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Overlooked formation of chlorinated coupling byproducts during phenol degradation with ferrate(VI) oxidation technology

3

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11

12 Abstract: Currently, ferrate(VI) oxidation technology (FOT) has been regarded as one of the most promising options for the degradation of emerging organic pollutants. However, the role 13 and transformation of chloride ions (Cl⁻) in FOT have not been well explored. The current study 14 15 aims to investigate the formation of chlorinated phenolic byproducts upon ferrate(VI) oxidation processes. The obtained results indicate that chlorides suffering ferrate(VI) attack will be 16 transformed to active chlorine species (ACS), which will subsequently lead to the formation of 17 highly toxic aromatic chlorinated byproducts. The identified byproducts include common 18 chlorinated phenolic derivatives, as well as complex chlorinated oligomer byproducts with 19 20 ether structures (mainly dimers and trimers). While the formation of common chlorophenols can be ascribed to the electrophilic substitution reactions mediated by ACS, the oligomer 21 byproducts are generated via coupling reactions between chlorinated phenoxy radicals. 22 23 ECOSAR software predicts that the generated chlorinated oligomer byproducts exhibit high ecotoxicological effects. As a whole, the above findings shed light on the potential risk of FOT 24 in real practice. 25

26 Keywords:

27 ferrate(VI) oxidation

28 chlorinated oligomers

29	toxicity calculation
30	reaction mechanism
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35

36 Introduction

Advanced oxidation process based on ferrate(VI) is currently one of the most promising 37 technologies to eliminate a wide spectrum of organic contaminants (Fan et al., 2023; Zhang et 38 al., 2023). This is mainly due to the high oxidation potential of ferrate(VI) ions (E^{θ} (FeO₄²⁻/Fe³⁺) 39 = 2.20 V), plus the excellent coagulation and adsorption performance of the *in situ* generated 40 ferric species (e.g., Fe(OH)₃). As a consequence, the common organic pollutants routinely 41 detected in aquatic systems can be effectively removed via ferrate(VI) oxidation technology 42 (FOT). For instance, Zhao et al. demonstrated the effectiveness of FOT in the degradation of 43 44 cylindrospermopsin and 6-hydroxymethyl uracil under neutral and alkaline pH conditions (Zhao et al., 2023). In another work, 99% removal efficiency of bisphenol E was achieved 45 within 3 min using FOT (Tian et al., 2022). In the case of drinking water purification, FOT had 46 often been employed as a pretreatment option (before the chlorine disinfection process) to 47 48 remove aqueous natural organic matter (NOM), to reduce the risk associated with the formation of chlorinated disinfection byproducts (DBPs) (Gan et al., 2015; Liu et al., 2020). As a result, 49 FOT has always been deemed a green and efficient option in the field of wastewater treatment. 50 A review of relevant literature indicates that current FOT research has focused on the 51 following aspects: 1) in situ preparation and characterization of ferrate(VI); 2) efficiency 52 promotion concerning the removal of organic pollutants; 3) parameter optimization and reaction 53 kinetics involved; 4) identification of the reaction byproducts and proposal of the oxidation 54 pathway; and 5) classification and evaluation of the toxicity of potential degradation byproducts 55 (Jiang, 2014; Cheng et al., 2023; He et al., 2022; He et al., 2023a; He et al., 2023b; Wang et al., 56 2023). Specifically, the last two aspects have received increasing research attention in recent 57

58 years. For example, the formation of toxic reaction intermediates can be linked to the presence 59 of co-existing inorganic ions present in wastewater effluents (e.g., Cl⁻, NO₂⁻) (Ji et al., 2019; Chen et al., 2015). It is well known that inorganic ions often co-exist with target organic 60 61 pollutants, leading to a complex system which does not easily allow the prediction of the treatment efficiency and an understanding of the mechanisms involved (An et al., 2023). For 62 example, chlorinated aromatic byproducts have recently been identified in other advanced 63 oxidation processes such as electrochemical oxidation with boron-doped diamond anode. In 64 65 chloride medium, the anodic oxidation of phenol will result in the generation of chlorinated aromatic oligomers as a consequence of electrophilic substitution and cross-coupling reactions. 66 It is thus reasonable to conclude similar byproducts may also be formed in FOT. However, to 67 date, the roles of inorganic ions during ferrate oxidation processes have not been well studied 68 (He et al., 2022). In particular, little attention has been paid to the role and transformation of 69 Cl⁻ in FOT. This is of vital concern since Cl⁻ can be oxidized forming active chlorine species 70 (ACS, e.g., Cl₂, HClO, and ClO⁻), due to the low redox potential of chlorine evolution reactions 71 72 $(E (Cl_2/Cl^-) = 1.36 V)$ (Cao et al., 2022). Once ACS are formed upon ferrate oxidation 73 processes, they will react with electron-rich organics to form highly toxic chlorinated organic 74 byproducts (Sun et al., 2022). These byproducts are considered important DBPs in water treatment processes, as they usually exhibit higher toxicity than their parent pollutant (An et al., 75 2023; Feng et al., 2023). It is thus reasonable to conclude that using FOT to treat chloride-76 77 containing organic wastewater may lead to the generation of toxic chlorinated DBPs. 78 Unfortunately, this risk has been overlooked by most previous reports, which necessitates the 79 urgent need for further studies.

In this context, the present study investigates the formation of chlorinated aromatic byproducts upon ferrate oxidation processes. Phenol (PhOH, C_6H_5OH) was chosen as the model compound to simulate the reactivity of aqueous natural organic matter (NOM). As expected, the results obtained further our understanding of the complex reactions involved in FOT.

84

86 1 Experimental

87 **1.1 Materials and reagents**

Reagent grade potassium ferrate (K_2FeO_4 , 99.5%) was obtained from Shanghai Yuanye Biotechnology Co., Ltd (Shanghai, China), and other chemicals (PhOH, NaCl, Na₂S₂O₃) were of the purest available quality from Wako (Japan). All solutions used in this study were carefully prepared with purified water from a Milli-Q system.

92

93 **1.2 Batch reaction experiments**

As mentioned above, the parameter optimization of FOT had been extensively examined 94 previously. Thus in the current work, the conditions employed for the batch reaction 95 96 experiments were chosen based on the results from a former correlative report (Graham et al., 97 2004) and some preliminary studies (not shown here). In brief, the batch oxidation experiments were carried out in pure water, in 200 mL beakers at 25°C (with an initial solution pH of 6.2). 98 For each entry, 0.10 g K₂FeO₄ was added to the 0.1 L aqueous solution containing 50 mg L^{-1} 99 100 phenol and varying concentrations of NaCl (1 mmol/L, 10 mmol/L and 50 mmol/L), which were mixed rapidly with a magnetic stirrer (400 r min⁻¹). For each entry, 5 mL samples were 101 taken from the system at reaction time of 60 min, and then filtered through 0.45 µm polyether 102 sulfone membrane and quenched with 0.50 mol/L Na₂S₂O₃ aqueous solution. Under these 103 104 conditions, the mineralization percentages of phenol obtained were located in the range of 30~80%. All experiments were carried out at least in duplicate, and the reported TOC values 105 were within the experimental error of +2%. 106

107

108 **1.3 Instruments and analysis**

109 The mineralization of phenol during ferrate oxidation was monitored using a Shimadzu TOC-110 L Total Organic Carbon analyzer (Japan). LC/MS analyses were conducted on a Waters 111 Acquity UPLC/SQD analyzer (USA). The LC column was a reversed-phase CSH C₁₈ column 112 (2.1 mm × 50 mm, 1.7 μ m, USA), and the column temperature was set at 35 °C. The mobile 113 phase was composed of acetonitrile and phosphate buffer (pH = 3.5) (70:30 v/v), and the flow 114 rate was 0.50 mL min⁻¹. For each test, the injection volume was 5 μ L. The MS conditions employed were: carrying and nebulizer gas (pure nitrogen) pressure of 30 psig, gas temperature of 350 °C, a Q-array RF voltage of 40 V and an interface voltage of - 4.0 V. Mass spectra in the m/z range of 50-1000 were recorded in negative mode electrospray source ionization (ESI-). The following criteria were employed for by-product identification: 1) the exact masses recorded; 2) the fragmentation patterns of ions; and 3) comparison with the information from several correlative reports (Chen et al, 2015; Zhang et al., 2018; Chen et al., 2019; Sun et al, 2022).

122

123 **1.4 Toxicity assessment**

The toxicity of DBPs was calculated using the Ecological Structure Activity Relationship (ECOSAR) software package (version 2.0). Chronic toxicity values (ChV) and acute toxicity values (including EC50 (96 h) for fish (48 h) and Daphnia (96 h) and green algae) were both calculated using ECOSAR. Thereafter, their ecotoxicity was graded using the globally harmonized chemical classification and labeling system.

129

130 **2 Results and discussion**

131 **2.1 Formation of chlorinated byproducts in FOT**

To our knowledge, this work is one of the very few attempts to elucidate the role and transformation of chloride ions in FOT. Previous correlative studies (of other advanced oxidation processes) have demonstrated that the initial chloride concentration is the most important parameter affecting degradation efficiency and byproduct formation (Chen et al, 2015; Zhang et al., 2018; Chen et al., 2019; Sun et al, 2022). Therefore, the effect of initial chloride concentration on ferrate(VI) oxidation of PhOH was primarily examined and discussed.

Results from TOC analysis revealed that the mineralization percentages of PhOH obtained at reaction time of 60 min were 53.5%, 48.2% and 38.3% for 1 mmol/L, 10 mmol/L and 50 mmol/L NaCl media, respectively. This phenomenon confirms that excessive chloride ions retard the mineralization of phenolic pollutants, which possibly indicates the formation of recalcitrant degradation byproducts. To confirm the hypothesis, samples also underwent LC/MS analysis. Briefly, this analysis allowed the identification of 19 major reaction

intermediates, with *m/z* range of 128 to 430 (Table 1). Example LC and MS spectra have been 144 provided in the supplementary materials (see Fig. 3 and Fig. SM-1). According to the ring 145 146 structural characteristics, these intermediates may be classified as monomer byproducts (1-11), dimer byproducts (12-17), and trimer byproducts (18,19). It should be mentioned that the trimer 147 products may have several possible structures for the differing coupling patterns between 148 phenyl radicals. Moreover, due to the lack of commercial standards, it is still difficult to 149 elucidate the very accurate structure of trimer byproducts, thus only one representative structure 150 151 has been provided. Table 1 illustrates the impact of chloride concentration on the generation of these byproducts, and the key findings include: (1) monomers constitute the major byproducts 152 in case of 1 mmol/L NaCl; (2) monomers and dimers are predominantly observed in 10 mmol/L 153 NaCl media; (3) trimers are only detected in chloride-rich environments (50 mmol/L NaCl); 154 and (4) as chloride concentration rises from 10 mmol/L to 50 mmol/L, PhOH suffering ferrate 155 attack will be transformed to coupling byproducts with larger molecular size and higher 156 halogenation degree. 157

The above results are in well accordance with those recorded in existing literature, which 158 159 demonstrate that the formation of byproducts is molar ratio of reactant dependent (Rush et al., 1995). More importantly, our results support the findings of previously published research 160 concerning the formation of chlorinated and non-chlorinated intermediates during phenol 161 degradation with potassium ferrate (Sun et al., 2016; Jiang et al., 2019; Wu et al., 2020). As 162 expected, some of the same intermediates $(\underline{1}-\underline{9})$ have also been identified in our study, 163 confirming the vital roles of ferrate ions, active oxygen radicals, and free chlorine species. 164 However, the formation of coupling byproducts (oligomers) in FOT has been neglected in most 165 previous works. It worth mentioning that the coupling reactions are rather common during 166 advanced oxidation of phenolic pollutants (Chen et al., 2015; Zhang et al., 2018; Chen et al., 167 168 2019; Ji et al., 2019). For instance, chlorinated oligomer byproducts have been previously identified during electrochemical advanced oxidation processes, as well as during the in situ 169 chemical oxidation mediated by activated persulfate (K₂S₂O₈) or peroxymonosulfate (KHSO₅) 170 (Chen et al., 2015; Zhang et al., 2018; Chen et al., 2019; Ji et al., 2019). Although the main 171 reactive agents involved in different advanced oxidation processes vary greatly from case to 172

173 case, the oxidation of phenol will always lead to formation of resonance-stabilized radicals 174 (Chen et al., 2015; Ji et al, 2019). The combination of these radicals with free radical or 175 intermediate will result in chlorinated or non-chlorinated coupling byproducts (with or without 176 ether bonds). Thus, we emphasize the importance of coupling reactions in advanced oxidation 177 of phenolic pollutants, especially when chlorides are present in the reaction systems.

The principles of radical chemistry and organic chemistry are frequently used to explore 178 the formation mechanism of the byproducts (Chen et al, 2015; Zhang et al., 2018; Chen et al., 179 180 2019; Sun et al, 2022). As shown in Fig. 1, the electrophilic substitution reactions involving ACS, along with the hydroxylation reactions mediated by ferrate ions and reactive oxygen 181 species (ROS, e.g., •OH), all contribute to the generation of monomeric byproducts. As reported 182 before (Chen et al., 2015; Chen et al, 2019; Ji et al., 2019), the attack of ACS at the ortho-, 183 para-, and hydroxyl-bearing positions of phenolic compounds will result in the formation of 184 chlorinated monomers (1, 2, 3, 4, 10). These byproducts may serve as important precursors for 185 the formation of dimeric and trimeric species. It has been reported that the reactions of ACS 186 and ROS with PhOH will generate resonance-stabilized radicals, of which the unpaired 187 188 electrons can be delocalized at the aromatic ring or oxygen atom (Fig. 2) (Ji et al., 2019). Fig. 4 reveals that the benzoquinone-phenol coupling reaction results in the formation of six dimeric 189 intermediates with ether bonds (<u>11</u>, <u>12</u>, <u>13</u>, <u>15</u>, <u>16</u>, and <u>17</u>). Meanwhile, an alternative dimeric 190 species (14) without ether bonds is also generated through the ortho- and phenoxy-radical 191 pathway. The structural features of the oligomer depicted in Fig. 4 suggest that the coupling 192 reaction may stop at dimer stage during such reactions. In other words, the generated dimer 193 byproducts are unable to participate in the further coupling reactions. However, our results 194 confirm that some of the dimer byproducts remain reactive during chlorination, leading to the 195 196 production of trimeric intermediates (18 and 19, both exhibit two ether bonds) (see Fig. 5). Here, it is worth highlighting that the trimeric intermediates may also be formed through 197 multiple monomer coupling reactions. Given that trimeric species are only generated in 198 chlorine-rich environment (50 mmol/L NaCl), it is thus reasonable to conclude that the presence 199 of abundant ACS is an important prerequisite for their formations. Interestingly, the absence of 200 higher-order oligomeric species (e.g., tetramers and pentamers) possibly reveals the inherent 201

202 constraints associated with such coupling reactions. In addition, the role of ROS is deemed as 203 insignificant in halide-rich media, which has been confirmed by the poor mineralization 204 performance recorded in case of 50 mmol/L NaCl (Rusevova Crincoli and Huling, 2020; He et 205 al., 2021; Zeng et al., 2023). Due to the lack of standard reagents, quantification of oligomer 206 byproducts cannot be conducted at current stage. Despite this, the high polarity and 207 hydrophobicity of the coupling byproducts suggest that they may be easily removed via 208 common adsorption technology.

209 Lastly, the simplified reaction sequence of phenol oxidation in K₂FeO₄/NaCl system is depicted in Fig. 6. According to this scheme, hydroxylation and chlorination of phenol give rise 210 to monomeric byproducts during initial stage of degradation. Subsequently, a portion of the 211 monomers will undergo coupling reactions to form dimeric intermediates, while the remaining 212 monomers are oxidized to carboxylic acids (and ultimately to harmless carbon dioxide and 213 water). As a result, the pH of the solution tends to decrease as oxidation reactions proceed, 214 possibly due to the generation of carboxylic acids (which are important intermediates for 215 phenolic pollutants). If abundant ACS are present in the reaction system, the coupling reaction 216 217 will continue to generate trimeric byproducts. Clearly, the coupling reactions facilitate the removal of phenol but retard the mineralization process. Therefore, the cleavage of ether bonds 218 in dimeric and trimeric intermediates should be considered as an important step concerning 219 phenol mineralization (Zhang et al., 2018). This hypothesis is supported by the co-existence of 220 monomeric, dimeric, and trimeric byproducts in chloride-rich system (see Table 1). 221

222

223 2.2 Environmental implications

As previously mentioned, chlorides are widely present in different environment matrix. It has been reported that in urban domestic wastewater, the concentration of chloride ions typically ranges from a few milligrams per liter (mg dm⁻³) to several tens of milligrams per liter (Zhang et al., 2018). In contrast, industrial processes such as electroplating and pharmaceutical production can result in higher chloride ion concentrations, possibly reaching several hundred milligrams per liter (Cao et al., 2022). Since ferrate ions in acidic conditions exhibit higher oxidation potential than chlorine evolution, the formation of active chlorine is almost inevitable 231 (Li et al., 2021). In our reaction system, the reactions between potassium ferrate and phenol 232 will lead to the formation ofchlorinated aromatic byproducts, including diphenyl ethers and biphenyl species. These byproducts are recognized as hazardous pollutants which pose great 233 234 threats to the aquatic ecosystems (Chen et al., 2015). As shown in Table 2, ECOSAR calculations demonstrate that polychlorinated aromatic byproducts exhibit significant 235 ecotoxicological impacts on aquatic organisms such as fish and daphnia (Zhang et al., 2023). 236 More importantly, these compounds are highly prone to bioaccumulation in both plants and 237 238 animals(Zhang et al., 2023). Polychlorinated aromatic oligomer byproducts (PCAOs) are known to exhibit high genotoxicity, carcinogenicity and mutagenicity, thereby posing 239 significant ecotoxicological risks in the aquatic environment (Chen et al. 2015; Sun et al., 2022; 240 Zhang et al., 2022). Further efforts are needed to prevent and control the formation of these 241 toxic aromatic byproducts, and the practice of removing most of the chloride ions from the 242 effluents before the oxidative treatment is highly recommended. 243

244

245 **2.3 Comparison with other advanced oxidation processes**

246 As previously mentioned, chlorinated aromatic byproducts had also been detected in other advanced wastewater treatment processes. Here, let us draw a special attention to the research 247 works concerning the formation of chlorinated byproducts during in situ chemical oxidation 248 mediated by sulfate radicals, as well as upon electrochemical oxidation with BDD anodes (Chen 249 250 et al, 2015; Chen et al., 2019). As can be seen from Table 3, the distribution of byproducts differ greatly from case to case, possibly due to the differing reactive agents involved in these 251 reaction systems. The main reactive oxidizing agents involved in these systems are: 1) ACS, 252 ferrate ions and hydroxyl radicals for FOT; 2) ACS and hydroxyl radicals for BDD technology; 253 254 and 3) ACS, sulfate radicals and hydroxyl radicals for *in situ* chemical oxidation mediated by PMS. For all cases, there is a competitive consumption of oxidants by parallel reactions with 255 PhOH and its degradation byproducts. It is thus reasonable to assume that the distribution of 256 the reactive species will greatly influence the formation of byproducts. 257

Briefly, **Table 3** highlights that: 1) common hydroxylated and chlorinated byproducts are formed in all cases, confirming the co-action of ACS and ROS during the oxidation processes;

260 2) ACS and ROS play equal roles during the *in situ* chemical oxidations processes; 3) compared 261 to that of ferrate oxidation, the electrochemical oxidation of phenol results in the formation of dimer byproducts with more complex molecular structure and higher chlorination degree; 4) 262 chlorinated dimer and trimer byproducts are rarely reported upon PMS activation processes (Ji 263 et al., 2019); and 5) the structural characteristics of the trimer byproduct (polychlorinated 264 dibenzo-p-dioxin) generated in BDD anode cells is quite different from those formed during 265 ferrate oxidation. As a whole, the different patterns recorded suggest that chloride concentration 266 267 and oxidation system do impact byproduct speciation, and higher chloride concentration conditions usually lead to coupling byproducts with more rings and higher halogenation degree. 268

269

270 **3 Conclusions**

Previous works had demonstrated the effectiveness and safety of ferrate(VI) oxidation technology in the degradation of diverse aqueous organic pollutants. Nevertheless, our findings indicated that ferrate(VI)-treated wastewater may contain toxic chlorinated aromatic byproducts. The main conclusions of the work are summarized as follows:

- A sequence of polychlorinated aromatic byproducts (including monomers, dimers and trimers) are all identified, confirming the critical role of cross-coupling reactions upon ferrate oxidation processes;
- The coupling reactions involved in ferrate oxidation processes usually stop at stage of
 trimers. Moreover, the presence of abundant chlorides is an important prerequisite for the
 formation of complex coupling byproducts;

The proposed reaction mechanisms provide new insights into the transformation of
 chlorine atoms upon ferrate oxidation processes. That is, how inorganic chlorine atoms are
 incorporated into the aromatic molecules, which consequently leading to the formation of
 coupling byproducts;

The transformation diagram of chloride ions during ferrate oxidation is a subject of ongoing
 interest, as the complex structure of natural organic matter presents a more intricate
 challenge than that of simple phenolic compounds. Thus, more phenolic pollutants (such

288	as bisphenol A and nitrophenol) should be employed in similar studies, to expand our
289	scientific understanding of this subject.
290	
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294	
295	Declaration of competing interest
296	The authors declare that they have no known competing financial interests or personal
297	relationships that could have appeared to influence the work reported in this paper.
298	
299	Appendix A Supplementary data
300	Supplementary material associated with this article can be found, in the online version, at
301	
302	References
303	An, Y., Ma, X.Y., Chen, W., Li, W., Yang, S., Chen, R., et al., 2023. The impact of inorganic
304	ions on the solar photolysis of chlorinated dissolved organic matter from different sources:
305	spectral characteristics, disinfection byproducts, and biotoxicities. J. Hazard. Mater. 451,
306	131135. https://doi.org/10.1016/j.jhazmat.2023.131135.
307	Cao, K., Chen, Z., Wu, Y., Mao, Y., Shi, Q., Chen, X., et al., 2022. The noteworthy chloride
308	ions in reclaimed water: harmful effects, concentration levels and control strategies. Water
309	Res. 215, 118271. https://doi.org/10.1016/j.watres.2022.118271.
310	Cheng, X., Lian, J., Liu, B., Zhu, X., Jin, Y., Zhang, L., et al., 2023. Integrated ferrate and
311	calcium sulfite to treat algae-laden water for controlling ultrafiltration membrane fouling:
312	high-efficiency oxidation and simultaneous cell integrity maintaining. Chem. Eng. J. 461,
313	141880. https://doi.org/10.1016/j.cej.2023.141880.
314	Fan, W., Zhang, X., Guo, P., Sheng, G., 2023. Highly efficient removal of phosphonates by
315	ferrate-induced oxidation coupled with in situ coagulation. J. Hazard. Mater. 451, 131104.

https://doi.org/10.1016/j.jhazmat.2023.131104. 316

- Feng, H., Liao, X., Yang, R., Chen, S., Zhang, Z., Tong, J., et al., 2023. Generation, toxicity,
 and reduction of chlorinated byproducts: overcome bottlenecks of electrochemical
 advanced oxidation technology to treat high chloride wastewater. Water Res. 230, 119531.
 https://doi.org/10.1016/j.watres.2022.119531.
- Graham, N., Jiang, C., Li, X., Jiang, J., Ma, J., 2004. The influence of ph on the degradation of
 phenol and chlorophenols by potassium ferrate. Chemosphere 56 (10), 949-956.
 https://doi.org/10.1016/j.chemosphere.2004.04.060.
- He, H., Liu, Y., Wang, L., Qiu, W., Li, D., Liu, Z., et al., 2023. Improvements of ferrate(vi)
 pretreatment on membrane flux and membrane rejection using cheap naclo reagent. Water
 Res. 229, 119520. https://doi.org/10.1016/j.watres.2022.119520.
- He, X., Chi, H., He, M., Zhang, B., Zhang, J., Wang, D., et al., 2021. Efficient removal of
 halogenated phenols by vacuum-uv system through combined photolysis and oh oxidation:
 efficiency, mechanism and economic analysis. J. Hazard. Mater. 403, 123286.
 https://doi.org/10.1016/j.jhazmat.2020.123286.
- Jiang, Y., Goodwill, J.E., Tobiason, J.E., Reckhow, D.A., 2019. Comparison of ferrate and ozone pre-oxidation on disinfection byproduct formation from chlorination and chloramination. Water Res. 156, 110-124. https://doi.org/10.1016/j.watres.2019.02.051.
- Rusevova Crincoli, K., Huling, S.G., 2020. Hydroxyl radical scavenging by solid mineral
 surfaces in oxidative treatment systems: rate constants and implications. Water Res. 169,
- 336 115240. https://doi.org/10.1016/j.watres.2019.115240.
- Sun, X., Zhang, Q., Liang, H., Ying, L., Xiangxu, M., Sharma, V.K., 2016. Ferrate(vi) as a
 greener oxidant: electrochemical generation and treatment of phenol. J. Hazard. Mater. 319,
 130-136. https://doi.org/10.1016/j.jhazmat.2015.12.020.
- 340 Tian, B., Wu, N., Pan, X., Wang, Z., Yan, C., Sharma, V.K., et al., 2022. Ferrate(vi) oxidation
- of bisphenol e-kinetics, removal performance, and dihydroxylation mechanism. Water Res.
- 342 210, 118025. https://doi.org/10.1016/j.watres.2021.118025.
- Wang, X., Wang, Y., Zheng, K., Tian, L., Zhu, T., Chen, X., et al., 2023. Enhancing methane
 production from waste activated sludge with heat-assisted potassium ferrate (pf)
 pretreatment: reaction kinetics and mechanisms. Sci. Total Environ. 860, 160441.

- https://doi.org/10.1016/j.scitotenv.2022.160441. 346
- Wu, S., Liu, H., Lin, Y., Yang, C., Lou, W., Sun, J., et al., 2020. Insights into mechanisms of 347 uv/ferrate oxidation for degradation of phenolic pollutants: role of superoxide radicals. 348 Chemosphere 244, 125490. https://doi.org/10.1016/j.chemosphere.2019.125490.
- 349
- Zeng, G., Shi, M., Dai, M., Zhou, Q., Luo, H., Lin, L., et al., 2023. Hydroxyl radicals in natural 350 waters: light/dark mechanisms, changes and scavenging effects. Sci. Total Environ. 868, 351 161533. https://doi.org/10.1016/j.scitotenv.2023.161533. 352
- 353 Zhang, C., Xian, J., Liu, M., Fu, D., 2018. Formation of brominated oligomers during phenol degradation on boron-doped diamond electrode. J. Hazard. Mater. 344, 123-135. 354 https://doi.org/10.1016/j.jhazmat.2017.10.010. 355
- Zhang, X., Zhu, X., Li, H., Wang, C., Zhang, T., 2023. Combination of peroxymonosulfate and 356 Fe(vi) for enhanced degradation of sulfamethoxazole: the overlooked roles of high-valent 357 iron species. Chem. Eng. J. 453, 139742. https://doi.org/10.1016/j.cej.2022.139742. 358
- Zhao, C., Arroyo-Mora, L.E., Decaprio, A.P., Dionysiou, D.D., O'Shea, K.E., Sharma, V.K., 359 2023. Ferrate(vi) mediated degradation of the potent cyanotoxin, cylindrospermopsin: 360 361 kinetics. products, and toxicity. Water Res. 233. 119773. https://doi.org/10.1016/j.watres.2023.119773. 362
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- 364

List of tables 365

Table 1 The distribution of reaction intermediates with respect to the initial chloride 366 367 concentration

By products	Chemical structure	<i>m/z</i> 1	mmol/L	10 mmol/L	50 mmol/L
1	OH Cl	128	\checkmark	\checkmark	\checkmark



128	\checkmark		\checkmark
162			
162		\checkmark	

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<u>10</u>	O U O O O O	124		\checkmark	
<u>11</u>	HO HO HO O O O HO	172	\checkmark	\checkmark	
<u>12</u>		234	\checkmark		
<u>13</u>		267	\checkmark	\checkmark	\checkmark
<u>14</u>	OH HO	186		\checkmark	
<u>15</u>	OH OH	186			
<u>16</u>	O OH	186			\checkmark
<u>17</u>	HO	202		\checkmark	\checkmark
<u>18</u>		360			
<u>19</u>		430			

Table 2 The acute and chronic toxicity of the oxidation by-products using ECOSAR program(Orange: very toxic; Pink: toxic; Blue: harmful; Green: not harmful)

			(B ,)			
	Fish	Daphnia	Green algae			Green algae
	LC ₅₀	LC ₅₀	EC ₅₀	Fish	Daphnia	
PhOH	27.7	9.64	2.40	2.61	0.969	4.53
<u>1</u>	24.7	14.9	14.2	2.59	1.71	4.23
<u>2</u>	13.7	6.35	1.21	1.37	0.715	2.67
<u>3</u>	13.7	6.35	1.21	1.37	0.715	2.67
<u>4</u>	6.24	3.88	0.566	0.671	0.489	1.46
<u>5</u>	2.72	2.27	0.253	0.313	0.320	0.759
<u>6</u>	1.15	1.28	0.110	0.141	0.203	0.384
<u>7</u>	49.2	685	8.15	33.8	280	0.881
<u>8</u>	6.17	42.5	2.92	3.23	15.6	0.410
<u>9</u>	0.095	0.738	0.047	0.0091	4.87	0.011
<u>10</u>	0.168	1.78	0.066	0.018	18.1	0.015
<u>11</u>	0.094	0.525	0.060	0.0079	2.17	0.014
<u>12</u>	12.2	25.7	17.4	0.599	2.55	14.4
<u>13</u>	6.07	10.0	6.40	0.251	0.994	6.23
<u>14</u>	3.34	19.1	2.10	1.63	6.81	0.316
<u>15</u>	7.99	4.81	0.724	0.853	0.598	1.83
<u>16</u>	2.12	1.86	0.198	0.246	0.268	0.610
<u>17</u>	7.69	54.6	3.49	4.08	20.1	0.484
<u>18</u>	0.470	0.345	0.176	0.011	0.034	0.304
<u>19</u>	0.105	0.048	0.021	0.0017	0.0047	0.052

Acute toxicity (mg/L)

Chronic toxicity (mg/L)

Byproducts	ucts Ferrate (VI) oxidation Electrochemical ox BDD ano		<i>In situ</i> chemical oxidation mediated by PMS
	$\begin{array}{c c} OH & OH & OH \\ \downarrow & Cl & \downarrow & \downarrow \\ Cl & Cl & Cl \end{array}$	OH Cl Cl	OH Cl
	OH OH OH OH OH CI CI CI OH OH OH	OH Cl Cl	OH Cl
Monomers	$\begin{array}{c} OH \\ Cl \\ \leftarrow \\ Cl \\ \leftarrow \\ Cl \\ Cl \\ O \end{array} \begin{array}{c} OH \\ \leftarrow \\ Cl \\ O \\ O \end{array}$	$\begin{array}{c} OH \\ Cl \\ Cl \\ Cl \end{array} \begin{array}{c} OH \\ Cl \\ Cl \end{array} \begin{array}{c} OH \\ Cl \\ Cl \\ Cl \end{array} \end{array}$	OH Cl
	O O O O H HO O O O O O O O O O O O O O		
		$ \begin{array}{c} OH \\ HO \\ HO \\ O \\ O \\ O \\ O \\ O \\ O \\ $	
	$\begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 $	HO HO Cl	
dimers	HO OH	HO CI HO CI HO CI	None
	HO OH HO		
		CI OH CI CI CI	

Table 3 Comparison of the byproducts generated in different advanced oxidation processes



Cl

Ċl

<u>5</u>

Cl

OH

OH

 $\int 0$

<u>11</u>





ferrate oxidation of phenol

Cl

380

Fig. 1 Formation mechanism of monomer byproducts (hydroxylated and chlorinated during 381

<u>10</u>



382

384

385



Fig. 2 Formation of phenoxy radicals and carbon centered radicals through resonance during
 ferrate oxidation of PhOH, and the coupling reactions can be formed by their
 combinations



Fig. 3 Some representative LC and MS spectra concerning the degradation byproducts ofphenol via FOT



410 Fig. 4 Formation mechanism of dimer byproducts (hydroxylated and chlorinated products)
411 during ferrate oxidation of phenol

412 Scheme 9



- 414 Scheme 10



Fig. 5 Produces of symmetric trimeric intermediates (<u>**18**</u> and <u>**19**</u>, both featuring two ether bonds)



Fig. 6 A simplified transformation sequence of phenol in K₂FeO₄/NaCl system