this study proposed the reaction mechanism of the modified persulfate</sub>

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25 activation process and it could be applied in neutral and weak-alkaline pH range.

26 **Keywords**

27 siderophore, iron complex, neutral pH, sulfate radical, AOPs

28 **Introduction**

29 Fe is an integral element for many living organisms including human, animal, plants and
30 microorganism. However, the most common forms of Fe are iron oxide and iron hydroxide which are
31 difficult to be utilized by organisms (Ratledge and Dover, 2000). The typical concentration of dissolved
32 Fe^{3+} in natural water environment is not higher than 10^{-18} M (Price and Morel, 1998) and it is far below
33 the optimal required concentration for the growth of microbes and plants, 10^{-5} - 10^{-7} M and 10^{-4} - 10^{-9} M,
34 respectively (Colombo et al. 2014). Thus, the siderophores are produced by cells and they are strong
35 complexing agents to utilize Fe^{3+} in the iron deficiency environment. Siderophores are natural
36 complexing agents and Fe(III)-siderophore complexes are usually formed at neutral pH.

37 As we well know, ferrous iron is an important activator in traditional Fenton reactions or sulfate
38 radical based advanced oxidation process. The presence of Fe^{2+} related to the photo-reduction of Fe^{3+}
39 from Fe(III) oxides and Fe(III)-complexes (Erel et al. 1993; Johnson et al. 1994). Fe(III)-siderophores,
40 typical iron complexes, could be considered as a potential candidate for Fe(II) formation. Passananti et
41 al. (2016) reported the formation of Fe(II) at pH 6.0 with the irradiation of Fe(III)-Pyoverdin under
42 simulated sunlight. Pyoverdin was a kind of siderophores and produced by the bacterial strain isolated
43 from cloudwater. The formation of Fe^{2+} from the irradiation of Fe(III)-siderophore was confirmed but
44 its application in persulfate activation was not reported as yet.

45 Desferrioxamine B (DFOB) is a well-known microbial siderophore which is synthesised by fungi
46 and could be found in soils (Farkas et al. 1997; Neubauer et al. 2000). The chemical structure was
47 shown in Fig. S1. It is a hydroxamate-based siderophore which could strongly chelate with Fe^{3+} . The

48 complexing constant of Fe(III)-DFOB is very high and it was $10^{30.6}$ (Neilands, 1981). Lin et al. (2018)
49 reported the hematite dissolution at different pH in the presence of siderophore DFOB and other three
50 complexing agents (oxalic, citric and malic acid). Total dissolved iron concentration was measured by
51 ICP-OES and the results showed DFOB had positive effect on hematite dissolution at pH 9.0 compared
52 with other organic acids. Borer et al. (2009) studied the dissolution of Lepidocrocite (γ -FeOOH) in the
53 presence of DFOB under different light irradiation. The results showed DFOB could increase the
54 formation of Fe(II) strongly with the decreasing wavelengths below 440 nm at pH 3.0 and Fe(II) was
55 still produced at pH 8.0. It seemed DFOB could not only chelate Fe^{3+} but also release Fe^{2+} with a wide
56 pH range. The characteristics and photoreactivity of Fe(III)-DFOB were investigated in this study. The
57 application of DFOB in persulfate activation for the degradation of pharmaceutical contaminants was
58 also studied.

59 Recently, sulfate radical ($\text{SO}_4^{\cdot-}$)-based advanced oxidation technologies have been intensively
60 investigated for the degradation of organic pollutants, including pharmaceuticals and personal care
61 products (PPCPs), endocrine disrupting chemicals (EDCs) and persistent organic pollutants (POPs)
62 (Lian et al. 2017; Fang et al. 2013; Takedastan et al. 2018; Wu et al. 2019a; Wu et al. 2019b). In this
63 study, Fe(III)-DFOB was introduced as the activator of persulfate (PS) under simulated sunlight
64 irradiation. Atenolol (ATL), a wide existence pharmaceutical compound (Ling et al., 2016), was chosen
65 as the model pollutant in this study. The effect of pH on ATL degradation was investigated in
66 light/PS/Fe(III)-DFOB system. The main radicals were identified. The laser flash photolysis
67 experiments were performed to evaluate the second-order reaction rate constant between $\text{SO}_4^{\cdot-}$ and
68 DFOB.

69

70 **Materials and methods**

71 **Chemicals**

72 Desferrioxamine B (DFOB) was purchased as the deferoxamine B mesylate
73 ($C_{25}H_{46}N_5O_8NH_2 \cdot CH_4SO_3$, $\geq 92.5\%$) from Sigma Aldrich. Ferric perchlorate hydrate ($Fe(ClO_4)_3 \cdot xH_2O$,
74 Fe content 10.0-12.5%) was also obtained from Sigma Aldrich and the exact concentration of Fe(III)
75 was determined by Ferrozine method (described in Analytical Methods section) before using. $Na_2S_2O_8$
76 (PS), NaOH, NaCl, $HClO_4$, CH_3COOH , Na_2CO_3 , CH_3COONa were analytical grade and purchased
77 from Sinopharm Chemical Reagent Co., Ltd. Ferrozine (97%) and terephthalic acid (TA) were
78 purchased from Sigma Aldrich. Atenolol (99%) was purchased from Dr. Ehrenstorfer GmbH. Methanol
79 (LC/MS grade) was provided by J&K Scientific Co., Ltd. Fe(III)-DFOB solutions were prepared by
80 mixing appropriate volumes of freshly prepared aqueous solutions of $Fe(ClO_4)_3$ and DFOB.

81 **Simulated sunlight assisted activation of persulfate by Fe(III)-DFOB**

82 The mixed solutions (ATL/Fe(III)-DFOB/PS) were irradiated in a 40 mL quartz bottle and the
83 temperature was constant (298 ± 2 K) controlled by water circulation. The reactor was placed at a fixed
84 point with 10 cm from the lamp. Two lamps were set in the middle and equipped with four filters
85 around to remove wavelengths lower than 290 nm. The purpose was to simulate the solar emission
86 spectrum. The emission spectrums and the energy of the lamps were shown in Fig. S2. The figure of
87 the reactor was shown in Fig. S3. The mixed solutions were continuously stirred during the reaction.
88 The reaction samples were taken at the fixed time intervals. The pH value of the solution was adjusted
89 with NaOH or $HClO_4$ which showed negligible effect on the kinetics of pollutant degradation
90 (Lipctnska-Kochany et al., 1995).

91 **Analytical Methods**

192 ATL concentration in the sample was determined by high performance liquid chromatography
193 (HPLC) system (DIONEX U3000, USA) equipped with a photodiode array detector (DAD). The
194 column was a C18 column (CNW, 5 μm \times 4.6 mm \times 250 mm). The mobile phase consisted of 0.01 M
195 $\text{CH}_3\text{COONH}_4$ and methanol (70:30). The flow rate was 0.8 ml/min and the detection wavelength was
196 224 nm. The detection limit of ATL concentration was 0.05 mg/L.

197 The concentration of Fe(II) was determined by Ferrozine method (Stookey, 1970). Fe(II) and
198 Ferrozine could form a stable carmine complex which had the maximum absorption wavelength at 562
199 nm. The molar absorption coefficient ($\epsilon_{562\text{ nm}}$) was reported as $2.79 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ (Berlett, et al. 2001).
200 The concentration of Fe(III) was determined as Fe(II) by adding ascorbic acid (0.05 M) to reduce all
201 the Fe(III) to Fe(II). The detection limit of Fe(II) concentration was 0.8 μM .

202 The steady-state concentration of hydroxyl radical (HO^\bullet) was measured with a chemical probe
203 (terephthalic acid, TA). TA was used to trap HO^\bullet and the products were 2HTA. It was measured by
204 HPLC with fluorescence detection ($\lambda_{\text{excitation}} = 315 \text{ nm}$, $\lambda_{\text{emission}} = 425 \text{ nm}$). The formation yield of 2HTA
205 was estimated as 0.28 (Charbouillot et al. 2011) and the HO^\bullet steady-state concentration was calculated
206 based on the literature (Li et al. 2016).

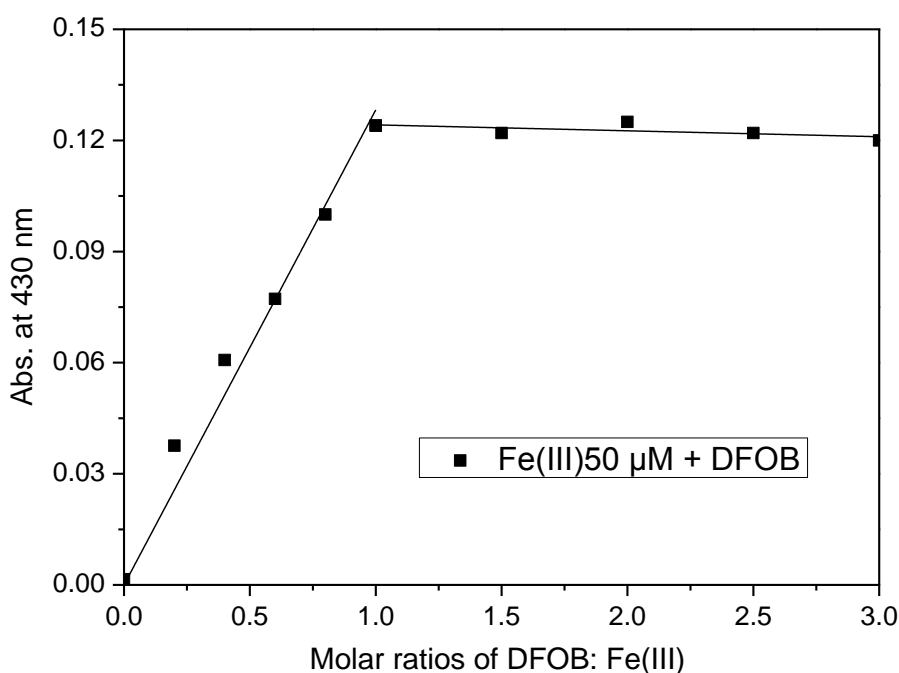
207 **Laser flash photolysis experiments**

208 The transient laser flash photolysis (LFP) experiments were performed to determine the second
209 order reaction rate constant for the reactions between DFOB and $\text{SO}_4^{\bullet-}$ ($k_{\text{DFOB}, \text{SO}_4^{\bullet-}}$). LFP was performed
210 with the excitation wavelength at 266 nm and using a Quanta Ray LAB-150-10 Nd:YAG laser. The
211 transient absorption spectrum of $\text{SO}_4^{\bullet-}$ at 0.3 μs was shown in Fig. S4. The detection wavelength of
212 $\text{SO}_4^{\bullet-}$ was 450 nm (George and Chovelon, 2002). The samples were mixed with DFOB and PS solution
213 just before the LFP experiment.

114 Results and Discussion

115 Characteristics of Fe(III)-DFOB complex

116 Fe(III)-DFOB complex was formed by Fe(III) and DFOB in specific proportion. The UV-vis
117 spectrums of Fe³⁺, DFOB and Fe(III)-DFOB were shown in Fig. S5 and the absorption peak of
118 Fe(III)-DFOB was at 430 nm. Job's Method (Job, 1928) was used to determine stoichiometry of the
119 binding event and it was performed to measure the proportion between Fe(III) and DFOB in this study.
120 The concentration of Fe(III) was held constant, but DFOB concentrations were varied. The absorbance
121 of Fe(III)-DFOB at 430 nm with different proportion between Fe(III) and DFOB was shown in Fig. 1.
122 The inflection point on the curve corresponded to the stoichiometry of the two binding partners. It
123 showed that Fe(III)-DFOB complex formed with the mole proportion 1:1.



124

125

126 Fig. 1 Effect of molar ratio on the binding of Fe(III) and DFOB (pH=6.5)

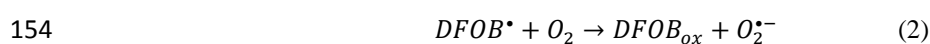
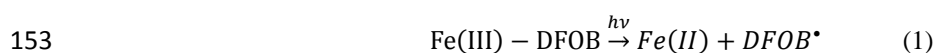
127 DFOB is a hydroxamate-based siderophore with three hydroxamate groups and a terminal primary

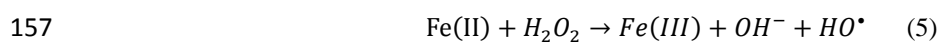
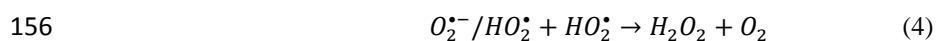
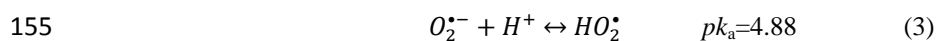
128 amine group. It had four pK_a associated to its structure including $pK_{a1} = 8.30$, $pK_{a2} = 9.00$, $pK_{a3} = 9.86$
129 and $pK_{a4} = 10.84$ (Farkas et al. 1999). Thus, DFOB was kept in molecular state in a large pH range. The
130 UV-vis spectra of Fe(III)-DFOB with different pH were shown in Fig. S6. The UV-vis spectra were not
131 affected by different pH showed Fe(III)-DFOB had a very stable form. It might be due to the strong
132 chelating ability of DFOB.

133 **Photochemical behavior of Fe(III)-DFOB complex**

134 The photoactivity of Fe(III)-DFOB was investigated following the degradation of ATL (2.5 mg/L)
135 and formation of Fe(II) in the presence of Fe(III)-DFOB (100 μ M) under simulated sunlight irradiation.
136 The results (Fig. S7) showed there was Fe(II) formation at pH 6.5 but almost no degradation of ATL.
137 The conversion rate from Fe(III) to Fe(II) was 10%.

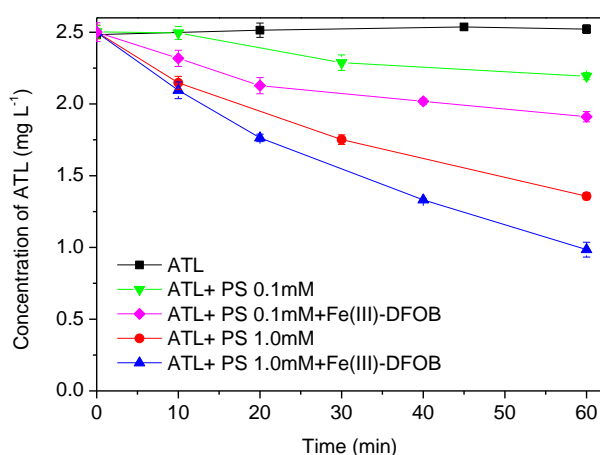
138 Accompanied by the Fe(II) formation, a series of reactive oxygen species (ROS) such as $HO_2^{\bullet}/O_2^{\bullet-}$,
139 H_2O_2 and HO^{\bullet} would usually be produced according to the photolysis mechanism of many
140 Fe(III)-complexes including Fe(III)-Oxalate (Liu et al. 2010), Fe(III)-Citrate (Feng et al. 2014),
141 Fe(III)-EDDS (Wu et al. 2014) and Fe(III)-Pyoverdin (Passananti et al. 2016). However, ATL was not
142 degraded in light/Fe(III)-DFOB system (Fig. S7). It should be due to the too low concentration of ATL
143 (9.4 μ M) compared with 100 μ M of DFOB. The ROS was quenched by DFOB. A more sensitive
144 chemical probe (terephthalic acid, TA) was used to trap HO^{\bullet} and the formation of 2HTA was shown in
145 Fig. S8. There was 9.3 μ g/L of 2HTA formed after 10 min irradiation of Fe(III)-DFOB. The
146 steady-state concentrations of HO^{\bullet} was calculated as 1.46×10^{-7} M. The formation of HO^{\bullet} could be
147 concluded as shown in Equation (1) to (5). Fe(III)-DFOB with simulated solar light irradiation
148 underwent a ligand-to-metal-charge-transfer (LMCT) leading to Fe(II) formation and organic ligand
149 radicals similar with other Fe(III)-complex (Passananti et al. 2016, Wu et al. 2014, Wang et al. 2012),
150 as shown in Eq. (1). With the reaction with oxygen, $HO_2^{\bullet}/O_2^{\bullet-}$ were formed (Eq. 2-3) and the
151 self-annihilation of them would produce H_2O_2 (Eq. 4) (Bielski et al. 1985). Finally, HO^{\bullet} was produced
152 by the classical Fenton reaction (Eq.5) (Walling and Goosen 1973).





158 **Application of DFOB in the activation of PS for ATL degradation at neutral pH**

159 According to the results mentioned above, Fe(II) would be produced from the photolysis of
 160 Fe(III)-DFOB. Thus, Fe(III)-DFOB was applied as the source of Fe(II) to activate PS to enhance the
 161 ATL degradation. Fig. 2 showed the degradation of ATL in light/Fe(III)-DFOB/PS system. The
 162 concentration of Fe(III)-DFOB was set as 15 μ M according to the results of pre-experiments (as shown
 163 in Table S1). There was almost no degradation of ATL with the directly photolysis. Meanwhile, it was
 164 not surprised to see that 12.4% and 45.7% of ATL was degraded after 60 min reaction in PS/light
 165 system with 0.1 and 1.0 mM PS. Because PS would be activated by simulated sunlight irradiation
 166 directly and $SO_4^{\bullet -}$ would be produced to oxidize ATL. The ATL degradation rate was increased to 24%
 167 and 60.8% with the addition of Fe(III)-DFOB at pH 6.5. It meant Fe(III)-DFOB could enhance the PS
 168 activation even in neutral pH.



169

170 Fig. 2 Degradation of ATL in Fe(III)-DFOB/PS system under simulated sunlight irradiation

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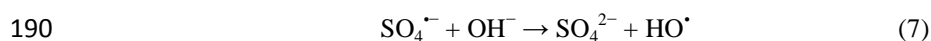
([Fe(III)-DFOB]=15 μ M, pH=6.5)

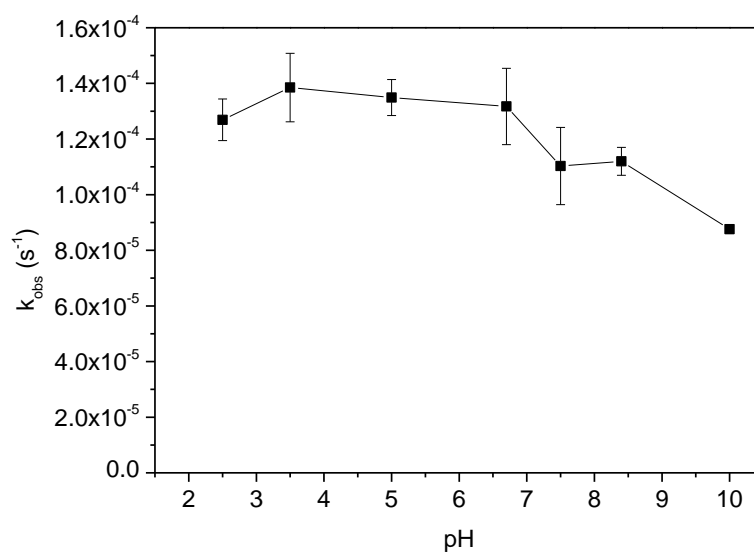
172 pH played an important role in chemical reaction, especially in iron participated oxidation
173 processes because it greatly influenced the speciation of ferric and ferrous iron. The degradation of
174 ATL was followed at different pH in light/PS/Fe(III)-DFOB system. The pseudo-first order reaction
175 rate constants for ATL degradation (k_{obs} , s^{-1}) were calculated according to Eq. (6) and the variety of k_{obs}
176 with different pH was shown in Fig. 3.

$$177 \quad C_t = C_0 e^{-k_{\text{obs}} t} \quad (6)$$

178 The k_{obs} was 1.269×10^{-4} , 1.385×10^{-4} , 1.349×10^{-4} , 1.317×10^{-4} , 1.103×10^{-4} , $1.1198 \times 10^{-4} \text{ s}^{-1}$
179 when the pH increased from 2.5 to 8.4. It was glad to see there was only slight fluctuation of ATL
180 degradation in such a large pH range. A inhibition was observed at pH 10.0 and the k_{obs} was decreased
181 to 0.876×10^{-4} . However, it was still better than the completely inhibition in UV/PS (Lin et al. 2011)
182 and Fe^{2+} /PS (Xu et al. 2010) processes.

183 It seems that DFOB could help the Fe(III) dissolve within the pH range of 2.5-8.4 and kept Fe(II)
184 formation. It was a breakthrough compared with the traditional/other Fenton-like processes (Xu et al.
185 2010; Kattel et al.2017; Costa et al. 2019) which could only be applied in acid pH range. The ATL
186 degradation was almost inhibited at pH 10.0. Because there was no Fe(II) formation due to the alkaline
187 condition. The radicals could only produce from the photolysis of PS. Moreover, many $\text{SO}_4^{\cdot-}$ were
188 converted to HO^{\cdot} as expressed in Eq. (7) which had a shorter life. It was also not conducive to ATL
189 degradation.





191

192 Fig. 3 The variety of ATL degradation efficiency in different pH conditions ($[ATL]=2.5$ mg/L,

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$[Fe(III)-DFOB]=15$ μ M, $[PS]= 500$ μ M, pH=6.5)

194 Identification of radicals

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Isopropanol (2-Pr) and ter-butyl alcohol (t-BuOH) with different initial concentrations were used as scavengers in light/PS/Fe(III)-DFOB system. 2-Pr was used as a quencher of both $SO_4^{\cdot-}$ and HO^{\cdot} (Buxton et al.,1988), while t-BuOH was as a scavenger for HO^{\cdot} , but not for $SO_4^{\cdot-}$ (Neta et al. 1988). 10 mM t-BuOH was added to quench HO^{\cdot} but not affect the reaction of $SO_4^{\cdot-}$. Different concentrations of 2-Pr were added to completely quench both radicals. The results were shown in Fig. 4. The results demonstrated that both $SO_4^{\cdot-}$ and HO^{\cdot} were responsible for ATL degradation, while $SO_4^{\cdot-}$ was the dominating one. The contribution percentage of each radical was about 85.5% and 14.5%.

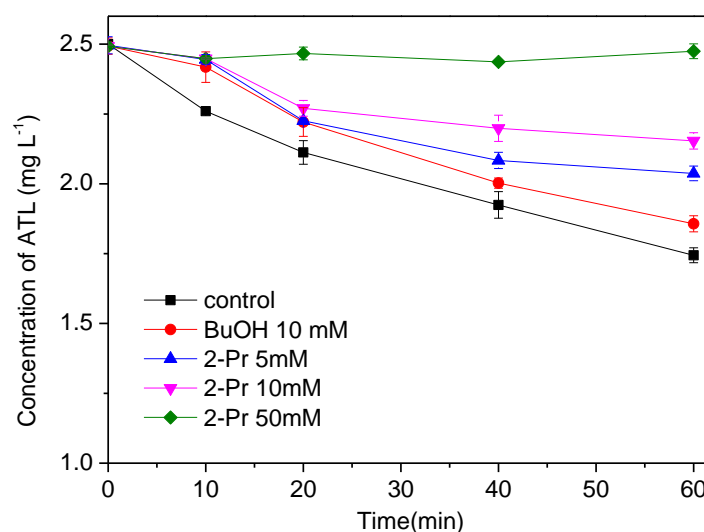
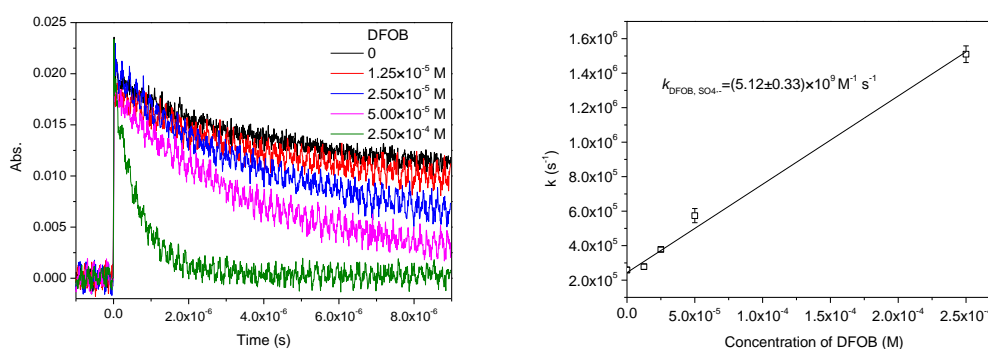


Fig. 4 Effect of different quenchers on ATL degradation

([Fe(III)]-DFOB = 15 μ M, [PS] = 500 μ M, pH = 6.5)

Determination of the second-order rate constant between $\text{SO}_4^{\cdot-}$ and DFOB

DFOB as an organic compound would competitively consume radicals. It was very important to estimate the second-order rate constant between $\text{SO}_4^{\cdot-}$ and DFOB ($k_{\text{SO}_4^{\cdot-}, \text{DFOB}}$). The transient decay spectra of $\text{SO}_4^{\cdot-}$ in the presence of DFOB were obtained via LFP experiments, as shown in Fig. 5(a). The different decay rate constants (k) were obtained when the increasing concentration of DFOB (C_{DFOB}) was added. Fig. 5(b) showed the linear relationship between k and C_{DFOB} . The $k_{\text{SO}_4^{\cdot-}, \text{DFOB}}$ was calculated as $(5.12 \pm 0.33) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. In our previous study (Wu et al. 2019a), $k_{\text{SO}_4^{\cdot-}, \text{ATL}}$ was estimated as $(8.7 \pm 0.6) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ with the same experimental method. It meant both the chelating agent and target pollutant had very high reactivity with $\text{SO}_4^{\cdot-}$. Although DFOB addition could enhance the production of Fe(II), the DFOB concentration should be strictly controlled to prevent it from consuming radicals.



216

217 Fig. 5 (a) The transient decay spectra of $\text{SO}_4^{\bullet-}$ with different DFOB concentration. (b) Relationship

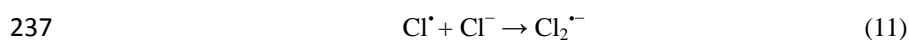
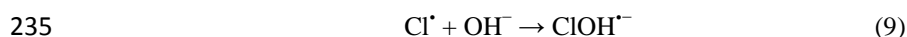
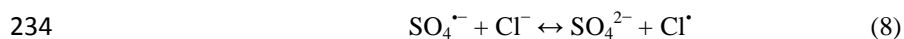
218 between the pseudo-first order decay of $\text{SO}_4^{\bullet-}$ and concentration of DFOB ($[\text{S}_2\text{O}_8^{2-}] = 5.0 \text{ mM}$; $\text{pH} =$

219 6.50)

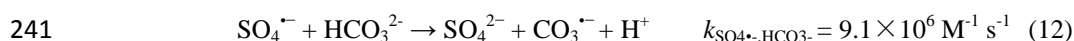
220 Effect of chloride and carbonate ion

221 Cl^- and $\text{HCO}_3^-/\text{CO}_3^{2-}$ were the most important anions in water treatment due to their obvious
 222 influence on the removal of target pollutants. The degradation of ATL with different concentration of
 223 Cl^- ($\text{pH}=6.5$) and HCO_3^- ($\text{pH}=8$) was investigated. The apparent first-order reaction rate constants of
 224 ATL degradation with Cl^- and HCO_3^- were calculated respectively, as shown in Table 1. The reaction
 225 condition was PS $500 \mu\text{M}$ and Fe(III)-DFOB $15 \mu\text{M}$.

226 As shown in Table 1, the addition of Cl^- had positive effect on ATL degradation. It was a
 227 coincident result with literatures (Wu et al. 2015, Wu et al. 2019a) when Cl^- was added at low
 228 concentrations range. Wu et al. (Wu et al. 2019b) used a calculation model to help explain the
 229 mechanism. The results of the calculation model showed that low concentrations of Cl^- transformed
 230 $\text{SO}_4^{\bullet-}$ into $\text{HO}^\bullet/\text{Cl}^\bullet$ but the further increased concentration of Cl^- could convert $\text{HO}^\bullet/\text{Cl}^\bullet$ into $\text{Cl}_2^{\bullet-}$ (with
 231 low reactivity) (Eq. 8-11). Moreover, the degradation of ATL in ATL/ Cl^- /light system (shown in Fig. S9)
 232 showed that Cl^\bullet could oxidize ATL directly. So the low concentrations of Cl^- in present study enhanced
 233 the degradation of ATL.



238 It was normal to see the inhibition of ATL degradation by adding HCO_3^- (Table 1). Because HCO_3^-
 239 would quench $\text{SO}_4^{\cdot-}$ to produce $\text{CO}_3^{\cdot-}$ which was a weak oxidative radical (Wu et al. 2015, Luo et al.
 240 2019).



242 Table 1 ATL degradation rate constant with different concentration of Cl^- and HCO_3^-

C_{Cl^-} (mg L ⁻¹)	k_{obs} (s ⁻¹)	$C_{\text{HCO}_3^-}$ (mg L ⁻¹)	k_{obs} (s ⁻¹)
0	1.317×10^{-4}	0	1.317×10^{-4}
10	1.487×10^{-4}	10	9.213×10^{-5}
50	1.658×10^{-4}	50	4.905×10^{-5}
100	2.119×10^{-4}	100	2.719×10^{-5}

243

244

245 Conclusions

246 Ferrous iron is the key parameter in PS activation process. A microbial siderophore
 247 Desferrioxamine B (DFOB) secreted by fungi was proposed to simultaneously complex with Fe^{3+} and
 248 generate Fe^{2+} under simulated sunlight irradiation. The molar proportion between Fe^{3+} and DFOB to
 249 form Fe(III)-DFOB complex was 1:1. The photolysis of Fe(III)-DFOB produced Fe(II) and HO^{\cdot} . The
 250 Fe(II) could be generated even in neutral pH. ATL as the target pollutant could be degraded in
 251 light/PS/Fe(III)-DFOB system and the degradation efficiency was kept stable with various pH (2.5-8.4).
 252 $\text{SO}_4^{\cdot-}$ was the dominating radical which responsible for ATL degradation. $k_{\text{DFOB}, \text{SO}_4^{\cdot-}}$ was measured as

253 $(5.12 \pm 0.33) \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ by LFP experiments. The high reaction rate constant further proved the both
254 positive and negative sides of DFOB in this reaction. But in any case, the pH range of the modified PS
255 activation process in this study was enlarged to neutral and weak-alkaline pH with a biodegradable
256 compound (DFOB). The chloride ion had slight enhancement of ATL degradation but carbonate ion had
257 inhibition effect. Although the degradation efficiency of ATL was not very high in the experimental
258 condition in this study, the mechanism and the role of DFOB were the focus of this research. The actual
259 work would be guided by the research results.

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