



HAL
open science

Toward a better understanding of peroxymonosulfate and peroxydisulfate activation using a nano zero-valent iron catalyst supported on graphitized carbon: Mechanisms and application to the degradation of estrogenic compounds in different water matrix

Minjuan Cai, Peng Cheng, Jinjun Li, Feng Wu, Mohamed Sarakha, Gilles Mailhot, Marcello Brigante

► **To cite this version:**

Minjuan Cai, Peng Cheng, Jinjun Li, Feng Wu, Mohamed Sarakha, et al.. Toward a better understanding of peroxymonosulfate and peroxydisulfate activation using a nano zero-valent iron catalyst supported on graphitized carbon: Mechanisms and application to the degradation of estrogenic compounds in different water matrix. *Journal of Cleaner Production*, 2023, 414, pp.137702. 10.1016/j.jclepro.2023.137702 . hal-04129222

HAL Id: hal-04129222

<https://hal.science/hal-04129222v1>

Submitted on 15 Jun 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution 4.0 International License

1 **Toward a better understanding of peroxymonosulfate and peroxydisulfate**
2 **activation using a nano zero-valent iron catalyst supported on graphitized**
3 **carbon: Mechanisms and application to the degradation of estrogenic**
4 **compounds in different water matrix**

5
6 **Minjuan Cai^{a,b}, Peng Cheng^b, Jinjun Li^{a*}, Feng Wu^a, Mohamed Sarakha^b, Gilles Mailhot^b,**
7 **Marcello Brigante^{b*}**

8
9 ^a Department of Environmental Engineering, School of Resources and Environmental Science,
10 Wuhan University, 430079, P. R. China

11 ^b Université Clermont Auvergne, CNRS, Institut de Chimie de Clermont-Ferrand, F-63000
12 Clermont-Ferrand, France.

13
14 **Abstract**

15 In this study, we employed nano zero-valent iron catalysts supported on graphitized carbon (GC-
16 nZVI) catalyst to efficiently degrade BPA under circumneutral pH conditions in both dark and
17 UVA radiation. The GC-nZVI catalyst was characterized using specific techniques (XPS, FTIR,
18 BET, etc.), and was used to activate both PS and PMS in solution. Although no significant BPA
19 degradation constant (k_{BPA}) was determined using PS/PMS or GC-nZVI alone, a significant
20 synergistic effect was observed in the system. Under dark conditions, k_{BPA} increased from 0.01 min^{-1}
21 to 0.17 when PS was used, both in the dark and under UVA. Notably, when PMS was present in
22 the system, the improvement was even higher with k_{BPA} reaching 0.18 and 0.26 min^{-1} under dark
23 and UVA conditions, respectively. To further support the synergistic effect, it was found that 80 %
24 of mineralization was achieved within 2 hours of UVA exposure.

25 Chemical quenching experiments were conducted using selective probes and kinetic modelling

26 showed that the activation of PS/PMS produced sulfate radicals ($\text{SO}_4^{\bullet-}$), hydroxyl radicals ($\cdot\text{OH}$)
27 and ferryl ions ($\text{Fe}^{\text{IV}}\text{O}^{2+}$) in both systems. Additionally, GC-nZVI/PMS system demonstrated good
28 stability in recycling experiments, with up to 70 % of BPA still being degraded after 3 cycled in 1
29 hour under UVA.

30 In conclusion, the degradation efficiencies of GC-nZVI/PMS and GC-nZVI/PS systems under dark
31 and UVA radiation were assessed for three different EDCs (BPA, E2, and EE2) in both tap and
32 sewage treatment plant waters.

33 This study has demonstrated that the highly efficient GC-nZVI /PS/UVA or GC-nZVI/PMS/UVA
34 system has significant potential for application in different water matrix, and our findings provide
35 insights into the design of heterogeneous Fenton-like and photo-Fenton-like catalysts.

36

37 **Keywords**

38 Advanced oxidation processes, Endocrine Disrupting Compounds, Fenton-like activation, Ferryl
39 ions, Radical formation

40

41 **Introduction**

42 Endocrine Disrupting Compounds (EDCs) are emerging environmental pollutants that include
43 various types of natural and synthetic compounds exhibiting adverse effects on reproduction
44 through mimicking or inhibiting the endocrine systems of animals and humans (Marty et al., 2011;
45 Wang et al., 2020). The presence of EDCs and the resulting adverse effects in aqueous media have
46 been widely demonstrated (Annamalai and Namasivayam, 2015; Giulivo et al., 2016; Kim et al.,
47 2018) and various technologies to decrease their concentration including adsorption/biosorption
48 (Ahmed et al., 2017), biochemical oxidation (Wang et al., 2022), ozonation (Esplugas et al., 2007),
49 and treatment with hypochlorite (Romanucci et al., 2020; Zarrelli et al., 2012) have been
50 investigated. For example, the oxidative degradation of some EDCs is associated with the

51 aromaticity of their structures, implying that hydrophobicity may be an important feature in their
52 study and control (Chang et al., 2009). Techniques such as treatment with activated carbon (AC)
53 (Ghazal et al., 2022) or membranes (Kimura et al., 2004; Wijekoon et al., 2014) can effectively
54 remove EDCs from water. However, all of these methods have some disadvantages such as long
55 reaction times, high cost, low efficiency, incomplete removal, and production of additional toxic
56 by-products. Recently, advanced oxidation processes (AOPs) (Jia et al., 2021a; Liu et al., 2022;
57 Phan et al., 2022; Thomas et al., 2021) have been explored, which show great promise for the
58 elimination of estrogenic compounds from aqueous solution, and they have been widely applied due
59 to the non-selectivity and high redox potential of $\cdot\text{OH}$.

60 In AOPs systems, the formation of strong and non-selective radicals such as $\cdot\text{OH}$ or $\text{SO}_4^{\cdot-}$ is
61 most prevalent. Through dehydrogenation and electron-transfer reactions between free radicals and
62 organic pollutants, the latter are oxidized and decomposed into small molecules, ultimately being
63 mineralized as carbon dioxide, water, and inorganic ions. $\text{SO}_4^{\cdot-}$ has similar or even higher redox
64 potential (2.5–3.1 V) and longer half-life (30–40 μs) than $\cdot\text{OH}$ (1.8–2.7 V and 20 ns respectively)
65 (Lin et al., 2020). Moreover, its oxidation reactions can proceed efficiently over a wider pH range
66 (from 2 to 8). Sulfate-based advanced oxidation processes (SR-AOPs) have shown excellent
67 performances in the removal of refractory organic pollutants from aqueous environments
68 (Giannakis et al., 2021; Jiang et al., 2019). Peroxymonosulfate (PMS) and peroxydisulfate (PS) are
69 important sources of sulfate radicals. Due to their cost-effectiveness, good solubility, and
70 environmentally benign, they have been widely studied and applied in environmental remediation.

71 Traditional activation catalysts for SR-AOPs are mainly based on transition metal ions (Jia et
72 al., 2021b; Wu et al., 2019; Zhou et al., 2014) (Fe, Co, Mn, etc.) , or heterogeneous photoactivation
73 (Gowrisankaran et al., 2022; Kakavandi et al., 2022; Khan et al., 2017) or ultrasound (Gujar et al.,
74 2023). Compared to other activation methods, transition metal activation has advantages of strong
75 activity and low energy consumption. However, single use of some of the activation techniques

76 mentioned above can leave SR-AOPs with limitations, such as the large number of free radicals
77 generated in a short period of time not being able to react sufficiently with the pollutant, but being
78 quenched directly, resulting in high chemical compounds consumption, high treatment cost and low
79 degradation efficiency of the AOPs system. The application of heterogeneous catalytic materials
80 can enhance the generation of free radicals and promote degradation efficiency. For example,
81 Takdastan et al. (Takdastan et al., 2018) prepared magnetite nanoparticles supported on carbon as a
82 heterostructure catalyst and combined it with UV light and ultrasonication to efficiently activate
83 PMS for the degradation of bisphenol A (BPA), achieving a removal efficiency of more than 90%
84 within 30 min. Compared to energy-based activation methods, activation of PMS/PS using
85 heterogeneous catalysts is simpler and more economical in terms of reactor/system configuration.
86 Iron-based materials are generally regarded as excellent heterogeneous catalysts because of their
87 non-toxicity, environmental benignity, low cost, and high catalytic activity, and so have become the
88 most studied materials in SR-AOPs (Li et al., 2020; Xu et al., 2018; Yan et al., 2019a).

89 Nano zero-valent iron (nZVI), which has been widely assessed as a replacement for iron
90 cations or iron oxides with a view to long-term use and potential reusability, has poor stability due
91 to its high surface energy (Sun et al., 2012). To circumvent this disadvantage, stable, porous
92 supports are usually used. The presence of carrier material also reduces the rate of oxidation of
93 nZVI by dissolved oxygen prior to application. Carbonaceous materials have been widely used due
94 to their high specific surface areas, adjustable pore sizes and low cost. Compared to AC, GC has
95 abundant π -electrons and its high affinity for organics favours the adsorption of organic matter on
96 its surface (Chen et al., 2021; Pan et al., 2021). Zhao et al. in a recent review reported that
97 generation of $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ can occur from the π -electrons in hybridized carbon of biochar-based
98 catalysts to PMS (Zhao et al., 2021).

99 This increases the contact between them and thereby improves the degradation efficiency of
100 AOPs. Moreover, nZVI can be uniformly dispersed on the carbon-based materials, and providing

101 more active sites. Carbon material can also be used as a substrate for the reduction of iron oxides to
102 nZVI. For example, Jiang et al. (Jiang et al., 2019) prepared an Fe functionalized biochar
103 composites that consisted of ZVI, porous carbon bearing abundant functional groups, and
104 nanofibers, which could activate PMS to efficiently remove BPA. B. Wang and co-workers (Wang
105 et al., 2021) investigated the p-nitrophenol degradation using PS activation by n-ZVI-loaded
106 biochar. The authors found a complete degradation after using 0.8g/L of catalysts and 1 mM of PS.
107 Tan and al. investigated the removal of levofloxacin using nZVI/carbon fiber by achieving a good
108 removal efficiency (~ 93 %) after 1h of reaction in the presence of 1 mM of PMS in the dark.
109 Furthermore, they indicated that this reaction was also due to the 50% adsorption obtained during
110 the first minutes of the reaction (Tan et al., 2021).

111 EDCs are represented by 17 α -estradiol (EE2), 17 β -estradiol (E2), and BPA. BPA is a
112 compound showing estrogenic activity at very low concentrations, and is of prime concern with
113 regard to water quality (Chang et al., 2009). These pollutants are stable in the environment, so it is
114 important to evaluate their degradation in aquatic systems. In this context, the main purpose of this
115 study is to assess the performance of nZVI supported on GC (GC-nZVI) for heterogeneous SR-
116 AOPs at circumneutral pH values. First, the BPA degradation kinetics and steady-state
117 concentration of different oxidant species, such as $\text{SO}_4^{\bullet-}$, $\cdot\text{OH}$, and $\text{Fe}^{\text{IV}}\text{O}^{2+}$ were determined to
118 assess their contributions to BPA degradation under thermal (dark) and UVA activation. Thereafter,
119 the use of GC-nZVI in the presence of PS and PMS was evaluated for the degradation of E2, EE2,
120 and BPA in tap and sewage treatment plant (STP) water samples. In our work, we use the thermal
121 reduction of zero-valent iron with carbon and metal-catalyzed graphitization to improve the
122 graphitization of the carbon carrier, and all the degradation data were measured after desorption.
123 Another originality is to have differentiated the adsorption from the degradation of selected
124 pollutants (which is not always done in other works) and to have quantified the reactive species
125 involved in the degradation in the dark and under UVA radiation. In addition, we have shown a

126 significant formation of the ferryl ion and determined its contribution to the selective degradation of
127 bisphenol A in solution.

128

129 **2. Materials and methods**

130 **2.1 Chemicals and irradiation setup**

131 The list of chemicals and photochemical setup are provided in Supplementary Material

132

133 **2.2 Synthesis and characterization**

134 Ferric nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$; 6.06 g, 9.09 or 12.12 g) was first dissolved in
135 Milli-Q water (25 mL) and then 3.0 g commercial activated carbon (from Sinopharm Chemical
136 Reagent Co., Ltd.; 3.0 g, giving Fe:C ratios $[\text{Fe}]/[\text{C}]_n$ of 0.06:1, 0.09:1, and 0.12:1, respectively)
137 was added. Each mixture was stirred at room temperature for 60 min, and then heated and stirred at
138 60 °C to evaporate the water, leaving a black solid. Each solid was placed in a corundum reactor in
139 a tubular furnace and heated for 1 h at 250 °C under a nitrogen flow of 30 mL min⁻¹, then heated to
140 900 °C at a rate of 10 °C min⁻¹ and maintained at this temperature for 2 h. Thereafter, it was
141 allowed to cool naturally to room temperature. To determine the total iron in the obtained samples,
142 portions (5 mg) were dissolved in concentrated HCl (30 mL). Each experiment was performed in
143 duplicate. Chemical analysis was performed with an Inductively Coupled Plasma Optical Emission
144 Spectroscopy (ICP-OES) analyzer (5800 Agilent) in radial and axial modes, using a wavelength of
145 238.2 nm for the quantitative determination.

146 The actual Fe:C ratios ($[\text{Fe}]/[\text{C}]_n = 0.06, 0.09$ and 0.12) in the samples was measured as 0.054,
147 0.073, and 0.096, respectively. So, the samples are denoted as 0.05-GC-nZVI, 0.07-GC-nZVI, and
148 0.10-GC-nZVI, respectively.

149 Functional groups on the surfaces of the samples were characterized by Fourier transform
150 infrared spectroscopy (FTIR, PerkinElmer 1725X, USA). The valence states of the constituent
151 elements were determined by X-ray diffraction (XRD) analysis, (D8 Advance, Bruker, Germany)

152 and X-ray photoelectron spectroscopy (XPS, Thermo-Fisher ESCALAB Xi+, USA), and binding
153 energies were calibrated with reference to the C 1s peak at 284.8 eV. Specific surface areas were
154 analyzed by recording Brunauer–Emmett–Teller (BET) nitrogen–adsorption-desorption isotherms.
155 The morphological and textural properties of the samples were characterized by field–emission
156 scanning electron microscopy (SEM; Tescan Mira3, Czech Republic, equipped with a Zeiss Sigma
157 300 analyzer) and transmission electron microscopy (TEM; H-7650, AMT40, Germany) with an
158 attachment for energy-dispersive X-ray (EDX) analysis for element mapping. The surface chemical
159 composition of the samples was analysed by Fourier transform infrared (FTIR) spectroscopy
160 (NICOLET 5700, Thermo Electron, USA). The order of their graphitic structures was examined by
161 Raman spectroscopy (514 nm) (LabRAM HR Evolution, HORIBA Scientific, France) and the
162 surface charged condition by zeta potential analysis (ZEN 3700 Zetasizer, Malvern, UK). Before
163 the zeta potential measurement, samples were prepared in Milli-Q water at a concentration of 0.5 g
164 L⁻¹. The suspension was adjusted to a pH range of 1 to 11 using NaOH or HCl solution and then
165 sonicated for 30 min.

166

167 **2.3 Experimental procedure**

168 The kinetics of EDCs degradation were investigated using a pseudo-first-order model ($\ln \frac{C_t}{C_0} =$
169 $-kt$), which allows better comparison of reaction constants (k, min^{-1}) under different conditions.
170 The error in the selected pollutant degradation rate constant was estimated from the scatter of the
171 experimental data about the fitting line.

172

173 **2.4 Quantification of chemical species**

174 Prior to analysis, each sample (2 mL) was basified with 1 M NaOH (1 mL, pH \approx 11) and filtered
175 through a 0.45 μm polytetrafluoroethylene syringe filter to desorb BPA so as to separate the
176 adsorption and degradation processes. This allowed us to determine the actual degradation of BPA
177 during the experiment.

178 The concentrations of BPA, E2, and EE2 during kinetic experiments were determined by high-
179 performance liquid chromatography (HPLC). The experiments were performed with UV detection
180 at 277 nm. A flow rate of 1 mL min⁻¹ was used with, as mobile phase, a mixture of water and
181 methanol (30:70, v/v). A Nucleodur 100-5 C18 column with dimensions of 250 mm×4.6 mm was
182 used. The retention time of BPA was 4 min. For determination of three EDCs (BPA, E2 and EE2)
183 in different water samples, the fluorescence detector settings were $\lambda_{\text{ex}} = 280$ nm and $\lambda_{\text{em}} = 305$ nm.
184 The mobile phase for isocratic elution comprised water and acetonitrile 50/50 (v/v) with a flow rate
185 of 1 mL min⁻¹. Under these conditions, the retention times of BPA, E2, and EE2 were 4.9, 7.1 and
186 7.6 min, respectively. By-products derived from BPA were determined by ultra-high-performance
187 liquid chromatography coupled to mass spectrometry (UHPLC-MS) and Ion Chromatography-Mass
188 spectrometry (IC-MS). More details are provided in the Supplementary Material.

189 Electron spin resonance (ESR) experiments were performed on a JES-X320 spectrometer. DMPO
190 (100 mM) was used as a radical probe for $\text{SO}_4^{\bullet-}$ and $\cdot\text{OH}$. ESR spectra were registered at room
191 temperature under the following operating conditions: modulation frequency 100 kHz, sweep width
192 0.5 mT, microwave power 1 mW, microwave frequency 9.15 GHz, and center field at 326.0 ± 5
193 mT.

194

195 **3. Results and discussion**

196 **3.1 Material characterization**

197 XRD patterns of GC-nZVI with different iron contents and pure ZVI are presented in Fig. S2a.
198 With increasing Fe proportion ($[\text{Fe}]/[\text{C}]_n$), the signals at $2\theta = 44.7^\circ$, 65.0° , and 82.4° , which are
199 corresponded to the peak of pure ZVI, attributable to the (110), (200), and (211) planes of metallic
200 iron, respectively (JCPDS No. 06-0696), gradually intensified. Further peaks at 43.7° and 50.9°
201 correspond to the Fe_3C (JCPDS No. 03-0400). The formation of Fe_3C was mainly due to the
202 reduction of pyrocarbon at high temperatures. However, the peak of GC could not be observed due

203 to the strong signal peak of zero-valent iron. After removing the iron from the GC-nZVI using
204 hydrochloric acid, there was a obvious signal peak at $2\theta = 26^\circ$, which can be thought of as graphite
205 crystal diffraction peak (JCPDS No. 26-1097). As given in the Raman spectra (Fig. S3), the G
206 bands and D bands were found in the sample, as a feature of graphitized materials. And the ratio of
207 the intensity of the D-band to the G-band (I_D/I_G), is also shown in the graph, and it can be seen that
208 the GC-0.10-GC-nZVI has the smallest ratio of the three catalysts, indicating that it has the least
209 amount of defective carbon and the highest degree of graphitization.

210 The derived textural properties were calculated by non-local density functional theory function
211 of SAIEUS software and compiled in Table S1 (the specific nitrogen adsorption and desorption
212 isotherms of the samples and pore size distributions are shown in Fig. S4). With the increase of Fe
213 proportion, S_{BET} and the micropore and mesopore volume decreased. This could be attributed to the
214 adsorption of ZVI on the carrier GC resulting in the blockage of the pores. It follows that the ZVI
215 particles were not accumulated on the surface of the carbon but dispersed in its pores (Lv et al.,
216 2011; Zhu et al., 2009). SEM image (Fig. S5) also clearly showed that at low iron loading, the iron
217 was preferentially dispersed in the pores of the carbon rather than on the surface, spreading to the
218 surface of the carbon when the iron was overloaded. In contrast, when there was no carbon carrier
219 (Fig. S5d), the ZVI tends to gather together and has a larger particle size. The corresponding EDS
220 elemental mappings (Fig. S6a–d) clearly illustrate the homogeneous distributions of C, O, and Fe in
221 the samples. The presence of O may be due to the formation of iron oxide on the surface of the
222 sample in contact with O_2 in the air. Moreover, the TEM image (Fig. S7a, b) revealed that ZVI in
223 the material was evenly dispersed on the carbon, which had a typical graphitized structure,
224 facilitating the transfer of photogenerated electrons (Wang et al., 2019b; Zhuang et al., 2017)

225 From the infrared spectrum of GC-nZVI in Figure S8, it can be seen that the sharp absorption
226 peak near 3436 cm^{-1} was caused by the stretching vibration of -OH in the supported iron compound.
227 At the same time, there was a strong absorption peak near 1630 cm^{-1} , which was formed by the

228 C=C stretching vibration of alkenes, and the peak at 1380 cm^{-1} was formed by the C-H deformation
229 vibration of alkanes and alkenes. The peak at 1100 cm^{-1} was assigned to the C-O groups; the
230 characteristic peak at 584 cm^{-1} was the Fe-O stretching vibration peak corresponding to Fe-O-H,
231 which further verifies nZVI successfully loaded on carbon (Su et al., 2016). The zeta potential of
232 the particles reflected the variation of surface charge with pH in aqueous solutions of different
233 acidity (Fig. S9). The zero point of charge (pHzpc) of 0.05-GC-nZVI, 0.07-GC-nZVI and 0.10-GC-
234 nZVI was observed at 3.25, 6.21 and 7.62, which were consistent with the results of previous
235 studies(Wang et al., 2019a) (Ren et al., 2021). The loaded iron significantly reduces the specific
236 surface area and hydrophobicity of the carbon. To investigate the impact of the loaded iron on
237 reactivity, batch experiments were conducted.

238

239 **3.2 Degradation of BPA using GC-nZVI with PS or PMS**

240 The activation of PS and PMS by 0.07-GC-nZVI was investigated through assessing the
241 efficiency of BPA degradation under different conditions. In the first step, BPA adsorption on 0.07-
242 GC-nZVI, AC and GC were tested at pH 7 (Fig. S10a). From the kinetic results it was clear that the
243 adsorption efficiency of GC was higher compared to AC. This was due to that the mesopore volume
244 of GC was larger than that of AC, which was more conducive to the dispersion of BPA in the pore,
245 as well as the high graphitisation of GC which facilitates the π - π interaction with the organics. The
246 decrease in adsorption efficiency of 0.07-GC-nZVI was due to iron blocking the pore structure of
247 GC, resulting in a decrease in the specific surface area of GC. But the data after desorption of the
248 three indicated that the material itself had no degradation effect on BPA. But it can be observed that
249 the adsorption was very fast, almost reaching equilibrium within 30 min. Therefore, the dark
250 reaction adsorption time in subsequent experiments was set at 30 min.

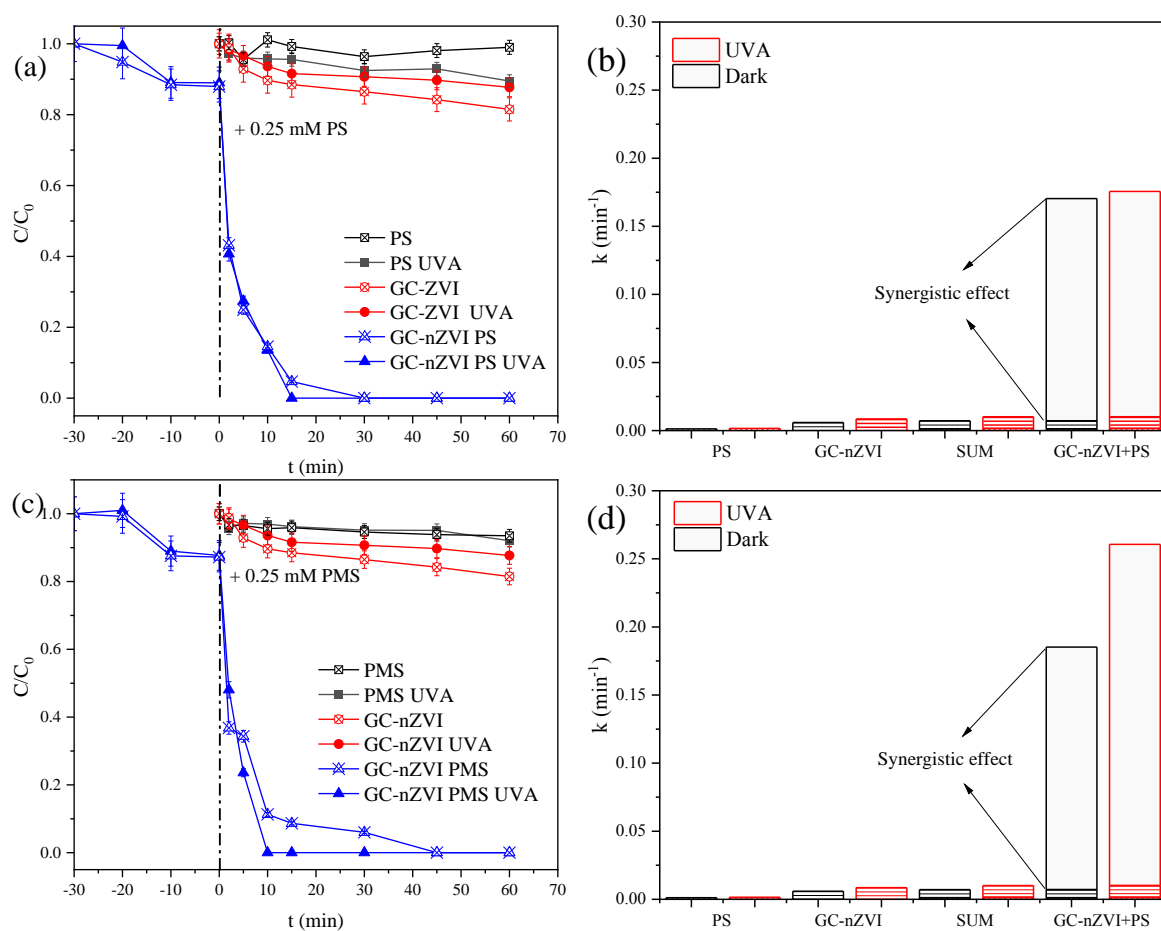
251 In order to correlate the effect of iron doping amount to the degradation of BPA in the presence
252 of PMS, a series of experiments was carried out as shown in Fig. S11. BPA was completely

253 degraded within 30 min in the presence of GC-nZVI ($[\text{Fe}]/[\text{C}]_n = 0.07$) and PMS, while BPA
254 removal efficiencies of 47% and 85% within 30 min were achieved with $[\text{Fe}]/[\text{C}]_n$ 0.05 and 0.10,
255 respectively. The results implied that an Fe to C ratio of 0.07 was optimal for BPA degradation.

256 To further optimize the BPA degradation efficiency of 0.07-GC-nZVI, the effects of pH and
257 oxidant concentration were investigated. As shown in Fig. S12, 0.07-GC-nZVI showed good
258 degradation efficiency as the pH was increased from 3 to 7. Under pH 3–7, most of the BPA was in
259 uncharged forms (Yan et al., 2019b). No effect of pH on BPA removal towards 0.07-GC-nZVI
260 composites may be attributed to no change in BPA species and surface charge of GC-nZVI (Fig.
261 S9). At a PMS concentration of 0.1 mM, the degradation efficiency reached 100% within 60 min.
262 When the PMS concentration was increased from 0.25 to 1.0 mM, the time for complete removal of
263 BPA was shortened to less than 30 min. Considering the cost and the fact that the pH of actual
264 environmental water is near-neutral, the conditions used in the subsequent experiments were 0.07-
265 GC-nZVI at $\text{pH}_0 = 7$ and an oxidant concentration of 0.25 mM.

266 In the PMS or PS systems under dark conditions (Fig. S13), BPA was slowly degraded by the
267 added ZVI after 60 min of treatment (20% with PMS, 15% with PS). In contrast, in the 0.07-GC-
268 nZVI/PS or 0.07-GC-nZVI/PMS systems, significant increases in removal efficiency were
269 observed, with complete removal of BPA within 45 min. And under UVA irradiation, without the
270 addition of catalysts and oxidants, there is no degradation effect on BPA. Blank experiments
271 showed that at most no BPA degradation was observed when PS and PMS used with or without
272 UVA irradiation, confirming the catalytic effect of 0.07-GC-nZVI. To confirm the role of GC in the
273 degradation effect of the catalyst, the removal and degradation effects of GC in different systems
274 were compared (Fig. S10b) and the results showed that the addition of oxidants or UVA irradiation
275 had little or no contribution to the removal of BPA. The data after desorption showed that the
276 addition of PS or PMS to the system only improved the degradation by about 5%, and then only by
277 8% after the addition of UVA. This suggests that the use of GC alone as a catalyst does not improve

278 the degradation of BPA. The BPA degradation constant (k , min^{-1}) (Fig 1c) increases considerably in
 279 the presence of GC-nZVI with the two oxidants (Fig. 1). Furthermore, in contrast to the system with
 280 PS, the use of UVA radiation using PMS accelerates the degradation of BPA from 0.185 min^{-1} to
 281 0.261 min^{-1} . This synergistic effect indicates the contribution of a photo-induced process that
 282 increases the production of oxidizing species.
 283



284
 285
 286 Fig. 1. BPA degradation efficiencies in different systems: (a) PS system, (b) PMS system and
 287 initial reaction rate constant in 10 min (c). Initial conditions: $[\text{BPA}] = 25 \mu\text{M}$, $[\text{PS}] =$
 288 $[\text{PMS}] = 0.25 \text{ mM}$, $[\text{catalyst}] = 0.05 \text{ g L}^{-1}$, $\text{pH}_0 = 7.0 \pm 0.1$.

289
 290 The catalytic ability of 0.07-GC-nZVI in different systems was also investigated. The

291 introduction of UVA in the 0.07-GC-nZVI/PS system (Fig. 1a) accelerated the BPA degradation
292 such that 100% degradation of BPA was achieved within 15 min instead of 30 min. A marked effect
293 was also observed in the ZVI/PS system, with BPA degradation increasing from 15% to 56% after
294 1 h. The introduction of UVA to the 0.07-GC-nZVI/PMS system (Fig. 1b) significantly reduced the
295 reaction time for complete degradation of BPA from 45 min to 10 min. Thus, it is clear that the
296 introduction of UVA promotes the generation of radicals, providing insight into the mechanism in
297 these two systems.

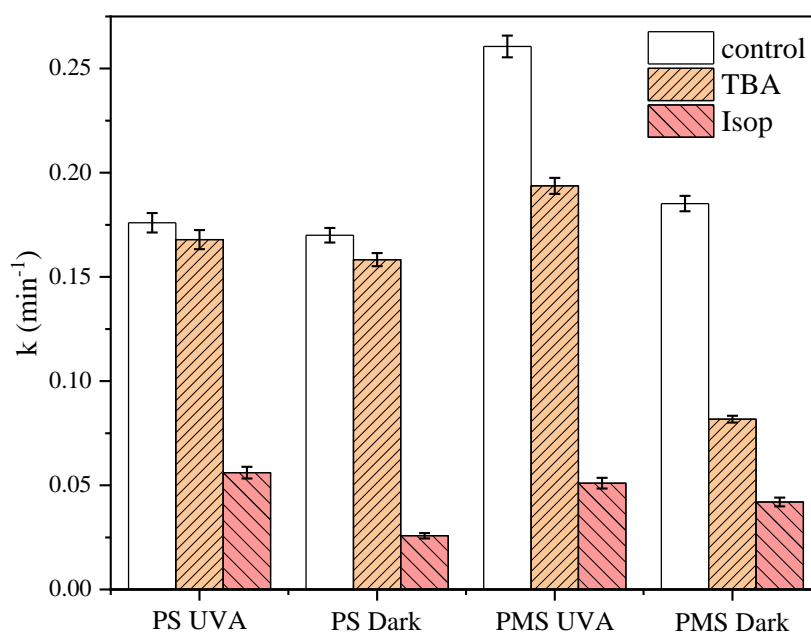
298

299 **3.3 Contributions of free radicals in different systems**

300 The contributions of radical species in the degradation of BPA were determined through
301 quenching experiments. Typically, PMS / PS generate $\text{SO}_4^{\bullet-}$ and $\cdot\text{OH}$ during the activation process.
302 At an appropriate concentration, isopropanol (Isop) can effectively quench $\text{SO}_4^{\bullet-}$ and $\cdot\text{OH}$ with
303 second-order rate constants of $k_{\text{Isop},\text{SO}_4^{\bullet-}} = 8.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{\text{isop}, \cdot\text{OH}} = 1.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, whereas
304 *tert*-butanol (TBA) can only quench $\cdot\text{OH}$ ($k_{\text{TBA}, \cdot\text{OH}} = 6.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$; $k_{\text{TBA},\text{SO}_4^{\bullet-}} = 8.3 \times$
305 $10^5 \text{ M}^{-1} \text{ s}^{-1}$) (Buxton et al., 1988; Huie et al., 1991). In the system 0.07-GC-nZVI + PS, the addition
306 of 5 mM TBA had almost no effect on BPA degradation, whereas in the presence of 40 mM Isop,
307 up to 62% inhibition was observed after 60 min of reaction (Fig. S14a). A similar trend was
308 observed under UVA irradiation, whereby inhibition by Isop was about 45% (Fig. S14b). When
309 0.25 mM PMS was used in the dark and under UVA irradiation, negligible effect on BPA removal
310 was observed in the presence of TBA (5 mM), whereas the BPA degradation efficiency was
311 inhibited by about 60% within 60 min under both dark and light conditions in the presence of Isop.

312 BPA degradation rate constants (k , min^{-1}) over the first 10 min in different reaction systems
313 are indicated in Fig. 2. In the presence of PS, the use of UVA led to an increase in k from 0.170 to
314 0.176 min^{-1} . In the presence of TBA, k was reduced by only about 7% (0.158 min^{-1} in the dark;
315 0.167 min^{-1} under UVA), further indicating that $\cdot\text{OH}$ was not dominant in the reaction. In the

316 presence of Isop, k decreased to 0.056 and 0.026 min^{-1} , respectively. A similar trend was observed
 317 when PMS was used, whereby the addition of Isop to the 0.07-GC-nZVI/PMS/UVA system led to a
 318 decrease in k from 0.261 to 0.051 min^{-1} . These findings suggest that the principal radical involved
 319 in the activation of PMS and PS by 0.07-GC-nZVI is $\text{SO}_4^{\bullet-}$. It is also evident that UVA irradiation
 320 increases the BPA degradation rate constant by promoting the generation of radicals, consistent
 321 with the results reported in Figure 1. In some paper, the formation of singlet oxygen through
 322 reactivity of iron with PS or PMS has been reported. In order to clarify this point, furfuryl alcohol
 323 (FFA) was used as a quencher, which was due to its reactivity with $^1\text{O}_2$ in addition to the also well
 324 known reactivities with HO^{\bullet} and $\text{SO}_4^{\bullet-}$. By comparing the quenching effects when FFA (0.5 mM)
 325 was used alone or in the presence of ISOP (40 mM) (see Fig. S15), we can see that no difference
 326 was determined, indicating that no $^1\text{O}_2$ was produced in this system.



327

328 Fig. 2. Effects of TBA and Isop on the degradation rate constants of BPA in different systems.

329 Initial conditions: $[\text{PS}] = [\text{PMS}] = 0.25 \text{ mM}$, $[\text{catalyst}] = 0.05 \text{ g L}^{-1}$, $[\text{TBA}] = 5 \text{ mM}$, $[\text{Isop}] = 40$
 330 mM , $\text{pH}_0 = 7.0 \pm 0.1$.

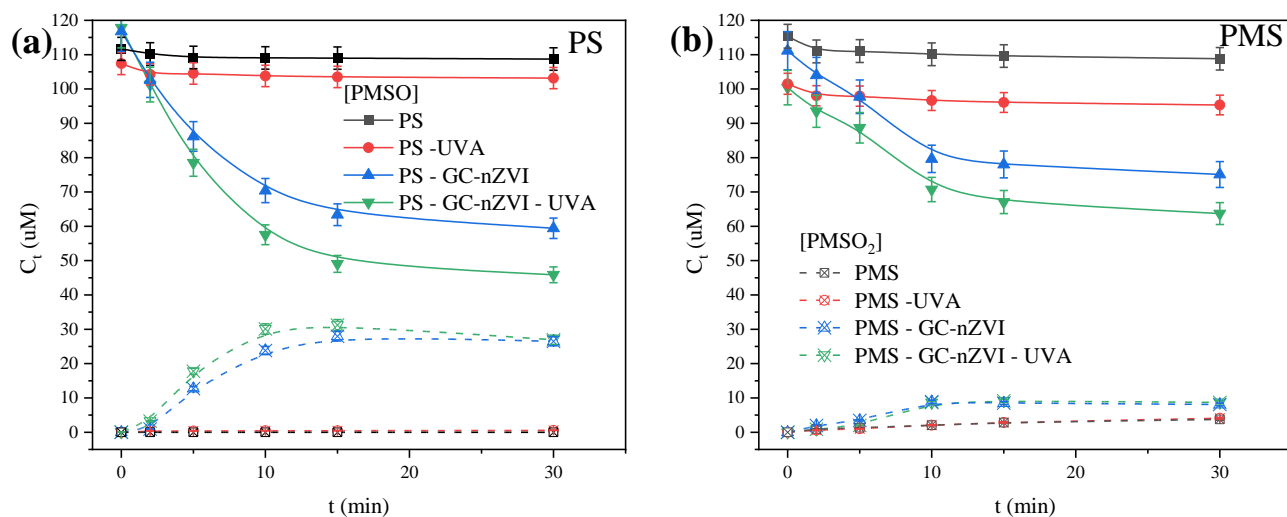
331

332 3.4 High-valent Iron species

333 The addition of Isop did not completely inhibit the degradation of BPA, suggesting that other
334 reactive species besides $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ were also generated. The formation of high-valent iron in
335 heterogeneous Fenton and Fenton-like processes has been reported in different works (Farinelli et
336 al., 2020; Litter and Slodowicz, 2017). PMSO has been reported as a chemical probe for ferryl ions
337 ($\text{Fe}^{\text{IV}}\text{O}^{2+}$) giving PMSO_2 as a product. Through an oxygen atom transfer mechanism, sulfoxide is
338 readily oxidized to the corresponding sulfone by high-valence metal oxygen species which differs
339 from the $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ mediated pathways. In order to assess whether the high-valent metal oxide
340 species [Fe^{IV}] were produced in the different systems, the production of PMSO_2 by selective
341 oxidation of PMSO was determined. As shown in Figure 3a, in the GC-nZVI/PS system, 57 μM
342 PMSO was oxidized after 30 min, and 26 μM PMSO_2 was produced. And after the addition of UVA
343 irradiation, 72 μM PMSO was oxidized and 27 μM PMSO_2 was produced.

344 Blank experiments showed neither degradation of PMSO nor production of PMSO_2 in the
345 presence of PS alone, with or without UVA irradiation, indicating that PS alone could not react with
346 PMSO. In the PMS system (Figure 3b), some oxidation of PMSO was observed with the production
347 of PMSO_2 . However, by calculating the percentage of $[\text{PMSO}_2]$ to $[\text{PMSO}]_0$, it transpired that 3%
348 and 4% of PMSO_2 were produced in the dark and light reactions, respectively, with corresponding
349 increases of 7% and 9% upon the addition of catalyst, suggesting a direct contribution of Fe^{IV} in the
350 PMS system. Thus, BPA degradation is not only attributable to radicals, but also to Fe^{IV} , and we
351 can argue that exposure to UVA promotes the degradation of PMSO and the generation of PMSO_2 ,
352 suggesting that the positive effect of UVA on BPA degradation is due to both the promotion of
353 radical production and Fe^{IV} .

354



355

356 Fig. 3. PMSO degradation and PMSO₂ formation in (a) PS system and (b) PMS system, [PS] =

357 [PMS] = 0.25 mM, [catalyst] = 0.05 g L⁻¹, pH₀ = 7.0 ± 0.1.

358

359 3.5 Steady state concentrations of reactive species

360 In order to determine the steady-state concentrations of each reactive species in the various

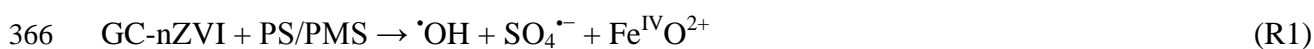
361 systems, a kinetic approach under different experimental conditions in the presence of PMSO and

362 TBA was employed. The first simplified step is the generation of $\cdot\text{OH}$, $\text{SO}_4^{\cdot-}$, and $\text{Fe}^{\text{IV}}\text{O}^{2+}$ through

363 the reaction of GC-nZVI with PS and PMS (R1). PMSO was used due to its reactivity with all

364 reactive species (R2–R4) and to quantify the generation of $\text{Fe}^{\text{IV}}\text{O}^{2+}$ in solution through the selective

365 formation of PMSO₂ (R4) while TBA was used as a selective $\cdot\text{OH}$ scavenger (R5).



371 Considering the rate constants of reactions between TBA and oxidant species such as $\cdot\text{OH}$,

372 $\text{SO}_4^{\cdot-}$, and $\text{Fe}^{\text{IV}}\text{O}^{2+}$ (6.0×10^8 , 8.4×10^5 and $6.0 \times 10^1 \text{ M}^{-1} \text{ s}^{-1}$), (Bakac et al., 2004; Buxton et al.,

373 1988; Neta et al., 1996) we can argue that 5 mM TBA is sufficient to selectively scavenge all

374 generated $\cdot\text{OH}$, while its effects on $\text{SO}_4^{\bullet-}$ and $\text{Fe}^{\text{IV}}\text{O}^{2+}$ are negligible.

375 The results presented in figure S16 show that the addition of 5 mM TBA partially inhibited the
376 degradation of PMSO when 0.07-GC-nZVI (0.05 g L^{-1}) was used in the presence of 0.25 mM PS,
377 decreasing the degradation rates of PMSO from $7.57 \times 10^{-8} \text{ M s}^{-1}$ and $9.96 \times 10^{-8} \text{ M s}^{-1}$ in the dark
378 and under UVA to $5.82 \times 10^{-8} \text{ M s}^{-1}$ and $6.11 \times 10^{-8} \text{ M s}^{-1}$, respectively. A similar effect was
379 observed when PMS was used, with decreases in the PMSO degradation rates from $5.14 \times 10^{-8} \text{ M}$
380 s^{-1} and $3.87 \times 10^{-8} \text{ M s}^{-1}$ to $3.84 \times 10^{-8} \text{ M s}^{-1}$ and $2.28 \times 10^{-8} \text{ M s}^{-1}$, respectively.

381 It can be concluded that, under the adopted conditions, the degradation of PMSO is due to the
382 combined effects of R3 and R4, as expressed by Eq. (1) (Fig. S16), where $\frac{d[\text{PMSO}]}{dt}$ is the
383 degradation rate of PMSO (M s^{-1}), and k_3 and k_4 are the second-order rate constants for reactions
384 between PMSO and $\text{SO}_4^{\bullet-}$ and $\text{Fe}^{\text{IV}}\text{O}^{2+}$, respectively.

$$385 \frac{d[\text{PMSO}]}{dt} = -k_3[\text{PMSO}][\text{SO}_4^{\bullet-}]_{\text{ss}} - k_4[\text{PMSO}][\text{Fe}^{\text{IV}}\text{O}^{2+}]_{\text{ss}} \quad (1)$$

386 The formation of PMSO_2 depends only on $\text{Fe}^{\text{IV}}\text{O}^{2+}$ and can be modelled according to Eq. (2)

$$387 \frac{d[\text{PMSO}_2]}{dt} = k_4[\text{PMSO}][\text{Fe}^{\text{IV}}\text{O}^{2+}]_{\text{ss}} \quad (2)$$

388 The steady state concentration of $\text{Fe}^{\text{IV}}\text{O}^{2+}$ ($[\text{Fe}^{\text{IV}}\text{O}^{2+}]_{\text{ss}}$) can then be calculated from Eq. (2) by
389 plotting the formation of PMSO_2 during the reaction period and considering the initial PMSO
390 concentration of $100 \mu\text{M}$ and $k_4 = 1.23 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ (Pestovsky and Bakac, 2006). This value has
391 been used to determine $[\text{SO}_4^{\bullet-}]_{\text{ss}}$ from Eq. (1). Finally, $[\text{Fe}^{\text{IV}}\text{O}^{2+}]_{\text{ss}}$ and $[\text{SO}_4^{\bullet-}]_{\text{ss}}$ were used to calculate
392 $[\text{HO}^{\bullet}]_{\text{ss}}$ according to Eq. (3) by plotting PMSO degradation without TBA.

$$393 \frac{d[\text{PMSO}]}{dt} = -k_2[\text{PMSO}][\text{HO}^{\bullet}]_{\text{ss}} - k_3[\text{PMSO}][\text{SO}_4^{\bullet-}]_{\text{ss}} - k_4[\text{PMSO}][\text{Fe}^{\text{IV}}\text{O}^{2+}]_{\text{ss}} \quad (3)$$

394 The steady state concentrations of each reactive species generated in the presence of PS and PMS in
395 the dark and under UVA irradiation are given in Table 2

396

397 Table 2. The concentrations of each reactive species generated in the presence of PS and PMS in

398 the dark and under UVA irradiation

	<i>PS</i>		<i>PMS</i>	
	Dark	Irradiation	Dark	Irradiation
$[\text{HO}^\bullet]_{\text{ss}} \text{ (M)}$	4.60×10^{-14}	9.39×10^{-14}	3.36×10^{-14}	5.07×10^{-14}
$[\text{SO}_4^{\bullet-}]_{\text{ss}} \text{ (M)}$	5.15×10^{-13}	1.57×10^{-13}	7.45×10^{-13}	4.59×10^{-13}
$[\text{Fe}^{\text{IV}}\text{O}^{2+}]_{\text{ss}} \text{ (M)}$	2.59×10^{-9}	3.71×10^{-9}	8.52×10^{-10}	4.64×10^{-10}

399

400 We also used EPR spectroscopy to detect variations in different reactive oxygen species (ROS)
401 contents in the GC-nZVI/PS and GC-nZVI/PMS systems. When DMPO was used as a trapping
402 agent, peaks due to DMPO-OH and DMPO-SO₄^{•-} could be detected but without DMPO-O₂^{•-}, as
403 shown in Fig. S17. However, in contrast to the quenching experiments, the signal intensity of SO₄^{•-}
404 was lower than that of [•]OH, which might be attributed to the much lower rate constant of the
405 reaction between DMPO and SO₄^{•-} ($k = 2.9 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$) compared to that of the reaction between
406 DMPO and [•]OH ($k = 2.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) (Wei et al., 2017). When TEMP was used as a trapping
407 agent (Fig. S18), no change in the ESR signal when only TEMP of TEMP + PS + GC-nZVI was
408 measured after 2 min of acquisition. So, we prove that there is no singlet oxygen in our
409 experimental system.

410

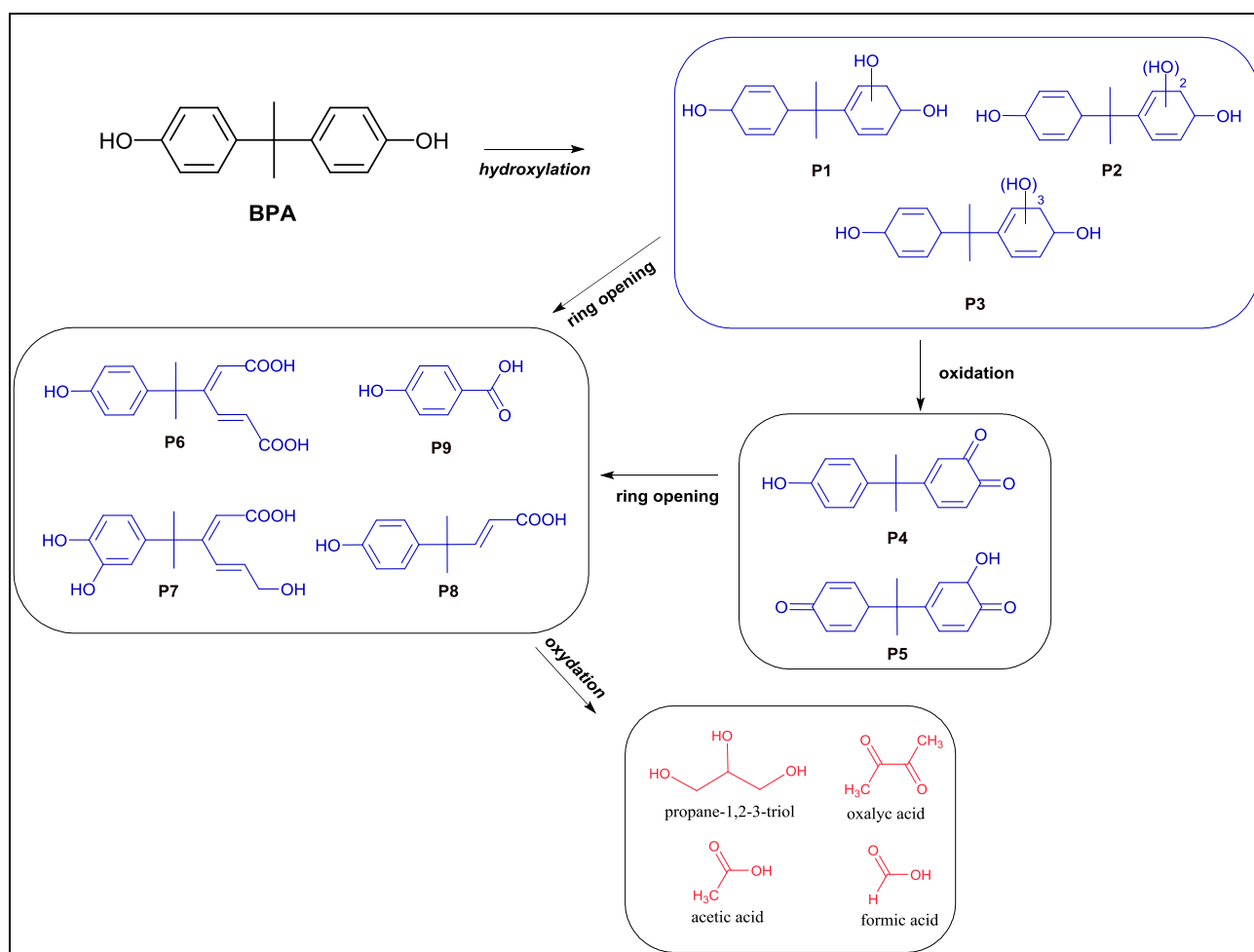
411 3.6 BPA degradation products and mineralization efficiency

412 In this study, BPA ($[\text{M}+\text{H}]^+$, m/z 299.1254) degradation products in the 0.07GC-nZVI + PS or
413 PMS systems were determined by LC-MS. Different compounds were identified based on m/z
414 values. A first class of different hydroxylated products generated from the attack of oxidant species
415 ([•]OH, SO₄^{•-}, and probably Fe^{IV}O²⁺) on the aromatic ring, forming a cyclohexadienyl radical rapidly,
416 were rapidly oxidized to hydroxylated derivatives such as P1 (monohydroxylated BPA; $[\text{M}-\text{H}]^-$,
417 m/z 243.0367), P2 (dihydroxylated BPA; $[\text{M}+\text{H}]^+$, m/z 261.0110), and P3 (trihydroxylated BPA;

418 $[M+H]^+$, m/z 277.1695) when PS and PMS were used as oxidant precursors. Further oxidation of
419 hydroxylated products generated P4 ($[M+H]^+$, m/z 244.1906) and P5 ($[M-H]^-$, m/z 241.0573).
420 Finally, aromatic ring-opening furnished P6 ($[M-H]^-$, m/z 277.1091), P7 ($[M-H]^-$, m/z 275.1696),
421 P8 ($[M-H]^-$, m/z 205.0899), and P9 ($[M-H]^-$, m/z 137.0234). (Fig. 4).

422 Efficient oxidation of organic molecules leads to the formation of short chain carboxylic acids
423 (CAs) before complete mineralization. We used IC-MS analysis to identify the main CAs generated
424 during BPA degradation using 0.07-GC-nZVI/PS/UVA. In order to improve the formation of CAs,
425 we increased the concentrations of all reactants in the solution (100 μM BPA, 0.2 g L^{-1} GC-nZVI
426 and 1 mM PMS). IC-MS results (Fig. S19a), indicated that intermediates such as oxalate, formate,
427 acetate, and propane-1,2,3-triol were generated during the reaction. As can be seen in Fig. S19b,
428 about 10 μM acetate and 100 μM formate were produced after the reaction had proceeded for 79 h,
429 while the concentration of oxalate was immeasurably low. However, it is interesting to note that
430 oxalic acids, which is able to complex iron in solution to generate a photolabile iron-oxalate
431 complex, first accumulated and was then slowly degraded in the solution, implicating it as a BPA
432 degradation product during GC-nZVI/PS/UVA activation.

433



434
435

436
437
438
439

Fig. 4: Suggested pathways of BPA degradation based on the LC-MS (blue) and IC-MS (red) analyses.

440

441

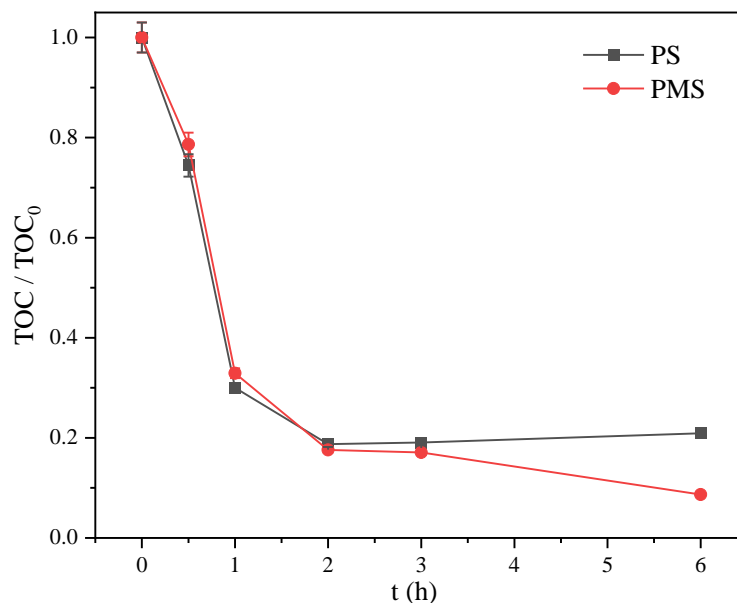
442

443

444

445

Total organic carbon (TOC) analysis was used as a measure of mineralization efficiency in our systems. Mineralization of BPA by 0.07-GC-nZVI catalyzed by PMS and PS were compared (Fig. 5). Both systems fully degraded BPA within 30 min, while up to 80% mineralization was achieved after 2 h, showing good efficiency of our process for the degradation and mineralization of BPA compared to other catalytic oxidation systems based on PMS or PS.



446

447 Fig. 5. TOC tests of GC-nZVI. Initial conditions: [BPA] = 25 μM , [PS] = [PMS] = 0.25 mM,
 448 [catalyst] = 0.05 g L⁻¹, pH₀ = 7.0 \pm 0.1, UVA.

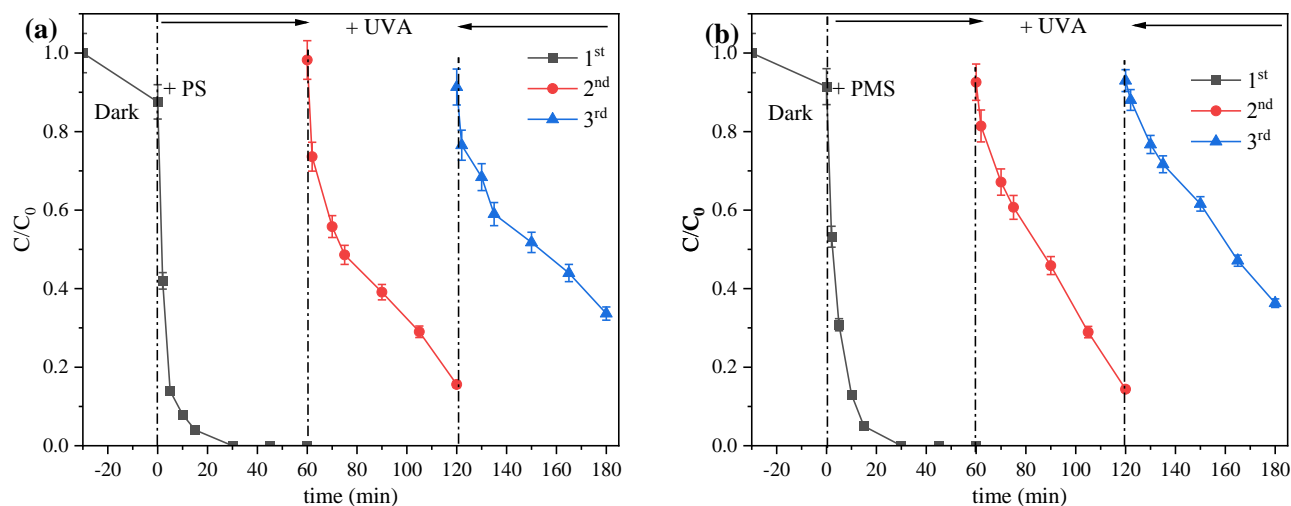
449

450 3.7 Recyclability and Suitability of GC-nZVI in PMS/PS activation

451 Catalyst stability is an important property for practical applications. For its assessment, we
 452 used twofold higher concentrations of each species in solution. Rrecycling experiments in this study
 453 were performed by directly adding fresh BPA and PS/PMS to the reaction solution for multiple
 454 runs. As shown in Figure 6, a slight decrease in degradation efficiency was observed in the second
 455 and third runs. This trend can be explained by considering different factors arising during the
 456 experimental procedure. (i) We did not wash the sample and add again PS/PMS during the cycle;
 457 only BPA was added to re-establish an initial concentration of 50 μM . Moreover, BPA by-products
 458 in the solution may play a competitive role in the oxidation of BPA. (ii) The GC-nZVI
 459 concentration decreased with each cycle. This problem was partially circumvented by increasing the
 460 initial GC-nZVI concentration. However, a loss of catalyst was incurred when samples were
 461 withdrawn for analysis. (iii) During each cycle, a fixed volume of BPA solution was added,
 462 resulting in an additional dilution of PS/PMS and GC-nZVI. Despite this, a removal efficiency of

463 70% was maintained after three runs at 60 min, indicating good stability and reusability of 0.07-
464 GC-nZVI.

465



467 Fig. 6. Reusability tests of GC-nZVI. Initial conditions: $[BPA]_0 = 50 \mu\text{M}$, $[PS] =$
468 $[PMS]_0 = 0.5 \text{ mM}$, $[\text{catalyst}] = 0.1 \text{ g L}^{-1}$, $\text{pH}_0 = 7.0 \pm 0.1$.

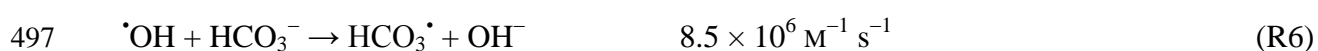
469

470 As shown in Fig. S2c, comparing the XRD patterns before and after reactions in the PS and
471 PMS systems, it can be seen that the peak due to ZVI ($2\theta = 44.7^\circ$) was significantly weakened,
472 which indicates that Fe showed a certain degree of dissolution during the reaction process.
473 Nevertheless, SEM and TEM images showed that the structure of the sample was not destroyed,
474 confirming the stability of the material (Figs. S6e, f and S7c, d). The FITR spectrum after the
475 reaction can see that the fluctuation at 1100 cm^{-1} was weakened, and the wavenumber at 584 cm^{-1}
476 was changed, which may be because the dissolution of iron affects the bonding effects between ZVI
477 and carbon (Yan et al., 2015).

478 XPS patterns clearly showed the presence of C, O, and Fe in both samples (Fig. S20a). The O
479 content of used GC-nZVI in the PS/PMS systems increased sharply to 23.8% and 25.9%,
480 respectively, as compared to 6.2% in the fresh GC-nZVI, which was presumably due to the
481 oxidation of Fe. Fe 2p core-level spectra (Fig. S20b–d) of the GC-nZVI indicated the presence of

482 Fe^0 (708.6 eV), Fe^{2+} (710.5 eV), and Fe^{3+} (711.6 and 713.2 eV) (Jiang et al., 2019). These results
483 indicate that part of the ZVI on the carbon surface was oxidized to Fe^{3+} and Fe^{2+} when exposed to
484 air, resulting in an attenuation of its peak (Zhang and Shen, 2020). After the reaction, the atom Fe^0
485 were oxidized and lost. However, it can be seen from the XRD results that this did not lead to
486 complete oxidation or dissolution of the ZVI in the material, but only a relative oxidation.

487 Inorganic anions and natural organic matter (NOM) are ubiquitous in the aqueous environment,
488 and also have significant impacts on the performance of AOPs. They can react with free radicals,
489 thus influencing the type and concentration of active species and leading to variations in the
490 removal efficiencies of target organic pollutants. As can be seen in Figure S21, different
491 concentrations of chloride ions (Cl^-) had no inhibitory effect on the degradation of BPA in the
492 different systems. However, high concentrations of hydrogen carbonate ions (HCO_3^-) exerted a
493 significant negative effect on the removal efficiency, as can be seen in Figure S22, although the
494 degradation of BPA did not decrease further when the HCO_3^- concentration was increased from 2 to
495 5 mM. This suggests that $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ produced in our system react with HCO_3^- to form weak
496 redox radical species [as expressed by reactions (6) and (7)]. .

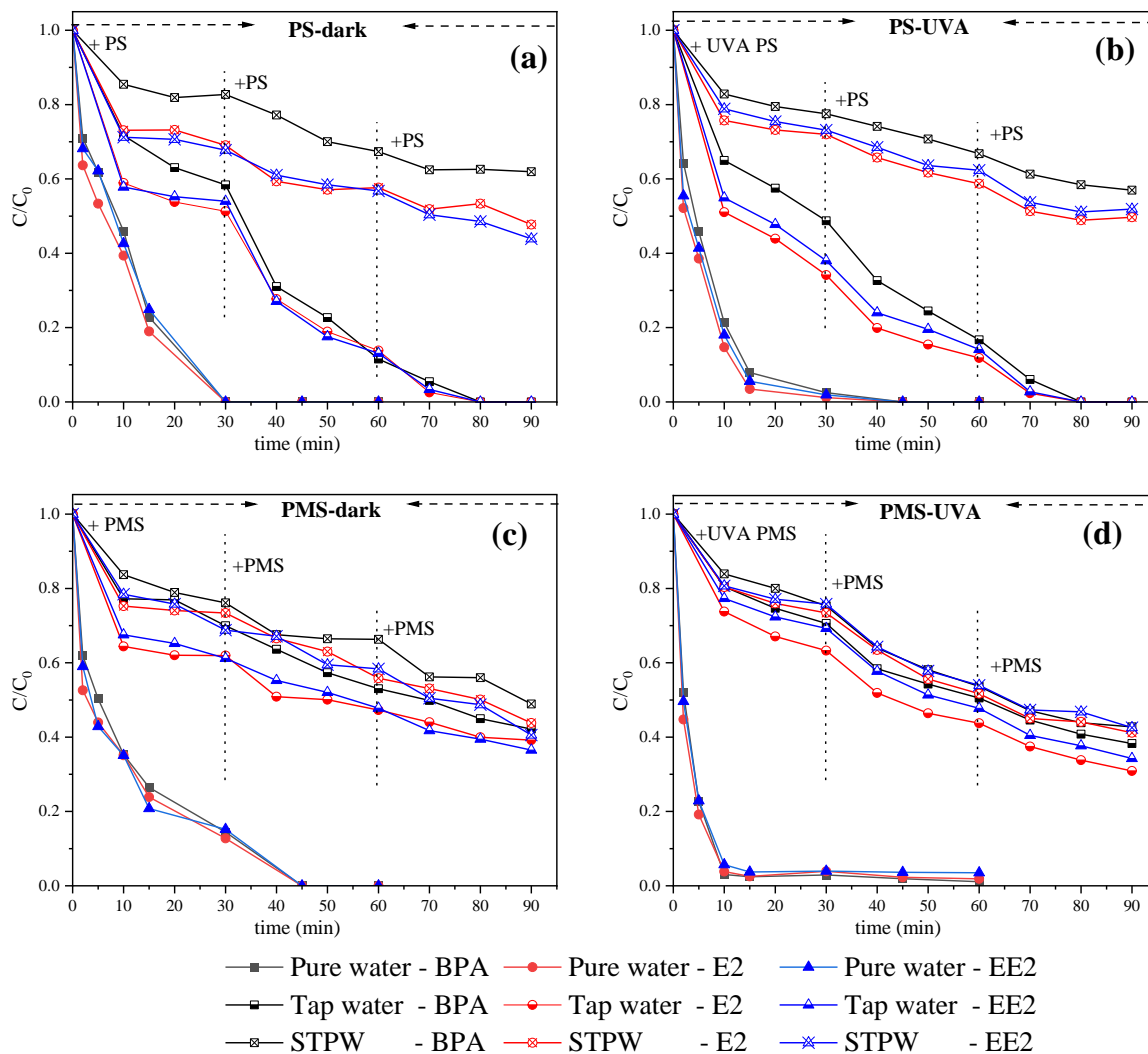


499 NOM in surface water is often considered to be a scavenger, leading to a reduction in the
500 degradation efficiency of target pollutants by competing with ROS in AOPs. Therefore, as a
501 representative of NOM, humic acid (HA) was considered in BPA degradation. In Figure S23, an
502 increase in HA concentration from 2 to $10 \text{ mg}_C \text{ L}^{-1}$ is seen to have a negative impact on the
503 efficiency of the degradation. At an HA concentration of $10 \text{ mg}_C \text{ L}^{-1}$, the BPA degradation rate
504 constants (k) of different reaction systems (Figure S24) were greatly reduced to around 0.05 min^{-1} ,
505 which may be attributed to competitive reactions of reactive species with HA and BPA.

506 The potential of GC-nZVI for practical application in PS and PMS systems was further
507 investigated by the degradation of different pollutants (BPA, E2, and EE2) in different water
508 samples (see Table S2 for detailed information on these water samples). The experiments were
509 carried out in the same way as described for BPA degradation, with an initial concentration of 5 μM
510 for all three pollutants.

511 As shown in Figure 7, the removal efficiencies in the different water sources were in the order:
512 pure water > tap water > STPW. In pure water, 100% removal was achieved within 60 min with the
513 addition of only 0.25 mM PS or PMS, which could be reduced to 15 min in the irradiated systems.
514 In both tap water and STPW, it can be observed that the degradation process slowed down after the
515 first addition of 0.25 mM PS/PMS after 30 min of reaction, but restarted with the addition of fresh
516 PS/PMS. This suggested that the reduction in degradation efficiency in both water samples was due
517 to the presence of inorganic or organic pollutants rapidly depleting the oxidant, and that better
518 degradation can be achieved under conditions of sufficient oxidant, while the catalyst can be used
519 continuously. The potential of 0.07-GC-nZVI for practical environmental remediation applications
520 remains significant.

521



522

523 Fig. 7. Photocatalytic activities in organic compounds degradation by GC-nZVI in various water
 524 samples with different systems: $[BPA] = [E2] = [EE2] = 5 \mu\text{M}$, $[PS]_0 = [PMS]_0 = 0.25 \text{ mM}$,
 525 $[\text{catalyst}] = 0.05 \text{ g L}^{-1}$, $\text{pH}_0 = 7.0 \pm 0.1$.

526

527 4. Conclusion

528 Nano zero-valent iron (nZVI) has been deposited on graphitized carbon (GC) to prepare
 529 catalysts suitable for environmental remediation. Of the prepared catalysts, 0.07-GC-nZVI
 530 exhibited high BPA removal efficiency in the presence of PMS or PS. BPA ($25 \mu\text{M}$) could be fully
 531 removed by 0.05 g L^{-1} 0.07-GC-nZVI in the presence of only 0.25 mM of PMS or PS within
 532 30 min. Compared with pure ZVI, it can be seen that GC significantly enhances the adsorption of
 533 compounds at the active sites. Exposure to UVA irradiation slightly improves the degradation

534 efficiency of BPA. Reactive species responsible for BPA degradation at near-neutral pH have been
535 systematically identified. Our results imply that the 0.07-GC-nZVI/PMS or PS systems generate
536 $\text{SO}_4^{\bullet-}$, $\cdot\text{OH}$, and Fe(IV) at steady-state concentrations ranging from 3.4×10^{-14} to 3.7×10^{-9} M.
537 Among them, $\text{SO}_4^{\bullet-}$ plays the dominant role in the degradation process. Moreover, 0.07-GC-nZVI
538 also demonstrated good stability and efficiency during application in tap and STP water samples.
539 This work provides new insight into heterogeneous Fenton and photo-Fenton catalytic degradation
540 processes, which offer good practical application potential.

541

542 **Acknowledgments**

543 Authors acknowledge the Ministry of Education of China for providing the financial support for
544 Minjuan CAI stay in France and PRC program CNRS/NSFC n°270437.

545

- 547 Ahmed, M.B., Zhou, J.L., Ngo, H.H., Guo, W., Thomaidis, N.S., Xu, J. 2017. Progress in the biological and chemical
548 treatment technologies for emerging contaminant removal from wastewater: A critical review. *Journal of*
549 *Hazardous Materials*, 323, 274-298.<https://doi.org/10.1016/j.jhazmat.2016.04.045>
- 550 Annamalai, J., Namasivayam, V. 2015. Endocrine disrupting chemicals in the atmosphere: Their effects on humans and
551 wildlife. *Environment International*, 76, 78-97.<https://doi.org/10.1016/j.envint.2014.12.006>
- 552 Bakac, A., Shi, C., Pestovsky, O. 2004. Acid-Catalyzed Oxidation of Iodide Ions by Superoxo Complexes of Rhodium
553 and Chromium. *Inorganic Chemistry*, 43, 5416-5421.[10.1021/ic049629j](https://doi.org/10.1021/ic049629j)
- 554 Buxton, G.V., Greenstock, C.L., Helman, W.P., Ross, A.B. 1988. Critical Review of rate constants for reactions of
555 hydrated electrons, hydrogen atoms and hydroxyl radicals ($\cdot\text{OH}/\cdot\text{O}^{\sup>}$) in Aqueous Solution.
556 *Journal of Physical and Chemical Reference Data*, 17, 513-886.[10.1063/1.555805](https://doi.org/10.1063/1.555805)
- 557 Chang, H.-S., Choo, K.-H., Lee, B., Choi, S.-J. 2009. The methods of identification, analysis, and removal of endocrine
558 disrupting compounds (EDCs) in water. *Journal of Hazardous Materials*, 172, 1-
559 12.<https://doi.org/10.1016/j.jhazmat.2009.06.135>
- 560 Chen, T., Fu, C., Liu, Y., Pan, F., Wu, F., You, Z., Li, J. 2021. Adsorption of volatile organic compounds by mesoporous
561 graphitized carbon: Enhanced organophilicity, humidity resistance, and mass transfer. *Separation and*
562 *Purification Technology*, 264, 118464.<https://doi.org/10.1016/j.seppur.2021.118464>
- 563 Esplugas, S., Bila, D.M., Krause, L.G.T., Dezotti, M. 2007. Ozonation and advanced oxidation technologies to remove
564 endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) in water
565 effluents. *Journal of Hazardous Materials*, 149, 631-642.<https://doi.org/10.1016/j.jhazmat.2007.07.073>
- 566 Farinelli, G., Minella, M., Pazzi, M., Giannakis, S., Pulgarin, C., Vione, D., Tiraferri, A. 2020. Natural iron ligands
567 promote a metal-based oxidation mechanism for the Fenton reaction in water environments. *Journal of*
568 *Hazardous Materials*, 393, 122413.<https://doi.org/10.1016/j.jhazmat.2020.122413>
- 569 Ghazal, H., Koumaki, E., Hoslett, J., Malamis, S., Katsou, E., Barcelo, D., Jouhara, H. 2022. Insights into current
570 physical, chemical and hybrid technologies used for the treatment of wastewater contaminated with
571 pharmaceuticals. *Journal of Cleaner Production*, 361, 132079.<https://doi.org/10.1016/j.jclepro.2022.132079>
- 572 Giannakis, S., Lin, K.-Y.A., Ghanbari, F. 2021. A review of the recent advances on the treatment of industrial
573 wastewaters by Sulfate Radical-based Advanced Oxidation Processes (SR-AOPs). *Chemical Engineering*
574 *Journal*, 406, 127083.<https://doi.org/10.1016/j.cej.2020.127083>
- 575 Giulivo, M., Lopez de Alda, M., Capri, E., Barceló, D. 2016. Human exposure to endocrine disrupting compounds:
576 Their role in reproductive systems, metabolic syndrome and breast cancer. A review. *Environmental Research*,
577 151, 251-264.<https://doi.org/10.1016/j.envres.2016.07.011>
- 578 Gowrisankaran, S., Thrinavukkarasu, G.K., Hanif, M.B., Liapun, V., Roch, T., Satrapinsky, L., Plesch, G., Motola, M.,
579 Monfort, O. (2022). Fe-Modified TiO₂ Nanotube Layer as a Photochemically Versatile Material for the
580 Degradation of Organic Pollutants in Water. In *Engineering Proceedings*, vol. 19).
- 581 Gujar, S.K., Divyapriya, G., Gogate, P.R., Nidheesh, P.V. 2023. Environmental applications of ultrasound activated
582 persulfate/peroxymonosulfate oxidation process in combination with other activating agents. *Critical Reviews*
583 *in Environmental Science and Technology*, 53, 802.[10.1080/10643389.2022.2085965](https://doi.org/10.1080/10643389.2022.2085965)
- 584 Huie, R.E., Clifton, C.L., Neta, P. 1991. Electron transfer reaction rates and equilibria of the carbonate and sulfate
585 radical anions. *International Journal of Radiation Applications and Instrumentation. Part C. Radiation Physics*
586 *and Chemistry*, 38, 477-481.[https://doi.org/10.1016/1359-0197\(91\)90065-A](https://doi.org/10.1016/1359-0197(91)90065-A)
- 587 Jia, D., Li, Q., Hanna, K., Mailhot, G., Brigante, M. 2021a. Efficient removal of estrogenic compounds in water by
588 Mn(III)-activated peroxymonosulfate: Mechanisms and application in sewage treatment plant water.
589 *Environmental Pollution*, 288, 117728.<https://doi.org/10.1016/j.envpol.2021.117728>
- 590 Jia, J., Wei, L., Li, F., Yu, C., Yang, K., Liang, T. 2021b. In situ growth of NiFe MOF/NF by controlling solvent
591 mixtures as efficient electrocatalyst in oxygen evolution. *Inorganic Chemistry Communications*, 128,
592 108605.<https://doi.org/10.1016/j.inoche.2021.108605>
- 593 Jiang, S.-F., Ling, L.-L., Chen, W.-J., Liu, W.-J., Li, D.-C., Jiang, H. 2019. High efficient removal of bisphenol A in a
594 peroxymonosulfate/iron functionalized biochar system: Mechanistic elucidation and quantification of the
595 contributors. *Chemical Engineering Journal*, 359, 572-583.<https://doi.org/10.1016/j.cej.2018.11.124>
- 596 Kakavandi, B., Alavi, S., Ghanbari, F., Ahmadi, M. 2022. Bisphenol A degradation by peroxymonosulfate photo-
597 activation coupled with carbon-based cobalt ferrite nanocomposite: Performance, upgrading synergy and
598 mechanistic pathway. *Chemosphere*, 287, 132024.<https://doi.org/10.1016/j.chemosphere.2021.132024>
- 599 Khan, S., He, X., Khan, J.A., Khan, H.M., Boccelli, D.L., Dionysiou, D.D. 2017. Kinetics and mechanism of sulfate
600 radical- and hydroxyl radical-induced degradation of highly chlorinated pesticide lindane in
601 UV/peroxymonosulfate system. *Chemical Engineering Journal*, 318, 135-
602 142.<https://doi.org/10.1016/j.cej.2016.05.150>
- 603 Kim, S., Eom, S., Kim, H.-J., Lee, J.J., Choi, G., Choi, S., Kim, S., Kim, S.Y., Cho, G., Kim, Y.D., Suh, E., Kim, S.K.,
604 Kim, S., Kim, G.-H., Moon, H.-B., Park, J., Kim, S., Choi, K., Eun, S.-H. 2018. Association between maternal

605 exposure to major phthalates, heavy metals, and persistent organic pollutants, and the neurodevelopmental
606 performances of their children at 1 to 2 years of age- CHECK cohort study. *Science of The Total Environment*,
607 624, 377-384. <https://doi.org/10.1016/j.scitotenv.2017.12.058>

608 Kimura, K., Toshima, S., Amy, G., Watanabe, Y. 2004. Rejection of neutral endocrine disrupting compounds (EDCs)
609 and pharmaceutical active compounds (PhACs) by RO membranes. *Journal of Membrane Science*, 245, 71-
610 78. <https://doi.org/10.1016/j.memsci.2004.07.018>

611 Li, Y., Yang, T., Qiu, S., Lin, W., Yan, J., Fan, S., Zhou, Q. 2020. Uniform N-coordinated single-atomic iron sites
612 dispersed in porous carbon framework to activate PMS for efficient BPA degradation via high-valent iron-oxo
613 species. *Chemical Engineering Journal*, 389, 124382. <https://doi.org/10.1016/j.cej.2020.124382>

614 Lin, Z., Qin, W., Sun, L., Yuan, X., Xia, D. 2020. Kinetics and mechanism of sulfate radical- and hydroxyl radical-
615 induced degradation of Bisphenol A in VUV/UV/peroxymonosulfate system. *Journal of Water Process
616 Engineering*, 38, 101636. <https://doi.org/10.1016/j.jwpe.2020.101636>

617 Litter, M.I., Slodowicz, M. 2017. An overview on heterogeneous Fenton and photoFenton reactions using zerovalent
618 iron materials. *20.doi:10.1515/jaots-2016-0164*

619 Liu, X., Li, H., Gao, S., Bai, Z., Tian, J. 2022. Peroxymonosulfate activation by different iron sulfides for bisphenol-A
620 degradation: Performance and mechanism. *Separation and Purification Technology*, 289,
621 120751. <https://doi.org/10.1016/j.seppur.2022.120751>

622 Lv, X., Xu, J., Jiang, G., Xu, X. 2011. Removal of chromium(VI) from wastewater by nanoscale zero-valent iron
623 particles supported on multiwalled carbon nanotubes. *Chemosphere*, 85, 1204-
624 1209. <https://doi.org/10.1016/j.chemosphere.2011.09.005>

625 Marty, M.S., Carney, E.W., Rowlands, J.C. 2011. Endocrine Disruption: Historical Perspectives and Its Impact on the
626 Future of Toxicology Testing. *Toxicological Sciences*, 120, S93-S108. [10.1093/toxsci/kfq329](https://doi.org/10.1093/toxsci/kfq329)

627 Neta, P., Grodkowski, J., Ross, A.B. 1996. Rate Constants for Reactions of Aliphatic Carbon-Centered Radicals in
628 Aqueous Solution. *Journal of Physical and Chemical Reference Data*, 25, 709-1050. [10.1063/1.555978](https://doi.org/10.1063/1.555978)

629 Pan, F., Chen, T., Cai, M., Wu, F., You, Z., Li, J. 2021. Fabrication of large-surface-area graphitized carbons by
630 potassium hydroxide-promoted catalytic graphitization. *Materials Research Bulletin*, 140,
631 111333. <https://doi.org/10.1016/j.materresbull.2021.111333>

632 Pestovsky, O., Bakac, A. 2006. Aqueous Ferryl(IV) Ion: Kinetics of Oxygen Atom Transfer To Substrates and Oxo
633 Exchange with Solvent Water. *Inorganic Chemistry*, 45, 814-820. [10.1021/ic051868z](https://doi.org/10.1021/ic051868z)

634 Phan, H.T.B., Nguyen, A.Q.K., Ahn, Y.-Y., Kim, K., Kim, S., Kim, J. 2022. Visible light-induced degradation of
635 propranolol with peroxymonosulfate as an oxidant and a radical precursor. *Separation and Purification
636 Technology*, 289, 120764. <https://doi.org/10.1016/j.seppur.2022.120764>

637 Ren, Y., Ma, J., Lee, Y., Han, Z., Cui, M., Wang, B., Long, M., Khim, J. 2021. Reaction of activated carbon zerovalent
638 iron with pentachlorophenol under anaerobic conditions. *Journal of Cleaner Production*, 297,
639 126748. <https://doi.org/10.1016/j.jclepro.2021.126748>

640 Romanucci, V., Siciliano, A., Guida, M., Libralato, G., Saviano, L., Luongo, G., Previtera, L., Di Fabio, G., Zarrelli, A.
641 2020. Disinfection by-products and ecotoxic risk associated with hypochlorite treatment of irbesartan. *Science
642 of The Total Environment*, 712, 135625. <https://doi.org/10.1016/j.scitotenv.2019.135625>

643 Su, H., Fang, Z., Tsang, P.E., Zheng, L., Cheng, W., Fang, J., Zhao, D. 2016. Remediation of hexavalent chromium
644 contaminated soil by biochar-supported zero-valent iron nanoparticles. *Journal of Hazardous Materials*, 318,
645 533-540. <https://doi.org/10.1016/j.jhazmat.2016.07.039>

646 Sun, H., Zhou, G., Liu, S., Ang, H.M., Tadé, M.O., Wang, S. 2012. Nano-Fe⁰ encapsulated in microcarbon spheres:
647 synthesis, characterization, and environmental applications. *ACS Appl Mater Interfaces*, 4, 6235-
648 6241. [10.1021/am301829u](https://doi.org/10.1021/am301829u)

649 Takdastan, A., Kakavandi, B., Azizi, M., Golshan, M. 2018. Efficient activation of peroxymonosulfate by using
650 ferrous oxide supported on carbon/UV/US system: A new approach into catalytic degradation of bisphenol
651 A. *Chemical Engineering Journal*, 331, 729-743. <https://doi.org/10.1016/j.cej.2017.09.021>

652 Tan, W., Ruan, Y., Diao, Z., Song, G., Su, M., Hou, L.a., Chen, D., Kong, L., Deng, H. 2021. Removal of levofloxacin
653 through adsorption and peroxymonosulfate activation using carbothermal reduction synthesized nZVI/carbon
654 fiber. *Chemosphere*, 280, 130626. <https://doi.org/10.1016/j.chemosphere.2021.130626>

655 Thomas, N., Dionysiou, D.D., Pillai, S.C. 2021. Heterogeneous Fenton catalysts: A review of recent advances. *Journal
656 of Hazardous Materials*, 404, 124082. <https://doi.org/10.1016/j.jhazmat.2020.124082>

657 Wang, B., Zhu, C., Ai, D., Fan, Z. 2021. Activation of persulfate by green nano-zero-valent iron-loaded biochar for the
658 removal of p-nitrophenol: Performance, mechanism and variables effects. *Journal of Hazardous Materials*, 417,
659 126106. <https://doi.org/10.1016/j.jhazmat.2021.126106>

660 Wang, L., Zhao, Y., Li, Y., Yao, B., Zhang, C., Zhang, W., Niu, L., Zhang, H. 2022. Fe-loaded biochar facilitates
661 simultaneous bisphenol A biodegradation and efficient nitrate reduction: Physicochemical properties and
662 biological mechanism. *Journal of Cleaner Production*, 372,
663 133814. <https://doi.org/10.1016/j.jclepro.2022.133814>

664 Wang, M., Cheng, W., Wan, T., Hu, B., Zhu, Y., Song, X., Sun, Y. 2019a. Mechanistic investigation of U(VI)

665 sequestration by zero-valent iron/activated carbon composites. *Chemical Engineering Journal*, 362, 99-
666 106.<https://doi.org/10.1016/j.cej.2018.12.138>

667 Wang, R., Ma, X., Liu, T., Li, Y., Song, L., Tjong, S.C., Cao, L., Wang, W., Yu, Q., Wang, Z. 2020. Degradation aspects
668 of endocrine disrupting chemicals: A review on photocatalytic processes and photocatalysts. *Applied Catalysis*
669 *A: General*, 597, 117547.<https://doi.org/10.1016/j.apcata.2020.117547>

670 Wang, S., Zhao, M., Zhou, M., Li, Y.C., Wang, J., Gao, B., Sato, S., Feng, K., Yin, W., Igalavithana, A.D., Oleszczuk, P.,
671 Wang, X., Ok, Y.S. 2019b. Biochar-supported nZVI (nZVI/BC) for contaminant removal from soil and water:
672 A critical review. *Journal of Hazardous Materials*, 373, 820-834.<https://doi.org/10.1016/j.jhazmat.2019.03.080>

673 Wei, Z., Villamena, F.A., Weavers, L.K. 2017. Kinetics and Mechanism of Ultrasonic Activation of Persulfate: An in
674 Situ EPR Spin Trapping Study. *Environmental Science & Technology*, 51, 3410-3417.[10.1021/acs.est.6b05392](https://doi.org/10.1021/acs.est.6b05392)

675 Wijekoon, K.C., Hai, F.I., Kang, J., Price, W.E., Cath, T.Y., Nghiem, L.D. 2014. Rejection and fate of trace organic
676 compounds (TrOCs) during membrane distillation. *Journal of Membrane Science*, 453, 636-
677 642.<https://doi.org/10.1016/j.memsci.2013.12.002>

678 Wu, Y., Monfort, O., Dong, W., Brigante, M., Mailhot, G. 2019. Enhancement of iron-mediated activation of persulfate
679 using catechin: From generation of reactive species to atenolol degradation in water. *Science of The Total*
680 *Environment*, 697, 134188.<https://doi.org/10.1016/j.scitotenv.2019.134188>

681 Xu, J., Wang, X., Pan, F., Qin, Y., Xia, J., Li, J., Wu, F. 2018. Synthesis of the mesoporous carbon-nano-zero-valent iron
682 composite and activation of sulfite for removal of organic pollutants. *Chemical Engineering Journal*, 353, 542-
683 549.<https://doi.org/10.1016/j.cej.2018.07.030>

684 Yan, J., Han, L., Gao, W., Xue, S., Chen, M. 2015. Biochar supported nanoscale zerovalent iron composite used as
685 persulfate activator for removing trichloroethylene. *Bioresource Technology*, 175, 269-
686 274.<https://doi.org/10.1016/j.biortech.2014.10.103>

687 Yan, S., Shi, Y., Tao, Y., Zhang, H. 2019a. Enhanced persulfate-mediated photocatalytic oxidation of bisphenol A using
688 bioelectricity and a g-C₃N₄/Fe₂O₃ heterojunction. *Chemical Engineering Journal*, 359, 933-
689 943.<https://doi.org/10.1016/j.cej.2018.11.093>

690 Yan, Z.-r., Zhu, Y.-y., Meng, H.-s., Wang, S.-y., Gan, L.-h., Li, X.-y., Xu, J., Zhang, W. 2019b. Insights into
691 thermodynamic mechanisms driving bisphenol A (BPA) binding to extracellular polymeric substances (EPS) of
692 activated sludge. *Science of The Total Environment*, 677, 502-
693 510.<https://doi.org/10.1016/j.scitotenv.2019.04.413>

694 Zarrelli, A., DellaGreca, M., Parolisi, A., Iesce, M.R., Cermola, F., Temussi, F., Isidori, M., Lavorgna, M., Passananti,
695 M., Previtiera, L. 2012. Chemical fate and genotoxic risk associated with hypochlorite treatment of nicotine.
696 *Science of The Total Environment*, 426, 132-138.<https://doi.org/10.1016/j.scitotenv.2012.03.047>

697 Zhang, L., Shen, S. 2020. Adsorption and catalytic degradation of sulfamethazine by mesoporous carbon loaded nano
698 zero valent iron. *Journal of Industrial and Engineering Chemistry*, 83, 123-
699 135.<https://doi.org/10.1016/j.jiec.2019.11.020>

700 Zhao, C., Shao, B., Yan, M., Liu, Z., Liang, Q., He, Q., Wu, T., Liu, Y., Pan, Y., Huang, J., Wang, J., Liang, J., Tang, L.
701 2021. Activation of peroxymonosulfate by biochar-based catalysts and applications in the degradation of
702 organic contaminants: A review. *Chemical Engineering Journal*, 416,
703 128829.<https://doi.org/10.1016/j.cej.2021.128829>

704 Zhou, D., Chen, L., Zhang, C., Yu, Y., Zhang, L., Wu, F. 2014. A novel photochemical system of ferrous sulfite complex:
705 Kinetics and mechanisms of rapid decolorization of Acid Orange 7 in aqueous solutions. *Water Research*, 57,
706 87-95.<https://doi.org/10.1016/j.watres.2014.03.016>

707 Zhu, H., Jia, Y., Wu, X., Wang, H. 2009. Removal of arsenic from water by supported nano zero-valent iron on activated
708 carbon. *Journal of Hazardous Materials*, 172, 1591-1596.<https://doi.org/10.1016/j.jhazmat.2009.08.031>

709 Zhuang, P., Lin, W., Tian, B., Shih, T.-m., Cai, W. 2017. Ultraviolet-light-induced electron transfer between chlorine
710 anions and graphene. *Carbon*, 123, 380-384.<https://doi.org/10.1016/j.carbon.2017.07.084>

711