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Yuan Gao, Wenxia Fan, Zhong Zhang, Yang Zhou, Zhu Zeng, et al.. Transformation mechanisms of iopamidol by iron/sulfite systems: Involvement of multiple reactive species and efficiency in real water. *Journal of Hazardous Materials*, 2022, 426, pp.128114. 10.1016/j.jhazmat.2021.128114. hal-03514438

HAL Id: hal-03514438

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Submitted on 9 Feb 2023

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1 Transformation mechanisms of iopamidol by
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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 3.5×10^6 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 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 μg
53 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/ H_2O_2 ,
68 $\text{O}_3/\text{H}_2\text{O}_2$ or O_3/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 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 (Na_2SO_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 (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 mg L^{-1} , UV_{254} absorbance of 0.075
124 cm^{-1} , Cl^- of 1.8 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 mg L^{-1} , UV_{254} absorbance of 0.083 cm^{-1} ,
126 Cl^- of 1.6 mM and pH of 6.8). After filtering through glass fiber membranes, these water
127 samples were stored at $4 \text{ }^\circ\text{C}$.

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 μM)
131 and sulfite (300 μM) were simultaneously added into stirring solutions containing IPM
132 and/or constituents (e.g., 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 ± 1 °C) in ambient atmosphere. The solution pH was adjusted with
140 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 μm 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 PMSO₂ 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

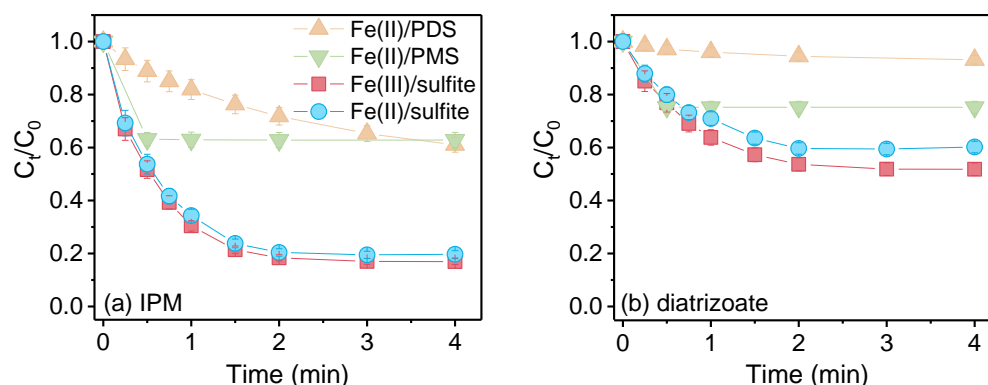
151 parameters were provided in Text S1. Electron paramagnetic resonance (EPR) analysis
152 using DMPO as a spin-trapping agent was performed on a Bruker A200 spectrometer,
153 and the detailed parameters were shown in Text S2. Fourier transform infrared
154 spectroscopy (FTIR) analysis was conducted on a Shimadzu IRTracer-100 and the
155 samples was prepared by vacuum filtration via 0.45 μm 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 μm 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 μM) and sulfite (300
166 μM) led to an efficient abatement of IPM (5 μM) at pH_{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 μ M, [Fe(II)] = [Fe(III)] = 50 μ M, [sulfite]
178 = [persulfates] (i.e., [PDS] or [PMS]) = 300 μ M, and $\text{pH}_{\text{ini}} = 4$.

179 Further, the effect of pH_{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 pH_{ini} increased

181 from 3 to 4, and then decreased when pH_{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 (pH_{final}) was shown in Figure S1b. To evaluate the

184 reaction kinetics at different pH_{ini} , the initial reaction rates k_{ini} over the first reaction

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

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

187 increased to pH_{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

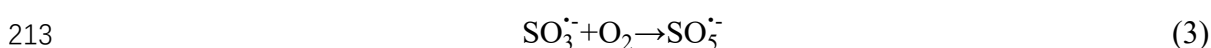
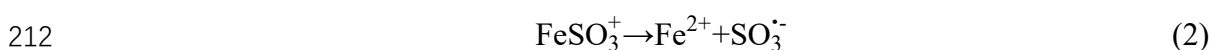
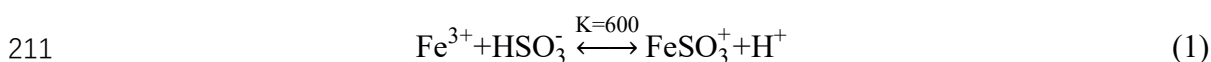
189 pH may facilitate the formation of sulfur dioxide, thus decreasing the effective

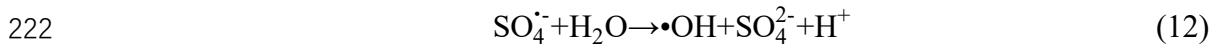
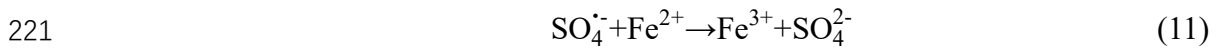
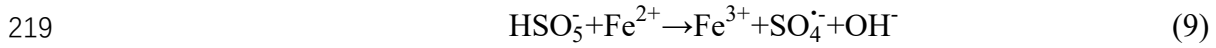
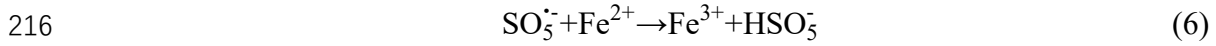
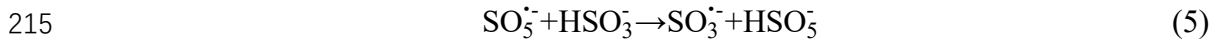
190 concentration of HSO_3^- . At higher pH, iron precipitation takes place, thereby decreasing

191 the dissolved iron concentration available for sulfite activation.

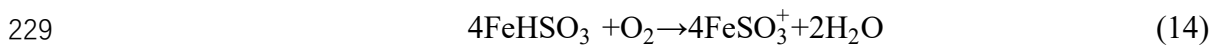
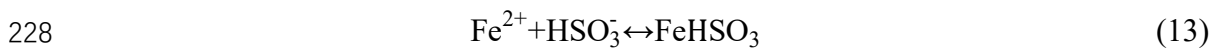
192 3.2 Identification of reactive radical species

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 (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 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 H_2O (Neta et al., 1988).





223 In the case of Fe(II), a rapid formation of 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.

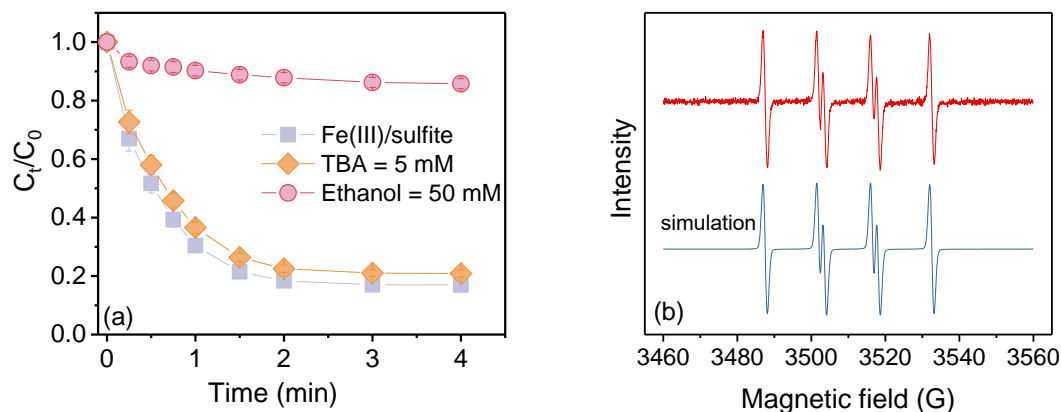


230 3.2.1 Role of $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ in IPM degradation

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-
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 3.4×10^9
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 μM) 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.

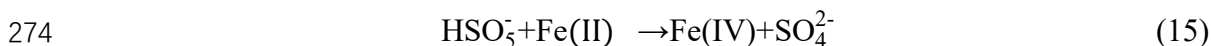


259

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 μM , [Fe(III)] = 50 μM , [sulfite] = 300 μM , $\text{pH}_{\text{ini}} = 4$, 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 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 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 (PMSO_2) via oxygen electron transfer. Comparatively, PMSO_2 was not
273 generated in the case of free radicals (Wang et al. 2018).

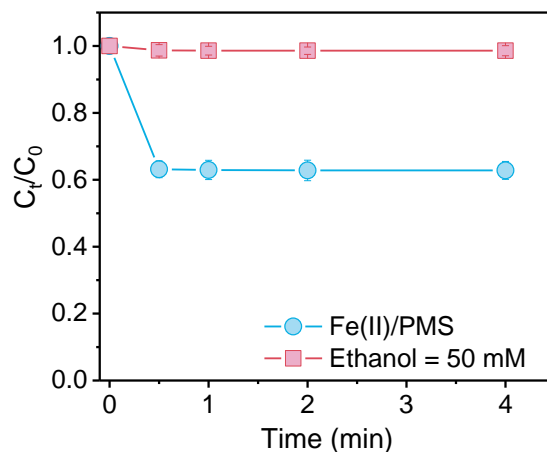


275 Thus, it is quite plausible that Fe(IV) was involved in the Fe(III)/sulfite system
276 generated from eq. 15. In order to verify this possibility, the degradation of methyl
277 phenyl sulfoxide (PMSO) in the Fe(III)/sulfite system was examined. As expected, the

278 formation of methyl phenyl sulfone (PMSO₂) (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 SO₄^{•-} 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 μ M, [Fe(II)] = 50 μ M, [PMS] = 300 μ M, pH_{ini} = 4,
 300 and [ethanol] = 50 mM.

301

302 3.2.2 Role of HSO_5^- , $\text{SO}_3^{\bullet-}$ and $\text{SO}_5^{\bullet-}$ in IPM degradation

303 Recently, 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 HSO_5^-

306 was found negligible (**Fig. 4a**), ruling out the contribution of HSO_5^- to IPM degradation

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

310 toward IPM. Less than 10% of IPM was degraded in the absence of O_2 , where $\text{SO}_3^{\bullet-}$

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

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

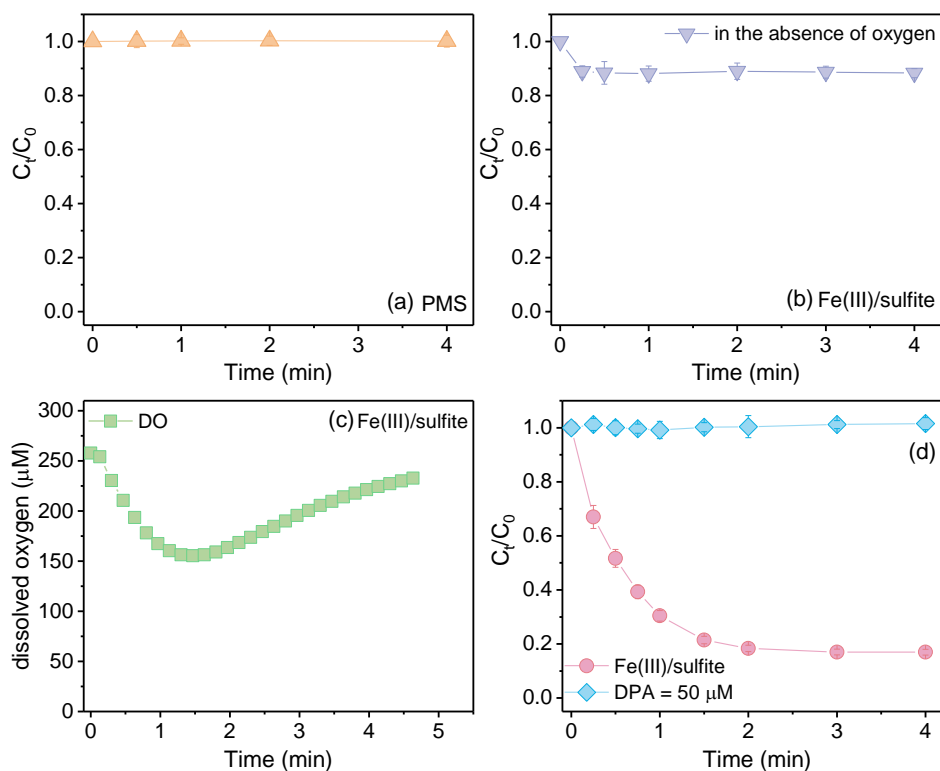
314 et al., 1998). The evolution of dissolved O_2 during the reaction was also monitored (**Fig.**

315 **4c**). The initial decrease of O_2 further confirmed the participation of O_2 (eq. 3) in the

316 Fe(III)/sulfite oxidation process, while further increase of O₂ level might be due to the
317 redissolution of O₂ under open atmosphere. Given the fast reaction of SO₃^{•-} with O₂
318 and the relatively high concentration of dissolved O₂ (≥ 155 μM under atmospheric
319 pressure), SO₃^{•-} would be quickly reacted with O₂ rather than with IPM.

320 SO₅^{•-}, 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 SO₅^{•-} was reported to be 1.2 × 10⁷ M⁻¹ s⁻¹, more than 10 times the rate constant for the
324 SO₃^{•-} reaction (~10⁶ M⁻¹ s⁻¹). Therefore, SO₅^{•-} might also participate in IPM oxidation
325 in the Fe(III)/sulfite system. In contrast to SO₄^{•-} and Fe(IV), SO₅^{•-} is relatively inert
326 toward ethanol with a low rate constant, ~10³ M⁻¹s⁻¹ (Neta et al., 1988). Thus, the IPM
327 degradation (~15%) observed in excess ethanol (**Fig. 2a**) could be resulted from the
328 contribution of SO₅^{•-}. Diphenylamine (DPA) with a relatively higher rate constant with
329 SO₅^{•-} is usually used as scavenger to terminate the contribution of SO₅^{•-} (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 SO₅^{•-} in IPM degradation in the iron/sulfite system.

334 Taken together, these findings suggest that multiple reactive species including
335 Fe(IV), SO₄^{•-}, and SO₅^{•-} could contribute to the IPM transformation in the iron/sulfite
336 system.



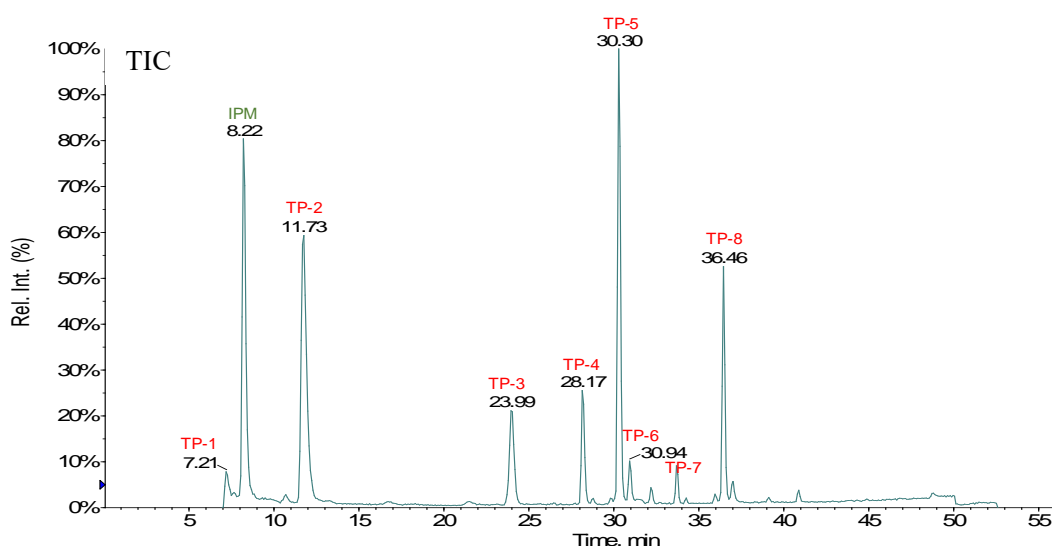
337

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 μM , [Fe(III)] = 50 μM , [sulfite] = 300
 342 μM , $\text{pH}_{\text{ini}} = 4$, and [PMS] = 300 μM for (a), or [DPA] = 50 μM for (d).
 343

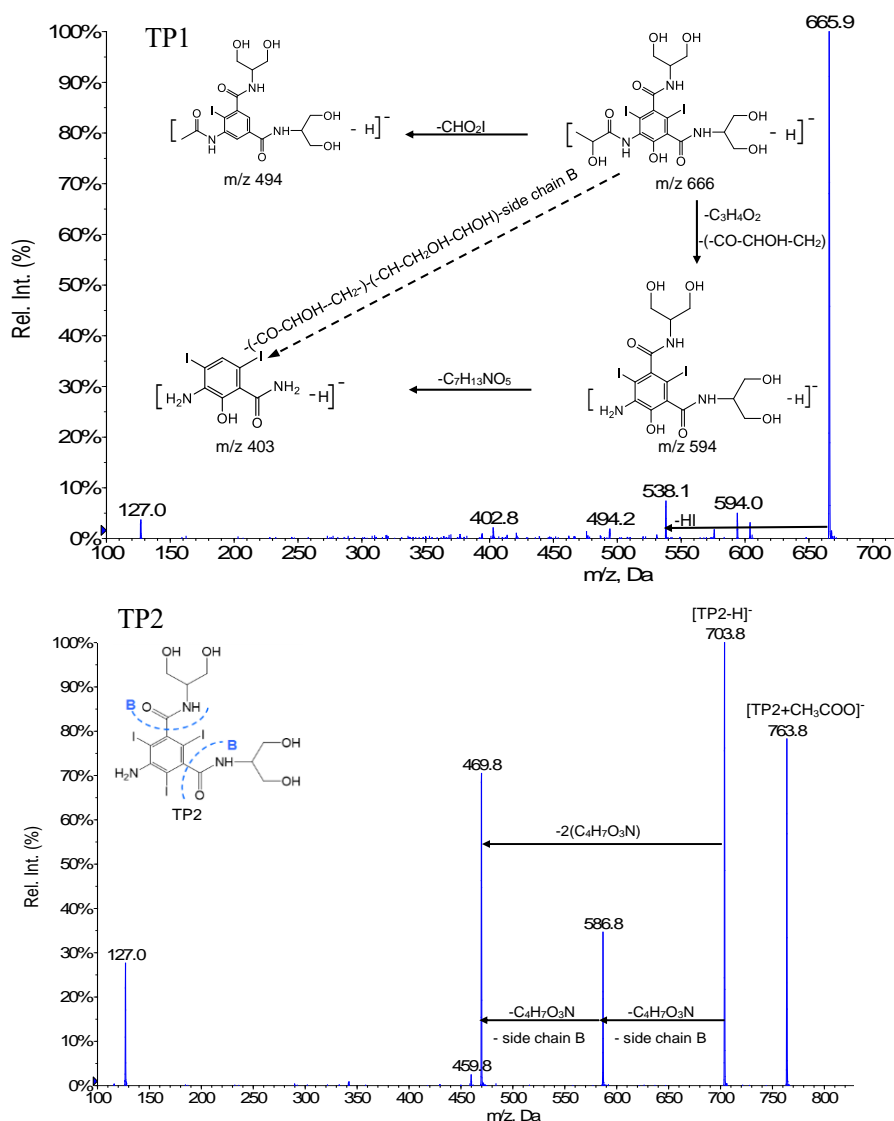
344 3.4 Transformation mechanism

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 [C₁₇H₂₂I₃N₃O₈] with the retention time of 8.22 min. This product was proposed to be
354 a hydroxylated product C₁₇H₂₃I₂N₃O₉, consistent with the nitrogen rule and its
355 fragments observed in the product ion scan spectra. The fragment ions of 72 (-CO-
356 CHOH-CH₂), 263 (-CO-CHOH-CH₂-, -CH-CH₂OH-CHOH-, -CO-NH-CH-CH₂OH-
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 CH₂OH-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 μ M,
 371 [Fe(III)] = 50 μ M, [sulfite] = 300 μ M, and $pH_{ini} = 4$

372

To further understand the transformation pathway, the transformation products of

373

IPM by $SO_4^{\bullet-}$, $SO_5^{\bullet-}$, 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 $SO_4^{\bullet-}$ production (Johnson et al., 2008;

376

Lee et al., 2020). The production of TP 2-6 was observed, indicating the oxidation role

377

of $SO_4^{\bullet-}$. To explore the TPs of IPM by $SO_5^{\bullet-}$, experiments were conducted in the

378

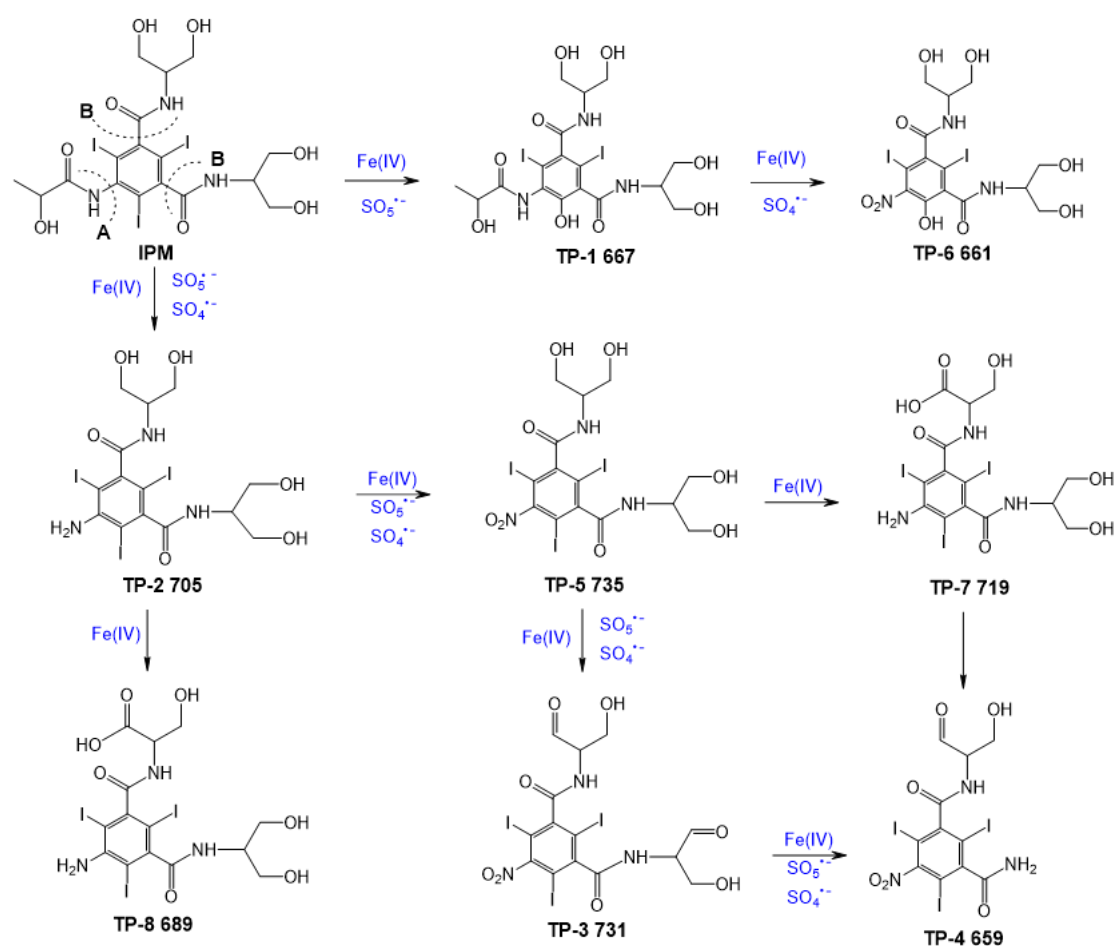
presence of 50 mM ethanol, where the contribution of $SO_4^{\bullet-}$ and Fe(IV) could be

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 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 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 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

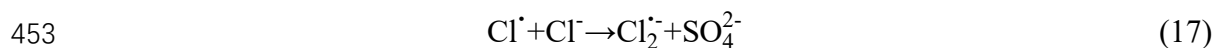
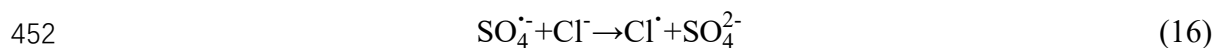
413 **3.5 Removal of TPs from solutions via pH adjustment**

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 μM to 0.3 μM 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 cm^{-1} were ascribed
426 to the OH stretching vibration of water molecules (Fig. S17). The peak around 1300
427 cm^{-1} could be ascribed to the antisymmetric stretching of NO_3^- (resulting from the iron
428 salt used, $\text{Fe}(\text{NO}_3)_3$). The peak near 800 cm^{-1} could be related to the OH bending modes
429 in FeOOH (Amini et al., 2021). In the presence of IPM, the new peaks around 2900
430 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 Fe^{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_{3/2} and Fe 2p_{1/2} (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

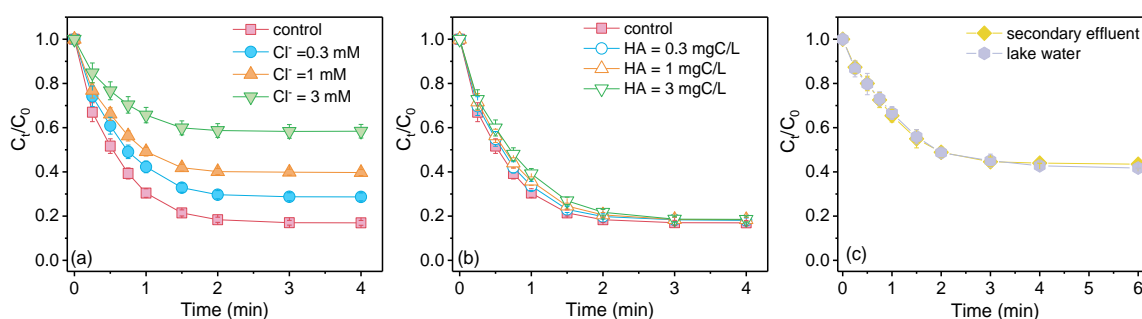
443 **Figure 7a** showed the effect of water matrix including Cl⁻ and humic acid (surrogate of
444 NOM) on the degradation of IPM in the Fe(III)/sulfite system. The presence of Cl⁻
445 suppressed the degradation of IPM to a certain extent. With the concentration of Cl⁻
446 increasing from 0 to 3 mg/L, the percentage of IPM degradation decreased from 85%
447 to 50%. Comparatively, the effect of Cl⁻ on heat/PDS (for SO₄^{•-} generation) and
448 Fe(II)/PMS systems was investigated. An inhibitory effect of Cl⁻ was observed in the
449 scenario of heat/PDS (Fig. S19). In previous studies, it has been documented that Cl⁻
450 could act as a radical scavenger for SO₄^{•-} (eqs 16-17) with the formation of chlorine
451 radicals (Cl[•] and Cl₂^{•-}) (Neta et al., 1988).



454 The rate constant for the reaction of Cl₂^{•-} with IPM was estimated to be 2.5 × 10⁶ M⁻¹s⁻¹
455 ¹, three orders of magnitude lower than that for the reaction of SO₄^{•-} with IPM (Zhao et
456 al., 2019). The inhibitory effect of Cl⁻ on heat/PDS system further suggested the
457 relatively lower reactivity of chlorine radicals towards IPM as compared to SO₄^{•-}. In

458 contrast, no difference in IPM degradation was observed in the Fe(II)/PMS system with
459 or without Cl⁻ (Fig. S20). This distinct difference in the impact of Cl⁻ 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⁻ has slight effect on Fe(IV) oxidation toward IPM. So, the
463 inhibitory effect of Cl⁻ on the iron/sulfite system involving multiple reactive
464 intermediates might be explained by that Cl⁻ captured SO₄^{•-} and chlorine radicals was
465 less reactive toward IPM as compared to SO₄^{•-}. Based on above findings, we could
466 speculate that the effect of Cl⁻ 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_{ini} = 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⁻¹, Cl⁻ 1.8 mM for secondary effluent, whereas DOC 12.6 mg L⁻¹, Cl⁻ 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), SO₄^{•-}, and SO₅^{•-} 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⁻, 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

509 **Acknowledgments**

510 This study was financially supported by the National Natural Science Foundation of
511 China (52000038 and 21906030), the Program for Guangdong Introducing Innovative
512 and Entrepreneurial Teams (2019ZT08L213), the Guangdong Basic and Applied Basic
513 Research Foundation (2019A1515110321 and 2019A1515011947), the Guangzhou
514 Science and Technology Project (202002030093), the Open Project of State Key
515 Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology
516 (No.HC202145), the Key Special Project for Introduced Talents Team of Southern
517 Marine Science and Engineering Guangdong Laboratory (GML2019ZD0403). Thanks
518 for the kind help of Dr. Tao Yang, Wei Song, Hang Bai and Zhengheng Yang regarding
519 the XPS、EPR and FTIR analysis

520

521

Reference

- 522 Amini, M., Mousazade, Y., Zand, Z., Bagherzadeh, M., and Najafpour, M.M. (2021).
523 Ultra-small and highly dispersive iron oxide hydroxide as an efficient catalyst for
524 oxidation reactions: a Swiss-army-knife catalyst. *Scientific Reports* *11*, 6642.
- 525 Brandt, Christian., and van Eldik, Rudi. (1995). Transition Metal-Catalyzed Oxidation
526 of Sulfur(IV) Oxides. Atmospheric-Relevant Processes and Mechanisms. *Chem. Rev.*
527 *95*, 119–190.
- 528 Brandt, C., Fabian, I., and van Eldik, R. (1994). Kinetics and Mechanism of the
529 Iron(III)-catalyzed Autoxidation of Sulfur(IV) Oxides in Aqueous Solution. Evidence
530 for the Redox Cycling of Iron in the Presence of Oxygen and Modeling of the Overall
531 Reaction Mechanism. *Inorg. Chem.* *33*, 687–701.
- 532 Buxton, G.V., Greenstock, C.L., Helman, W.P., and Ross, A.B. (1988). Critical Review
533 of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl
534 radicals ($\cdot\text{OH}/\cdot\text{O}^-$ in Aqueous Solution. *Journal of Physical and Chemical Reference*
535 *Data* *17*, 513–886.
- 536 Cao, Y., Qiu, W., Li, J., Zhao, Y., Jiang, J., and Pang, S. (2021). Sulfite enhanced
537 transformation of iopamidol by UV photolysis in the presence of oxygen: Role of
538 oxysulfur radicals. *Water Research* *189*, 116625.
- 539 Chan, T.W., Graham, N.J.D., and Chu, W. (2010). Degradation of iopromide by
540 combined UV irradiation and peroxydisulfate. *Journal of Hazardous Materials* *181*,
541 508–513.
- 542 Chen, L., Peng, X., Liu, J., Li, J., and Wu, F. (2012). Decolorization of Orange II in

543 Aqueous Solution by an Fe(II)/sulfite System: Replacement of Persulfate. *Ind. Eng.*
544 *Chem. Res.* *51*, 13632–13638.

545 Dong, H., Wei, G., Yin, D., and Guan, X. (2020). Mechanistic insight into the generation
546 of reactive oxygen species in sulfite activation with Fe(III) for contaminants
547 degradation. *Journal of Hazardous Materials* *384*, 121497.

548 Duirk, S.E., Lindell, C., Cornelison, C.C., Kormos, J., Ternes, T.A., Attene-Ramos, M.,
549 Osiol, J., Wagner, E.D., Plewa, M.J., and Richardson, S.D. (2011). Formation of Toxic
550 Iodinated Disinfection By-Products from Compounds Used in Medical Imaging.
551 *Environ. Sci. Technol.* *45*, 6845–6854.

552 Ens, W., Senner, F., Gyax, B., and Schlotterbeck, G. (2014). Development, validation,
553 and application of a novel LC-MS/MS trace analysis method for the simultaneous
554 quantification of seven iodinated X-ray contrast media and three artificial sweeteners
555 in surface, ground, and drinking water. *Anal Bioanal Chem* *406*, 2789–2798.

556 Fronaeus, S., Berglund, J., and Elding, L.I. (1998). Iron–Manganese Redox Processes
557 and Synergism in the Mechanism for Manganese-Catalyzed Autoxidation of Hydrogen
558 Sulfite. *Inorg. Chem.* *37*, 4939–4944.

559 Gara, P.M.D., Bosio, G.N., Gonzalez, M.C., and Mártire, D.O. (2008). Kinetics of the
560 sulfate radical-mediated photo-oxidation of humic substances. *International Journal of*
561 *Chemical Kinetics* *40*, 19–24.

562 Guo, Y., Lou, X., Fang, C., Xiao, D., Wang, Z., and Liu, J. (2013). Novel Photo-Sulfite
563 System: Toward Simultaneous Transformations of Inorganic and Organic Pollutants.
564 *Environ. Sci. Technol.* *47*, 11174–11181.

565 Huie, R.E., and Neta, P. (1984). Chemical behavior of sulfur trioxide(1-) (SO_3^-) and
566 sulfur pentoxide(1-) (SO_5^-) radicals in aqueous solutions. *J. Phys. Chem.* *88*, 5665–
567 5669.

568 Jacobsen, F., Holcman, J., and Sehested, K. (1998). Reactions of the ferryl ion with
569 some compounds found in cloud water. *International Journal of Chemical Kinetics* *30*,
570 215–221.

571 Jeong, J., Jung, J., Cooper, W.J., and Song, W. (2010). Degradation mechanisms and
572 kinetic studies for the treatment of X-ray contrast media compounds by advanced
573 oxidation/reduction processes. *Water Research* *44*, 4391–4398.

574 Johnson, R.L., Tratnyek, P.G., and Johnson, R.O. (2008). Persulfate Persistence under
575 Thermal Activation Conditions. *Environ. Sci. Technol.* *42*, 9350–9356.

576 Kormos, J.L., Schulz, M., and Ternes, T.A. (2011). Occurrence of Iodinated X-ray
577 Contrast Media and Their Biotransformation Products in the Urban Water Cycle.
578 *Environ. Sci. Technol.* *45*, 8723–8732.

579 Lee, J., von Gunten, U., and Kim, J.-H. (2020). Persulfate-Based Advanced Oxidation:
580 Critical Assessment of Opportunities and Roadblocks. *Environ. Sci. Technol.* *54*, 3064–
581 3081.

582 Liang, S., Zhu, L., Hua, J., Duan, W., Yang, P.-T., Wang, S.-L., Wei, C., Liu, C., and
583 Feng, C. (2020). $\text{Fe}^{2+}/\text{HClO}$ Reaction Produces FeIVO_2^+ : An Enhanced Advanced
584 Oxidation Process. *Environ. Sci. Technol.* *54*, 6406–6414.

585 Lutze, H.V., Bircher, S., Rapp, I., Kerlin, N., Bakkour, R., Geisler, M., von Sonntag, C.,
586 and Schmidt, T.C. (2015). Degradation of Chlorotriazine Pesticides by Sulfate Radicals

587 and the Influence of Organic Matter. *Environ. Sci. Technol.* *49*, 1673–1680.

588 Mao, Y., Dong, H., Liu, S., Zhang, L., and Qiang, Z. (2020). Accelerated oxidation of
589 iopamidol by ozone/peroxymonosulfate (O₃/PMS) process: Kinetics, mechanism, and
590 simultaneous reduction of iodinated disinfection by-product formation potential. *Water*
591 *Research* *173*, 115615.

592 Mártire, D.O., Caregnato, P., Furlong, J., Allegretti, P., and Gonzalez, M.C. (2002).
593 Kinetic study of the reactions of oxoiron(IV) with aromatic substrates in aqueous
594 solutions. *International Journal of Chemical Kinetics* *34*, 488–494.

595 Mottley, C., and Mason, R.P. (1988). Sulfate anion free radical formation by the
596 peroxidation of (Bi)sulfite and its reaction with hydroxyl radical scavengers. *Arch*
597 *Biochem Biophys* *267*, 681–689.

598 Neta, P., and Huie, R.E. (1985a). Free-radical chemistry of sulfite. *Environ Health*
599 *Perspect* *64*, 209–217.

600 Neta, P., and Huie, R.E. (1985b). One-electron redox reactions involving sulfite ions
601 and aromatic amines. *J. Phys. Chem.* *89*, 1783–1787.

602 Neta, P., Huie, R.E., and Ross, A.B. (1988). Rate Constants for Reactions of Inorganic
603 Radicals in Aqueous Solution. *Journal of Physical and Chemical Reference Data* *17*,
604 1027–1284.

605 Pantelaki, I., and Voutsas, D. (2018). Formation of iodinated THMs during chlorination
606 of water and wastewater in the presence of different iodine sources. *Science of The*
607 *Total Environment* *613–614*, 389–397.

608 Pérez, S., Eichhorn, P., Celiz, M.D., and Aga, D.S. (2006). Structural Characterization

609 of Metabolites of the X-ray Contrast Agent Iopromide in Activated Sludge Using Ion
610 Trap Mass Spectrometry. *Anal. Chem.* *78*, 1866–1874.

611 Pestovsky, O., and Bakac, A. (2004). Reactivity of Aqueous Fe(IV) in Hydride and
612 Hydrogen Atom Transfer Reactions. *J. Am. Chem. Soc.* *126*, 13757–13764.

613 Putschew, A., Wischnack, S., and Jekel, M. (2000). Occurrence of triiodinated X-ray
614 contrast agents in the aquatic environment. *Science of The Total Environment* *255*,
615 129–134.

616 Richardson, M.J., and Johnston, J.H. (2007). Sorption and binding of nanocrystalline
617 gold by Merino wool fibres—An XPS study. *Journal of Colloid and Interface Science*
618 *310*, 425–430.

619 Saptari, V. (2003). *Fourier transform spectroscopy instrumentation engineering* (SPIE
620 *Optical Engineering Press Bellingham Washington, DC*).

621 Ternes, T.A., and Hirsch, R. (2000). Occurrence and Behavior of X-ray Contrast Media
622 in Sewage Facilities and the Aquatic Environment. *Environ. Sci. Technol.* *34*, 2741–
623 2748.

624 Ternes, T.A., Stüber, J., Herrmann, N., McDowell, D., Ried, A., Kampmann, M., and
625 Teiser, B. (2003). Ozonation: a tool for removal of pharmaceuticals, contrast media and
626 musk fragrances from wastewater? *Water Research* *37*, 1976–1982.

627 Tian, F.-X., Xu, B., Lin, Y.-L., Hu, C.-Y., Zhang, T.-Y., Xia, S.-J., Chu, W.-H., and Gao,
628 N.-Y. (2017). Chlor(am)ination of iopamidol: Kinetics, pathways and disinfection by-
629 products formation. *Chemosphere* *184*, 489–497.

630 Wang, Z., Jiang, J., Pang, S., Zhou, Y., Guan, C., Gao, Y., Li, J., Yang, Y., Qiu, W., and

631 Jiang, C. (2018). Is Sulfate Radical Really Generated from Peroxydisulfate Activated
632 by Iron(II) for Environmental Decontamination? *Environ. Sci. Technol.* *52*, 11276–
633 11284.

634 Wendel, F.M., Lütke Eversloh, C., Machek, E.J., Duirk, S.E., Plewa, M.J., Richardson,
635 S.D., and Ternes, T.A. (2014). Transformation of Iopamidol during Chlorination.
636 *Environ. Sci. Technol.* *48*, 12689–12697.

637 Xu, Z., Li, X., Hu, X., and Yin, D. (2017). Distribution and relevance of iodinated X-
638 ray contrast media and iodinated trihalomethanes in an aquatic environment.
639 *Chemosphere* *184*, 253–260.

640 Yang, T., Wu, S., Liu, C., Liu, Y., Zhang, H., Cheng, H., Wang, L., Guo, L., Li, Y., Liu,
641 M., et al. (2021). Efficient Degradation of Organoarsenic by UV/Chlorine Treatment:
642 Kinetics, Mechanism, Enhanced Arsenic Removal, and Cytotoxicity. *Environ. Sci.*
643 *Technol.* *55*, 2037–2047.

644 Yermakov, A.N., and Purmal, A.P. (2003). Iron-Catalyzed Oxidation of Sulfite: From
645 Established Results to a New Understanding. *Progress in Reaction Kinetics and*
646 *Mechanism* *28*, 189–256.

647 Yu, Y., Li, S., Peng, X., Yang, S., Zhu, Y., Chen, L., Wu, F., and Mailhot, G. (2016).
648 Efficient oxidation of bisphenol A with oxysulfur radicals generated by iron-catalyzed
649 autoxidation of sulfite at circumneutral pH under UV irradiation. *Environ Chem Lett*
650 *14*, 527–532.

651 Yuan, Y., Yang, S., Zhou, D., and Wu, F. (2016). A simple Cr(VI)–S(IV)–O₂ system for
652 rapid and simultaneous reduction of Cr(VI) and oxidative degradation of organic

653 pollutants. *Journal of Hazardous Materials* 307, 294–301.

654 Yuan, Y., Luo, T., Xu, J., Li, J., Wu, F., Brigante, M., and Mailhot, G. (2019). Enhanced
655 oxidation of aniline using Fe(III)-S(IV) system: Role of different oxysulfur radicals.
656 *Chemical Engineering Journal* 362, 183–189.

657 Zhao, X., Jiang, J., Pang, S., Guan, C., Li, J., Wang, Z., Ma, J., and Luo, C. (2019).
658 Degradation of iopamidol by three UV-based oxidation processes: Kinetics, pathways,
659 and formation of iodinated disinfection byproducts. *Chemosphere* 221, 270–277.

660 Zhou, D., Chen, L., Li, J., and Wu, F. (2018a). Transition metal catalyzed sulfite auto-
661 oxidation systems for oxidative decontamination in waters: A state-of-the-art
662 minireview. *Chemical Engineering Journal* 346, 726–738.

663 Zhou, Y., Gao, Y., Pang, S.-Y., Jiang, J., Yang, Y., Ma, J., Yang, Y., Duan, J., and Guo,
664 Q. (2018b). Oxidation of fluoroquinolone antibiotics by peroxymonosulfate without
665 activation: Kinetics, products, and antibacterial deactivation. *Water Research* 145, 210–
666 219.

667 Zhou, Y., Jiang, J., Gao, Y., Pang, S.-Y., Ma, J., Duan, J., Guo, Q., Li, J., and Yang, Y.
668 (2018c). Oxidation of steroid estrogens by peroxymonosulfate (PMS) and effect of
669 bromide and chloride ions: Kinetics, products, and modeling. *Water Research* 138, 56–
670 66.

671