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# Exploring the viability of peracetic acid-mediated antibiotic degradation in wastewater through activation with electrogenerated HClO



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#### ABSTRACT

Electrochemical advanced oxidation processes (EAOPs) face challenging conditions in chloride media, owing to the co-generation of undesirable Cl-disinfection byproducts (Cl-DBPs). Herein, the synergistic activation between in-situ electrogenerated HClO and peracetic acid (PAA)-based reactive species in actual wastewater is discussed. A metal-free graphene-modified graphite felt (graphene/GF) cathode is used for the first time to achieve the electrochemically-mediated activation of PAA. The PAA/Cl<sup>-</sup> system allowed a near-complete sulfamethoxazole (SMX) degradation ( $k_{obs} = 0.49 \text{ min}^{-1}$ ) in only 5 min in a model solution, inducing 32.7- and 8.2-fold rise in  $k_{obs}$  as compared to single PAA and Cl<sup>-</sup> systems, respectively. Such enhancement is attributed to the occurrence of  ${}^{1}O_{2}$  (25.5 µmol L<sup>-1</sup> after 5 min of electrolysis) from the thermodynamically favored reaction between HClO and PAA-based reactive species. The antibiotic degradation in a complex water matrix was further considered. The SMX removal is slightly susceptible to the coexisting natural organic matter, with both the acute cytotoxicity (ACT) and the yield of 12 DBPs decreasing by 29.4 % and 37.3 %, respectively. According to calculations, HClO accumulation and organic Cl-addition reactions are thermodynamically unfavored. This study provides a scenario-oriented paradigm for PAA-based electrochemical treatment technology, being particularly appealing for treating wastewater rich in Cl<sup>-</sup> ion, which may derive in toxic Cl-DBPs.

#### 1. Introduction

Due to their high oxidation ability (Ao et al., 2021), antibacterial activity (Cao et al., 2023), superior disinfection efficiency (Kim and Huang, 2021), and lower generation of halogenated disinfection byproducts (DBPs) (Shah et al., 2015), peracetic acid (PAA)-based advanced oxidation processes (AOPs) have become a research hotspot for the efficient treatment of antibiotics in wastewater (Ao et al., 2021; Dai et al., 2022b; Manoli et al., 2022; Miao et al., 2022). On the other hand, the electrochemically-assisted AOPs (i.e., EAOPs) have remarkable advantages such as simplicity for operation, eco-friendliness, and high efficiency. They also have the potential to activate various relatively mild oxidants such as hydrogen peroxide (Lin et al., 2016; Xia et al., 2023), persulfate (Tirira et al., 2023), and peracetic acid (PAA) (Lu et al., 2024; Yuan et al., 2021). The peroxide bond energy of PAA (159 kJ mol<sup>-1</sup>) is lower than that of peroxymonosulfate (317 kJ mol<sup>-1</sup>) and

hydrogen peroxide (213 kJ mol<sup>-1</sup>) (Kong et al., 2022; Zhang et al., 2022a), making PAA activation thermodynamically feasible. In PAA electro–activation, free radicals with prevalence of hydroxyl radicals (\*OH) and organic radicals (R-O\*) are generated by electron gain at the cathode rather than electron loss at the anode (Lu et al., 2024). Our previous findings suggest that PAA electro–activation tends to be more efficient than its equivalent non-electrochemical counterpart (Lu et al., 2024), thereby leading to a 10-fold reduction in required PAA dosage for complete drug removal (PAA/contaminant ratio  $\geq$  20:1 in some AOPs vs. 2:1 in our EAOP system) (Cheng et al., 2023; Li et al., 2021; Lin et al., 2021; Lu et al., 2024; Wang et al., 2021a). This is advantageous because the main limitation of PAA, which is the increased total organic carbon and biochemical oxygen demand, is drastically minimized in an electrochemical system (Shah et al., 2015).

To date, numerous studies have focused on the use of transition metals for PAA activation, including homogeneous (e.g., Ru(III) (Li

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et al., 2021), Co(II) (Du et al., 2022), Cu(II) (Wang et al., 2021a), Mn(II) (Rothbart et al., 2012), Fe(II) (Cheng et al., 2023; Kim et al., 2019; Lin et al., 2021), Fe(III) (Kim et al., 2022), and Fe(IV) (Manoli et al., 2022)) and heterogeneous (e.g., MnO<sub>2</sub> (Rokhina et al., 2013), CoFe<sub>2</sub>O<sub>4</sub> (Wang et al., 2021b), CuO (Zhang et al., 2022a), single-atom Fe-g-C<sub>3</sub>N<sub>4</sub> nanotubes (Chen et al., 2022)) catalysts. However, their practical application is rather limited due to high energy consumption and secondary pollution caused by unavoidable leaching (Ao et al., 2021; Kim et al., 2022, 2019). Carbonaceous catalysts are presumably more advantageous thanks to their unique chemical and thermal stability, cost-effectiveness and availability (Miao et al., 2022; Tian et al., 2023; Wu et al., 2022; Zhou et al., 2015). To our knowledge, there is little research on carbon-based PAA catalysts. Activated carbon fibers were first used to activate PAA, yielding <sup>•</sup>OH and R–O<sup>•</sup> that served for the removal of dyes (Zhou et al., 2015), drugs (Dai et al., 2022a), and p-chlorophenol (Wu et al., 2022). In electrochemical systems, only 'OH and two kinds of  $R-O^{\bullet}$  (i.e.,  $CH_3CO_2^{\bullet}$  and  $CH_3CO_3^{\bullet}$ ) have been detected when using a graphite plate (Yuan et al., 2021) or graphene-based material as the cathode (Lu et al., 2024). These studies revealed relatively low values of kinetic constants, thus requiring 20–30 min for completely degrade the organic contaminants under the action of radicals as sole reactive species. It is thus presumed that the performance of the PAA-based process could be significantly enhanced in the presence of nonradical oxidants (Kong et al., 2022; Miao et al., 2022; Wang et al., 2023), suggesting that the introduction of a nonradical process might be the key for enhancing the PAA-based EAOP.

As a typical nonradical,  ${}^{1}O_{2}$  with a high standard redox potential  $(E^0(^1O_2/H_2O) = 2.17 \text{ V vs. SHE})$  value possesses an unoccupied  $\pi^*$ orbital, resulting in high selectivity toward electron-rich substances (Wang et al., 2024). Moreover, long–lived diffusible <sup>1</sup>O<sub>2</sub> exhibits high tolerance to water matrices, thereby inhibiting the generation of toxic byproducts (Feng et al., 2023). In this context, the reaction between HClO and H<sub>2</sub>O<sub>2</sub> has been explored by several scholars, since it is an important source for the <sup>1</sup>O<sub>2</sub> production in EAOPs performed in chloride media (reaction (1)) (Chen et al., 2023; Liu et al., 2023; Shah et al., 2015). However, a major drawback of EAOPs is the rapid anodic oxidation of Cl<sup>-</sup> to free available chlorine (FAC, i.e., Cl<sub>2</sub>, HClO/ClO<sup>-</sup>) (reaction (2) and (3)) (Haider et al., 2023), which is considered to be responsible for the halogenation reaction to form Cl-DBPs (Liu et al., 2023). Given that Cl<sup>-</sup> is a major anion found in all natural waters, the formation of chlorinated byproducts represents a major challenge for the safe application of EAOPs. This means that, although the presence of Cl<sup>-</sup> accelerates the contaminants removal (Liu et al., 2023), it concomitantly increases the risk of generating Cl-DBPs in saline water (Lin et al., 2020; Radjenović et al., 2012; Sergienko et al., 2019).

 $HClO + H_2O_2 \rightarrow H^+ + Cl^- + {}^1O_2 + H_2O$ (1)

$$2\mathrm{Cl}^- \to \mathrm{Cl}_{2(\mathrm{aq})} + 2\mathrm{e}^- \tag{2}$$

 $E^0 = 1.36$  V vs standard hydrogen electrode (SHE)

$$Cl_{2(aq)} + H_2O \rightarrow HClO + Cl^- + H^+$$
 (3)

Some studies have reported that PAA–based AOP has a lower risk of DBPs generation (Ao et al., 2021; Miao et al., 2022; Shah et al., 2015; Wang et al., 2021b), but only limited information is available on their formation during PAA treatment. In EAOPs, the in-situ electrogenerated HClO can be rapidly consumed to produce  ${}^{1}O_{2}$  (reaction (1)). PAA solution is a mixture of PAA, H<sub>2</sub>O<sub>2</sub> and acetic acid, where H<sub>2</sub>O<sub>2</sub> reacts rapidly with HClO ( $k = 4.4 - 195.5 \times 10^{7} \text{ M}^{-1} \text{ s}^{-1}$ , depending on pH) (Lu et al., 2022). Shah et al.(2015) demonstrated that increasing the H<sub>2</sub>O<sub>2</sub> concentration until [PAA] < [H<sub>2</sub>O<sub>2</sub>] effectively reduced the steady–state concentration of HClO, reducing the Cl–DBPs accumulation. Unexpectedly, in our previous study on the PAA–based EAOP, the production of FAC and AOCl during the treatment of chlorinated antibiotic wastewater was decreased by 83.5 % and 82.7 %, respectively (Lu

et al., 2024), despite the small  $H_2O_2$  percentage in the PAA solution ([PAA]/[H<sub>2</sub>O<sub>2</sub>] = 3.125). This suggests not just  $H_2O_2$  can react with HClO, some other HClO–consuming reaction may exist. In fact, the mechanism is still a mystery, the current research does not go further on this processes, and the phenomenon we found needs to be well explained. Based on the above, we hypothesize that electrogenerated HClO could also be activated by PAA–based reactive species, yet it has never been studied before.

Herein, a new mechanism for the synergistic activation between PAA solution and electrogenerated HClO in chloride media is proposed. The kinetic and thermodynamic evidences are explored experimentally as well as via DFT calculations. A metal-free graphene–modified graphite felt (graphene/GF) cathode was used for the first time to achieve the electro–activation of PAA. The reactive species (radical and nonradical) and their concentrations in a PAA/Cl<sup>-</sup> electrochemical system are systematically studied, and the interaction between such species and chlorine is evaluated by analyzing DBPs and toxicity when treating simulated and actual Cl<sup>-</sup>-rich wastewater.

#### 2. Experimental

#### 2.1. Cathode synthesis and modification

Graphene/GF was synthesized by using a previously reported modified Hummer's method (Lu et al., 2023, 2024; Ma et al., 2020), which involved GF cleaning and pre-treatment, followed by its in-situ modification. The procedure is detailed in Text S1 of Supporting Information (SI).

#### 2.2. Reagents and experimental setup

PAA stock solution (2.5 M PAA + 0.8 M  $H_2O_2$  + 8.8 M acetic acid) was stored at 4 °C and prepared once a week (Lu et al., 2024). Simultaneous determination of PAA and  $H_2O_2$  was carried out using iodometric spectrophotometry (Xiao et al., 2019). The PAA solution preparation as well as the list of chemicals and reagents are provided in Text S2.

All experiments were conducted in a 100-mL undivided cylindrical glass cell equipped with a Hg/HgCl<sub>2</sub> reference electrode (S.C.E, model 150, CHI, China), whereas boron-doped diamond (BDD) and graphene/GF (1 cm  $\times$  3 cm) were used as the anode and cathode, respectively (Fig. S1a). A CHI660E electrochemical analyzer was set in potentiostatic mode. The electrolyte (20 mM NaCl) was always deaerated with argon to avoid cathodic competition between H<sub>2</sub>O<sub>2</sub> production via oxygen reduction reaction (ORR) and PAA activation. The experimental procedure in detail is described in Text S3.

#### 2.3. Characterization and analytical methods

Cyclic voltammetry (20 mV s<sup>-1</sup>) was carried out at room temperature using a CHI660E electrochemical analyzer with the same standard three–electrode configuration as that employed for the degradation experiments. Before voltammetric measurements, the open circuit potential was recorded for at least 10 min to achieve a steady state. Electrode characterization, analytical methods and computational details are found in Text S4–S14.

#### 3. Results and discussion

#### 3.1. Morphological and structural characterization

Graphene/GF was obtained by in-situ graphenization of GF (modified Hummer's method) (Lu et al., 2024; Ma et al., 2018). As shown in Fig. 1a, the pristine GF exhibited a well-developed woven carbon fiber structure with a clean and smooth surface. In contrast, a layer of lamellar structure was found on the surface of graphene-modified carbon fibers



**Fig. 1.** Morphology and characterization of GF and graphene/GF. SEM images of (a) pristine GF and (b) graphene/GF. (c) Raman spectra and  $I_D/I_G$  by calculating the area of the *D*- and *G*-bands. (d) XRD patterns. (e) FT-IR spectra. (f) XPS survey spectra. High resolution XPS spectra: (g) C 1s, (h) O 1s, and (i) N 1s.

with diameters ranging from 1 to 10 µm (Fig. 1b). Raman spectra demonstrate the graphenization of GF (Fig. 1c). The disordered band (D band,  $\sim 1351 \text{ cm}^{-1}$ ) aroused from amorphous carbon and edges, and in-plane vibrations of the graphite lattice (G band,  $\sim$ 1595 cm<sup>-1</sup>) were also found (Cui et al., 2022). Graphenization leads to a high degree of surface structural defects in graphene/GF, and the increased  $I_D/I_G$  (1.17 to 1.51) is evidenced, which is essential for enhanced electron transfer processes (Zhang et al., 2022). For graphene/GF, two peaks were observed at  $25.6^{\circ}$  and  $43.2^{\circ}$ , corresponding to the (002) and (100) planes of carbon with a typical graphene structure (Fig. 1d). In FT-IR spectra (Fig. 1e), the absorption peaks at 3393.1 and 2942.8  $\text{cm}^{-1}$  are related to the O- H and saturated C-H stretching vibrations, whereas the peaks at 1072.2 and 1537 cm<sup>-1</sup> represent the C-O and C=O vibrations. These results suggest a higher content of oxygen functional groups, as confirmed by XPS survey spectra (Fig. 1f). As shown in Fig. 1g, h, the graphene/GF surface is rich in oxygen functionalities,

especially C=O. Previous studies have used the ratio of the C—O to C=O groups as the indicators of the catalytic activity for PAA activation (Dai et al., 2022a), which indirectly proves that functional groups can participate in PAA activation. Moreover, nitrogen was successfully introduced on the graphene/GF surface (Fig. 1i); the high content of pyridinic–N and pyrrolic–N at defective sites are expected to contribute to remarkable electrochemical activity (Yang et al., 2018), showing great potential to activate PAA rapidly. The long-term stability of the electrodes is verified (Fig. S1b).

## 3.2. Reactive species generation during the PAA electro–activation in ${\it Cl}^-$ media

The electrochemical performance and reaction mechanism in the PAA/Cl<sup>-</sup> system were evaluated based on the formation of reactive oxygen species (ROS) and the degradation of SMX. Through detailed

batch experiments, for the fastest SMX removal, the main operation parameters were optimized, as discussed in detail in Text S15 and Fig. S3, S4, yielding the following values: cathode potential of -1.0 V vs. SCE, solution pH 3.0, and  $[NaCl]_0/[PAA]_0 = 400$ . In Fig. 2a, b, it can be seen that SMX was barely degraded by PAA/Cl<sup>-</sup> alone and PAA/SO<sub>4</sub><sup>2-</sup> alone without current supply. The electrolytic trials enhanced the SMX degradation, but the SMX degradation kinetics of <sup>•</sup>OH produced by BDD anode is slow (electrolysis in sulfate medium yielded  $k_{obs} = 0.00801$ min<sup>-1</sup>). Fig. S5 confirms that PAA can be electro-activated by graphene/ GF, but the cathode potential cannot be excessively negative because H<sub>2</sub> bubble formation (Fig. S6) would be detrimental. As depicted in Fig. 2a, b, the presence of Cl<sup>-</sup> accelerated the SMX degradation, owing to the rapid oxidation of Cl<sup>-</sup> at BDD (reaction (4)), thereby undergoing a series of chain reactions to produce active chlorine species and chlorine oxyanions (Lin et al., 2020; Mascia et al., 2010). The removal was significantly accelerated when PAA was present ( $k_{obs} = 0.49 \text{ min}^{-1}$ ). The degree of interaction between electrolysis, PAA and Cl<sup>-</sup> was quantified by calculating the synergy index (S) (eq. (S5)) (Ren et al., 2022). The results showed that  $S_{PAA/Cl}^-$  was 58.6, which exceeded the sum of  $S_{PAA}$ (1.8) and  $S_{Cl}^-$  (6.9); as a result, the PAA/Cl<sup>-</sup> system exhibited a 32.7and 8.2-fold rise in  $k_{\rm obs}$  as compared to single PAA and Cl<sup>-</sup> systems (Fig. 2b), confirming the great contribution of PAA during the treatment of Cl-containing solutions. The high performance of the PAA/Clelectrochemical system for degrading other typical contaminants (naproxen, ibuprofen, and ciprofloxacin) was corroborated (Fig. S7) (Lu et al., 2024).

$$\text{Cl}^- \rightarrow \text{HClO}/\text{ClO}^- \rightarrow \text{ClO}_2^- \rightarrow \text{ClO}_2^- \rightarrow \text{ClO}_3^- \rightarrow \text{ClO}_4^-$$
 (4)

A range of quenchers was used to clarify the contribution of ROS (Fig. S2a and S2d). Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> serves to remove all reactive species. MeOH ( $k_{MeOH}$ ,  $_{OH} = (1.2 - 2.8) \times 10^{9} M^{-1} s^{-1}$ ) and 2,4–HD ( $k_{2,4-HD}$ ,  $_{OH} = 1 \times 10^{10} M^{-1} s^{-1}$ ;  $k_{2,4-HD}$ ,  $_{CH3CO3\bullet} > 5 \times 10^{8} M^{-1} s^{-1}$ ) (Chen et al., 2022) can quickly quench <sup>•</sup>OH and R–O<sup>•</sup>, whereas tertiary butyl alcohol (TBA) reacts with <sup>•</sup>OH ( $k_{TBA}$ ,  $_{OH} = (3.3 - 7.6) \times 10^{8} M^{-1} s^{-1}$ ) at a much greater rate as compared to R–O<sup>•</sup> due to the absence of  $\alpha$ -H in TBA molecule (Zhang et al., 2022a, 2024), so they can be used to distinguish <sup>•</sup>OH and R–O<sup>•</sup>. In addition, CH<sub>3</sub>CO<sup>•</sup><sub>3</sub> is considered to be the most

important R–O<sup>•</sup> in PAA–based AOP (Ao et al., 2021; Kim and Huang, 2021), and Mn<sup>2+</sup> was proved to be its selective quencher (Zhang et al., 2022a). Due to the error caused by the direct reaction of furfuryl alcohol (FFA) with PAA (Wu et al., 2023), *L*–histidine was selected to certified the exist of <sup>1</sup>O<sub>2</sub> ( $k_1$  (<sup>1</sup>O<sub>2</sub>/*L*–histidine =  $3.2 \times 10^8$  M<sup>-1</sup> s<sup>-1</sup>);  $k_2$  (<sup>•</sup>OH/L–histidine =  $5.0 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>)) by comparing the masking amount of l-histidine and TBA (Chen et al., 2023), while (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> is used to quench HClO (*k* (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>/HClO =  $10^4$ – $10^5$  M<sup>-1</sup> s<sup>-1</sup>) (Liu et al., 2023). Fig. 2d, e show that electron paramagnetic resonance (EPR) spectra without quenchers exhibit a triplet peak signal (1:1:1,  $\alpha$ N = 16.9 G, g = 2.0054) from TEMP–<sup>1</sup>O<sub>2</sub> and a quadruplet (1:2:2:1,  $\alpha$ N =  $\alpha$ H = 14.9 G, g = 2.0068) from DMPO–•OH. Note that high PAA at high concentrations (> 200 µM) may react with TEMP, resulting in an overestimated EPR signal intensity (Wu et al., 2023), but this source of error was negligible in this study because of the lower PAA contents.

In the PAA/Cl<sup>-</sup> system, no DMPO-<sup>•</sup>OH signal was detected with excess MeOH, 2,4–HD and TBA, while the signal of  $\text{TEMP}^{-1}\text{O}_2$  was always observed (Fig. 2e). And SMX removal could not be completely quenched in these 3 groups (Fig.S2a and S2b), which means that <sup>•</sup>OH is not the only reason for SMX removal. The presence of <sup>1</sup>O<sub>2</sub> in the PAA/Clsystem can be revealed by comparing the SMX removal inhibited by L-histidine and TBA (Fig. S2a and S2b). The decrease in SMX removal with excess  $(NH_4)_2SO_4$  was close to the  ${}^1O_2$  quenching result achieved by comparing L-histidine and TBA. Moreover, no  $\text{TEMP}^{-1}\text{O}_2$  was detected with excess (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, suggesting that the disappear of HClO leading a very low  ${}^{1}O_{2}$  production. The Mn<sup>2+</sup> for quenching CH<sub>3</sub>CO<sub>3</sub> showed a minor influence on SMX removal (Fig. S2a), and no DMPO-R-O<sup>•</sup> signal was detected when HClO was accumulated (i.e., trials without (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>). These results meaning that when PAA and Cl<sup>-</sup> exist in electrochemical system, R- O<sup>•</sup> shows little SMX removal because of the potential consumption of R-O<sup>•</sup>/PAA by HClO. In contrast to PAA-based AOP reports (Dai et al., 2022a; Wu et al., 2022; Yuan et al., 2021; Zhou et al., 2015) and our previous results (Lu et al., 2024), FAC, OH and <sup>1</sup>O<sub>2</sub> appear as the dominant ROS in the PAA/Cl<sup>-</sup> electrochemical system, instead of <sup>•</sup>OH and R-O<sup>•</sup> (Text S17). Specifically, the H<sub>2</sub>O<sub>2</sub> present in PAA solution reacts with HClO at a high rate (reaction (1)) (Chen et al., 2023; Liu et al., 2023; Shah et al., 2015). Comparisons of FAC accumulation in PAA, H<sub>2</sub>O<sub>2</sub> and acetic acid solution



Fig. 2. Performance and reactive species in the PAA/Cl<sup>-</sup> electrochemical system. (a) Normalized SMX concentration decays, and (b) comparison of observed rate constants ( $k_{obs}$ ) under different experiment conditions. (c) Quantitative determination of the <sup>•</sup>OH and <sup>1</sup>O<sub>2</sub> concentrations. (d,e) EPR spectra found using different scavengers in the PAA/Cl<sup>-</sup> electrochemical system at 5 min of electrolysis. Experimental conditions:  $[NaCl]_0 = [Na_2SO_4]_0 = 20 \text{ mM}$ ,  $[PAA]_0 = 50 \mu M$ ,  $[SMX]_0 = 25 \mu M$ ,  $[Mn^{2+}]_0 = 10 \text{ mM}$ ,  $[TBA]_0 = [MeOH]_0 = [2,4-HD]_0 = [L-Histidine]_0 = [(NH_4)_2SO_4]_0 = [Na_2S_2O_3]_0 = 50 \text{ mM}$ , cathodic potential of -1.0 V vs. SCE, initial pH 3.0  $\pm$  0.1, argon atmosphere.

revealed that the HClO does not consume acetic acid, but PAA and H<sub>2</sub>O<sub>2</sub> cause a strong decrease (especially PAA) in accumulated HClO concentration (Fig. S8). This result means, H<sub>2</sub>O<sub>2</sub>, which has been reported (Feng et al., 2023; Lu et al., 2022; Shah et al., 2015) is not the only HClO consumption factor in the PAA/Cl<sup>-</sup> system. From a thermodynamic standpoint, PAA as well as CH<sub>3</sub>CO<sub>3</sub><sup>•</sup> have the potential to react with HClO and yield  ${}^{1}O_{2}$  (reaction (5) and (6)) ( $E^{0}({}^{\bullet}OH) = 2.8 \text{ V vs. SHE}, E^{0}(H_{2}O_{2})$ = 1.78 V vs. SHE,  $E^{0}(PAA) = 1.96$  V vs. SHE,  $E^{0}(CH_{3}CO_{3}^{\bullet}) = 1.6$  V vs. SHE) (Kim et al., 2020). Indeed, this have been verified to be thermodynamically spontaneous (see DFT calculations below), leading to a <sup>1</sup>O<sub>2</sub> production in the PAA/Cl- system. According to quantitative EPR spectrometry (Eaton et al., 2010), the cumulative <sup>1</sup>O<sub>2</sub> concentration was rapidly increased to 25.52  $\mu$ mol L<sup>-1</sup> after 5 min (Fig. 2c). The <sup>1</sup>O<sub>2</sub> production rate herein was up to 5.1  $\mu$ mol L<sup>-1</sup> min<sup>-1</sup>, which is 1.16–1.55 times compared to H<sub>2</sub>O<sub>2</sub> activation rate (Zhang et al., 2021; Zhao and Zhao, 2019). Note that the  ${}^{1}O_{2}$  measured concentration is the value after its quenching by H<sub>2</sub>O.

 $HClO + CH_3CO(O)O^{\bullet} \rightarrow Cl^- + {}^1O_2 + CH_3COOH$ (5)

$$HClO + CH_3CO(O)OH \rightarrow HCl + {}^{1}O_2 + CH_3COOH$$
(6)

To give firm evidence for  ${}^{1}O_{2}$  contribution, solvent-dependent experiments (from pure H<sub>2</sub>O to pure D<sub>2</sub>O) were performed, expecting to extend the  ${}^{1}O_{2}$  lifetime in D<sub>2</sub>O (Wu et al., 2023). Increasing the D<sub>2</sub>O volume ratio in the medium significantly accelerated the SMX degradation in the PAA/Cl<sup>-</sup> system (Fig. S9a). In 100 % D<sub>2</sub>O, leads to a

2.53–fold rise in  $k_{obs}$  as compared to 100 % H<sub>2</sub>O (Fig. S9b), which is similar to some reports (Huang et al., 2022; Luo et al., 2019). Notably, as calculated according to the study by Jiang et al. (2017), the elevation of  $k_{obs}$  in 100 % D<sub>2</sub>O is not sufficient to demonstrate that degradation is exclusively attributable to <sup>1</sup>O<sub>2</sub>, suggesting that <sup>•</sup>OH produced by the BDD anode as well as FAC are also non-negligible factors for SMX removal.

Additionally, Fukui index of SMX was calculated to predict ROS attack (reactions (S6–S8)). As a result (Fig. S2c), the sulfonamide and aniline groups of SMX are most susceptible to radical ( $^{\circ}$ OH) and electrophilic ( $^{1}O_{2}$ ) attack, which is consistent with the reported degradation mechanism of SMX (Lu et al., 2024; Xie et al., 2023; Zhang et al., 2023). Note that in PAA/Cl<sup>-</sup> system, chlorine radicals can lead to a Cl–addition reaction that generates organochlorine products, which typically lead to an increase in toxicity (Jasper et al., 2017; Lin et al., 2020; Lu et al., 2023; Sergienko et al., 2019). Therefore, their accumulation in Cl<sup>-</sup> media must be carefully assessed.

#### 3.3. Reduced production of inorganic chlorine products

The reaction rate constant of Cl<sup>-</sup> with PAA is low (reaction (7), 1.47  $\times 10^{-5}$  M<sup>-1</sup> s<sup>-1</sup>) and hence (Farinelli et al., 2022), the FAC produced in this study was mainly attributed to anodic oxidation (reaction (2) and (3)). Note that the cathodic potential is used here to precisely control the PAA electro-activation, because the anodic chlorine evolution potential of BDD is low and HClO can be readily produced (Norra and Radjenovic,



Fig. 3. Reduced production of inorganic chlorine in the PAA/Cl<sup>-</sup> electrochemical system. Concentration of (a) FAC and (b) total chlorine (TC, sum of FAC and combined chlorine) over time at different cathode potential. (c) Comparison of FAC and TC production with/without PAA. (d) CV curves to show Cl<sup>-</sup> oxidation. (e) UV/Vis spectra of HClO. (f) Comparison of Cl<sup>-</sup> evolution and ClO<sub>3</sub><sup>-</sup> and ClO<sub>4</sub><sup>-</sup> production with/without PAA. (g) Acute cytotoxicity, (h) TOC values, and (i) SMX concentration decays during electrolysis in different media. Experimental conditions: [NaCl]<sub>0</sub> = 20 mM, [PAA]<sub>0</sub> = 50  $\mu$ M, [SMX]<sub>0</sub> = 25  $\mu$ M, cathodic potential of -1.0 V vs. SCE, initial pH 3.0  $\pm$  0.1, argon atmosphere.

2021). Normally, the electrochemical production of FAC and TC in Cl<sup>-</sup> media increases continuously at greater applied potential or current (Lin et al., 2020; Luna-Trujillo et al., 2020; Norra et al., 2022; Norra and Radjenovic, 2021), but in the presence of PAA, their accumulation was reduced to varying degrees (Fig. 3a–c). In particular, a larger cathode potential from -0.2 V to -1.0 V vs. SCE reduced the concentration of FAC and TC by 74.6 % and 77.3 %, respectively, whereas a more negative value (-1.4 V vs. SCE) failed to achive further concentration decay of FAC (18.4 %) and TC (16.5 %) (Fig. 3c). This means that an excessively negative potential is detrimental to PAA activation (Text S15) (Lu et al., 2024), allowing a weak consumption of the electrogenerated HClO, which also agreed well with the  ${}^{1}O_{2}$  analysis (Fig. S2a–f). In addition, Cl<sup>-</sup> led to an oxidation current at the anode (Fig. 3d), which was attenuated after the addition of PAA.

$$CH_{3}CO(0)OH + Cl^{-} \rightarrow CH_{3}COOH + ClO^{-}$$
(7)

Due to the high toxicity of HClO on *Vibrio fischeri*,  $Na_2S_2O_3$  was chosen to remove HClO from samples for acute cytotoxicity test (ACT, Text S12) (Lu et al., 2023, 2024). UV/Vis spectra of the samples from electrolytic trials at -1.0 V vs. SCE show the attenuation of the absorption peak of HClO/ClO<sup>-</sup> in the presence of PAA (Fig. 3e, without  $Na_2S_2O_3$ ), which led to a more rapid reduction of ACT during SMX degradation (Fig. 3g, with  $Na_2S_2O_3$ ). Although PAA introduces TOC

(2.625 mg L<sup>-1</sup> at 50  $\mu$ M PAA), the PAA/Cl<sup>-</sup> system achieved 90.2 % TOC removal (Fig. 3h). Notably, when SMX was completely degraded (Fig. 3i, 6 min), PAA was depleted as the electrolysis time increased, leading to the accumulation of inorganic halogenation products that could not be removed by Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (Fig. 3f, ClO<sub>x</sub><sup>-</sup>, x = 2 - 4 or organochlorides), and thus a rise in ACT occurred (Fig. 3g).

HClO is a key precursor for the formation of chlorate  $(ClO_3^-)$  and perchlorate  $(ClO_4^-)$  from chlorine oxidation (reaction (4)), and the low potentials cannot avoid their accumulation (Norra and Radjenovic, 2021). Especially in the case of high oxidation power anodes like BDD,  $Cl^-$  is gradually oxidized. As shown in Fig. 3f,  $ClO_3^-$  and  $ClO_4^-$  were measured in concentrations up to 0.092 and 0.031 mM without PAA, and 0.054 and 0.021 mM in PAA/Cl<sup>-</sup> system. Note that the decrease in the concentration of  $Cl^-$  is much greater than the equivalent concentration as inorganic chlorine, suggesting that some organochlorine is also generated.

### 3.4. Degradation of SMX and reduced production of organochlorine products

The UV/Vis spectra of solutions were recorded during electrolysis (Fig. S10), and the typical UV indicators were calculated (Table S1 and S2). The results showed that the  $UV_{269}$  signal, related to the SMX



**Fig. 4. Degradation products and toxicity evolution.** Structures of SMX and products, and proposed degradation pathways in (a) PAA/Cl<sup>-</sup> and (b) Cl<sup>-</sup> electrochemical systems, where [O] is an oxidation reaction. (c) Acute toxicity to *Fathead minnow*, (d) growth inhibition, and (e) bioaccumulation factor of SMX degradation products in PAA/Cl<sup>-</sup> and Cl<sup>-</sup> electrochemical systems. Experimental conditions:  $[NaCl]_0 = 20 \text{ mM}$ ,  $[PAA]_0 = 50 \text{ }\mu\text{M}$ ,  $[SMX]_0 = 25 \text{ }\mu\text{M}$ , cathode potential of -1.0 V vs. SCE, initial pH 3.0  $\pm$  0.1, argon atmosphere.

structure (some transition products may overlap), as well the indicators related to C=O\C=C and the substituents ( $E_{265}/E_{465}$  and  $E_{253}/E_{203}$ ) decreased, and the benzene ring was gradually opened ( $A_{200-300}$  decreased, especially in PAA/Cl<sup>-</sup> system). To investigate the different degradation pathways in both Cl<sup>-</sup> media, the evolution of transformation products (TPs) was examined using LC–MS (Fig. S11–S13) and SPME–GC/MS (Table S3 and S4). As shown in Fig. 4a and 3b, as well as in the list of initial oxidation products (Fig. S14, Table S5), the following three reaction routes can be distinguished: (i) Cl–addition reaction (TP<sub>m/z</sub> 286.01), (ii) *H*–abstraction reaction (TP<sub>m/z</sub> 172.01). The three pathways are identified in the PAA/Cl<sup>-</sup> system, but only two in Cl<sup>-</sup> medium (Fig. 4a, b). A detailed analysis of the degradation pathways is presented in Text S18. Overall, with PAA, SMX is oxidized mainly through *H*–abstraction reaction and sulfonamide cleavage. Without

PAA, more chlorinated products are obtained: chloro–SMX ( $TP_{m/z}$  <sub>286.01</sub>), dichloro–SMX ( $TP_{m/z}$  <sub>319.97</sub>), and dichlorohydroquinone ( $TP_{m/z}$  <sub>176.95</sub>). The SPME–GC/MS results (Table S3 and S4) show that PAA resulted in a reduction of organochlorine products, while smaller molecules of organochlorine products were found in the absence of PAA (retention times of 18.69, 20.05, and 35.1 min; Table S4).

Organochlorine products are expected to contribute to effluent toxicity and hence, the acute toxicity, developmental toxicity, and bioaccumulation factor of SMX and its products were evaluated using toxicity estimation software tool (T.E.S.T., Text S8), based on quantitative structure–activity relationship (QSAR) prediction. As a result, most of the TPs from the PAA/Cl<sup>-</sup> system were in the "not harmful" region (Fig. 4c–e), whereas those from Cl<sup>-</sup> medium were harmful, toxic and even "very toxic", which is mainly due to organochlorine products. As mentioned above, PAA could not completely impede the



**Fig. 5.** Mechanistic study of SMX degradation and synergistic activation between PAA and HClO. (a) Molecular orbital energies of  ${}^{\circ}$ OH,  ${}^{1}O_{2}$ , SMX and the oxidation products from Cl–addition reaction, *H*–abstraction reaction, and sulfonamide group cleavage. Blue and red lines account for HOMO and LUMO energy levels, respectively. (b) The Gibbs free energy profile of the dominant reactions for SMX oxidation. (c) Schematic Gibbs free energy diagram for the synergistic activation between PAA and HClO.

accumulation of organochlorine products (Fig. 4a), but avoided presence of dichloro–SMX and dichlorohydroquinone. Their acute toxicity to *Fathead minnow* and growth inhibition of *T. pyriformis* reached "very toxic" levels, and had a higher bioaccumulation factor. This means that the addition of PAA in  $Cl^-$  media can reduce the production of organochlorine products and hence, their potential toxicity. This conclusion is supported by the changes in ACT values (Fig. 3g).

#### 3.5. Mechanistic study

Theoretical approaches were used to elucidate the reaction mechanisms for the above experiments. Specific models are proposed for the three reaction pathways (Fig. S14): (i) Cl–addition reaction (INT1 and INT2), (ii) H–abstraction reaction (INT3), and (iii) sulfonamide group cleavage (INT4–INT7). The highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO), and the Gibbs free energy of the reactions were calculated in gas phase at B3LYP (Becke, 1993)/6 – 31G(d) (Hehre et al., 1972) level of theory at 298.15 K and 1 atm with Grimme's D3 dispersion correction (Text S14) (Grimme et al., 2010). Note that the radicals and nonradicals in the reaction mechanism are proposed based on the previous studies (Du et al., 2022; Feng et al., 2023; Haider et al., 2023; Kong et al., 2022) and the experimental results of this study.

Electrophilic reactions usually occur by electron transfer from the pollutant HOMO to the ROS LUMO, whereas nucleophilic reactions do the opposite (Kong et al., 2022). The HOMO–LUMO gap informs about the electron transfer capacity in a given system (Feng et al., 2023; Kong et al., 2022; Zhang et al., 2022b). As shown in Fig. 5a and S13, the narrow HOMO–LUMO gap suggests that °OH and <sup>1</sup>O<sub>2</sub> thermodynamically favor electrophilic rather than nucleophilic attack. The gaps of SMX<sub>HOMO</sub> (-1.47 eV) with <sup>1</sup>O<sub>2,LUMO</sub> (-4.88 eV) and °OH<sub>LUMO</sub> (1.88 eV) are 3.41 eV and 3.35 eV, respectively, which suggests that both are thermodynamically favored for electrophilic attack. In addition, the HOMO–LUMO gaps between <sup>1</sup>O<sub>2</sub> and the initial TPs (i.e., 0.01-3.33 eV) are all smaller than those of °OH (i.e., 3.43-7.15 eV), suggesting that the attack of <sup>1</sup>O<sub>2</sub> is much more favorable for further mineralization. Similar conclusions can be drawn considering a nucleophilic attack (Fig. S15, Text S19) (Wang et al., 2024).

Fig. 5b shows the Gibbs free energy ( $\Delta G$ ) profile of the dominant reactions for SMX oxidation, which can add further insights from a thermodynamic viewpoint. Among the three reaction mechanisms, only the sulfonamide group cleavage via <sup>•</sup>OH and the H-abstraction reaction via  ${}^{1}O_{2}$  have negative  $\Delta G$ , implying that they are spontaneous reactions. This is confirmed in Fig. S14. This justifies why the thermodynamically unfavored Cl-addition reaction products are rarely detected in the PAA/Cl<sup>-</sup> system. Notably, three reaction steps from HClO to  ${}^{1}O_{2}$  are downhill in  $\Delta G$  (reaction (1), (5) and (6), Fig. 5c), with the following free energy changes:  $\Delta G$ -CH<sub>3</sub>CO(O)O<sup>•</sup> (-2.41 eV),  $\Delta G$ -H<sub>2</sub>O<sub>2</sub> (-2.95 eV), and  $\Delta G$ -CH<sub>3</sub>CO(O)OH (-3.12 eV), which means that all the activation pathways are favored in the PAA/Cl<sup>-</sup> system. In summary, electrogenerated HClO, which is thought to be critical in leading to Cl-addition reaction (Norra et al., 2022; Norra and Radjenovic, 2021), produces <sup>1</sup>O<sub>2</sub> through synergistic activation with the PAA solution (i.e., H<sub>2</sub>O<sub>2</sub>, CH<sub>3</sub>CO(O)O<sup>•</sup>, and CH<sub>3</sub>CO(O)OH). Moreover, owing to the  $\Delta G >$ 0 of Cl-addition reaction, the production of organochlorine products is thermodynamically impeded. The overall DFT observations prove that the introduction of PAA for the electrochemical treatment of organics in Cl<sup>-</sup> media boosts <sup>1</sup>O<sub>2</sub> and reduces the chlorine byproducts, which agree perfectly with experimental evidences.

### 3.6. Treatment of actual chlorinated antibiotic wastewater and toxicity assessment

To examine the resilience of the PAA/Cl<sup>-</sup> electrochemical system in complex water matrices, the performance and the accumulation of DBPs was investigated using actual urban wastewater containing inorganic ions and dissolved organic matter (DOM), with SMX spiked at a concentration of 25  $\mu$ M. For actual application, the pH of wastewater has not been adjusted (initial pH: 6.9  $\pm$  0.1). The changes of water quality parameters (COD, TOC, TON, AOCl, etc.) are summarized in Table S6. From Fig. 6a, b, it is evident that PAA accelerates SMX and TOC removal in this complex water matrix. Compared to simulated solutions, the  $k_{obs}$ for SMX and TOC removal declined by 8.2 % and 73.1 %, respectively, when treating actual wastewater, suggesting that although  ${}^{1}O_{2}$  is highly selective for SMX removal, DOM content affects the mineralization efficiency. In the presence of PAA, the ACT decreased by 29.4% and reached a minimum with complete SMX removal.

Up to 12 DBPs were identified during the electrolysis, including trichloromethane (TCM), trichloroacetonitrile (TCAN), bromodichloromethane (BDCM), chloral hydrate (CH), dichloroacetonitrile (DCAN), 11-dichloro-2-propanone (DCP), trichloronitromethane (TCNM), dibromochloromethane (DBCM), bromochloroacetonitrile (BCAN), 1,1,1-trichloroacetone (TCP), tribromomethane (TBM), and dibromoacetonitrile (BDAN) (Fig. 6c and 6d). In comparison, the total concentration of DBPs decreased by 37.3 % in the presence of PAA, with special reduction in the Cl-DBPs yield. Interestingly, the cytotoxicity and DBPs concentration in the PAA/Cl<sup>-</sup> system increase as the PAA solution is consumed during the extended electrolysis time, which is not conducive to obtaining a low-risk effluent. Note that haloacetic acids (HAAs) were not considered in detail because of the low PAA dosing and the fact that the ACT of HAAs for several target microorganisms was in general one order of magnitude lower than that of most of the 12 DBPs identified (Table S7 and Fig. S18).

Notably, TN in this study mainly consisted of NH<sup>+</sup><sub>4</sub>–N, and the N–H bond has a high reactivity with FAC, which is usually removed quickly in electrolytic trials in Cl<sup>-</sup> media (Lu et al., 2023, 2024) (Table S6). Furthermore, the organic substances removal was evaluated by UV/Vis spectrophotometry, HPLC and fluorescence analysis (3D–EEM). In the PAA/Cl<sup>-</sup> system, the peak at 269 nm associated with antibiotics was quickly removed (Fig. S16), as confirmed in the chromatograms of Fig. S17. In 3D–EEM (Fig. 6e-h), a rapid removal of fluorescent organics can be observed. In particular, the transformation of fluorescent organics (from region IV to region I, II, III, V) was poorer without PAA, which was manifested by the lower TOC removal (58.6 %<sub>without PAA</sub> < 88.0 % with PAA).

#### 4. Conclusions

Developing a PAA-based system with robust and detoxifying ability in actual Cl<sup>-</sup> media, whose advanced treatment by <sup>•</sup>OH-based AOPs may be dangerous due to the potential production of HClO and its tendency to accumulate Cl-DBPs, is of great interest for water decontamination. Here, a new strategy for boosting <sup>1</sup>O<sub>2</sub> production via synergistic activation between PAA and electrogenerated HClO is described. High oxidation effectiveness in simulated wastewater is attributed to the concomitance of both radical (<sup>•</sup>OH) and nonradical (<sup>1</sup>O<sub>2</sub>) mechanisms. In the PAA/Cl<sup>-</sup> system, a low accumulation of HClO/ClO<sup>-</sup> and Cl-DBPs is found, which depends strongly on the synergistic activation promoted by PAA, CH<sub>3</sub>CO<sub>3</sub>, and H<sub>2</sub>O<sub>2</sub>. All these possible activation reactions are thermodynamically spontaneous, which is meaningful for boosting <sup>1</sup>O<sub>2</sub> and minimize the accumulation of chlorinated products. The mechanism was verified by treating a complex wastewater, achieving rapid contaminants removal and effectively reducing 37.3 % yield of dissolved DBPs. This study provides a scenario-oriented paradigm for PAA-based electrochemical treatment in actual Cl<sup>-</sup> media. Our findings shed light on the performance prediction and regulation of conventional EAOPs, and extends the understanding of PAA-based water treatment strategies.

Note that despite the 41.3 % and 32.3 % reductions in  $\text{ClO}_3^-$  and  $\text{ClO}_4^-$  (substances added to the Chinese drinking water quality standards in 2022), the outlet concentrations are still above the limits (0.7 and 0.07 mg l<sup>-1</sup>, respectively). Future studies will address three strategies to



Fig. 6. Performance for treatment of actual chlorinated antibiotic wastewater via electrolysis in PAA/Cl<sup>-</sup> system. Comparison of acute cytotoxicity change, SMX removal and TOC decay in (a) PAA/Cl<sup>-</sup> and (b) Cl<sup>-</sup> system. Comparison of time-course of 12 dissolved DBPs (see text for names) during electrolysis in (c) PAA/Cl<sup>-</sup> and (d) Cl<sup>-</sup> system. Three–dimensional excitation and emission matrix: (e) before, and after 10 min of treatment in (f) PAA/Cl<sup>-</sup> and (g) Cl<sup>-</sup>. (h) Changes of fluorescence volume percentage. Experimental conditions:  $[Cl<sup>-</sup>]_0 = 1166 \pm 17.1 \text{ mg L}^{-1}$ ,  $[PAA]_0 = 50 \mu\text{M}$ ,  $[SMX]_0 = 25 \mu\text{M}$ , cathodic potential of -1.0 V vs. SCE, initial pH 6.9  $\pm$  0.1, argon atmosphere.

decrease the content of final chlorine by–products: (i) use of a less powerful anode, to favor the first oxidation of Cl<sup>-</sup> oxidation but not the subsequent steps(Norra et al., 2022), (ii) optimize the PAA/Cl<sup>-</sup> system structure and shorten the electrolysis time, and (iii) add an adsorptive dechlorination step at the reactor outlet (Norra and Radjenovic, 2021). It is suggested that the applicability range of the PAA/Cl<sup>-</sup> system, in terms of Cl<sup>-</sup> content, is preliminary studied for each target wastewater, since the required PAA concentration to minimize the Cl–DBPs will depend on the generated HClO to be counterbalanced.

#### CRediT authorship contribution statement

Wang Lu: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. Nan Chen: Supervision, Resources, Project administration, Funding acquisition. Chuanping Feng: Writing – review & editing, Supervision. Ignasi Sirés: Writing – review & editing, Writing – original draft, Validation, Funding acquisition, Formal analysis. Ning An: Software, Investigation. Haotian Mu: Investigation.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

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#### Supplementary materials

Supplementary material associated with this article can be found, in

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