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## Transformation mechanisms of iopamidol by iron/sulfite systems: Involvement of multiple reactive species and efficiency in real water

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4

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## 20 **Abstract**

21 Although the ability of iron/sulfite system for decontamination purposes has been  
22 investigated, the complex reactive species generated and the underlying transformation  
23 mechanisms remain elusive. Here, we have comprehensively examined the  
24 transformation of iopamidol (IPM), a representative of iodinated X-ray contrast media,  
25 by iron catalyzed sulfite oxidation process under different water chemistry conditions.  
26 Multiple reactive intermediates including Fe(IV),  $\text{SO}_4^{\cdot-}$ , and  $\text{SO}_5^{\cdot-}$  were identified by  
27 conducting a series of experiments. Eight transformation products were detected by  
28 mass spectrometry analysis, and correlation with the nature of involved reactive species  
29 has been made. Further, the transformation pathway including amide hydrolysis,  
30 deiodination, amino and hydroxyl groups oxidation was proposed. Interestingly, these  
31 transformation products could be removed through adsorption to iron precipitates  
32 formed via pH adjustment. Combining Fourier transform infrared spectroscopy and X-  
33 ray photoelectron spectroscopy, we revealed an effective way to reduce the amount of  
34 transformation products in the treated solutions. Since the iron/sulfite process appears  
35 to be less sensitive to natural organic matter, it exhibited very good efficiency for IPM  
36 removal in real water samples, even with a high organic carbon loading. These findings  
37 may have strong implications in the development of novel oxidation process based on  
38 the sulfite/iron systems for wastewater treatment.

39

## 40 **Keywords**

41 Iodinated X-ray contrast media; sulfur radicals; Fe(IV); organic carbon

## 42 **1. Introduction**

43 Iodinated X-ray contrast media (ICM), used for medical imaging of internal organs,  
44 blood vessels and soft tissues, are the most widely administered intravascular  
45 pharmaceuticals with the worldwide consumption of  $3.5 \times 10^6$  kg per year (Duirk et al.,  
46 2011). This class of pharmaceuticals are specifically designed to be metabolically stable  
47 and almost completely excreted from the body via urine or faeces (Pérez et al., 2006).  
48 Due to their high solubility and poor biodegradability, conventional wastewater  
49 treatments are not effective in abating ICM, resulting in their occurrence in surface  
50 water and even drinking water ranging from  $\text{ng L}^{-1}$  to  $\mu\text{g L}^{-1}$  (Kormos et al., 2011;  
51 Putschew et al., 2000; Ternes and Hirsch, 2000; Xu et al., 2017). Iopamidol (IPM), a  
52 representative of ICM, is the most frequently detected at concentration level up to  $\mu\text{g}$   
53  $\text{L}^{-1}$ . Because of their high environmental concentrations and potential to leak through  
54 wastewater treatment plants and even reach drinking water, ICM has become chemicals  
55 of emerging concern to the public. Although ICM is believed not to be harmful, any  
56 subtle effects of mixtures, their metabolites, or other micropollutants are currently  
57 unknown and may pose ecological or human health issues (Ens et al., 2014).  
58 Considering their low biodegradability, ICM may also accumulate in the environment.  
59 Also, ICM might serve as the iodine source promoting the formation of iodinated by-  
60 products (Duirk et al., 2011; Pantelaki and Voutsas, 2018). For this reason, removal of  
61 ICM in water has been the subject of numerous studies (Cao et al., 2021; Chan et al.,  
62 2010; Jeong et al., 2010; Mao et al., 2020; Ternes et al., 2003; Tian et al., 2017; Wendel  
63 et al., 2014, Zhao et al., 2019).

64 Recently, ozone, chlorine, and chlorine dioxide were used as selective oxidant to  
65 remove ICM, which showed very limited efficiency with the maximum rate constant  
66 up the order of  $10 \text{ M}^{-1}\text{s}^{-1}$  (Ternes et al., 2003; Tian et al., 2017; Wendel et al., 2014).  
67 However, hydroxyl ( $\bullet\text{OH}$ ) and sulfate radicals ( $\text{SO}_4^{\bullet-}$ ) generated from UV/ $\text{H}_2\text{O}_2$ ,  
68  $\text{O}_3/\text{H}_2\text{O}_2$  or  $\text{O}_3/\text{PMS}$  systems were found to be able to transform ICM compounds with  
69 the reaction rate constant of  $\sim 10^9 \text{ M}^{-1}\text{s}^{-1}$  (Chan et al., 2010; Jeong et al., 2010; Mao et  
70 al., 2020). As compared to  $\bullet\text{OH}$ ,  $\text{SO}_4^{\bullet-}$  has been reported to be less influenced by natural  
71 organic matter in real water matrix (Gara et al., 2008; Lutze et al., 2015). Thus, sulfate  
72 radical based oxidation technologies could be considered as promising for ICM  
73 removal in wastewater.

74 Transition metal catalyzed sulfite is one of the possibilities for  $\text{SO}_4^{\bullet-}$  generation  
75 through chain propagation reactions (Brandt et al., 1994; Yermakov and Purmal, 2003).  
76 As compared to persulfates (peroxydisulfate and peroxymonosulfate), commonly  
77 employed as  $\text{SO}_4^{\bullet-}$  precursor, sulfite takes the advantage of lower toxicity and  
78 competitive price. For instance, the  $\text{LD}_{50}$  (oral, rat) of sulfite is 3560 mg/kg, three times  
79 higher than that of peroxydisulfate (802 mg/kg) (Zhou et al., 2018a). Among various  
80 transition metals, iron is the most widely used one for environmental application  
81 because of its cost effectiveness and environmentally friendly nature. This iron-  
82 catalyzed sulfite oxidation process in the atmospheric liquid phase has been extensively  
83 investigated due to its implication on the generation of acid rain (Brandt and van Eldik,  
84 1995). Recently, the iron/sulfite system has been investigated for water contaminants  
85 removal (e.g., dyes, aniline, and carbamazepine) (Chen et al., 2012; Dong et al., 2020;

86 Yu et al., 2016; Yuan et al., 2019). In these studies, multiple reactive intermediates  
87 including  $\text{SO}_4^{\bullet-}$ ,  $\bullet\text{OH}$  and peroxomonosulfate radical ( $\text{SO}_5^{\bullet-}$ ) were proposed to be the  
88 candidates of potential oxidant. For instance, Chen et al. (2012) reported that the  
89 efficient decolorization of orange II in the Fe(II)/sulfite system was mainly attributed  
90 to the contribution of  $\text{SO}_4^{\bullet-}$ , while  $\bullet\text{OH}$  and  $\text{SO}_5^{\bullet-}$  contribution were considered as  
91 minor. Other reports showed that the combination of Fe(II) or Fe(III) and sulfite could  
92 generate  $\text{SO}_5^{\bullet-}$ ,  $\text{SO}_4^{\bullet-}$  or  $\bullet\text{OH}$ , and then effectively remove organic contaminants  
93 (Dong et al., 2020; Yuan et al., 2019). Although the good ability of the iron/sulfite  
94 system for contamination removal has been investigated, the underlying mechanisms  
95 of generation of reactive species and target compound degradation remain elusive. In  
96 addition, very little is known about the application of this process for ICM  
97 transformation, and much less on the influence of key factors (*e.g.*, pH and water matrix)  
98 on the removal performance.

99 In this work, the performance and mechanism of the iron/sulfite system for the  
100 degradation of IPM were investigated for the first time. The primary objectives of the  
101 present work were to (i) assess the oxidation efficiency of the iron/sulfite system in  
102 IPM transformation; (ii) identify the reactive intermediates responsible for IPM  
103 degradation; (iii) elucidate the reaction mechanism based on the identified oxidation  
104 products; (iv) evaluate the influence of pH adjustment of the resulting solutions and  
105 water matrix on the performance of the iron/sulfite system.

## 106 **2. Experimental Section**

### 107 **2.1. Materials**

108 All chemicals were of analytical purity or higher and used without further purification  
109 unless otherwise stated. IPM (98%) was obtained from Macklin Biochemical Co., Ltd.  
110 Sodium sulfite ( $\text{Na}_2\text{SO}_3$ ; AR,  $\geq 97.0\%$ ) and ethanol (AR,  $\geq 95.0\%$ ) were purchased  
111 from Chemical Reagent Co. Ltd. Iron nitrate nonahydrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , AR),  
112 ferrous sulfate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ; AR,  $\geq 99.0\%$ ), and tert-butyl alcohol  
113 (TBA  $>99.5\%$ ) were purchased from Aladdin Biochemical Co., Ltd.  
114 Peroxymonosulfate (PMS, available as Oxone), methyl phenyl sulfoxide (PMSO,  $\geq$   
115  $97\%$ ) and methyl phenyl sulfone ( $\text{PMSO}_2$ ; GC,  $\geq 98\%$ ), humic acid (HA) and acetic  
116 acid for HPLC were obtained from Sigma-Aldrich. Methanol and acetonitrile of  
117 chromatographic grad were obtained from Merck KGaA. All solutions were prepared  
118 using deionized (DI) water ( $18.2 \text{ M}\Omega \cdot \text{cm}$ ) from a Millipore purification system. The  
119 stock solutions of HA were purified by repeated pH adjustment, filtration, and  
120 precipitation. Stock solutions of sulfite and ferrous sulfate were freshly prepared before  
121 experiments. Real water samples were taken from the filtered water of secondary  
122 effluent of Lijiao Wastewater Treatment Plant (located in Haizhu district of Guangzhou  
123 in China; Dissolved organic carbon (DOC) of  $5.6 \text{ mg L}^{-1}$ ,  $\text{UV}_{254}$  absorbance of  $0.075$   
124  $\text{cm}^{-1}$ ,  $\text{Cl}^-$  of  $1.8 \text{ mM}$  and pH of  $7.3$ ) and central lake in Guangzhou (GPS coordinate of  
125  $23^\circ 03' 07.3'' \text{N} / 113^\circ 23' 21.8'' \text{E}$ ; DOC of  $12.6 \text{ mg L}^{-1}$ ,  $\text{UV}_{254}$  absorbance of  $0.083 \text{ cm}^{-1}$ ,  
126  $\text{Cl}^-$  of  $1.6 \text{ mM}$  and pH of  $6.8$ ). After filtering through glass fiber membranes, these water  
127 samples were stored at  $4^\circ \text{C}$ .

## 128 **2.2. Experimental procedure**

129 Batch experiments were conducted in open beakers with 100 mL capacity under  
130 magnetic stirring. To initiate the reactions, predetermined amounts of iron ion (50  $\mu\text{M}$ )  
131 and sulfite (300  $\mu\text{M}$ ) were simultaneously added into stirring solutions containing IPM  
132 and/or constituents (e.g.,  $\text{Cl}^-$  and humic acid) of interest at desirable concentrations. At  
133 specific time intervals, reaction solution was sampled and quenched by excess methanol  
134 for the following measurement of IPM or the analysis of transformation products.  
135 Experiments in real waters were conducted following the similar procedure as that in  
136 synthetic solutions except that a relatively low concentration of IPM (500 nM) was used  
137 to simulate environmental levels.

138 Unless otherwise stated, the experiments in this study were conducted at controlled  
139 temperature ( $25 \pm 1$  °C) in ambient atmosphere. The solution pH was adjusted with  
140  $\text{HClO}_4$  and NaOH. To ensure reproducibility, the experiments were conducted in  
141 triplicates with results presented as the average data and the relative standard deviations  
142 were also presented.

### 143 **2.3. Analytical Methods**

144 IPM was quantified by using a Waters Alliance e2695 HPLC. The separation was  
145 achieved by a Waters XBridge C18 column (4.6 $\times$ 250 mm, 5 $\mu\text{m}$  particle size) and the  
146 mobile phase consisted of 0.1% acetic acid and methanol with a ratio of 90:10 (v/v) at  
147 a flow rate of 0.5 mL/min. The wavelength for IPM was set at 242 nm. PMSO and  
148 PMSO<sub>2</sub> were analyzed by HPLC/UV at 230 and 215 nm, with the eluent of 0.1% acetic  
149 acid and acetonitrile at a flow rate of 1 mL/min. A Sciex QTrap 5500 MS with an ESI  
150 source was used for products identification and quantification. The MS instrumental



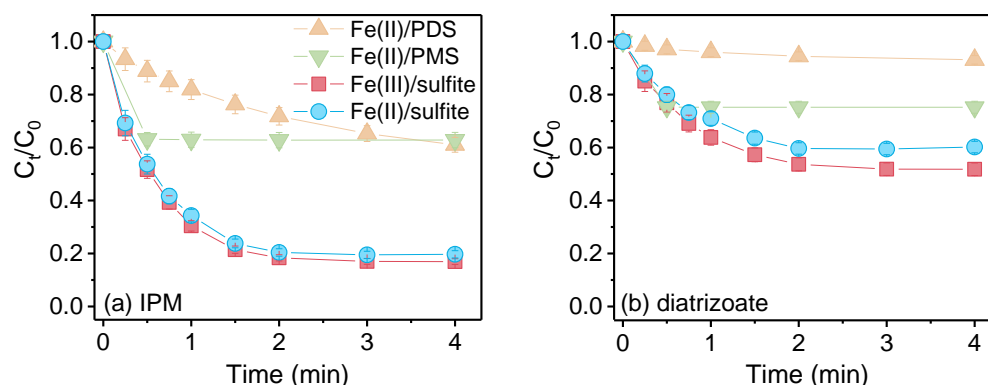
151 parameters were provided in Text S1. Electron paramagnetic resonance (EPR) analysis  
152 using DMPO as a spin-trapping agent was performed on a Bruker A200 spectrometer,  
153 and the detailed parameters were shown in Text S2. Fourier transform infrared  
154 spectroscopy (FTIR) analysis was conducted on a Shimadzu IRTracer-100 and the  
155 samples was prepared by vacuum filtration via 0.45  $\mu\text{m}$  filters. X-ray photoelectron  
156 spectrometer (XPS) was conducted on a Thermo Fisher Escalab 250Xi and the samples  
157 was prepared by vacuum filtration via 0.45  $\mu\text{m}$  filters followed by vacuum drying. The  
158 DOC content of HA stock solution was determined using Shimadzu TOC-L. Solution  
159 pH was measured with Leici PHS-3C pH-meter (Shanghai INESA Scientific  
160 Instrument Co.Ltd). Dissolved oxygen was detected using Hach HQ40d Portable  
161 Meters. Absorbance was measured by Hach DR6000 Spectrophotometer.

### 162 **3. Results and Discussion**

#### 163 **3.1 Degradation of IPM by iron/sulfite**

164 **Figure 1** comparatively showed the degradation of IPM in the Fe/sulfite as well as  
165 Fe(II)/persulfates (PDS or PMS). The combination of Fe(III) (50  $\mu\text{M}$ ) and sulfite (300  
166  $\mu\text{M}$ ) led to an efficient abatement of IPM (5  $\mu\text{M}$ ) at  $\text{pH}_{\text{ini}}$  4, where  $\sim 85\%$  removal of  
167 IPM was achieved. Interestingly, Fe(II)/sulfite exhibited a similar reactivity toward  
168 IPM removal. Comparatively, Fe(II)/PMS and Fe(II)/PDS systems only achieved  $\sim 40\%$   
169 removal under the same conditions. Similar findings were obtained in the case of  
170 diatrizoate, a relatively refractory ICM. The removal percentage of diatrizoate in the  
171 iron/sulfite system ( $\sim 50\%$ ) was at least more than twice that in the Fe(II)/PMS and  
172 Fe(II)/PDS systems ( $< 25\%$ ) (**Fig. 1**). These findings indicated the higher oxidation

173 efficiency of iron/sulfite system in ICM abatement as compared to commonly used  
174 iron-based Fenton-like AOPs.



175

176 **Fig. 1** Degradation of IPM (a) or diatrizoate (b) in the iron/sulfite and iron/persulfates  
177 systems. Experimental conditions: [IPM] = 5  $\mu$ M, [Fe(II)] = [Fe(III)] = 50  $\mu$ M, [sulfite]  
178 = [persulfates] (i.e., [PDS] or [PMS]) = 300  $\mu$ M, and  $\text{pH}_{\text{ini}} = 4$ .

179 Further, the effect of  $\text{pH}_{\text{ini}}$  on the performance of Fe(III)/sulfite system was examined.

180 It was found that efficiency of Fe(III)/sulfite system increased first as  $\text{pH}_{\text{ini}}$  increased

181 from 3 to 4, and then decreased when  $\text{pH}_{\text{ini}}$  further increased and became negligible at

182 higher pH values (7 and 9) (Fig. S1a). The pH variation was also measured and the

183 solution pH at the end of reaction ( $\text{pH}_{\text{final}}$ ) was shown in Figure S1b. To evaluate the

184 reaction kinetics at different  $\text{pH}_{\text{ini}}$ , the initial reaction rates  $k_{\text{ini}}$  over the first reaction

185 time (within 1 min) was determined. The  $k_{\text{ini}}$  value first increased from 0.80 to 1.23

186  $\text{min}^{-1}$  as  $\text{pH}_{\text{ini}}$  increased from 3 to 4, and then decreased to 0.08  $\text{min}^{-1}$  as pH further

187 increased to  $\text{pH}_{\text{ini}}$  9. This could be probably due to the combined effect of pH on the

188 distribution of sulfite species and iron speciation in solution (Guo et al., 2013). Acidic

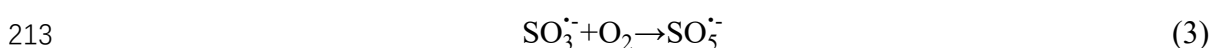
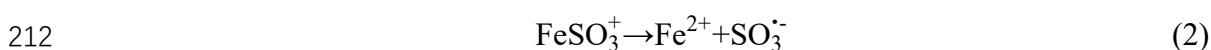
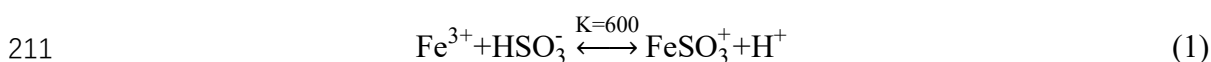
189 pH may facilitate the formation of sulfur dioxide, thus decreasing the effective

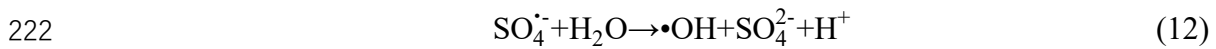
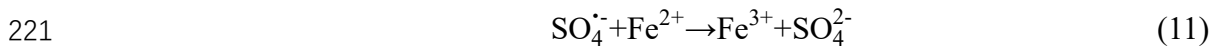
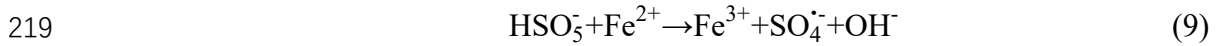
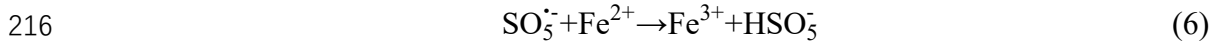
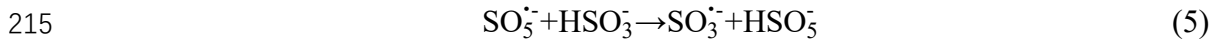
190 concentration of  $\text{HSO}_3^-$ . At higher pH, iron precipitation takes place, thereby decreasing

191 the dissolved iron concentration available for sulfite activation.

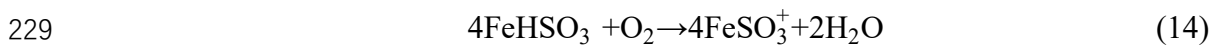
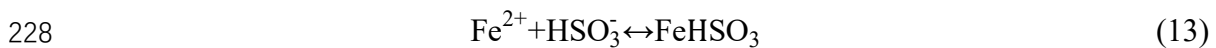
## 192 3.2 Identification of reactive radical species

193 Preliminary experiments showed that negligible degradation of IPM was observed in  
194 the case of Fe(III) or sulfite alone (Fig. S2). Therefore, Fe(III)-induced activation of  
195 sulfite is likely to occur for the generation of reactive species. A radical mechanism has  
196 been well reported for the complex reaction of Fe(III) catalyzed sulfite auto-oxidation  
197 (eqs. 1-12) (Brandt et al., 1994). The fast formation of Fe(III)-sulfite complex ( $K_{\text{Fe(III)-sulfite}} = 600$ ) and its subsequent decomposition to Fe(II) and  $\text{SO}_3^{\bullet-}$  is considered as the  
198 core of the reactions (eqs. 1-2), which participate to the generation of  $\text{SO}_3^{\bullet-}$  as the  
199 initiation step of catalytic sulfite oxidation. In the present work, the degradation of IPM  
200 was completely inhibited with the addition of EDTA and pyrophosphate, stronger  
201 chelators for iron (e.g.,  $K_{\text{Fe(III)-EDTA}} = 10^{24.23}$ ) (Fig. S3). Then, the generated  $\text{SO}_3^{\bullet-}$  may  
202 combine quickly with oxygen ( $\text{O}_2$ ) leading to the formation of  $\text{SO}_5^{\bullet-}$  (eq. 3). This  
203 reactive species may oxidize either sulfite or Fe(II) resulting in the production of sulfur-  
204 containing intermediates including  $\text{SO}_4^{\bullet-}$ ,  $\text{SO}_3^{\bullet-}$  and  $\text{HSO}_5^-$  (peroxymonosulfate ion)  
205 (eqs. 4-6). These intermediates could further induce several redox processes such as  
206 oxidizing sulfite or Fe(II) (eqs. 7-12). This was consistent with the evolution of sulfite  
207 (continuous degradation) and Fe(II) (initial increase concentration and then decrease)  
208 observed during the reaction in the present study (Fig. S4). In addition,  $\bullet\text{OH}$  might be  
209 generated from the reaction of  $\text{SO}_4^{\bullet-}$  and  $\text{H}_2\text{O}$  (Neta et al., 1988).





223 In the case of Fe(II), a rapid formation of  $\text{FeSO}_3^+$  is possible (eqs. 13-14) (Chen  
 224 et al., 2012; Guo et al., 2013), which would in turn follow the same reaction chain (eqs.  
 225 2-12). Therefore, the same reactive species should be involved in Fe(II)/sulfite and  
 226 Fe(III)/sulfite systems, thereby explaining their similar performance in IPM  
 227 degradation as observed in Figure 1a.

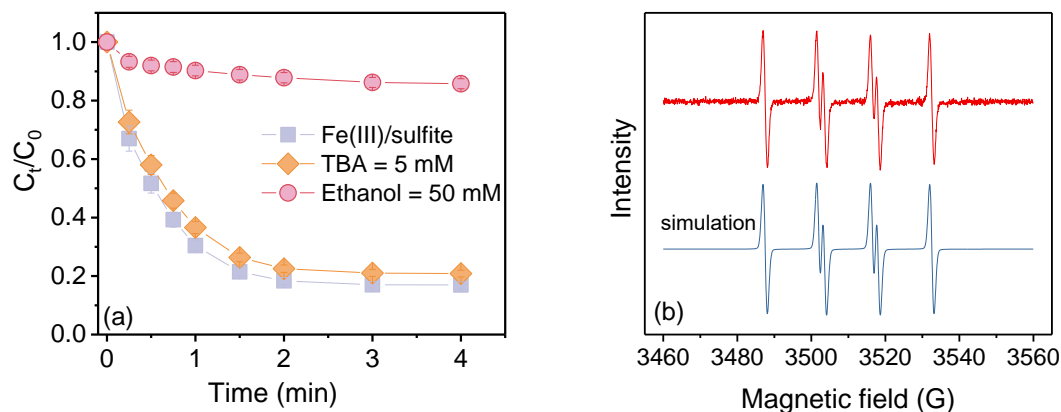


### 230 3.2.1 Role of $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ in IPM degradation

231 According to eqs. 1-12,  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$  were usually considered as the primary reactive  
 232 species responsible for contaminant degradation in the iron ions/sulfite system (Chen  
 233 et al., 2012; Dong et al., 2020). To gain further insights into the role of  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$   
 234 in IPM degradation, alcohol scavenging experiments were conducted. The inhibitory  
 235 effects of ethanol and TBA (commonly used scavengers) could be used as a mean to

236 verify the contribution of  $\text{SO}_4^{\bullet-}$  and  $\bullet\text{OH}$ . Ethanol could react quickly with both  $\text{SO}_4^{\bullet-}$   
237 and  $\bullet\text{OH}$  with the rate constants of  $1.6\text{-}7.7 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$  and  $1.2\text{-}2.8 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$  (Buxton  
238 et al., 1988; Neta et al., 1988). TBA could effectively scavenge  $\bullet\text{OH}$  with the rate  $3.8\text{-}$   
239  $7.6 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ , which was about 3 orders of magnitude higher than the rate constant  
240 for the reaction of TBA and  $\text{SO}_4^{\bullet-}$  ( $4.0\text{-}9.1 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ ) (Buxton et al., 1988; Neta et  
241 al., 1988). The rate constants for the reaction of IPM with  $\bullet\text{OH}$  and  $\text{SO}_4^{\bullet-}$  are  $3.4 \times 10^9$   
242  $\text{M}^{-1}\text{s}^{-1}$  and  $1.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$  as reported in literature (Jeong et al., 2010; Mao et al., 2020).  
243 Theoretically, the addition of 5 mM TBA or 50 mM ethanol could almost completely  
244 suppress the degradation of IPM (5  $\mu\text{M}$ ) by  $\bullet\text{OH}$  or  $\text{SO}_4^{\bullet-}$  ( $k_{\text{OH}^{\bullet}\text{-TBA}}[\text{TBA}] >$   
245  $100k_{\text{OH}^{\bullet}\text{-IPM}}[\text{IPM}]$ ,  $k_{\text{SO}_4^{\bullet-}\text{-ethanol}}[\text{ethanol}] > 100k_{\text{SO}_4^{\bullet-}\text{-IPM}}[\text{IPM}]$ ; details in Text S3). As  
246 shown in **Figure 2a**, 5 mM TBA slightly affected the degradation of IPM, excluding  
247 the involvement of  $\bullet\text{OH}$ . This might be due to the slow formation rate of  $\text{SO}_4^{\bullet-}$  from  
248 the reaction of  $\bullet\text{OH}$  with water ( $<6 \text{ M}^{-1} \text{ s}^{-1}$ , eq. 12). This finding was also confirmed  
249 by the EPR analysis where characteristic spectrum of the hydroxyl radical was not  
250 observed in the Fe(III)/sulfite system (**Fig. 2b**). Comparatively, ethanol considerably  
251 suppressed the degradation of IPM, suggesting the possible involvement of  $\text{SO}_4^{\bullet-}$ .  
252 Although the signal of  $\text{DMPO}/\text{SO}_4^{\bullet-}$  was not observed, the characteristic spectrum of  
253 EPR analysis for the  $\text{DMPO}/\text{SO}_3^{\bullet-}$  adduct ( $\alpha^{\text{N}} = 14.7 \text{ G}$ ,  $\alpha^{\text{H}} = 15.9 \text{ G}$ ) was detected (**Fig.**  
254 **2b**) (Mottley and Mason, 1988). The absence of  $\text{DMPO}/\text{SO}_4^{\bullet-}$  signal might be due to  
255 the high concentration of DMPO, which could completely trap  $\text{SO}_3^{\bullet-}$  and thus inhibited  
256  $\text{SO}_4^{\bullet-}$  generation (eqs 3-9) (Yuan et al., 2016). Interestingly,  $\sim 15\%$  IPM removal was still  
257 achieved in the presence of 50 mM ethanol, suggesting that other reactive species could

258 be involved in the Fe(III)/sulfite system.

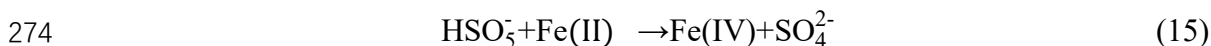


259

260 **Fig. 2** Effect of alcohol scavengers on IPM degradation in the Fe(III)/sulfite system as  
261 well as the EPR spectra obtained from the Fe(III)/sulfite/DMPO system (red line) and  
262 the simulation of DMPO- $\text{SO}_3^{\cdot-}$  adduct (blue line). Experimental conditions: [IPM] = 5  
263  $\mu\text{M}$ , [Fe(III)] = 50  $\mu\text{M}$ , [sulfite] = 300  $\mu\text{M}$ ,  $\text{pH}_{\text{ini}} = 4$ , and [TBA] = 5 mM, [ethanol] =  
264 50 mM for (a), or [DMPO] = 10 mM for (b).

### 265 3.2.2 Role of Fe(IV) in IPM degradation

266 In previous studies, the reaction of  $\text{HSO}_5^-$  (*i.e.*, monoanion form of PMS) and Fe(II)  
267 depicted as eq. 9 was usually considered as the main source for  $\text{SO}_4^{\cdot-}$  in the  
268 Fe(III)/sulfite system (Chen et al., 2012; Dong et al., 2020). However, Fe(IV) has been  
269 reported to be the primary oxidant in the Fe(II)/PMS, generated from Fe(II) and  $\text{HSO}_5^-$ ,  
270 in a recent work (Wang et al. 2018) (eq. 15). This Fe(IV) generation has been proposed  
271 based on conversion reaction of methyl phenyl sulfoxide (PMSO) to methyl phenyl  
272 sulfone ( $\text{PMSO}_2$ ) via oxygen electron transfer. Comparatively,  $\text{PMSO}_2$  was not  
273 generated in the case of free radicals (Wang et al. 2018).

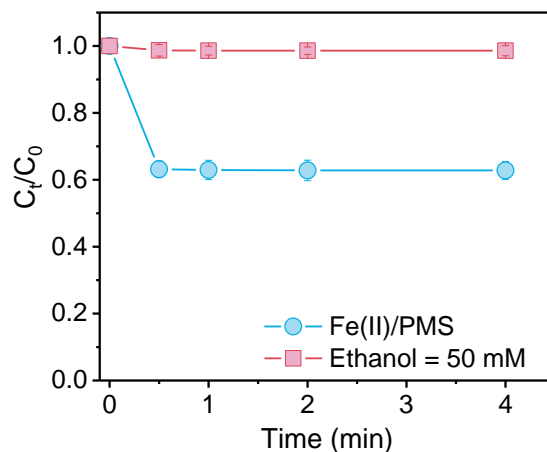


275 Thus, it is quite plausible that Fe(IV) was involved in the Fe(III)/sulfite system  
276 generated from eq. 15. In order to verify this possibility, the degradation of methyl  
277 phenyl sulfoxide (PMSO) in the Fe(III)/sulfite system was examined. As expected, the

278 formation of methyl phenyl sulfone (PMSO<sub>2</sub>) (1.1 μM) was observed from the  
279 transformation of 2.8 μM PMSO, suggesting the involvement of other reactive  
280 intermediates (possibly Fe(IV)) in the Fe(III)/sulfite system.

281 Fe(IV) is known to serve as an oxidant with considerable selectivity. For instance,  
282 the rate constants for the reaction of Fe(IV) with phenol and dimethyl sulfoxide (DMSO)  
283 were reported to be  $k_{\text{phenol}} = 4 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$  and  $k_{\text{DMSO}} = 1.26 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ ,  
284 respectively (Jacobsen et al., 1998; Mártire et al., 2002). To evaluate the oxidizing  
285 ability of Fe(IV) toward IPM, the degradation of IPM in the Fe(II)/PMS and  
286 Fe(II)/HOCl systems was examined, wherein Fe(IV) has been reported to be the  
287 primary oxidant (Fig.3 and Fig. S5). Significant IPM degradation was observed  
288 suggesting that Fe(IV) could contribute to IPM removal in the Fe(III)/sulfite system.

289 Interestingly, 50 mM ethanol was found to completely inhibit the degradation of  
290 IPM in the Fe(II)/PMS system (**Fig. 3**), underscoring the role of ethanol as an effective  
291 scavenger for Fe(IV). This was also consistent with previous work on the inhibitory  
292 effect of ethanol on the Fe(II)/ozone and Fe(II)/HOCl systems, where Fe(IV) served as  
293 the main reactive intermediates (Liang et al., 2020; Pestovsky and Bakac, 2004).  
294 However, partial inhibition was observed in the Fe(III)/sulfite system upon addition of  
295 50 mM ethanol (**Fig. 2a**), suggesting that other reactive intermediates, in addition to  
296 SO<sub>4</sub><sup>•-</sup> and Fe(IV), may exist in the Fe(III)/sulfite system.



297

298 **Fig. 3** Effect of alcohol scavengers on IPM degradation in the Fe(II)/PMS.  
 299 Experimental conditions: [IPM] = 5  $\mu$ M, [Fe(II)] = 50  $\mu$ M, [PMS] = 300  $\mu$ M, pH<sub>ini</sub> = 4,  
 300 and [ethanol] = 50 mM.

301

### 302 3.2.2 Role of $\text{HSO}_5^-$ , $\text{SO}_3^{\cdot-}$ and $\text{SO}_5^{\cdot-}$ in IPM degradation

303 Recently,  $\text{HSO}_5^-$  (*i.e.*, monoanion form of PMS) was found to be a mild oxidant towards

304 organic compounds such as estrogens and antibiotics with the rate constants ranging

305 from 0.5-30  $\text{M}^{-1}\text{s}^{-1}$  (Zhou et al., 2018b, 2018c). Here, the degradation of IPM by  $\text{HSO}_5^-$

306 was found negligible (**Fig. 4a**), ruling out the contribution of  $\text{HSO}_5^-$  to IPM degradation

307 in the iron/sulfite system.  $\text{SO}_3^{\cdot-}$  with a redox potential of  $E(\text{SO}_3^{\cdot-}/\text{HSO}_3^-) = 0.84$  V (vs.

308 NHE) could act as a weak oxidant or a strong reductant (Neta and Huie, 1985a).

309 Experiments were conducted in anaerobic condition to examine the reactivity of  $\text{SO}_3^{\cdot-}$

310 toward IPM. Less than 10% of IPM was degraded in the absence of  $\text{O}_2$ , where  $\text{SO}_3^{\cdot-}$

311 served as the predominant oxidant (**Fig. 4b**), underscoring the minor role of  $\text{SO}_3^{\cdot-}$  in

312 IPM degradation. However, it should be noted that  $\text{SO}_3^{\cdot-}$  could quickly react with  $\text{O}_2$

313 with the second-order rate constant up to  $2.5 \times 10^9 \text{M}^{-1}\text{s}^{-1}$  as described in eq. 3 (Fronaeus

314 et al., 1998). The evolution of dissolved  $\text{O}_2$  during the reaction was also monitored (**Fig.**

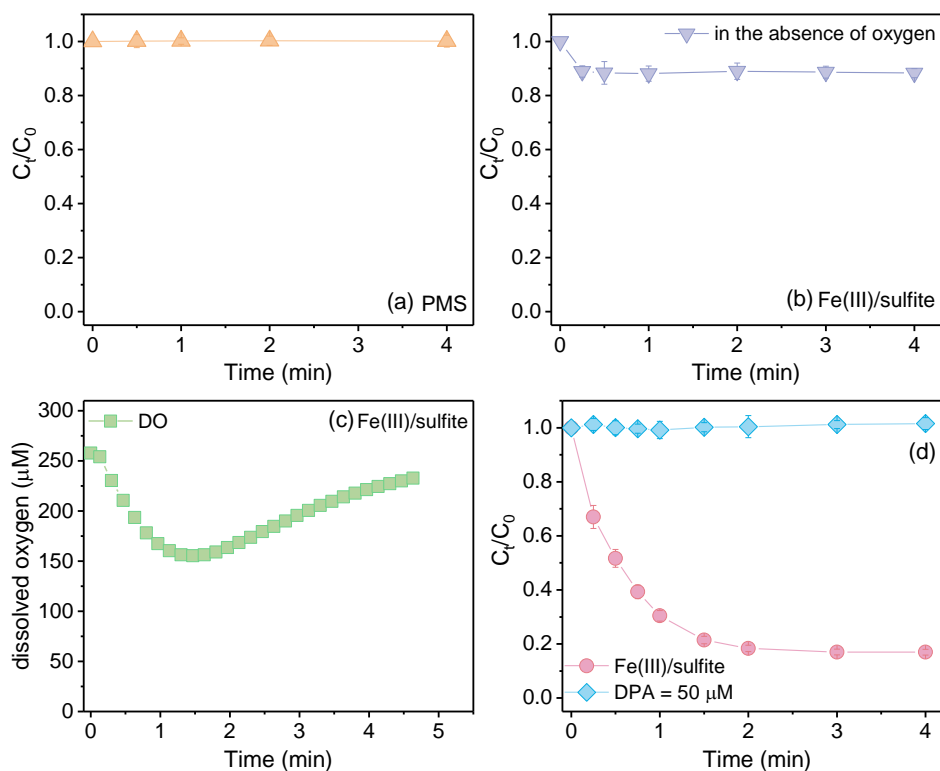
315 **4c**). The initial decrease of  $\text{O}_2$  further confirmed the participation of  $\text{O}_2$  (eq. 3) in the



316 Fe(III)/sulfite oxidation process, while further increase of O<sub>2</sub> level might be due to the  
317 redissolution of O<sub>2</sub> under open atmosphere. Given the fast reaction of SO<sub>3</sub><sup>•-</sup> with O<sub>2</sub>  
318 and the relatively high concentration of dissolved O<sub>2</sub> (≥ 155 μM under atmospheric  
319 pressure), SO<sub>3</sub><sup>•-</sup> would be quickly reacted with O<sub>2</sub> rather than with IPM.

320 SO<sub>5</sub><sup>•-</sup>, a relatively stronger oxidant, has been reported to react effectively with  
321 several organics such as aromatic amines and hydroxyphenols (Huie and Neta, 1984;  
322 Neta and Huie, 1985b). For instance, the rate constants for the reaction of Trolox with  
323 SO<sub>5</sub><sup>•-</sup> was reported to be 1.2 × 10<sup>7</sup> M<sup>-1</sup> s<sup>-1</sup>, more than 10 times the rate constant for the  
324 SO<sub>3</sub><sup>•-</sup> reaction (~10<sup>6</sup> M<sup>-1</sup> s<sup>-1</sup>). Therefore, SO<sub>5</sub><sup>•-</sup> might also participate in IPM oxidation  
325 in the Fe(III)/sulfite system. In contrast to SO<sub>4</sub><sup>•-</sup> and Fe(IV), SO<sub>5</sub><sup>•-</sup> is relatively inert  
326 toward ethanol with a low rate constant, ~10<sup>3</sup> M<sup>-1</sup>s<sup>-1</sup> (Neta et al., 1988). Thus, the IPM  
327 degradation (~15%) observed in excess ethanol (**Fig. 2a**) could be resulted from the  
328 contribution of SO<sub>5</sub><sup>•-</sup>. Diphenylamine (DPA) with a relatively higher rate constant with  
329 SO<sub>5</sub><sup>•-</sup> is usually used as scavenger to terminate the contribution of SO<sub>5</sub><sup>•-</sup> (Neta and Huie,  
330 1985b; Yuan et al., 2019). Here, the effect of DPA on IPM degradation in the  
331 Fe(III)/sulfite system was examined. In contrast to the partial inhibitory effect of  
332 ethanol, IPM was completely suppressed in the presence of 50 μM DPA (**Fig.4d**),  
333 further suggesting the role of SO<sub>5</sub><sup>•-</sup> in IPM degradation in the iron/sulfite system.

334 Taken together, these findings suggest that multiple reactive species including  
335 Fe(IV), SO<sub>4</sub><sup>•-</sup>, and SO<sub>5</sub><sup>•-</sup> could contribute to the IPM transformation in the iron/sulfite  
336 system.



337

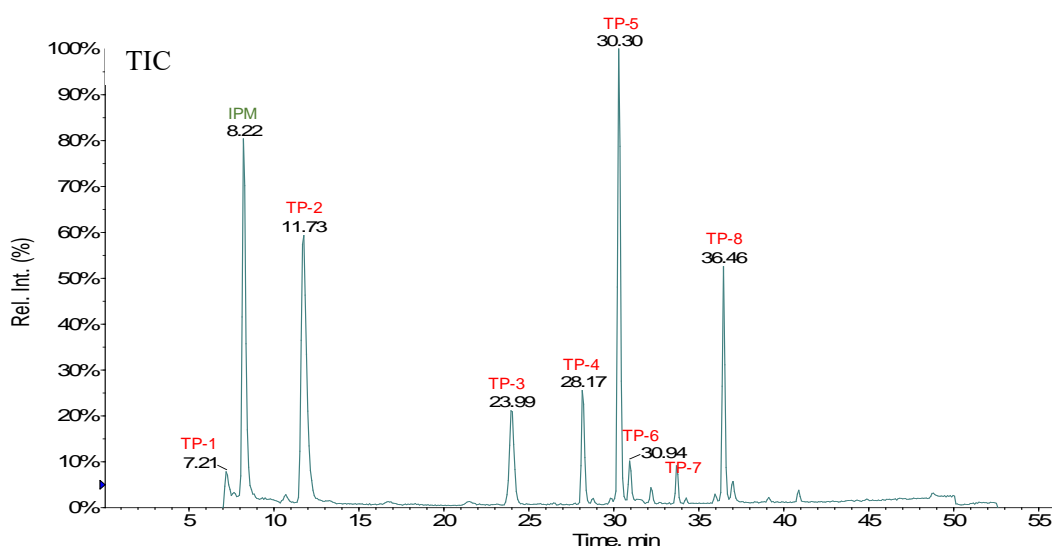
338 **Fig. 4** Oxidation of IPM by PMS under open atmosphere (a), by Fe(III)/sulfite  
 339 in the absence of oxygen (b), evolution of oxygen during Fe(III)/sulfite system and  
 340 effect of DPA on the degradation of IPM in the Fe(III)/sulfite system under a open  
 341 atmosphere. Experimental conditions: [IPM] = 5  $\mu$ M, [Fe(III)] = 50  $\mu$ M, [sulfite] = 300  
 342  $\mu$ M, pH<sub>ini</sub> = 4, and [PMS] = 300  $\mu$ M for (a), or [DPA] = 50  $\mu$ M for (d).

343

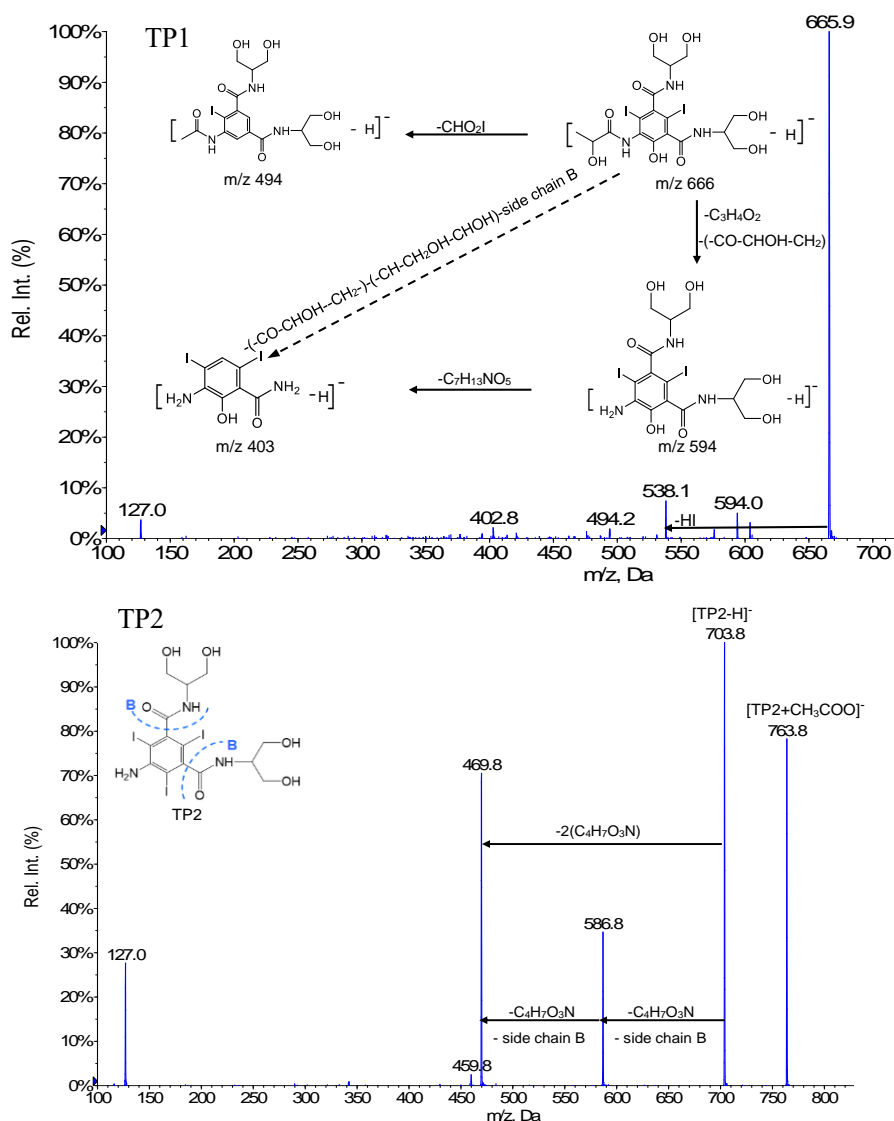
### 344 3.4 Transformation mechanism

345 ESI-MS at precursor ion scan (PIS) mode was used to selectively detect polar  
 346 halogenated compounds. Given three iodine atoms in IPM, this approach setting  
 347 precursor ion at m/z 127 was used to detect the primary transformation products of IPM  
 348 in the Fe(III)/sulfite system. **Figure 5** showed the HPLC/ESI-MS chromatogram of  
 349 IPM after the treatment of Fe(III)/sulfite with eight new peaks corresponding to  
 350 transformation products (TPs). These TPs were further identified based on their  
 351 molecular mass and MS/MS fragmentations. For instance, TP 1 eluting at 7.21 min had  
 352 the molecular ion of m/z 667, 110 Da loss as compared to IPM of m/z 777 (as

353 [C<sub>17</sub>H<sub>22</sub>I<sub>3</sub>N<sub>3</sub>O<sub>8</sub>] with the retention time of 8.22 min. This product was proposed to be  
354 a hydroxylated product C<sub>17</sub>H<sub>23</sub>I<sub>2</sub>N<sub>3</sub>O<sub>9</sub>, consistent with the nitrogen rule and its  
355 fragments observed in the product ion scan spectra. The fragment ions of 72 (-CO-  
356 CHOH-CH<sub>2</sub>), 263 (-CO-CHOH-CH<sub>2</sub>-, -CH-CH<sub>2</sub>OH-CHOH-, -CO-NH-CH-CH<sub>2</sub>OH-  
357 CHOH-) indicated the intact acylamino side chain A and carboxamide side chains B.  
358 TP 2 at the retention time of 11.73 min has the molecular ion of m/z 705. Two major  
359 products m/z 587 (-117) and m/z 467 (-324) were observed in its product ion scan  
360 spectra, corresponding to the successive loss of two side chain B (-CO-NH-CH-  
361 CH<sub>2</sub>OH-CHOH-). This finding indicated carboxamide side chains were intact in this  
362 product and it might be generated from the cleavage of C-N bond in the amide moiety  
363 of acylamino side chain A. Following similar procedure, other TPs were identified (Fig.  
364 S6-S11) and their information including retention time, molecular mass, chemical  
365 formula and proposed molecular structure were shown in **Table 1**.



366



367

368

369 **Fig.5** The HPLC/ESI-MS chromatograms of IPM after the treatment of Fe(III)/sulfite  
 370 and fragmentation pattern of TP-1 and TP-2. Experimental condition: [IPM] = 5  $\mu\text{M}$ ,  
 371 [Fe(III)] = 50  $\mu\text{M}$ , [sulfite] = 300  $\mu\text{M}$ , and  $\text{pH}_{\text{ini}} = 4$

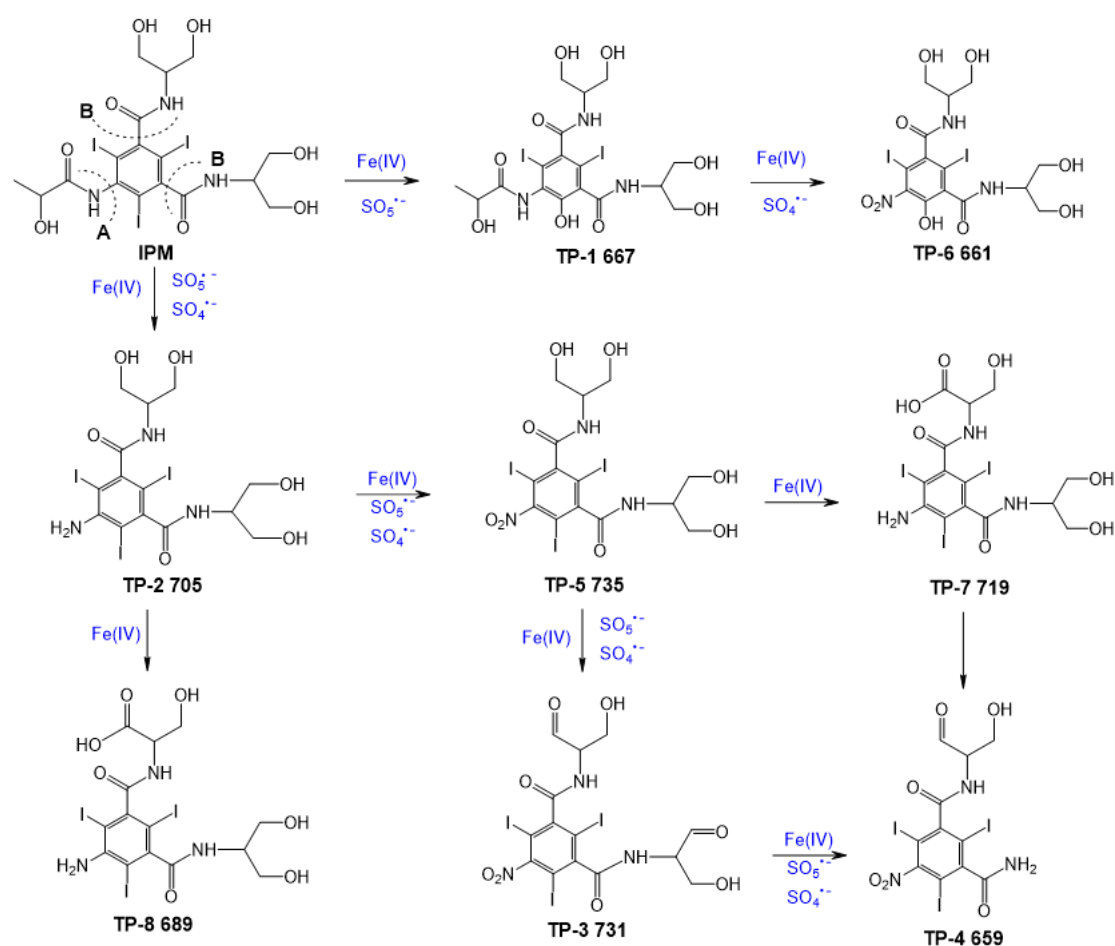
372 To further understand the transformation pathway, the transformation products of  
 373 IPM by  $\text{SO}_4^{\bullet-}$ ,  $\text{SO}_5^{\bullet-}$ , and Fe(IV) were comparatively detected. Figure S12 exhibited  
 374 the HPLC/ESI-MS chromatograms of IPM after the treatment of Heat/PDS, which has  
 375 been acknowledged as the common approach for  $\text{SO}_4^{\bullet-}$  production (Johnson et al., 2008;  
 376 Lee et al., 2020). The production of TP 2-6 was observed, indicating the oxidation role  
 377 of  $\text{SO}_4^{\bullet-}$ . To explore the TPs of IPM by  $\text{SO}_5^{\bullet-}$ , experiments were conducted in the  
 378 presence of 50 mM ethanol, where the contribution of  $\text{SO}_4^{\bullet-}$  and Fe(IV) could be

379 terminated and  $\text{SO}_5^{\bullet-}$  would act as the sole oxidant. TP 1-5 were generated indicated  
380 the  $\text{SO}_5^{\bullet-}$  role in the formation of these products (Fig. S13). Further, the transformation  
381 products of IPM in the Fe(II)/PMS system were also detected to distinguish the products  
382 generated from Fe(IV) in the Fe(III)/sulfite system (Fig. S14). As expected, the  
383 generation of TP 7 and 8 other than TP 1-6 were observed in the case of Fe(IV), further  
384 indicating the participation of Fe(IV) in IPM degradation during Fe(III)/sulfite process.  
385 In addition, the difference in the production formation in the Heat/PDS system  
386 (acknowledged  $\text{SO}_4^{\bullet-}$  system) and Fe(II)/PMS system again indicated the involvement  
387 of Fe(IV) in the Fe(II)/PMS system, supporting the formation of Fe(IV) from the  
388 reaction of Fe(II) and  $\text{HSO}_5^-$  (eq 15).

389 The time course profiles of products identified in the Fe(III)/sulfite were also  
390 monitored by HPLC/ESI MS at multiple reaction monitoring (MRM) mode. As could  
391 be seen in Figure S15, the formation of TP 1 (MW 667) and TP 3 (MW 731) was  
392 followed by their decay over time. The other products were gradually accumulated and  
393 reached plateau during the reaction time, which could be generated from the oxidation  
394 of TP 1 and TP 3 in the Fe(III)/sulfite system. Here, due to the lack of commercial  
395 standards, we cannot determine the absolute concentration of each TP, and only peak  
396 areas were used for data interpretation.

397 Based on these identified products, the transformation mechanism for IPM  
398 oxidation by the Fe(III)/sulfite system was tentatively proposed as shown in **Figure 6**.  
399 IPM would likely be oxidized by Fe(IV) or  $\text{SO}_5^{\bullet-}$  leading to the formation of  
400 hydroxylated TP 1 (MW667), which was further transformed to TP 6 (MW 661) via

401 the cleavage of C-N bond in the amide moiety of acylamino side chain A. In parallel,  
 402 IPM could be attacked by  $\text{SO}_4^{\cdot-}$ ,  $\text{SO}_5^{\cdot-}$  or  $\text{Fe(IV)}$  at the acylamino side chain and thus  
 403 TP 2 (MW 705) could be generated from IPM by the cleavage of side chain A at the  
 404 amide C-N bond. Subsequently, TP 5 (MW 735) is likely generated from TP 705  
 405 through amino groups oxidation to a nitro group, which further transforms to TP 7 (MW  
 406 719) via amide hydrolysis at amide C-N bond of side chains B. The oxidation of  
 407 hydroxyl groups to carbonyl groups occurs in TP 5 and TP 7, leading to the formation  
 408 of TP 3 (MW 731) and TP 4 (MW 659). Also, TP 2 (MW 705) may be transformed by  
 409  $\text{Fe(IV)}$  through hydroxyl groups oxidation into TP 8 (MW 689) with carboxylic group.



410

411 **Fig. 6** Proposed pathway of IPM in the Fe(III)/sulfite process.

412

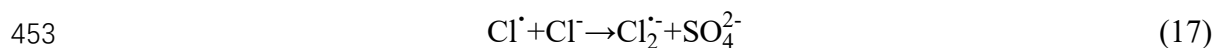
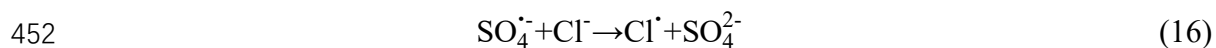
413 **3.5 Removal of TPs from solutions via pH adjustment**

414 Considering the hydrolysis of iron ion in neutral and alkaline conditions, the formation  
415 of iron precipitates through pH adjustment increasing up to neutral 7 and their removal  
416 capability towards transformation products were investigated. Interestingly, TP 3, TP  
417 4, TP 7, TP 8 was not detected after pH adjustment to 7. The concentration of iodide  
418 before and after pH adjustment was also compared. An efficient iodide removal (~80%)  
419 was also observed, where the iodide in solutions decreased from 1.8  $\mu\text{M}$  to 0.3  $\mu\text{M}$  after  
420 pH adjustment (Fig.S16). These findings indicated that the transformation products of  
421 IPM as well as the iodide released from IPM during iron/sulfite process might be  
422 effectively removed through adsorption and/or coprecipitation with iron species. To  
423 further confirm this, FTIR and XPS were conducted to characterize the precipitates  
424 obtained in the Fe(III)/sulfite system after the pH adjustment. In the control group  
425 without IPM, the FTIR band recorded at 3400 and the peak at 1640  $\text{cm}^{-1}$  were ascribed  
426 to the OH stretching vibration of water molecules (Fig. S17). The peak around 1300  
427  $\text{cm}^{-1}$  could be ascribed to the antisymmetric stretching of  $\text{NO}_3^-$  (resulting from the iron  
428 salt used,  $\text{Fe}(\text{NO}_3)_3$ ). The peak near 800  $\text{cm}^{-1}$  could be related to the OH bending modes  
429 in  $\text{FeOOH}$  (Amini et al., 2021). In the presence of IPM, the new peaks around 2900  
430  $\text{cm}^{-1}$  were ascribed to the alkane C-H. Also, the band around 1050 might be ascribed  
431 to C-OH stretching vibration or =CH (Saptari, 2003). The variation observed in the  
432 FTIR spectra with vs without IPM addition might be resulted from the alkane and  
433 alcohol functional groups or aromatic ring present in the transformation products. XPS  
434 analysis also indicated that  $\text{Fe}^{\text{III}}$ -precipitates were indeed generated in the Fe(III)/sulfite  
435 system via pH adjustment (Fig. S18). The peaks around 711 and 725 eV could be

436 attributed to Fe 2p<sub>3/2</sub> and Fe 2p<sub>1/2</sub> (Richardson and Johnston, 2007; Yang et al., 2021).  
437 No difference was observed in presence or absence of IPM, possible due to the low  
438 relative amount of organic products as compared to precipitates. Collectively, these  
439 results showed that adsorption of iodide-containing transformation products and iodide  
440 to iron precipitates could be considered as a way to reduce the to reduce the amount of  
441 transformation products in the treated solutions.

### 442 3.6 Effects of water matrix

443 **Figure 7a** showed the effect of water matrix including Cl<sup>-</sup> and humic acid (surrogate of  
444 NOM) on the degradation of IPM in the Fe(III)/sulfite system. The presence of Cl<sup>-</sup>  
445 suppressed the degradation of IPM to a certain extent. With the concentration of Cl<sup>-</sup>  
446 increasing from 0 to 3 mg/L, the percentage of IPM degradation decreased from 85%  
447 to 50%. Comparatively, the effect of Cl<sup>-</sup> on heat/PDS (for SO<sub>4</sub><sup>•-</sup> generation) and  
448 Fe(II)/PMS systems was investigated. An inhibitory effect of Cl<sup>-</sup> was observed in the  
449 scenario of heat/PDS (Fig. S19). In previous studies, it has been documented that Cl<sup>-</sup>  
450 could act as a radical scavenger for SO<sub>4</sub><sup>•-</sup> (eqs 16-17) with the formation of chlorine  
451 radicals (Cl<sup>•</sup> and Cl<sub>2</sub><sup>•-</sup>) (Neta et al., 1988).

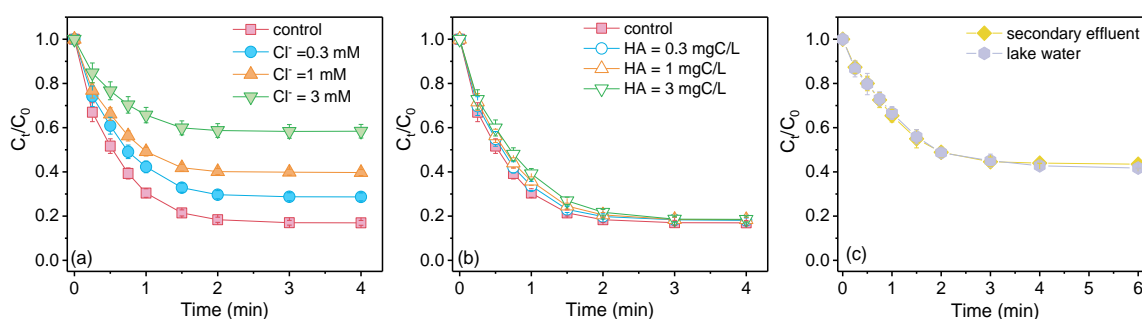


454 The rate constant for the reaction of Cl<sub>2</sub><sup>•-</sup> with IPM was estimated to be 2.5 × 10<sup>6</sup> M<sup>-1</sup>s<sup>-1</sup>  
455 <sup>1</sup>, three orders of magnitude lower than that for the reaction of SO<sub>4</sub><sup>•-</sup> with IPM (Zhao et  
456 al., 2019). The inhibitory effect of Cl<sup>-</sup> on heat/PDS system further suggested the  
457 relatively lower reactivity of chlorine radicals towards IPM as compared to SO<sub>4</sub><sup>•-</sup>. In



458 contrast, no difference in IPM degradation was observed in the Fe(II)/PMS system with  
 459 or without Cl<sup>-</sup> (Fig. S20). This distinct difference in the impact of Cl<sup>-</sup> on Fe(II)/PMS vs  
 460 heat/PDS system might be another indication for that Fe(IV) was the primary oxidant  
 461 in the Fe(II)/PMS system, otherwise a inhibitory effect should be observed. In turn, this  
 462 findings indicated that Cl<sup>-</sup> has slight effect on Fe(IV) oxidation toward IPM. So, the  
 463 inhibitory effect of Cl<sup>-</sup> on the iron/sulfite system involving multiple reactive  
 464 intermediates might be explained by that Cl<sup>-</sup> captured SO<sub>4</sub><sup>•-</sup> and chlorine radicals was  
 465 less reactive toward IPM as compared to SO<sub>4</sub><sup>•-</sup>. Based on above findings, we could  
 466 speculate that the effect of Cl<sup>-</sup> on the iron/sulfite system was likely related to the  
 467 reactivity of chlorine radicals towards contaminants.

468 As shown in **Figure 7b**, the degradation of IPM was slightly affected by humic acid  
 469 (HA), where the percentage of IPM degradation stayed at ~80% when humic acid  
 470 amount increased from 0.3 to 3 mg C/L. This finding indicated that the oxidation of  
 471 IPM by reactive intermediates involved in the Fe(III)/sulfite system are slightly  
 472 affected by HA.



473 **Fig. 7** Effect of chloride (a) and humic acid (b) on the degradation of IPM by the  
 474 Fe(III)/sulfite system as well as the degradation of IPM in real water samples (c).  
 475 Experimental condition: [Fe(III)] = 50 μM, [sulfite] = 300 μM, pH<sub>ini</sub> = 4, [IPM] = 5 μM for  
 476 (a) and (b), [IPM] = 500 nM for (c) to simulate environmental levels.  
 478

479 Further experiments were conducted to evaluate the performance of Fe(III)/sulfite  
480 system in two real water matrixes. As shown in **Figure 7c**, ~65% of IPM removal were  
481 achieved in both filtered secondary effluent and lake water samples. Since these water  
482 samples have similar chloride content but differ in organic carbon content (DOC 5.6  
483 mg L<sup>-1</sup>, Cl<sup>-</sup> 1.8 mM for secondary effluent, whereas DOC 12.6 mg L<sup>-1</sup>, Cl<sup>-</sup> 1.6 mM for  
484 central lake), these results corroborate the above-mentioned findings, *i.e.* the efficiency  
485 of iron/sulfite system is less sensitive to natural organic matter, compared to chloride  
486 ions. Collectively, these results suggest that the Fe(III)/sulfite system is highly selective  
487 and effective for IPM removal, and could be applied in real waters containing high  
488 organic carbon content.

#### 489 **4. Conclusion**

490 In this work, the performance of iron/sulfite system in IPM transformation as well as  
491 the mechanism were examined for the first time. Effective abatement of IPM was  
492 achieved by the iron/sulfite system, and the removal percentage was at least more than  
493 twice as compared to Fe(II)/PMS and Fe(II)/PDS systems. Multiple reactive species  
494 including Fe(IV), SO<sub>4</sub><sup>•-</sup>, and SO<sub>5</sub><sup>•-</sup> contributed to the degradation of IPM in the  
495 iron/sulfite system. The transformation pathways including amide hydrolysis,  
496 deiodination, amino and hydroxyl groups oxidation were proposed for the degradation  
497 of IPM based on the identification of a total of eight transformation products. In  
498 addition, iron precipitates generated via pH adjustment could effectively remove  
499 transformation products as well as the iodide in the resulting solutions. In contrast to  
500 Cl<sup>-</sup>, humic acid had a negligible impact on the IPM removal in the Fe(III)/sulfite system.

501 As a result, the iron/sulfite process exhibited a good efficiency for IPM removal in real  
502 water samples, even with a high organic carbon loading. Considering the low cost and  
503 good performance of the iron ions/sulfite system, this advanced oxidation process may  
504 be considered as a promising technology and an alternative for Fenton-like AOPs  
505 (Fe(II)/PMS and Fe(II)/PDS) in remediation of contaminated wastewater. In addition,  
506 this novel technology might be used as a possible pre-oxidation of IPM, in order to  
507 reduce the potential formation of iodinated by-products originated from ICM.

508

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520

521

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