



THE UNIVERSITY *of* EDINBURGH

Edinburgh Research Explorer

Co-generation of hydroxyl and sulfate radicals via homogeneous and heterogeneous bi-catalysis with the EO-PS-EF tri-coupling system for efficient removal of refractory organic pollutants

Citation for published version:

Yang, W, Deng, Z, Liu, L, Zhou, K, E, P, Meng, L, Ma, L & Wei, Q 2023, 'Co-generation of hydroxyl and sulfate radicals via homogeneous and heterogeneous bi-catalysis with the EO-PS-EF tri-coupling system for efficient removal of refractory organic pollutants', *Water Research*, vol. 243, 120312. <https://doi.org/10.1016/j.watres.2023.120312>

Digital Object Identifier (DOI):

[10.1016/j.watres.2023.120312](https://doi.org/10.1016/j.watres.2023.120312)

Link:

[Link to publication record in Edinburgh Research Explorer](#)

Document Version:

Peer reviewed version

Published In:

Water Research

General rights

Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact openaccess@ed.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.



Co-generation of hydroxyl and sulfate radicals via homogeneous and heterogeneous bi-catalysis with the EO-PS-EF tri-coupling system for efficient removal of refractory organic pollutants

Wanlin Yang^a, Zejun Deng^{a,*}, Libin Liu^a, Kechao Zhou^a, Sharel P. E^b, Lingcong Meng^c, Li Ma^{a,*}, Qiuping Wei^{a,*}

^aSchool of Materials Science and Engineering, State Key Laboratory of Powder Metallurgy, Central South University, Changsha 410083, P.R. China

^bSchool of Engineering, University of Edinburgh, Edinburgh, EH9 3DW

^cSchool of Chemistry, University of Edinburgh, David Brewster Rd, Edinburgh EH9 3FJ

*Corresponding author:

E-mail address: zejun.deng@csu.edu.cn (Dr. Z. Deng); marycupm@csu.edu.cn (Dr. L. Ma); qiupwei@csu.edu.cn (Dr. Q. Wei).

Abstract: Advanced oxidation processes are commonly considered one of the most effective techniques to degrade refractory organic pollutants, but the limitation of a single process usually makes it insufficient to achieve the desired treatment. This work introduces, for the first time, a highly-efficient coupled advanced oxidation process, namely Electro-Oxidation—Persulfate—Electro-Fenton (EO-PS-EF). Leveraging the EO-PS-EF tri-coupling system, diverse contaminants can be highly efficiently removed with the help of reactive hydroxyl and sulfate radicals generated via homogeneous and heterogeneous bi-catalysis, as certified by radical quenching and electron spin resonance. Concerning degradation of tetracycline (TC), the EO-PS-EF system witnessed a fast pseudo-first-order reaction kinetic constant of $2.54 \times 10^{-3} \text{ s}^{-1}$, ten times that of a single EO system and three-to-four times that of a binary system (EO-PS or EO-EF). In addition, critical parameters (e.g., electrolyte, pH and temperature) are systematically investigated. Surprisingly, after 100 repetitive trials TC removal can still reach 100% within 30 minutes and no apparent morphological changes to electrode materials were observed, demonstrating its long-term stability. Finally, its universality was demonstrated with effective degradation of diverse refractory contaminants (i.e., antibiotics, dyes and pesticides).

Keywords: Electro-Oxidation—Persulfate—Electro-Fenton; Hydroxyl and sulfate radicals; Mechanism; Degradation pathway; Application potential

1 Introduction

Environmentally-related contaminants (e.g., antibiotics, pesticides, industrial chemicals and persistent organic pollutants) are emerging and ubiquitous in the environment, such as the soil, surface water and groundwater, causing devastating threats to the ecological environment and human health. The environmental damage and biological toxicity of these emerging contaminants have developed into a challenging multidisciplinary issue and are yet to be resolved (Johnson et al., 2020; Liu et al., 2021b). Hydroxyl radicals-based advanced oxidation processes (AOPs), also known as deep oxidation processes, are considered one of the most effective techniques to decompose these environmental pollutants owing to their fast reaction rate and capability of completely removing and recycling the treated wastewater (Lu et al., 2022; Zheng et al., 2022). The outstanding feature of AOPs results from the generation of hydroxyl radicals ($\cdot\text{OH}$) with a strong oxidizing ability through homogeneous or heterogeneous catalysis, which is considered the most powerful oxidant to degrade refractory organic pollutants in water.

Among AOPs, the Fenton method is prone to generate $\cdot\text{OH}$ via the homogeneous reaction between Fe^{2+} and H_2O_2 , but at the cost of large consumption of H_2O_2 and the production of iron sludge. In addition, this method is only applicable to the limited acidic water pH condition, which significantly narrows the industrial applications toward wastewater treatment. In contrast, no additional H_2O_2 needs supplemented throughout Electro-Fenton (EF) process (Lin et al., 2022). This is because H_2O_2 can be continuously produced by electroreduction of O_2 at the cathode with high overpotentials, followed by a homogeneous reaction with additive Fe^{2+} to generate homogeneous $\cdot\text{OH}$, and the oxidant (Fe^{3+}) can be reversibly reduced back to Fe^{2+} , as described in Eqs. (1-3) respectively, thus creating a catalytic loop to accelerate the removal of water contaminants (Hu et al., 2021; Liu et al., 2019; Liu et al., 2021a). In addition, heterogeneous $\cdot\text{OH}$ can be generated via Electro-Oxidation (EO) of H_2O on the surface of a “non-active” anode, among which boron-doped diamond (BDD) exhibited the highest $\cdot\text{OH}$ generation efficiency and is considered the ideal anode material for wastewater treatment (see Eq. (4)) (Du et al., 2021). Synergistic effects of combining EO and EF were observed, and this bi-coupling system was capable of greatly enhancing the removal of refractory organic pollutants, such as synthetic wastewater and real wastewater, owing to the dual catalytic treatment via homogeneous $\cdot\text{OH}$ and heterogeneous BDD($\cdot\text{OH}$) (Nidheesh et al., 2022). However, EO-EF still encountered unsatisfactory limitations such as strict pH control, loss of soluble iron catalyst due to ferric hydroxide precipitation and relatively high energy costs (He and Zhou, 2017).

Sulfate radicals-based AOPs have recently received widespread attention because sulfate radicals ($\text{SO}_4^{\cdot-}$) exhibit apparent advantages over $\cdot\text{OH}$, including relatively higher generation potentials ($E^0 = 2.5\text{-}3.1 \text{ V}$ versus $1.9\text{-}2.7 \text{ V}$), stronger selectivity, and longer lifespan (30-40 μs versus 20 ns) respectively. It is noted that $\text{SO}_4^{\cdot-}$ can diffuse further to react with contaminants in bulk solution due to its considerably long lifetime (Yang et al., 2021). $\text{SO}_4^{\cdot-}$ is generally produced by breaking the peroxygen bond in

peroxymonosulfate or peroxydisulfate. The latest research demonstrated that it could be generated by persulfate (PS) via homogeneous or heterogeneous catalysis with the help of transition metals, electricity, heat, ultrasound, ultraviolet light and quinones (Wang and Wang, 2022). In terms of homogeneous catalysis, Fe^{2+} is considered one of the best candidates for activating PS to generate $\text{SO}_4^{\cdot-}$ due to its environmental soundness, high abundance, low cost and high efficiency (see Eq. (5)), as previously reported in the treatment of organic pollutants (Hou et al., 2021; Xiao et al., 2020). As for heterogeneous catalysis, $\text{SO}_4^{\cdot-}$ can be efficiently generated via electroreduction of PS (see Eq. (6)) and electrooxidation of SO_4^{2-} (see Eq. (7)), during which PS can be regenerated via electrochemical oxidation of SO_4^{2-} (see Eq. (8)), creating a catalytic loop to greatly reduce the addition of PS (Divyapriya and Nidheesh, 2021). In addition, the introduction of PS in the electrolyte can increase its conductivity and thus the response current (or reduce the cell voltage), which in turn promotes the mass transport of the system and accelerates the degradation efficiency.

Previous studies demonstrated that the combination of EO and PS (EO-PS) allowed the simultaneous generation of heterogeneous $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ during electrochemical activation of PS using BDD anode or graphite felt (GF) cathode and demonstrated the synergistic degradation efficiency toward refractory organic pollutants (Bu et al., 2019; Song et al., 2018; Zhi et al., 2020). Arellano et al. (Arellano et al., 2019) introduced the catalyst of iron-based minerals in the EO-PS system for activation of peroxymonosulfate and achieved effective degradation of 1-butyl-1-methylpyrrolidinium chloride. Until now, little research was reported regarding the co-activation of PS by the BDD anode and the GF cathode at the same time, not to mention the synergistic coupling effect in complicated wastewater environments while introducing EF in this system.

Herein, the Electro-Oxidation—Persulfate—Electro-Fenton (EO-PS-EF) triple coupling system was proposed to efficiently degrade refractory organic pollutants via homogeneous and heterogeneous catalytic co-generation of $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$. Taking TC as the benchmark pollutant, the performance of the single system and the coupled system were systematically compared to assess the coupling effect. Effects of seven key parameters, including the concentration of PS and Fe^{2+} , air flow rate, the species and concentration of inorganic anion, solution pH and temperature, on the degradation performance are considered based on TC removal rate and kinetics. Reactive species in the coupling system are identified by radical quenching and electron spin resonance spectroscopy. The intermediates during TC degradation were analyzed and identified by liquid chromatography-mass spectrometry to determine the possible degradation pathway. In addition, degradation performance (i.e., energy consumption analysis, long-term degradation stability and degradation selectivity) toward additional organic pollutants, including Orange G (OG), Reactive Blue 19 (RB-19), 2,4-Dichlorophenoxyacetic acid (2,4-D) and Atrazine (ATZ), were investigated via the established EO-PS-EF system.

2 Materials and methods

2.1 Chemicals and materials

Tetracycline (TC, >95%), Reactive Blue 19 (RB-19, ≥99.5%), Orange G (OG, ≥96%), Atrazine (ATZ, 97%), 2,4-Dichlorophenoxyacetic acid (2,4-D, 97%), Methanol (MeOH, 99.5%), tert-Butanol (TBA, ≥98%), and 5,5-Dimethyl-1-pyrroline-N-oxide (DMPO, 97%) were purchased from McLean, China. Sodium persulfate (PS, 98%), Ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, ≥99%), Sodium sulfate (Na_2SO_4 , 99%), Sodium chloride (NaCl, 99.5%), Sodium phosphate (Na_3PO_4 , 98%), Sodium carbonate (Na_2CO_3 , ≥99.8%), Sodium nitrate (NaNO_3 , ≥99%), Sodium hydroxide (NaOH, 96%), Sulfuric acid (H_2SO_4 , 98%) were purchased from Sinopharm, China. All chemicals were used without further purification. All solutions were prepared with ultrapure water (UPT-I-10T, ACCEXP, China). Graphite felt (GF, 3 mm thickness) was purchased from Jinglong Special Carbon, China. The preparation of flat Ti/BDD used in this work referred to the previous work (Yang et al., 2022a).

2.2 Electrochemical degradation

The electrochemical reactor consisted of a cylindrical electrolytic cell, anode, cathode, DC power supply (RD-2030, Suzhou Wanruida, China), collector-type thermostatic heating magnetic stirrer (DF-101S, Shanghai Lichen Bonsi, China) and air pump (SB-748, Zhongshan Songbao, China) (see Scheme 1). The anode was BDD or 304 stainless steel (SS) electrode, and the cathode was GF or SS electrode. The anode and cathode were placed in parallel with an equal geometric area of 4 cm^2 and an interspace of 1 cm. A uniformly distributed aeration device connected to the air pump was placed right below the cathode.

All degradation experiments were performed with a constant direct current model at the fixed value of 0.2 A and the reactor was under constant stirring with a speed of 300 rpm. Before electrochemical degradation, the electrode system was pre-cleaned with a constant current of 0.2 A for 30 min in 50 mM Na_2SO_4 solution. The volume of simulated wastewater is 0.25 L and the initial concentration of organic pollutants is 0.1 mM. The solution pH was adjusted with the concentrated H_2SO_4 and NaOH, and a water bath maintained the reactor temperature. Prior to the degradation experiment, the solution was saturated with O_2 pumped by the compressed air at a flow rate of 0.25 L min^{-1} for 15 min to ensure the electrosynthesis of H_2O_2 . The subsequent O_2 concentration was maintained by air supply at various flow rates. Samples were collected at fixed five-minute intervals for analytical determinations, and the initial sample was used as the control. All experiments were repeated at least three times and the averaged data are shown in the text.

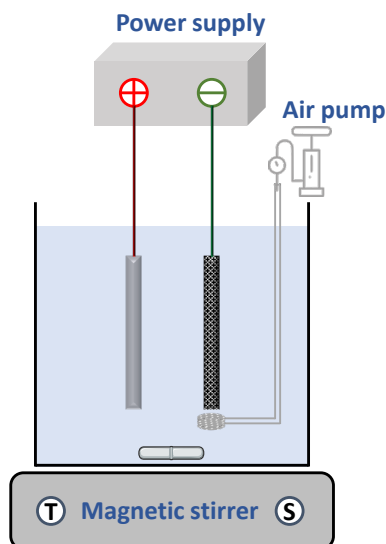
2.3 Analysis methods

TC, ATZ and 2,4-D concentrations were measured by high-performance liquid chromatography (HPLC, Agilent LC1290) with an adjustable wavelength UV detector, equipped with an ACE, UltraCore C18 column ($2.1 \times 75\text{ mm}$, $2.5\ \mu\text{m}$). Before analysis, water samples were filtered using Whatman PTFE membranes ($0.22\ \mu\text{m}$). Detailed analytical parameters were provided in the

113 supplementary materials (see Table S1). The concentrations of OG and RB-19 were measured by UV-visible spectrophotometer
114 (UV-8000S, METASH, China) based on the absorbance at the maximum absorption wavelength (478 nm and 596 nm, respec-
115 tively). The physicochemical information of these refractory organic pollutants is presented in Table S2.

116 TC degradation intermediates were characterized by liquid chromatography-mass spectrometry (LC-MS, Agilent LC1290-
117 QQQ-6470) at the column temperature of 40°C and the autosampler temperature of 25°C. The sample was analyzed by elec-
118 trospray ionization (ESI) in a positive mode over a mass range of 30-600 amu. The supplementary materials refer to mobile
119 phase ratios, gradient elution parameters, and other LC-MS detection information.

120 The electron spin resonance (ESR, Bruker A300, Germany) was used to detect transient free radicals in the system. At the
121 specified reaction time intervals, 100 μL of the solution near the anode surface was injected into 50 μL of 100 mM DMPO trap
122 using a capillary tube. The ESR measurements were performed with a power of 6.32 mW, a central field of 3510 G, a sweep
123 width of 100 G, and microwave and modulation frequencies of 9.87 GHz and 100 GHz respectively.



124
125 **Scheme 1.** Schematic illustration of the electrochemical reactor.

126 **3 Results and discussion**

127 **3.1 Establishment of the EO-PS-EF tri-coupling system**

128 **3.1.1 Synergistic effects of the EO-PS bi-coupling system**

129 Fig. 1 gradually illustrates the establishment of the EO-PS bi-coupling system according to the degradation performance
130 of TC, that is, the removal of TC and corresponding degradation kinetics. Note that statistical analysis of the TC removal by heat
131 map is first introduced to clearly compare and uncover the effects of diverse parameters on the degradation performance.
132 Three key control experiments are first presented in which almost no TC removal after 30 min was observed by GF adsorption
133 or PS alone, or both (see the top panel in Fig. 1), indicating that GF and PS themselves cannot physicochemically remove TC and
134 the unbiased GF cannot activate PS to generate the active radical species, in agreement with the observation from the unbiased
135 BDD electrode (Song et al., 2018).

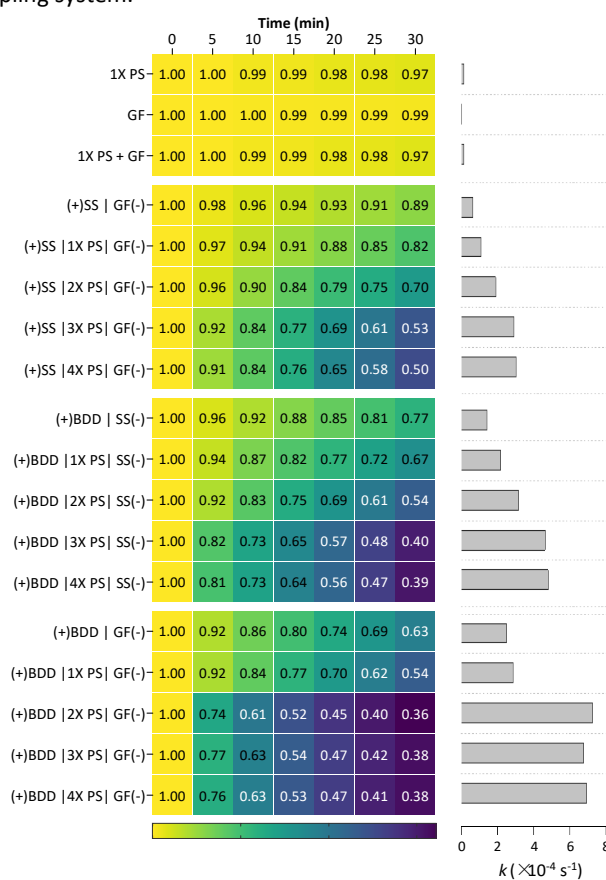
136 Previous works indicated that the BDD anode and the GF cathode could activate PS through different reaction mecha-
137 nisms. Thus, in order to uncover this claim and clarify the contribution of PS activation at the BDD anode and GF cathode toward
138 TC degradation, control experiments were carried out with the stainless steel (SS) electrode, which is difficult to activate PS (Bu
139 et al., 2019). (i) When SS and GF were used as anode and cathode respectively, named as (+)SS|GF(-), partial degradation of TC
140 (11% at 30 min) was observed, which is mainly attributed to the direct oxidation on the SS anode. The addition of 10 mM PS,
141 (+)SS|1X PS|GF(-), increased the TC removal from 11% to 18% at 30 min, and the reaction rate constant (k) increased from 6.52
142 $\times 10^{-5} \text{ s}^{-1}$ to $1.09 \times 10^{-4} \text{ s}^{-1}$. The enhanced TC removal was probably attributed to the effective activation of PS at the GF cathode.
143 (ii) When BDD and SS were used as anode and cathode, (+)BDD|SS(-), the TC removal without and with adding 10 mM PS
144 increased to 23% and 33%, accounting for the 12% and 15% increase compared to the counterparts of (+)SS|GF(-), respectively.
145 The improved capability toward TC removal presumably results from the activation of PS on the BDD anode and the GF, while
146 the former exhibited a superior activation performance (10% enhancement ratio after adding 10 mM) than the latter (7% en-
147 hancement ratio), indicating the difference in the electro-activation mechanism of PS on the BDD anode and the GF cathode.
148 In addition, the TC removal increased with increasing PS concentrations from 10 mM to 40 mM for both (+)BDD|SS(-) and
149 (+)SS|GF(-) systems, along with enhanced reaction rate constant at high PS concentrations.

150 At the GF cathode, PS activation to produce $\text{SO}_4^{\cdot -}$ is attributed to electrochemical reduction via direct electron transfer
151 (DET). Moreover, superoxide anion ($\text{O}_2^{\cdot -}$), which is converted from electrons captured by dissolved O_2 (from the pumping air
152 and oxygen evolution at the anode) at the cathode surface, is a crucial intermediate for PS activation at the GF cathode (Eq. (9)
153 and Eq. (10)) (Bu et al., 2019). A recent study proposed that anodic discharge at the BDD anode could convert adsorbed PS
154 molecules into a special transition state structure PS^* (Eq. (11)), which could degrade pollutants as a non-radical oxidation

155 pathway (Song et al., 2018). At the same time, PS* molecules can promote ·OH production and enhance DET reactions through
 156 water hydrolysis at the BDD anode. Notably, $\text{SO}_4^{\cdot-}$ and PS can be generated through electrochemical activation of SO_4^{2-} , HSO_4^-
 157 or H_2SO_4 owing to the powerful oxidizing capacity of the BDD anode (Divyapriya and Nidheesh, 2021). Meanwhile, the decom-
 158 position of $\text{SO}_4^{\cdot-}$ and PS will produce a large amount of SO_4^{2-} , which can ensure the recycling of $\text{SO}_4^{2-}/\text{PS}/\text{SO}_4^{\cdot-}$ to a certain extent.
 159 The catalytic activation loop of SO_4^{2-} , PS and $\text{SO}_4^{\cdot-}$ on the BDD anode endows its better TC degradation performance than the
 160 GF cathode activation.

161 To investigate the activation of PS at both the BDD anode and the GF cathode, 10 mM PS was added to the (+)BDD|GF(-)
 162 system, and TC removal, before and after PS addition, was observed to be 37% and 46%, respectively. The addition of PS in-
 163 creased the degradation rate constant from $2.50 \times 10^{-4} \text{ s}^{-1}$ to $2.88 \times 10^{-4} \text{ s}^{-1}$, and a synergistic effect of activating PS at the EO-
 164 PS bi-coupling system was observed. Later, the effect of PS concentrations (i.e., 10, 20, 30 and 40 mM) on the (+)BDD|GF(-)
 165 system was investigated. As the concentration increased from 10 mM to 20 mM, the TC removal increased from 46% to 64%
 166 and the reaction rate constant was found to increase from $2.88 \times 10^{-4} \text{ s}^{-1}$ to $7.24 \times 10^{-4} \text{ s}^{-1}$ respectively, attributed to a significant
 167 increase in the activation numbers of PS molecules with increasing concentrations. However, as the concentration continuously
 168 increased to 30 mM and 40 mM, the TC removal did not expect to increase but in return, a slight inhibition was observed. These
 169 results can be explained by the reorganization of $\text{SO}_4^{\cdot-}$ and the consumption of $\text{SO}_4^{\cdot-}$ (or ·OH) with excess PS (Eqs. (12-14)), as
 170 observed in previous works (Divyapriya and Nidheesh, 2021; Zhang et al., 2021; Zhu et al., 2018). In a nutshell, the PS can
 171 greatly promote TC removal at relatively low concentrations (e.g., less than 20 mM), but excess PS ($\geq 30 \text{ mM}$) adversely inhib-
 172 ited its removal. Note that the (+)BDD|GF(-) system exhibits faster TC degradation efficiency than the systems of (+)BDD|SS(-)
 173 and (+)SS|GF(-) under the identical addition of PS for all concentrations.

174 The subsequent studies will be carried out under the optimal PS concentration (i.e., 20 mM) on the (+)BDD|GF(-) system,
 175 which is named the EO-PS bi-coupling system.



176
 177 **Fig. 1. Establishment of the EO-PS bi-coupling system.** (a) Comparative heat map showing the removal rate of TC under various
 178 process parameters. 1X, 2X, 3X and 4X PS correspond to 10, 20, 30 and 40 mM PS. The symbol (+) and (-) refers to the anode
 179 and cathode respectively. The solution contains 50 mM Na_2SO_4 electrolyte, and pH and temperature are maintained at 7 and
 180 20 °C, respectively. (b) Corresponding pseudo-first-order reaction rate constants.

181 3.1.2 Synergistic effects of the EO-PS-EF tri-coupling system

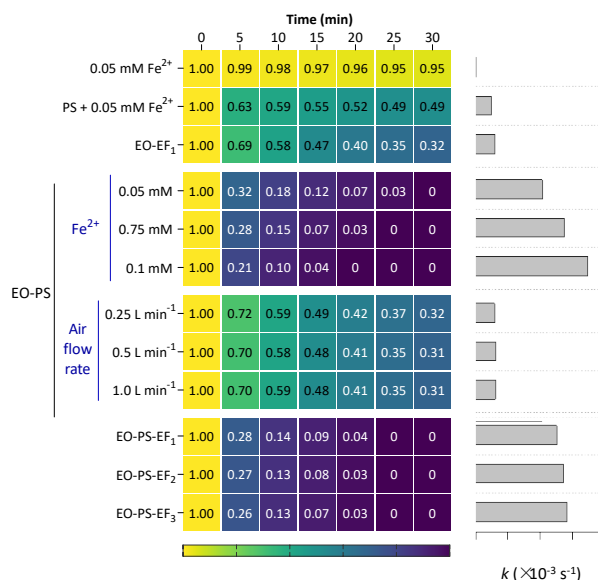
182 In the tri-coupling system, Fe^{2+} and air are considered homogeneous and heterogeneous catalytic co-generation of ·OH
 183 and $\text{SO}_4^{\cdot-}$. Fig. 2 gradually illustrates the establishment of the EO-PS-EF tri-coupling system. In the EO-PS bi-coupling system, as
 184 the Fe^{2+} concentration increased from 0 to 0.1 mM, the TC removal in 5 min increased from 26% to 79%, and the reaction rate
 185 constant increased from $7.24 \times 10^{-4} \text{ s}^{-1}$ to $3.51 \times 10^{-3} \text{ s}^{-1}$. It was observed that the degradation of TC by the EO-PS- Fe^{2+} system
 186 has two-stage reaction kinetic characteristics, with an initial slump and a later decay. In the initial stage, the homogeneous
 187 catalytic reaction between Fe^{2+} and PS with a reaction rate constant of up to $4.84 \times 10^{-4} \text{ s}^{-1}$ led to the rapid generation of $\text{SO}_4^{\cdot-}$,

188 greatly accelerating the TC removal. After that, most of Fe^{2+} was oxidized to Fe^{3+} , and the reactive oxygen species were mainly
 189 supplied via heterogeneous electrochemical reactions with a relatively slow reaction rate, mainly including exclusive BDD ano-
 190 dization ($k = 2.50 \times 10^{-4} \text{ s}^{-1}$) and electro-activation of PS ($k = 4.74 \times 10^{-4} \text{ s}^{-1}$). In addition, the competing intermediates during the
 191 latter period reacted with the reactive species, partially accounting for the decay of TC removal. Thus, TC removal rates dra-
 192 matically decreased during the heterogeneous reaction period. This phenomenon was also observed from the control experi-
 193 ment with only 0.05 mM Fe^{2+} and 20 mM PS, during which 37% of TC was degraded within 5 min, but only 14% of TC was
 194 removed in the following 25 min.

195 It was noted that Fe(II) and Fe(III) ions have a strong tendency to complex with TC due to the complexation sites of N-type
 196 and O-type structures on the A-ring of the TC molecule. The complexation of Fe(II) and TC could accelerate the oxidation of
 197 Fe(II), thus promoting the degradation of TC (Zhang et al., 2022). As shown in the control experiment, 0.05 mM Fe^{2+} exclusively
 198 achieved 5% TC removal within 30 min owing to the generation of reactive oxygen species (mainly $\cdot\text{OH}$) while the Fe(II)-TC
 199 complex was oxidized to the Fe(III)-TC complex by dissolved oxygen. In addition, the Fe(III)-TC complex could spontaneously
 200 transfer to TC oxidation intermediates and Fe(II) (Wang et al., 2016). Thus, the Fe cycle was established between the Fe(II),
 201 Fe(III), Fe(II)-TC and Fe(III)-TC, thus promoting TC removal.

202 The EF system mainly involves the reaction of Fe^{2+} and H_2O_2 to generate $\cdot\text{OH}$. The formation of H_2O_2 can be achieved by
 203 the electrochemical reduction of O_2 at the GF cathode. The EO-EF system was established by adding 0.05 mM Fe^{2+} and the
 204 pumping air at a flow rate of 0.25 L min^{-1} to the EO system, which has slightly enhanced degradation performance than the EO-
 205 PS system, accounting for 5% higher TC removal. This may be related to the amount of catalysts (Fe^{2+} , aeration and PS), the
 206 complexation effect of Fe-TC and the selective oxidation of the dominant active species in different systems. Two parameters of
 207 the concentration of Fe^{2+} and the airflow rate were considered to optimize the EO-PS-EF system. Note that as the Fe^{2+} con-
 208 centration doubled, only 11% of increasing TC removal rate was observed at 5 min and all those concentrations (0.05, 0.75 and
 209 0.1 mM) could achieve 100% of TC removal within a considerable time (less than 30 minutes). Thus, 0.05 mM of Fe^{2+} is chosen
 210 for subsequent studies to facilitate comparison and reduce the addition of chemicals. The airflow rate itself did not exhibit the
 211 apparent enhancement after addition, only with a 4% improved TC removal rate compared to the bare EO-PS system, and the
 212 degradation performance remained unchanged with increasing concentrations (see the 3rd panel in Fig. 2). However, after
 213 adding 0.05 mM of Fe^{2+} , Fenton reactions can occur after aeration due to the presence of Fe^{2+} , and the degradation perfor-
 214 mance of this system greatly increased, constituting a powerful EF system. Undeniably, the introduction of oxygen has a pro-
 215 nounced enhancement effect on the EO-PS-EF system, as observed from the comparison of EO-PS- Fe^{2+} (0.05 mM Fe^{2+}) and EO-
 216 PS-EF₁ (0.05 mM Fe^{2+} + 0.25 L min^{-1} Air), with the increment ratio of reaction kinetic constant up to 22% (from $2.08 \times 10^{-3} \text{ s}^{-1}$ to
 217 $2.54 \times 10^{-3} \text{ s}^{-1}$). However, the effect of continuous enhancement is less significant when the oxygen flow rate further increases
 218 from 0.25 L min^{-1} to 1 L min^{-1} (see the bottom panel in Fig. 2). The reason why the degradation of TC did not increase under a
 219 high airflow rate could be attributed to the competition of oxygen reduction reaction, hydrogen evolution reaction and PS
 220 activation reaction at the GF cathode. In addition, extremely high air flow rates might fill a large amount of air in the reactor,
 221 which could hinder electrode/solution contact or even ion transfer. Thus, the airflow rate of 0.25 L min^{-1} was suggested for
 222 subsequent studies.

223 In summary, the EO-PS-EF tri-coupling system was successfully established, which could achieve homogeneous and hetero-
 224 geneous catalytic co-generation of $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ and exhibit powerful degradation performance for TC.



225
 226 **Fig. 2. Establishment of the EO-PS-EF tri-coupling system.** (a) Degradation of TC by 0.05 mM Fe^{2+} , 20 mM PS + 0.05 mM Fe^{2+} ,
 227 EO-EF₁ (0.05 mM Fe^{2+} + 0.25 L min^{-1} Air), EO-PS- Fe^{2+} (0.05, 0.75 and 0.1 mM Fe^{2+}), EO-PS-Air flow rate ($0.25, 0.5$ and 1 L min^{-1}),
 228 EO-PS-EF₁ (0.05 mM Fe^{2+} + 0.25 L min^{-1} Air), EO-PS-EF₂ (0.05 mM Fe^{2+} + 0.5 L min^{-1} Air) and EO-PS-EF₃ (0.05 mM Fe^{2+} + 1 L min^{-1}
 229 Air). The solution contains 50 mM Na_2SO_4 electrolyte, and pH is fixed at 7 and temperature at $20 \text{ }^\circ\text{C}$. (b) Corresponding pseudo-
 230 first-order reaction rate constants.

232

233

234

235

236

237

238

239

240

241

242

243

244

245

246

247

248

249

250

251

252

253

254

255

256

257

258

259

260

261

262

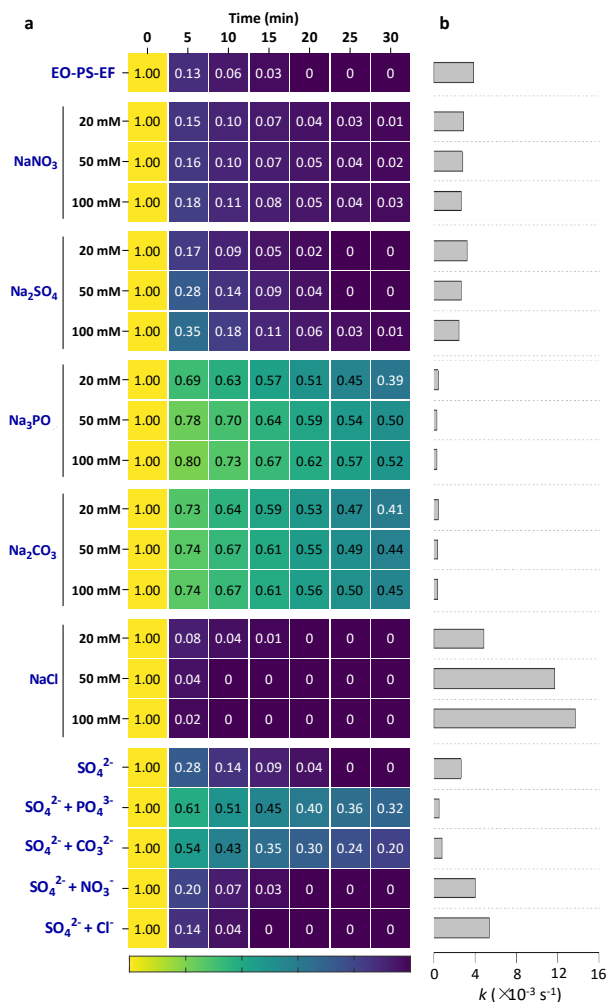
263

264

Inorganic anions often act as radical scavengers for the radical-based AOPs and are thus considered. Five common inorganic anion species (NO_3^- , SO_4^{2-} , PO_4^{3-} , CO_3^{2-} and Cl^-) with various concentrations (0, 20, 50 and 100 mM) were comparatively considered, as shown in Fig. 3. NO_3^- , SO_4^{2-} , PO_4^{3-} and CO_3^{2-} adversely inhibited the degradation performance of the EO-PS-EF system, with the inhibition effect of $\text{NO}_3^- < \text{SO}_4^{2-} < \text{CO}_3^{2-} < \text{PO}_4^{3-}$. The inhibition phenomenon was improved with increasing ion concentrations, which is more pronounced with SO_4^{2-} and PO_4^{3-} . In contrast, the introduction of Cl^- could promote the removal of TC molecules in the EO-PS-EF system, and the degradation performance was enhanced with increasing concentrations. Among the inhibition ions, NO_3^- has minimal effect on TC removal, and this results from the relatively low reaction rate constant for quenching active radicals (e.g., $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$). Meanwhile, a high overpotential is required for the oxidation of NO_3^- to NO_3^{\cdot} (see Eqs. (15-17)), as indicated in the previous works (Bu et al., 2018; Huang et al., 2021; Lee et al., 2020). The inhibition effect of SO_4^{2-} was possibly attributed to the limited active adsorption sites on the BDD surface and the competitive adsorption between SO_4^{2-} and PS partially rendered the electro-activation of PS (Cai et al., 2019a; Ding et al., 2020). Under neutral pH, PO_4^{3-} exists in the forms of H_2PO_4^- and HPO_4^{2-} that are not only powerful scavengers of $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$, but also affect charge consumption (Eqs. (18-23)) (Bu et al., 2018; Wang and Wang, 2020; Xu et al., 2017). The resulting phosphate reactive species (e.g., $\text{HPO}_4^{\cdot-}$, $\text{H}_2\text{PO}_4^{\cdot}$) have too low activities to oxidatively degrade organic pollutants, thus leading to the slump in the degradation performance of the EO-PS-EF system. Similarly, CO_3^{2-} is mainly present in the form of HCO_3^- which is also recognized as a powerful free radical scavenger, and the resulting bicarbonate radical (HCO_3^{\cdot}) has low degradation capability (k ranges between 4×10^6 and $1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) toward organic matters. In addition to scavenging free radicals, HCO_3^- can consume electrons to produce HCO_3^{\cdot} with low oxidative capacity (Eqs. (24-26)) (Lee et al., 2020; Wang and Wang, 2020). The formation of these low reactive oxygen species (ROS) may be responsible for the pronounced inhibition effect of PO_4^{3-} and CO_3^{2-} . Moreover, the competitive adsorption between negatively charged anion species and PS might inhibit PS adsorption and activation.

Interestingly that the presence of Cl^- promoted the degradation of TC in the EO-PS-EF system, and the promotion effect increased with increasing concentrations. This corresponds to the production of highly reactive and strongly selective reactive chlorine species (RCS), which are highly susceptible to addition, substitution or oxidation reactions with organic compounds with unsaturated bonds and electron-rich groups. It has been demonstrated that RCS reacts faster with certain phenolic compounds (e.g., benzoic acid, bisphenol A) than $\cdot\text{OH}$ and/or $\text{SO}_4^{\cdot-}$ (Chen et al., 2022). Cl^- can react with $\text{SO}_4^{\cdot-}$ to form chlorine radicals (Cl^{\cdot}) and then dichlorine radical (Cl_2^{\cdot}), and the chlorine products (e.g., Cl^{\cdot} and Cl_2^{\cdot}) can promote the production of $\cdot\text{OH}$ through the reaction, thus accelerating TC removal (see Eq. (27-33)) (Farhat et al., 2017; Oyekunle et al., 2021).

In addition, the influence of the introduction of NO_3^- , PO_4^{3-} , CO_3^{2-} and Cl^- with the same molar concentration on the performance of the system was also studied with 50 mM Na_2SO_4 as the background electrolyte. Its TC removal rate resulted from the mixed effect of the two salts, which was similar to a compromise effect. In general, almost all inorganic anions are capable of consuming electrons and scavenging free radicals with different reaction rates and producing reactive species with varying redox capabilities. The difference in oxidation capacity of these reactive species with respect to the target contaminants determines their impact on water treatment performance.



265
266
267
268
269

Fig. 3. Effects of inorganic anion species and concentration on the degradation performance of the EO-PS-EF tri-coupling system. (a) Effects of five individual inorganic anions (NO₃⁻, SO₄²⁻, PO₄³⁻, CO₃²⁻ and Cl⁻) at various concentrations (0, 20, 50 and 100 mM) on TC removal. The control experiment (EO-PS-EF₁ without 50 mM Na₂SO₄) was shown on the top panel. (b) Corresponding pseudo-first-order reaction rate constants.

Table 1 Elementary reactions during the EO-PS-EF system.

No.	Reaction equation	E^0 or k	Ref.
1	$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	$E^0 = 0.67$ V vs. RHE	(Hu et al., 2021)
2	$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^-$	$k = 40-80$ $M^{-1} s^{-1}$	(Liu et al., 2021a)
3	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	$E^0 = 0.77$ V vs. RHE	(Liu et al., 2019)
4	$BDD + H_2O \rightarrow BDD(\cdot OH) + H^+ + e^-$	$E^0 = 1.9-2.7$ V vs. RHE	(Du et al., 2021)
5	$Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{\cdot-} + SO_4^{2-}$	$k = 20-30$ $M^{-1} s^{-1}$	(Xiao et al., 2020)
6	$S_2O_8^{2-} + e^- \rightarrow SO_4^{\cdot-} + SO_4^{2-}$	-	(Divyapriya and Nidheesh, 2021)
7	$SO_4^{\cdot-} \rightarrow SO_4^- + e^-$	$E^0 = 2.5-3.1$ V vs. RHE	(Divyapriya and Nidheesh, 2021)
8	$2SO_4^{\cdot-} \rightarrow S_2O_8^{2-} + 2e^-$	$E^0 = 2.01$ V vs. RHE	(Divyapriya and Nidheesh, 2021)
9	$O_2 + e^- \rightarrow O_2^-$	-	(Bu et al., 2019)
10	$O_2^- + S_2O_8^{2-} \rightarrow O_2 + SO_4^- + SO_4^{2-}$	-	(Bu et al., 2019)
11	$BDD + PS \rightarrow BDD(PS^{\cdot})$	-	(Song et al., 2018)
12	$2SO_4^{\cdot-} \rightarrow S_2O_8^{2-}$	$k = 7.6 \times 10^8$ $M^{-1} s^{-1}$	(Divyapriya and Nidheesh, 2021)
13	$S_2O_8^{2-} + SO_4^- \rightarrow S_2O_8^- + SO_4^{2-}$	$k = 6.3 \times 10^5$ $M^{-1} s^{-1}$	(Zhu et al., 2018)
14	$S_2O_8^{2-} + \cdot OH \rightarrow S_2O_8^- + OH^-$	$k = 1.4 \times 10^7$ $M^{-1} s^{-1}$	(Zhu et al., 2018)
15	$NO_3^- + \cdot OH \rightarrow NO_3 + OH^-$	$k < 5.0 \times 10^5$ $M^{-1} s^{-1}$	(Huang et al., 2021)
16	$NO_3^- + SO_4^{\cdot-} \rightarrow NO_3 + SO_4^{2-}$	$k = 5.5 \times 10^5$ $M^{-1} s^{-1}$	(Huang et al., 2021)
17	$NO_3^- \rightarrow NO_3 + e^-$	$E^0 = 2.3-2.5$ V vs. RHE	(Bu et al., 2018)
18	$H_2PO_4^- + \cdot OH \rightarrow H_2PO_4 + OH^-$	$k = 2.2 \times 10^6$ $M^{-1} s^{-1}$	(Wang and Wang, 2020)
19	$H_2PO_4^- + SO_4^- \rightarrow H_2PO_4 + SO_4^{2-}$	$k < 7 \times 10^4$ $M^{-1} s^{-1}$	(Wang and Wang, 2020)
20	$HPO_4^{2-} + \cdot OH \rightarrow HPO_4^- + OH^-$	$k = 8.0 \times 10^5$ $M^{-1} s^{-1}$	(Wang and Wang, 2020)
21	$HPO_4^{2-} + SO_4^- \rightarrow HPO_4^- + SO_4^{2-}$	$k = 1.2 \times 10^6$ $M^{-1} s^{-1}$	(Wang and Wang, 2020)
22	$H_2PO_4^- \rightarrow H_2PO_4 + e^-$	-	(Bu et al., 2018)
23	$HPO_4^{2-} \rightarrow HPO_4^- + e^-$	-	(Bu et al., 2018)
24	$HCO_3^- + \cdot OH \rightarrow HCO_3 + OH^-$	$k = 8.5 \times 10^6$ $M^{-1} s^{-1}$	(Lee et al., 2020)
25	$HCO_3^- + SO_4^- \rightarrow HCO_3 + SO_4^{2-}$	$k = 9.1 \times 10^6$ $M^{-1} s^{-1}$	(Wang and Wang, 2020)
26	$HCO_3^- \rightarrow HCO_3 + e^-$	$E^0 = 1.7$ V vs. RHE	(Wang and Wang, 2020)
27	$Cl^- \rightarrow Cl + e^-$	$E^0 = 2.41$ V vs. RHE	(Farhat et al., 2017)
28	$2Cl^- \rightarrow Cl_2 + e^-$	$E^0 = 2.09$ V vs. RHE	(Farhat et al., 2017)
29	$Cl^- + SO_4^- \rightarrow Cl + SO_4^{2-}$	$k = 3.2 \times 10^8$ $M^{-1} s^{-1}$	(Farhat et al., 2017)
30	$Cl^- + Cl^- \rightarrow Cl_2^-$	$k = 6.5 \times 10^9$ $M^{-1} s^{-1}$	(Farhat et al., 2017)
31	$Cl^- + OH^- \rightarrow HOCl^-$	$k = 1.8 \times 10^{10}$ $M^{-1} s^{-1}$	(Farhat et al., 2017)
32	$Cl_2^- + OH^- \rightarrow HOCl^- + Cl^-$	$k = 4.5 \times 10^7$ $M^{-1} s^{-1}$	(Farhat et al., 2017)
33	$HOCl^- \rightarrow \cdot OH + Cl^-$	$k = 6.1 \times 10^9$ $M^{-1} s^{-1}$	(Farhat et al., 2017)
34	$SO_4^{\cdot-} + H_2O \rightarrow SO_4^{2-} + \cdot OH + H^+$	$k < 2.0 \times 10^3$ $M^{-1} s^{-1}$	(Gao et al., 2020)
35	$SO_4^{\cdot-} + OH^- \rightarrow SO_4^{2-} + \cdot OH$	$k = 6.5 \times 10^7$ $M^{-1} s^{-1}$	(Gao et al., 2020)
36	$S_2O_8^{2-} + Heat \rightarrow 2SO_4^{\cdot-}$	-	(Tian et al., 2022)

Note: E^0 : Standard reduction potential, k : reaction rate constant

271

272

3.3 Effect of pH and temperature

273

274

275

276

277

278

279

280

281

282

283

284

285

286

287

288

289

290

291

292

293

294

295

296

297

298

299

300

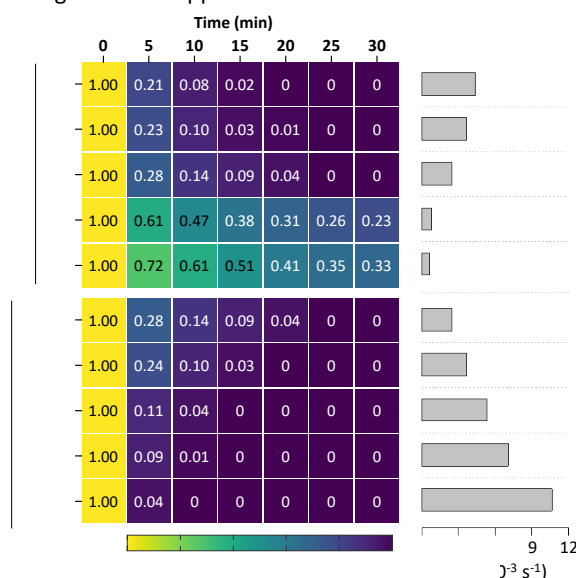
Fig. 4 shows the TC removal of the EO-PS-EF system with respect to pH (top panel) and temperature (bottom panel). The degradation efficiency of TC improves with increasing acidity but decreases with alkalinity. TC removal was observed to be highly efficient in neutral and acidic conditions, and the TC removal reached 96%, 99% and 100% after 20 min at pH of 7, 5 and 3, respectively. However, the TC removal decreased to 69% and 59% at pH of 9 and 11, respectively.

TC molecules have three types of pH-relevant functional groups with different protonation and deprotonation constants ($pK_a = 3.3, 7.7$ and 9.7), and their forms vary with changing pH, as shown in Fig. S1 (Gao et al., 2022b; Lalliansanga et al., 2022). At pH = 3, most TC molecules were protonated and existed in the cationic form of TCH^+ , while at pH = 5 it remained unchanged. At the neutral condition (pH = 7), some TC molecules were transformed into a monovalent anion (TC $^-$). In contrast, as pH increased to 9, the TC mainly existed in the form of TC $^-$, while the form of a divalent anion (TC $^{2-}$) dominated at a pH of 11. When TC species are positively charged, the negative charge on the GF cathode surface facilitates TC adsorption. Also, the lower pH favors the adsorption of PS anions on the cathode, which in turn promotes the generation of $SO_4^{\cdot-}$ (Liu et al., 2018).

The iron species present in the EO-PS-EF tri-coupling system is closely related to solution pH (Dihingia and Tiwari, 2022; Gabriel et al., 2021). On the one hand, iron species are present under alkaline environments in the form of hydroxide complexes such as $FeOH^+$, $Fe(OH)_2^+$, $Fe(OH)_3$ and $Fe(OH)_4^-$, leading to a decrease in the concentration of active Fe^{2+} . The stronger alkaline, the lower the concentration of Fe^{2+} , as shown in Fig. S2. However, Fe^{2+} participated in the generation of $SO_4^{\cdot-}$ from PS and $\cdot OH$ from H_2O_2 . Thus, the degradation performance of the EO-PS-EF tri-coupling system toward TC would be severely inhibited due to the loss of Fe^{2+} in alkaline environments. On the other hand, $SO_4^{\cdot-}$ dominated in acidic conditions while SO_4^- could be converted to $\cdot OH$ in neutral and alkaline conditions, and $\cdot OH$ would dominate in relatively concentrated alkaline conditions (see Eq. (34) and Eq. (35)) (Gao et al., 2020). However, the generation potential of $\cdot OH$ decreased and the oxygen evolution reaction increased under alkaline environments, leading to a decrease in the degradation performance of the EO-PS-EF tri-coupling system. In general, low pH contributes to the removal of TC in EO-PS-EF systems as a result of a comprehensive evaluation of multiple factors.

Later, the critical factor, temperature, was considered under the solution pH of 7. As expected, the degradation performance of the EO-PS-EF system increased with increasing temperatures from 20 °C to 60 °C, and the TC removal within 5 min increased from 72% to 96%, and the reaction rate constant was increased from $2.54 \times 10^{-3} s^{-1}$ to $1.07 \times 10^{-2} s^{-1}$, respectively. The increase in temperature increased the average kinetic energy of molecules and thus the collision frequency between reactant molecules, increasing the mass transfer and accelerating the activation of PS through the heat to generate more $SO_4^{\cdot-}$ (see Eq. (36)) (Tian et al., 2022). Nevertheless, high temperatures would reduce the solubility of oxygen in the water and adversely

301 reduce the yield of H₂O₂, unavoidably increasing energy consumption. A balance between removal efficiency and energy con-
 302 sumption should be addressed concerning industrial applications.

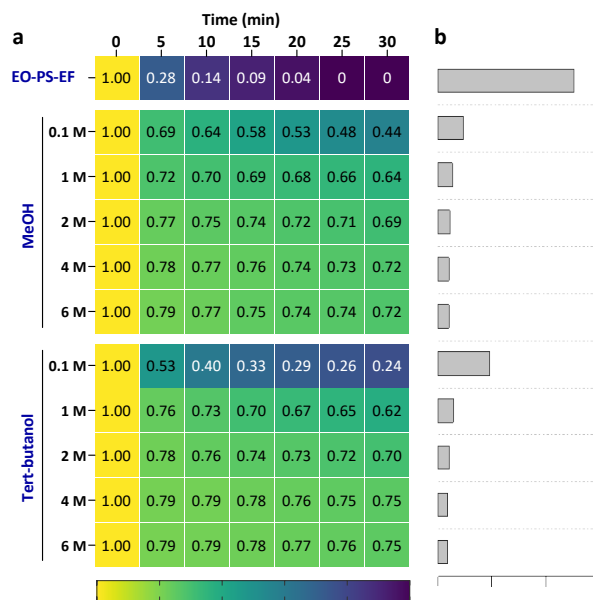


303 **Fig. 4. Effects of pH and temperature on the degradation performance of the EO-PS-EF tri-coupling system.** (a) The effect of
 304 pH (3, 5, 7, 9 and 11) and temperature (20, 30, 40, 50 and 60 °C) on TC removal in the EO-PS-EF₁ system. The solution pH and
 305 temperature were leveled off throughout the degradation period. (b) Corresponding pseudo-first-order reaction rate constants.
 306

307 3.4 Identification of the major reactive species

308 3.4.1 Free radicals quenching

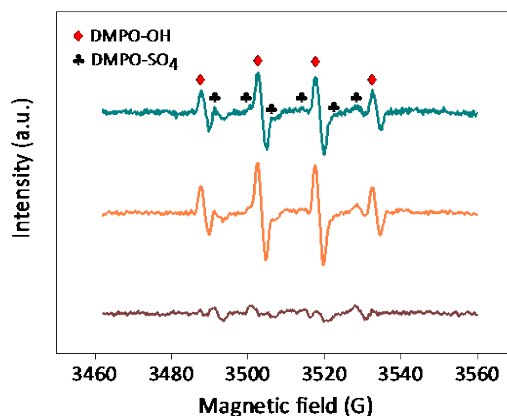
309 MeOH has equivalently high reaction rates to ·OH and SO₄^{·-} ($k_{\text{OH}} = 9.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, $k_{\text{SO}_4^{\cdot-}} = 1.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$) and was widely
 310 used as a scavenger for hydroxyl and sulfate radicals. The reaction rate constant between TBA and ·OH ($k_{\text{OH}} = 3.8\text{-}7.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$)
 311 is three orders of magnitude higher than that between TBA and SO₄^{·-} ($k_{\text{SO}_4^{\cdot-}} = 4.0\text{-}9.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$). Thus, TBA was chosen
 312 as a ·OH scavenger (Cai et al., 2019b). The electro-generated active radical species usually exist in the vicinity of the electrode
 313 surface, which is different from those homogeneous radical species existed in the bulk solution. Thus, quenching equal concen-
 314 trations of heterogeneous radical species required higher concentrations of a scavenger than quenching homogeneous radical
 315 species, as previously reported (Song et al., 2018). The EO-PS-EF system involves homogeneous catalytic and electrochemical
 316 reactions, producing homogeneous and heterogeneous radical species. Therefore, the contribution of free radicals evaluated by
 317 free radical scavenging studies is of great significance for understanding the reaction mechanism of the EO-PS-EF system. Fig.
 318 5 shows the effects of radical scavenger concentrations (0.1, 1, 2, 4 and 6 M) on the TC degradation performance of the EO-PS-
 319 EF system. As the scavenger concentrations increased from 0.1 M to 6 M, the effect of inhibiting TC removal increased. When
 320 the concentration of MeOH and TBA was greater than 1 M, the inhibition did not change significantly with further increasing
 321 quenchers. Furthermore, we found comparable quenching effects for high-concentration MeOH and TBA, which conflicts with
 322 the basic assumption that the added high-concentration quenchers only remove their target active species. This may be related
 323 to the confounding effects of high-concentration quenchers that interfere with reactive species production and quench non-
 324 target reactive species as reported in the literature (Gao et al., 2022a). For the case of 0.1 M MeOH and 0.1 M TBA, the remain-
 325 ing TC accounts for 44% and 24%, respectively. According to the previous study, it can be distinguished that the respective
 326 contributions of ·OH and SO₄^{·-} were 61.6% and 19.3% respectively (Cai et al., 2019b).



327
328 **Fig. 5. Free radicals quenching reactions.** (a) Effects of MeOH and TBA concentrations on TC removal in EO-PS-EF system. (b)
329 Corresponding pseudo-first-order reaction rate constants.

330 3.4.2 Electron Spin Resonance

331 The reactive radicals involved in the EO-PS-EF system were directly determined by the ESR spectroscopy (see Fig. 6). Typical
332 DMPO-OH and DMPO-SO₄ adduct signals were observed based on their hyperfine coupling constants (DMPO-OH: a_H = a_N = 14.9
333 G; DMPO-SO₄: a_N = 13.2 G, a_H = 9.6 G, a_H = 1.48 G, a_H = 0.78 G) (Gao et al., 2020). The signal of the DMPO-SO₄ adduct was lower
334 than that of the DMPO-OH adduct in ESR spectrum. This might result from that SO₄^{•-} could be converted into ·OH under neutral
335 and alkaline pH. Besides, the DMPO-SO₄ adduct could also undergo a rapid nucleophilic substitution reaction with H₂O/OH⁻
336 forming the DMPO-OH adduct (Gao et al., 2020). According to the relative intensities of the adduct signals, it can be seen that
337 the concentration of free radicals increases with the prolongation of the reaction time, resulting from the accumulation of free
338 radicals. The free radical concentration decreased to a certain extent when the reaction time was further prolonged due to the
339 quenching reaction. In conclusion, ·OH and SO₄^{•-} are the dominant reactive species in the EO-PS-EF system.



340
341 **Fig. 6. ESR spectrum recorded at different reaction times of the EO-PS-EF system.**

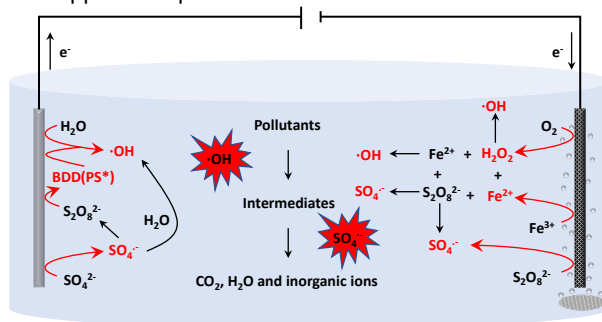
342 3.5 Degradation mechanism and the pathways

343 3.5.1 Analysis of the plausible mechanism

344 Scheme 2 schematically shows the possible degradation mechanism of the EO-PS-EF system. As an ideal anode material,
345 BDD has more substantial oxidation capability and longer service life than other anode materials (e.g., PbO₂, SnO₂, mixed-metal
346 oxides and Ti₄O₇) and can generate heterogeneous ·OH and SO₄^{•-} by anodizing H₂O, PS and SO₄²⁻. GF is a commercial EF cathode
347 material with low cost, large specific surface area, and stable production yield of H₂O₂, and also allows for cathodic electro-
348 activation of PS. When Fe³⁺ was reduced to Fe²⁺ on the GF surface, the reduced Fe²⁺ would react with PS to generate homoge-
349 neous SO₄^{•-}. The spontaneous aqueous chemical reactions of Fe²⁺, H₂O₂ and PS in the bulk solution can generate homogene-
350 ous ·OH and SO₄^{•-}, respectively. In summary, it is obvious that the homogeneous and heterogeneous catalytic co-generation of ·OH

351
352

and $\text{SO}_4^{\cdot-}$ is a reasonable mechanism to efficiently remove refractory organic pollutants. Notably, Fe cycling and PS cycling in the EO-PS-EF system might expand its application potential.



353
354

Scheme 2. Schematic illustration of the plausible degradation mechanism of the EO-PS-EF system.

355

3.5.2 Possible degradation intermediates and pathways

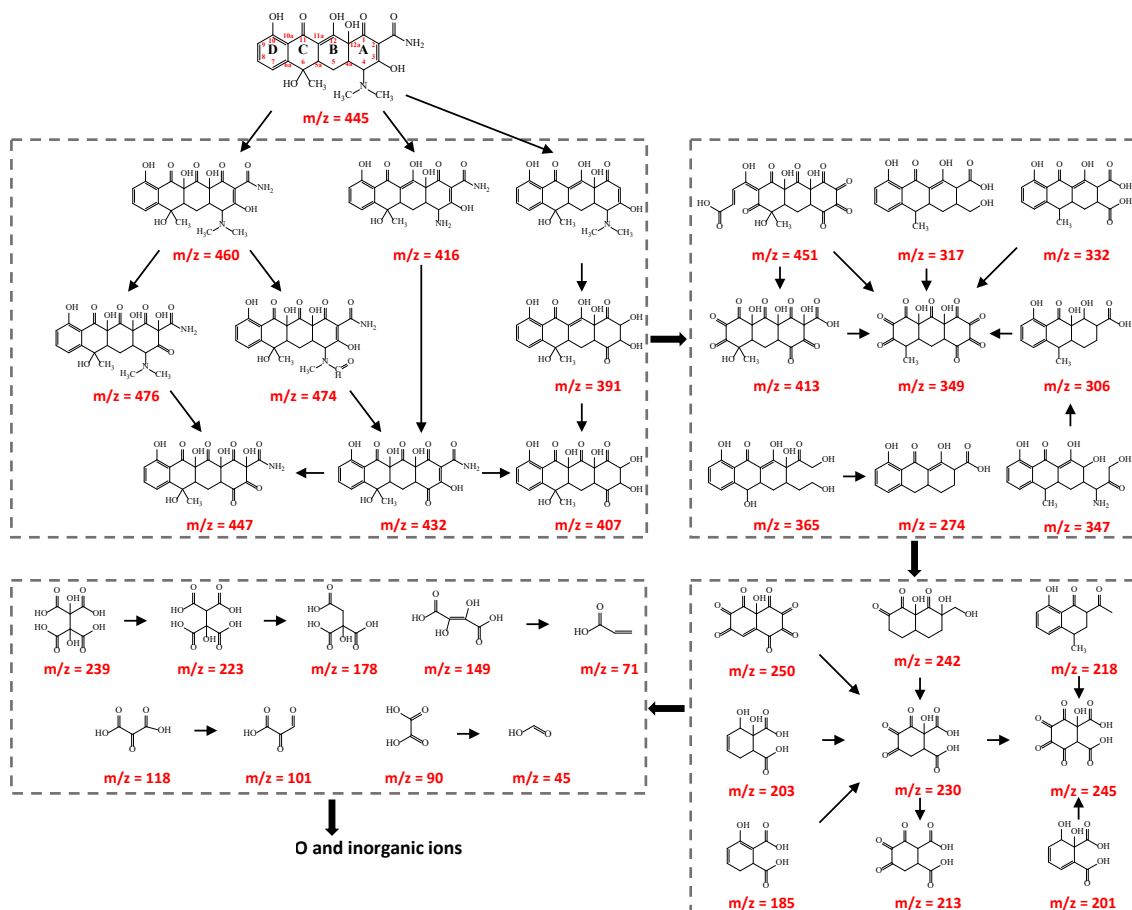
356

The degradation intermediates of TC were analyzed and identified by LC-MS, which provided a theoretical basis for the degradation pathways and mechanism of TC in the EO-PS-EF system. Various oxidation by-products were detected during TC degradation due to the complexity of TC molecules. 36 intermediates were identified by total ion flow chromatograms and mass spectra with different residence times (Fig. S3 and Table S4). Intermediates were classified into five types such as tetracyclic, tricyclic, bicyclic, monocyclic and short-chain carboxylic acids, according to their structures. Combined with the mechanism of the major reactive species ($\cdot\text{OH}$, $\text{SO}_4^{\cdot-}$ and electrons) reacting with organics, a possible degradation pathway of TC in the EO-PS-EF system was proposed (Scheme. 3). Four functional groups can be identified based on the chemical structural formula of TC, including the amide group ($-\text{C}(\text{O})-\text{NH}_2$) and dimethylamino group ($-\text{N}(\text{CH}_3)_2$) at the C2 position and C4 position of the A ring, the phenolic hydroxyl group ($-\text{OH}$) at the D ring (C10 position) and two conjugated double bond systems of ketone group ($\text{R}_1-\text{C}(\text{O})-\text{R}_2$) and enol group ($-\text{C}=\text{C}-\text{OH}$) across the ABC ring (Yang et al., 2022b). The electron clouds at these functional group positions were denser and more easily attacked by reactive species to undergo reactions such as electron transfer, double bond addition or hydrogen extraction.

368

The reaction of TC and reactive species will produce three primary intermediates with $m/z = 460$, $m/z = 416$ and $m/z = 401$. The $m/z = 460$ primary intermediate was produced by cycloaddition of the double bond (C11a-C12 position) in the TC molecule (Barhoumi et al., 2017; Liang et al., 2018). The $m/z = 416$ primary intermediate was produced by the demethylation of dimethylamino ($-\text{N}(\text{CH}_3)_2$) (C4 position). The $m/z = 401$ primary intermediate was produced by dedimethylamidation (C2 position). The double bond (C2-C3 position) of the $m/z = 460$ primary intermediate can generate the $m/z = 476$ intermediate by cycloaddition, further removing the dimethylamino group (C4 position) to produce $m/z = 447$ intermediate. In addition, the dimethylamino group ($-\text{N}(\text{CH}_3)_2$) (C4 position) of the $m/z = 460$ primary intermediate can also undergo an aldehyde conversion reaction to generate the $m/z = 474$ intermediate, followed by the oxidation of dimethylamino to generate $m/z = 432$ intermediate. The $m/z = 432$ intermediate can also be generated from the $m/z = 416$ primary intermediate by deamination (C4 position) and cycloaddition (C11a-C12 position). The $m/z = 432$ intermediate can be produced by cycloaddition (double bond at C2-C3 position) and deamidation reaction (C2 position) to produce $m/z = 447$ and $m/z = 407$ intermediates. The $m/z = 401$ primary intermediate then underwent a cycloaddition reaction (C2 position) and removal of the dimethylamino group (C4 position) to generate the $m/z = 391$ intermediate, which was further subjected to a cycloaddition reaction (C11a-C12 position) can produce $m/z = 407$ intermediate. Overall, TC molecules formed 9 tetracyclic intermediates in the EO-PS-EF system through cycloaddition, demethylation, deamidation, and deamination reactions. The above tetracyclic intermediates generated 9 tricyclic intermediates ($m/z = 451$, $m/z = 413$, $m/z = 365$, $m/z = 349$, $m/z = 347$, $m/z = 332$, $m/z = 317$, $m/z = 306$ and $m/z = 274$). The ring-opening positions are located at C7-C8, C1-C2, C3-C4 and C1-C12a. Some tricyclic intermediates can be generated by cycloaddition, dehydroxylation, carbonylation or decarboxylation of other tricyclic intermediates. For example, the $m/z = 349$ intermediate can be produced by oxidation of the $m/z = 451$, $m/z = 413$, $m/z = 332$, $m/z = 317$ and $m/z = 306$ intermediates. Further ring opening of these tricyclic intermediates will yield bicyclic ($m/z = 250$, $m/z = 242$, $m/z = 218$) and monocyclic intermediates ($m/z = 245$, $m/z = 230$, $m/z = 213$, $m/z = 203$, $m/z = 201$ and $m/z = 185$). Among them, some intermediates can be produced by the oxidation of other intermediates. For instance, $m/z = 230$ intermediates can be generated from $m/z = 250$, $m/z = 242$, $m/z = 203$ and $m/z = 185$ intermediates. Nine short-chain carboxylic acids were identified ($m/z = 239$, $m/z = 223$, $m/z = 178$, $m/z = 149$, $m/z = 118$, $m/z = 101$, $m/z = 90$, $m/z = 71$, $m/z = 45$). $m/z = 239$ can yield $m/z = 223$ and $m/z = 178$ intermediates by sequential oxidation. $m/z = 149$ can be oxidized to produce $m/z = 71$. $m/z = 118$ can be further oxidized to produce $m/z = 101$. $m/z = 90$ can be oxidized to produce $m/z = 45$. Finally, all intermediates might be gradually mineralized into CO_2 , H_2O and inorganic ions (Li et al., 2019).

394



Scheme 3. The possible degradation intermediates and pathways of TC in the EO-PS-EF system.

395
396

397 3.6 Application potential of EO-PS-EF system

398 3.6.1 Energy consumption

399 The electric energy efficiency of these AOPs (i.e., EO, EO-PS, EO-EF and EO-PS-EF) was evaluated based on the energy
 400 consumption per cubic meter of contaminant removal (EC, kWh m⁻³) according to reference (Wei et al., 2020). Under the power
 401 consumption of 1.65 kWh m⁻³, the TC removal of the EO, EO-PS, EO-EF and EO-PS-EF systems was 21%, 60%, 55%, and 100%,
 402 respectively (Fig. 7). For the fixed TC removal of 37%, the power consumption of EO, EO-PS, EO-EF and EO-PS-EF systems were
 403 calculated to be 3.04, 0.62, 0.75 and 0.17 kWh m⁻³, respectively. This result indicated that the EO-PS-EF coupling process
 404 provided significant advantages over other processes in terms of pollutant removal and energy consumption. Moreover, Table S5
 405 listed a comparison of the EO-PS-EF method with the reported AOPs for the degradation of TC, indicating that the proposed
 406 EO-PS-EF method exhibits significantly faster pollutant removal and lower energy consumption than other methods.

407
408
409

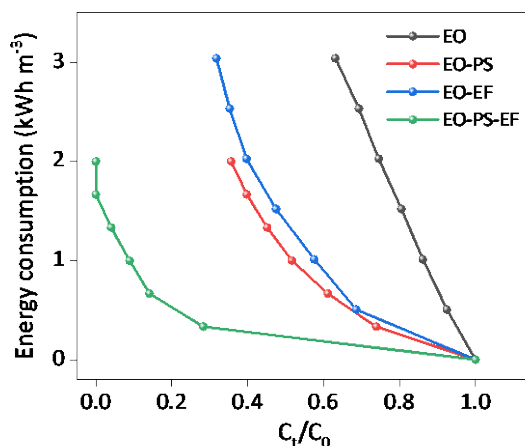


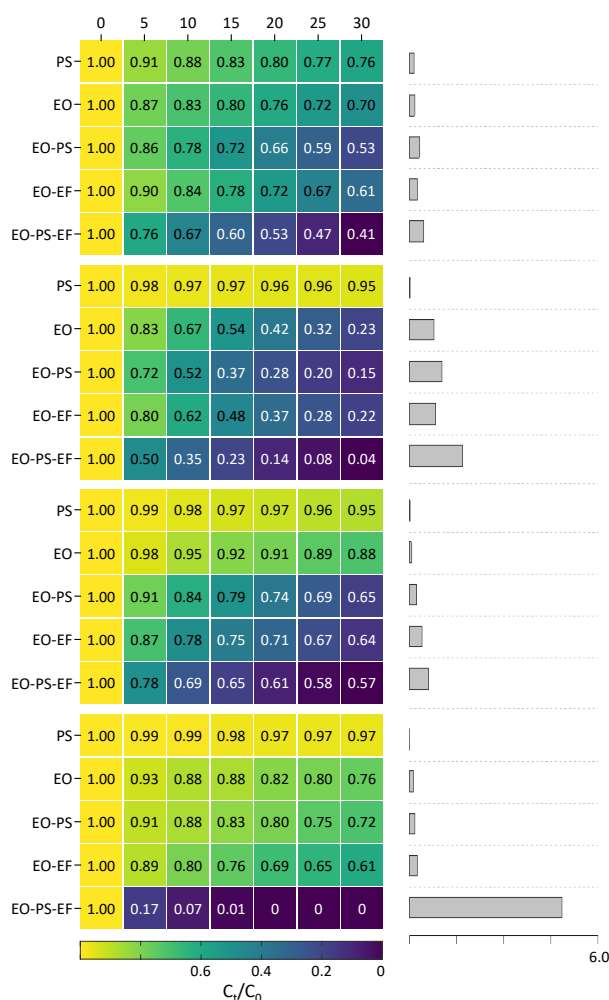
Fig. 7. Comparison of energy consumption related to TC removal rate collected from the EO, EO-PS, EO-EF and EO-PS-EF systems individually.

410 3.6.2 Long-term stability

411 The long-term stability of the EO-PS-EF system was considered via repetitive measurements up to 100 times to assess its
 412 possible practical applications. Fig. S4 shows repetitive TC removal results taken at the 1st, 25th, 50th, 75th and 100th run. With
 413 one-hundred repetitive measurements, the TC degradation performance of the EO-PS-EF tri-coupling system was almost kept
 414 unchangeable with only a 5% difference between all runs. In addition, no apparent changes were found in the surface mor-
 415 phologies, phase composition and potential windows of the BDD anode and GF cathode before and after the 100th degradation
 416 experiment (Fig. S5 and S6). The degradation tests and experimental observations demonstrated that the EO-PS-EF tri-coupling
 417 system had considerably long-term repetitive stability and could run for a quite long lifetime.

418 3.6.3 Selective degradation of RB-19, OG, ATZ and 2,4-D

419 Different structural refractory organic pollutants, including Azo dyes (RB-19 and OG) and organochlorine pesticides (ATZ
 420 and 2,4-D), were selected as target pollutants to assess the degradation performance of the EO-PS-EF system (see Fig. 8). Other
 421 single and bi-coupling systems were also compared including PS, EO, EO-EF and EO-PS. The degradation performance for Azo
 422 dyes (RB-19 and OG) are EO-PS-EF > EO-PS > EO-EF > EO > PS, while for organochlorine pesticides (ATZ and 2,4-D) it follows
 423 with EO-PS-EF > EO-EF > EO-PS > EO > PS. The comparative results indicate that the bi-coupling system exhibited higher degra-
 424 dation performance than the single system for all Azo dyes and organochlorine pesticides, while the EO-PS-EF significantly
 425 improved degradation performance than other single and bi-coupling systems, especially for OG and 2,4-D. The tri-coupling
 426 system exhibited exceptional selectivity for 2,4-D that was degraded entirely at around 15 min, with over five times the degra-
 427 dation performance of the other systems. The selectivity preference results from the pollutant structures. The degradation rate
 428 is 2,4-D > TC > OG > RB-19 > ATZ for the EO-PS-EF tri-coupling system. This provides an experimental database for the application
 429 of the EO-PS-EF system to treat various organic pollutants.



430 **Fig. 8.** Comparison of degradation performance of organic pollutants with the PS, EO, EO-PS, EO-EF and EO-PS-EF systems
 431 individually, including (a) RB-19, (b) OG, (c) ATZ and (d) 2,4-D. (e) Corresponding pseudo-first-order reaction rate constants.
 432

433 4 Conclusions

434 In summary, the EO-PS-EF tri-coupling system based on BDD anode and GF cathode was established for the first time,
 435 which efficiently removed pollutants by homogeneous and heterogeneous catalytic co-generation of $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$. Compared

436 with PS, EO, EO-PS and EO-EF systems, the EO-PS-EF system can significantly improve pollutant removal efficiency and reduce
437 energy consumption. Adjustment of PS concentration, Fe²⁺ concentration and air flow rate can optimize EO-PS-EF system per-
438 formance. NO₃⁻, SO₄²⁻, PO₄³⁻ and CO₃²⁻ had different degrees of inhibition on pollutant removal through radicals quenching and
439 electron consumption. However, Cl⁻ showed a significant promotion effect by generating highly reactive and selective RCS.
440 Besides, low pH and high temperature can facilitate the removal of contaminants. The possible coupling mechanisms and TC
441 degradation pathways of the EO-PS-EF system were revealed based on TC degradation rate constants, radical quenching, ESR
442 and LC-MS data. The high pollution removal efficiency, low energy consumption, long-term cycle stability, and efficient degra-
443 dation of various pollutants of the EO-PS-EF system demonstrated its potential for practical applications. This study developed
444 an economic, efficient and stable coupling process for removing various emerging pollutants and provided a theoretical basis
445 and experimental foundation for understanding the synergistic mechanism and designing new coupling processes.

446 Author Contributions

447 W. Yang: Investigation, Conceptualization, Writing - original draft, Writing - review & editing; Z. Deng: Conceptualization, Vali-
448 dation, Data Curation, Writing - original draft, Writing - review & editing; L. Liu: Resources, Supervision; K. Zhou: Analysis, Sug-
449 gestion, Resources; S. P. E: Suggestion, Resources; L. Meng: Suggestion, Resources; L. Ma: Resources, Supervision; Q. Wei:
450 Conceptualization, Resources, Funding acquisition, Supervision, Project administration.

451 Notes

452 The authors declare no competing financial interest.

453 Acknowledgments

454 We gratefully acknowledge the National Key Research and Development Program of China (No.2021YFB3701800), the
455 National Natural Science Foundation of China (No. 52202056, No. 52274370, No. 52071345, No. 51874370), the Province Key
456 Research and Development Program of Guangdong (No. 2020B010185001), the Province High-tech Industry Science and Tech-
457 nology Innovation Leading Plan of Hunan (No. 2022GK4037, No. 2022GK4047) and the Independent and Open projects of the
458 State Key Laboratory of Powder Metallurgy (No. 621022230) for financial support.

459 References

- 460 Arellano, M., Sanroman, M.A. and Pazos, M. 2019. Electro-assisted activation of peroxymonosulfate by iron-based minerals
461 for the degradation of 1-butyl-1-methylpyrrolidinium chloride. *Sep. Purif. Technol.* 208, 34-41.
- 462 Barhoumi, N., Olvera-Vargas, H., Oturan, N., Huguenot, D., Gadri, A., Ammar, S., Brillas, E. and Oturan, M.A. 2017. Kinetics of
463 oxidative degradation/mineralization pathways of the antibiotic tetracycline by the novel heterogeneous electro-Fenton
464 process with solid catalyst chalcopyrite. *Appl. Catal. B: Environ.* 209, 637-647.
- 465 Bu, L.J., Ding, J., Zhu, N.Y., Kong, M.H., Wu, Y.T., Shi, Z., Zhou, S.Q. and Dionysiou, D.D. 2019. Unraveling different mechanisms
466 of persulfate activation by graphite felt anode and cathode to destruct contaminants of emerging concern. *Appl. Catal. B:*
467 *Environ.* 253, 140-148.
- 468 Bu, L.J., Zhu, S.M. and Zhou, S.Q. 2018. Degradation of atrazine by electrochemically activated persulfate using BDD anode:
469 Role of radicals and influencing factors. *Chemosphere* 195, 236-244.
- 470 Cai, J., Niu, T., Shi, P. and Zhao, G. 2019a. Boron-Doped Diamond for Hydroxyl Radical and Sulfate Radical Anion
471 Electrogeneration, Transformation, and Voltage-Free Sustainable Oxidation. *Small* 15 (48), 1900153.
- 472 Cai, J.J., Zhou, M.H., Pan, Y.W., Du, X.D. and Lu, X.Y. 2019b. Extremely efficient electrochemical degradation of organic
473 pollutants with co-generation of hydroxyl and sulfate radicals on Blue-TiO₂ nanotubes anode. *Appl. Catal. B: Environ.* 257,
474 117902.
- 475 Chen, C.Y., Wu, Z.H., Hou, S.D., Wang, A.N. and Fang, J.Y. 2022. Transformation of gemfibrozil by the interaction of chloride
476 with sulfate radicals: Radical chemistry, transient intermediates and pathways. *Water Res.* 209, 117944.
- 477 Dihingia, H. and Tiwari, D. 2022. Impact and implications of nanocatalyst in the Fenton-like processes for remediation of
478 aquatic environment contaminated with micro-pollutants: A critical review. *J. Water Process Eng.* 45, 102500.
- 479 Ding, J., Bu, L.J., Zhao, Q.L., Kabutey, F.T., Wei, L.L. and Dionysiou, D.D. 2020. Electrochemical activation of persulfate on BDD
480 and DSA anodes: Electrolyte influence, kinetics and mechanisms in the degradation of bisphenol A. *J. Hazard. Mater.* 388,
481 121789.
- 482 Divyapriya, G. and Nidheesh, P.V. 2021. Electrochemically generated sulfate radicals by boron doped diamond and its
483 environmental applications. *Curr. Opin. Solid St. M.* 25 (3), 100921.
- 484 Du, X.D., Oturan, M.A., Zhou, M.H., Belkessa, N., Su, P., Cai, J.J., Trelu, P.E. and Mousset, E. 2021. Nanostructured electrodes
485 for electrocatalytic advanced oxidation processes: From materials preparation to mechanisms understanding and
486 wastewater treatment applications. *Appl. Catal. B: Environ.* 296, 120332.
- 487 Farhat, A., Keller, J., Tait, S. and Radjenovic, J. 2017. Assessment of the impact of chloride on the formation of chlorinated by-
488 products in the presence and absence of electrochemically activated sulfate. *Chem. Eng. J.* 330, 1265-1271.
- 489 Gabriel, G.V.D., Pitombo, L.M., Rosa, L.M.T., Navarrete, A.A., Botero, W.G., do Carmo, J.B. and de Oliveira, L.C. 2021. The
490 environmental importance of iron speciation in soils: evaluation of classic methodologies. *Environ. Monit. Assess.* 193 (2),
491 63.

492 Gao, H.Y., Huang, C.H., Mao, L., Shao, B., Shao, J., Yan, Z.Y., Tang, M. and Zhu, B.Z. 2020. First Direct and Unequivocal Electron
493 Spin Resonance Spin-Trapping Evidence for pH-Dependent Production of Hydroxyl Radicals from Sulfate Radicals. *Environ.*
494 *Sci. Technol.* 54 (21), 14046-14056.

495 Gao, L.W., Guo, Y., Zhan, J.H., Yu, G. and Wang, Y.J. 2022a. Assessment of the validity of the quenching method for evaluating
496 the role of reactive species in pollutant abatement during the persulfate-based process. *Water Res.* 221, 118730.

497 Gao, P., Ju, C., Tang, Z. and Qin, Y. 2022b. Enhanced adsorption of tetracycline on polypropylene and polyethylene
498 microplastics after anaerobically microbial-mediated aging process. *J. Hazard. Mater. Adv.* 6, 100075.

499 He, H.Q. and Zhou, Z. 2017. Electro-Fenton process for water and wastewater treatment. *Crit. Rev. Env. Sci. Tec.* 47 (21), 2100-
500 2131.

501 Hou, K.J., Pi, Z.J., Yao, F.B., Wu, B., He, L., Li, X.M., Wang, D.B., Dong, H.R. and Yang, Q. 2021. A critical review on the
502 mechanisms of persulfate activation by iron-based materials: Clarifying some ambiguity and controversies. *Chem. Eng. J.*
503 407, 127078.

504 Hu, J.J., Wang, S., Yu, J.Q., Nie, W.K., Sun, J. and Wang, S.B. 2021. Duet Fe₃C and FeN_x Sites for H₂O₂ Generation and Activation
505 toward Enhanced Electro-Fenton Performance in Wastewater Treatment, *Environ. Sci. Technol.* 55 (2), 1260-1269.

506 Huang, W.Q., Xiao, S., Zhong, H., Yan, M. and Yang, X. 2021. Activation of persulfates by carbonaceous materials: A review.
507 *Chem. Eng. J.* 418, 129297.

508 Johnson, A.C., Jin, X.W., Nakada, N. and Sumpter, J.P. 2020. Learning from the past and considering the future of chemicals in
509 the environment. *Science* 367 (6476), 384-387.

510 Lalliansanga, Tiwari, D., Lee, S.-M. and Kim, D.-J. 2022. Photocatalytic degradation of amoxicillin and tetracycline by template
511 synthesized nano-structured Ce³⁺@TiO₂ thin film catalyst, *Environ. Res.* 210, 112914.

512 Lee, J., von Gunten, U. and Kim, J.H. 2020. Persulfate-Based Advanced Oxidation: Critical Assessment of Opportunities and
513 Roadblocks. *Environ. Sci. Technol.* 54 (6), 3064-3081.

514 Li, Z.L., Guo, C.S., Lyu, J.C., Hu, Z. and Ge, M. 2019. Tetracycline degradation by persulfate activated with magnetic Cu/CuFe₂O₄
515 composite: Efficiency, stability, mechanism and degradation pathway. *J. Hazard. Mater.* 373, 85-96.

516 Liang, S.T., Lin, H., Yan, X.F. and Huang, Q.G. 2018. Electro-oxidation of tetracycline by a Magneli phase Ti₄O₇ porous anode:
517 Kinetics, products, and toxicity. *Chem. Eng. J.* 332, 628-636.

518 Lin, Y.H., Huo, P.F., Li, F.Y., Chen, X.M., Jiang, Y., Zhang, Y.F., Ni, B.J., Zhou, M.H. and Yang, L.Y. 2022. A critical review on
519 cathode modification methods for efficient Electro-Fenton degradation of persistent organic pollutants. *Chem. Eng. J.* 450,
520 137948.

521 Liu, C.F., Huang, C.P., Hu, C.C. and Huang, C.P. 2019. A dual TiO₂/Ti-stainless steel anode for the degradation of orange G in a
522 coupling photoelectrochemical and photo-electro-Fenton system. *Sci. Total Environ.* 659, 221-229.

523 Liu, M.Y., Feng, Z.Y., Luan, X.M., Chu, W.H., Zhao, H.Y. and Zhao, G.H. 2021a. Accelerated Fe²⁺ Regeneration in an Effective
524 Electro-Fenton Process by Boosting Internal Electron Transfer to a Nitrogen-Conjugated Fe(III) Complex. *Environ. Sci.*
525 *Technol.* 55 (9), 6042-6051.

526 Liu, Q.F., Li, L., Zhang, X.M., Saini, A., Li, W.L., Hung, H., Hao, C.Y., Li, K., Lee, P., Wentzell, J.J.B., Huo, C.Y., Li, S.M., Harner, T.
527 and Liggio, J. 2021b. Uncovering global-scale risks from commercial chemicals in air. *Nature* 600 (7889), 456-461.

528 Liu, Z., Zhao, C., Wang, P., Zheng, H.L., Sun, Y.J. and Dionysiou, D.D. 2018. Removal of carbamazepine in water by electro-
529 activated carbon fiber-peroxydisulfate: Comparison, optimization, recycle, and mechanism study. *Chem. Eng. J.* 343, 28-
530 36.

531 Lu, J., Hou, R., Wang, Y., Zhou, L. and Yuan, Y. 2022. Surfactant-sodium dodecyl sulfate enhanced degradation of polystyrene
532 microplastics with an energy-saving electrochemical advanced oxidation process (EAOP) strategy. *Water Res.* 226, 119277.

533 Nidheesh, P.V., Ganiyu, S.O., Martinez-Huitle, C.A., Mousset, E., Olvera-Vargas, H., Trellu, C., Zhou, M.H. and Oturan, M.A. 2022.
534 Recent advances in electro-Fenton process and its emerging applications. *Crit. Rev. Env. Sci. Tec.*

535 Oyekunle, D.T., Cai, J.Y., Gendy, E.A. and Chen, Z.Q. 2021. Impact of chloride ions on activated persulfates based advanced
536 oxidation process (AOPs): A mini review. *Chemosphere* 280, 130949.

537 Song, H.R., Yan, L.X., Jiang, J., Ma, J., Zhang, Z.X., Zhang, J.M., Liu, P.X. and Yang, T. 2018. Electrochemical activation of
538 persulfates at BDD anode: Radical or nonradical oxidation? *Water Res.* 128, 393-401.

539 Tian, K., Hu, L.M., Li, L.T., Zheng, Q.Z., Xin, Y.J. and Zhang, G.S. 2022. Recent advances in persulfate-based advanced oxidation
540 processes for organic wastewater treatment. *Chinese Chem. Lett.* 33 (10), 4461-4477.

541 Wang, B. and Wang, Y. 2022. A comprehensive review on persulfate activation treatment of wastewater. *Sci. Total Environ.*
542 831, 154906.

543 Wang, H., Yao, H., Sun, P.Z., Li, D.S. and Huang, C.H. 2016. Transformation of Tetracycline Antibiotics and Fe(II) and Fe(III)
544 Species Induced by Their Complexation. *Environ. Sci. Technol.* 50 (1), 145-153.

545 Wang, J.L. and Wang, S.Z. 2020. Reactive species in advanced oxidation processes: Formation, identification and reaction
546 mechanism. *Chem. Eng. J.* 401, 126158.

547 Wei, Q.P., Liu, G.S., Zhu, C.W., Zhou, B., Mei, R.Q., Ma, L., Zhang, L., Yang, W.L., Ye, W.T., Zhou, K.C. and Yu, Z.M. 2020. Ordered
548 structures with functional units (OSFU) enabled highly robust diamond anode for electrochemical decomposing of organic
549 pollutants. *Chem. Eng. J.* 397, 125465.

550 Xiao, S., Cheng, M., Zhong, H., Liu, Z.F., Liu, Y., Yang, X. and Liang, Q.H. 2020. Iron-mediated activation of persulfate and
551 peroxymonosulfate in both homogeneous and heterogeneous ways: A review. *Chem. Eng. J.* 384, 123265.

552 Xu, Y., Lin, H., Li, Y.K. and Zhang, H. 2017. The mechanism and efficiency of MnO₂ activated persulfate process coupled with
553 electrolysis. *Sci. Total Environ.* 609, 644-654.

554 Yang, J.L., Zhu, M.S. and Dionysiou, D.D. 2021. What is the role of light in persulfate-based advanced oxidation for water
555 treatment? *Water Res.* 189, 116627.

556 Yang, W.L., Deng, Z.J., Wang, Y.J., Ma, L., Zhou, K.C., Liu, L.B. and Wei, Q.P. 2022a. Porous boron-doped diamond for efficient
557 electrocatalytic elimination of azo dye Orange G. *Sep. Purif. Technol.* 293, 121100.

558 Yang, W.L., Tan, J.L., Chen, Y.H., Li, Z.S., Liu, F.M., Long, H.Y., Wei, Q.P., Liu, L.B., Ma, L., Zhou, K.C. and Yu, Z.M. 2022b.
559 Relationship between substrate type and BDD electrode structure, performance and antibiotic tetracycline mineralization.
560 *J. Alloy. Compd.* 890, 161760.

561 Zhang, P.Y., Zhang, X.F., Zhao, X.D., Jing, G.H. and Zhou, Z.M. 2022. Activation of peracetic acid with zero-valent iron for
562 tetracycline abatement: The role of Fe(II) complexation with tetracycline. *J. Hazard. Mater.* 424, 127653.

563 Zhang, W.W., He, Y.C., Li, C., Hu, X.X., Yang, S., You, X.Y. and Liang, W.Y. 2021. Persulfate activation using Co/AC particle
564 electrodes and synergistic effects on humic acid degradation. *Appl. Catal. B: Environ.* 285, 119848.

565 Zheng, N.C., He, X., Zhou, Q., Wang, R.L., Zhang, X.R., Hu, R.T. and Hu, Z.F. 2022. Generation of reactive chlorine species via
566 molecular oxygen activation on a copper chloride loaded hydrothermal carbonaceous carbon for advanced oxidation
567 process. *Appl. Catal. B: Environ.* 319, 121918.

568 Zhi, D., Lin, Y.H., Jiang, L., Zhou, Y.Y., Huang, A.Q., Yang, J. and Luo, L. 2020. Remediation of persistent organic pollutants in
569 aqueous systems by electrochemical activation of persulfates: A review. *J. Environ. Manage.* 260, 110125.

570 Zhu, C.Y., Zhu, F.X., Liu, C., Chen, N., Zhou, D.M., Fang, G.D. and Gao, J. 2018. Reductive Hexachloroethane Degradation by
571 $S_2O_8^{2-}$ with Thermal Activation of Persulfate under Anaerobic Conditions. *Environ. Sci. Technol.* 52 (15), 8548-8557.