

Contents lists available at ScienceDirect

# Water Research



journal homepage: www.elsevier.com/locate/watres

# Degradation of antibiotics and profiling of transformation products upon peracetic acid–mediated treatment of electrochlorinated groundwater in a flow–through reactor

Wang Lu<sup>a,b</sup>, Nan Chen<sup>b,\*</sup>, Chuanping Feng<sup>b</sup>, Gong Zhang<sup>c</sup>, Ignasi Sirés<sup>a,\*</sup>

<sup>a</sup> Laboratori d'Electroquímica dels Materials i del Medi Ambient, Departament de Ciència de Materials i Química Física, Secció de Química Física, Facultat de Química, Universitat de Barcelona, 08028 Barcelona, Spain

<sup>b</sup> School of Water Resources and Environment, MOE Key Laboratory of Groundwater Circulation and Environmental Evolution, China University of Geosciences (Beijing), Beijing, 100083, People's Republic of China

<sup>c</sup> College of Environment, Center for Water and Ecology, State Key Joint Laboratory of Environment Simulation and Pollution Control, College of Environment, Tsinghua University, Beijing 100084, China

#### ARTICLE INFO

Keywords: Antibiotic residues EAOPs FT–ICR MS Peracetic acid Transformation products

# ABSTRACT

Preventing the formation of hazardous chlorinated transformation products (Cl-TPs) when applying the electrochemical advanced oxidation processes (EAOPs) is a major challenge for ensuring their broader scale-up. In this context, the addition of peracetic acid (PAA) can potentially contribute to reduce the risk of Cl-TPs, but the associated transformation pathways remain insufficiently understood. Here, PAA-mediated electrochlorination process was found to reduce typical Cl-TPs (e.g., chloroform below 60  $\mu$ g L<sup>-1</sup>) by 26.9 %~80.8 %. Under optimized conditions, an innovative PAA-based treatment in a single-pass flow-through electrochemical reactor achieves the removal of four mixed antibiotics with low specific energy consumption (5.3 Wh mmol<sup>-1</sup>). The antibiotics concentration in the effluent remained below the detection limit within 10 operation cycles. In addition, reductions in Cl-TPs were achieved in both simulated and actual groundwater, meeting the 2022 Chinese drinking water quality standards. Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) revealed that PAA-based electrochlorination preferentially removed highly unsaturated heavy byproducts (O/C < 0.3, MW > 400 Da), and the CHOCl formulae number decreased by 59 %. The transformation pathways of Cl--TPs were mainly identified as decarbonylation, dihydroxylation, and hydrogenation. Moreover, the possible halogenation pathways number showed a significant decrease of 77.9 %. These findings provide deeper insights into the degradation mechanisms and Cl-TPs minimization during PAA-mediated electrochemical antibiotic degradation, shedding light on the transformation processes in diverse environmental scenarios.

#### 1. Introduction

The widespread use of mixed antibiotics in human and veterinary medicine has led to their frequent detection in groundwater (Wu et al., 2022) and even in tap water (Ben et al., 2020). For example, in the groundwater of Xiongan New Area, China, the average concentration of antibiotics reached  $79.22 \pm 56.46$  ng L<sup>-1</sup>(Fu et al., 2022). The presence of these emerging contaminants in natural water not only poses risks associated with the dissemination of antibiotic resistant genes but also represents a significant threat to ecological balance and human health (Chen et al., 2022; Lu et al., 2023; Thomas et al., 2024; Wang et al., 2024). Pollution by antibiotics can lead to the disorder of the microbiota

that maintains the balance of metabolism (Zhang et al., 2015), and damages many important organs, the human nervous system and gastrointestinal tract (Arulkumaran et al., 2020). Consequently, there is an urgent need for more efficient and eco–friendly technologies.

Electrochemically–assisted AOPs (i.e., EAOPs) have garnered increasing attention for the decentralized and distributed treatment of contaminated water because of their low footprint, compact and modular design, and ease of automation (Brillas et al., 2009; Deng et al., 2023; Zuo et al., 2023). Nonetheless, a challenging aspect of EAOPs is their safe application in water containing chloride ions, which are ubiquitous in sewage from coastal cities and groundwater supplies (Baptista-Pires et al., 2021; Jiang et al., 2024; Liu et al., 2024; Norra

\* Corresponding authors. E-mail addresses: chennan@cugb.edu.cn (N. Chen), i.sires@ub.edu (I. Sirés).

https://doi.org/10.1016/j.watres.2025.124013

Received 19 April 2025; Received in revised form 2 June 2025; Accepted 11 June 2025 Available online 11 June 2025

0043-1354/© 2025 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC license (http://creativecommons.org/licenses/by-nc/4.0/).

et al., 2022). Chloride ion concentrations in domestic and industrial wastewater can reach thousands of mg  $L^{-1}$  (Cuervo Lumbaque et al., 2022; Norra and Radjenovic, 2021; Radjenović et al., 2012). Accordingly, EAOPs can produce chlorine (Choi et al., 2023), leading to the formation of carcinogenic and mutagenic chlorine–containing transformation products (Cl–TPs) such as trihalomethanes, haloacetic acid, and haloacetonitrile. These byproducts introduce potential risks to both human health and ecosystems, highlighting the need for careful consideration and mitigation strategies when applying EAOPs to chloride–containing water (Jiang et al., 2024; Shah et al., 2015).

Recently, the feasibility of electroactivating peracetic acid (PAA) has been progressively demonstrated, encompassing either indirect activation via the continuous production of Fe(II) through electrically accelerated Fe(III)/Fe(II) cycles (Zhang et al., 2024d), or direct activation at the cathode (Zou et al., 2024). We showed that the thermodynamic tendency of peroxy group in PAA molecules to cleave upon electron gain underscores this process (Lu et al., 2024a). Notably, PAA electroactivation exhibits superior efficiency compared to non-electrochemical routes (Lu et al., 2024a, 2024b), leading to a lower need of PAA dosage for complete antibiotic removal and, which in turn mitigates concerns regarding increases in total organic carbon (TOC) and biological oxygen demand. Furthermore, PAA can synergistically interact with electrogenerated HClO to produce <sup>1</sup>O<sub>2</sub>, which facilitates thermodynamically spontaneous reactions (1)-(3) (Lu et al., 2024b; Shah et al., 2015), resulting in minimal HClO accumulation and thermodynamically unfavored organic Cl-addition reactions, thus inhibiting Cl-TPs. This provides a promising approach for developing PAA-based systems with robust detoxification capabilities in actual chloride-containing media, where AOPs relying on the action of hydroxyl radicals (<sup>•</sup>OH) may pose risks due to the potential HClO formation and Cl-TPs accumulation.

Despite the promising results reported in a growing number of batch experiments on antibiotic removal (Yuan et al., 2021; Zhang et al., 2024d; Zou et al., 2024), the industrial application of these technologies necessitates high-rate performance over extended periods. In batch experiments typically conducted in stirred-tank reactors, poor mass transport causes that the H<sup>+</sup> produced during oxygen evolution reaction remains near the anode surface, lowering the local pH value and triggering a large cell pH gradient (Zhang et al., 2024b). This increases the thermodynamic potential of both anode and cathode and raises the cell voltage. For sustainable operation of PAA-mediated EAOPs, the implementation of a continuous flow-through system is thus imperative. Moreover, the complexity of dissolved organic matter (DOM) in actual water remains a challenge because of its unclear conversion to halogenated organic matter and degradation behavior. Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS), has great potential for elucidating the impact of PAA-electroactivation on DOM transformation, especially for resolving the composition of toxic TPs at the molecular level (Li et al., 2024b; Wu et al., 2024; Zhang et al., 2024a). It provides detailed molecular information, including O/C ratios, double bond equivalents (DBE), and aromaticity indices (AI), among other (Lu et al., 2021; Zhang et al., 2021, 2024a). Distinguishing between natural and effluent organics in water samples could yield insightful differences in toxic TPs profiling (Lu et al., 2021). Although some reports have claimed the reduced yields of specific Cl-TPs in PAA-mediated EAOPs, there remains a wealth of information to be uncovered regarding the quantities and transformations of toxic TPs.

$$CH_3CO(0)O^{-} + HClO \rightarrow CH_3COOH + Cl^{-} + {}^1O_2$$
(1)

 $CH_{3}CO(O)OH + HClO \rightarrow CH_{3}COOH + HCl + {}^{1}O_{2}$ <sup>(2)</sup>

$$H_2O_2 + HClO \rightarrow HCl + H_2O + {}^1O_2 \tag{3}$$

In this study, a graphene–modified graphite felt (graphene/GF) cathode was synthesized using a previously established protocol (Lu

et al., 2024b). A BDD/Nb mesh anode paired with the graphene/GF cathode was employed for the electrochemical water treatment in a single-pass, flow-through reactor. To evaluate the efficacy of this system, four representative antibiotics were selected as model pollutants, spiked into simulated water and actual groundwater: (i) Amoxicillin (AMX) as penicillin example (Lu et al., 2023); (ii) sulfamethoxazole (SMX) as sulfonamide (Chen et al., 2022; Qian et al., 2022); (iii) ciprofloxacin (CIP) as quinolone (Chen et al., 2024; Xie et al., 2023); and (iv) oxytetracycline (OTC) as tetracycline (Thomas et al., 2024; Zhang et al., 2024c). Additionally, 15 typical toxic TPs were monitored to assess their inhibition when adding PAA in the system. Moreover, the DOM composition of the aqueous sample during the PAA-mediated treatment was characterized via FT-ICR MS. The feasibility of formulae in terms of transformation was quantified, and potential transformation pathways along with their associated molecular structures were summarized and proposed.

# 2. Materials and methods

# 2.1. Chemicals and reagents

Details regarding the preparation of the PAA solution, along with a comprehensive list of chemicals and reagents utilized, are provided in Text S1.

## 2.2. The flow-through system setup

Electrochemical experiments employing PAA were performed within a parallel-plate flow-through reactor, characterized by a diameter of 5 cm and an exposed area of 19.6 cm<sup>2</sup>. The reactor operated in a single--pass (i.e., continuous) mode, with flow rates set at 3.24, 6.48, and 12.96 mL min<sup>-1</sup> using a digital peristaltic pump (GILSON, USA). This configuration resulted in hydraulic residence times (HRTs) of 10.0, 5.0  $h^{-1}$ and 2.5 min, and effluent fluxes of 99.2, 198.4 and 396.7 L m<sup>-2</sup> (LMH), respectively. The anode was a BDD/Nb mesh (diameter of 50 mm, thickness of 1.4 mm), with a coating thickness of 5  $\mu$ m, and a boron content of 2500 mg g<sup>-1</sup> (mesh coated on both sides, excluding the edges). The graphene/GF cathode was prepared as described in Text S2 (Lu et al., 2024b). This cathode, with an approximate thickness of 0.5 cm, was put in contact with a three-dimensional (3D) stainless steel current collector (Fig. S1). Prior to each experiment, initial runs were executed at open circuit (OC<sub>0</sub>) to assess potential antibiotic losses due to adsorption onto the electrodes. At the end of each experiment, effluent samples were collected after the current was stopped (i.e., OC<sub>final</sub>), enabling the evaluation of overall antibiotic loss attributable solely to electrosorption (i.e., in the absence of subsequent degradation). To determine the impact of anodic current on antibiotic removal, experiments were conducted at varying flow rates in constant-current mode, with applied anodic current densities in the range of 0.1-20 mA cm<sup>-2</sup> (calculated based on the electrode water flow-through area) using an AMEL 2053 power supply. Samples were collected after each bed volume at each current setting. Given the presence of PAA and electrogenerated chlorine in the system, an excess of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (0.5 mM) was pre-added to sampling tubes to quench reactions in all effluents exiting the reactor.

#### 2.3. Water sampling and analytical procedures

Two types of actual Cl<sup>-</sup>-containing groundwater (GW1 and GW2) was collected in July 2024 (details in Text S1). The samples were sealed, transported in polyethylene drums, and refrigerated at 4 °C for storage. Prior to experiments, AMX, CIP, OTC, and SMX were added to the groundwater as model pollutants at a concentration of 0.025 mM, respectively.

Antibiotic concentrations were quantified using high–performance liquid chromatography (HPLC, Waters–1525, USA), using a C18 column of 5  $\mu$ m (4.6 mm  $\times$  250 mm) and UV detection. The analysis detailed can be found in Table S1. Analytical methods and computational details are outlined in Text S3–S9.

#### 2.4. Molecular characterization by FT-ICR MS

Molecular information was obtained using a Bruker Solarix 15T FT–ICR MS system (Bruker, Germany) with an electrospray ionization source. Formula assignments adhered to the constraints of  $^{12}C_{0-60}$ ,  $^{13}C_{0-1}$ ,  $^{14}H_{0-120}$ ,  $^{16}O_{0-50}$ ,  $^{14}N_{0-5}$ ,  $^{32}S_{0-2}$ ,  $^{35}Cl_{0-3}$ ,  $^{37}Cl_{0-1}$ ,  $^{79}Br_{0-3}$ ,  $^{81}Br_{0-1}$ , and H/C  $\leq 2.25$ , O/C  $\leq 1.15$ , in accordance with known chemical rules. Formulae containing Cl or Br atoms were validated based on their natural abundance (ratios of  $^{37}Cl/^{35}Cl$  and  $^{79}Br/^{81}Br$ ). Operational procedures, details to minimize potential biases caused by ionization efficiency or matrix effects, and calculations for determining the modified aromaticity index (AI\_mod), nominal oxidation state of carbon (NOSC), and double bond equivalent minus oxygen (DBE–O) are presented in Text S10.

# 3. Results and discussion

#### 3.1. Optimization of PAA-mediated treatment in the flow-through system

Density functional theory (DFT) calculations have revealed that chemical interaction between PAA-based reactants and the electrogenerated HClO is thermodynamically favored (Lu et al., 2024b). The concentration of electrogenerated HClO under optimized conditions was tested using N,N-diethyl-p-phenylenediamine method, yielding 1.1  $\pm$ 0.1 mg  $L^{-1}$  (i.e., 19.1  $\mu M$  ). Preliminary experiments, wherein 50  $\mu M$  PAA and 19.1  $\mu$ M HClO were directly introduced into an SMX solution without current supply, demonstrated a mere 45.8 % drug removal within 5 min (Fig. S2), highlighting the pivotal role of electrolysis in the process. Fig. S3 compares the typical cell voltages observed in batch and flow-through systems during electrolysis. Despite variations influenced by current density, electrolyte composition, and reactor design, the batch reactors exhibit consistently higher total cell voltages compared to most continuous-flow reactors (Li et al., 2024a). For sustained antibiotic removal in industrial settings, the adoption of a continuous flow--through system is imperative.

The electrode arrangement may exert a profound influence on the generation of oxidant species. Specifically, reactive oxygen species (ROS) and free available chlorine (FAC) generated at the anode can undergo further cathodic reduction in an anode-to-cathode (A-to-C) flow configuration. Conversely, In a cathode-to-anode (C-to-A) setup, PAA may become initially activated at the cathode, followed by reaction with FAC produced at the anode to form <sup>1</sup>O<sub>2</sub> (Lu et al., 2024b), potentially accelerating the antibiotic removal. The impact of the electrode arrangement on SMX removal was assessed at a low current density (j =0.5 mA cm<sup>-2</sup>) (Fig. S4). A significant 75.5 %  $\pm$  2 % removal of SMX was obtained with the C-to-A configuration, representing a 14.3 % increase over the A-to-C direction (which reached 61.2 %  $\pm$  3 % SMX removal). These findings underscore the advantage of initiating PAA activation at the cathode to produce ROS, prior to its passage through the anode for synergistic activation with HClO, in PAA-mediated electrochlorination performed in flow-through systems. The influence of key operation parameters in such system is discussed hereby.

#### 3.1.1. Current density

Typically, antibiotics with low logD values exhibit limited adsorption onto graphene–based electrodes. As evidenced in Table S2, all four studied antibiotics displayed low logD values ranging from -4.25 to -0.56. Consequently, during the OC<sub>0</sub> stage, the adsorption of these drugs on electrodes or other reactor components can be neglected. To assess the system performance, current densities spanning from 0.1 to 20 mA cm<sup>-2</sup> were evaluated for SMX as target pollutant (Fig. S5). The removal of this drug reached a saturation point at  $j \ge 2.5$  mA cm<sup>-2</sup> (Fig. S5). That is, at j = 2.5 mA cm<sup>-2</sup>, the SMX concentration achieved in the effluent was lower than the HPLC detection limit. Further increasing *j* essentially leads to an increase in the low-grade heat within the electrochemical system and to a larger pH gradient between the electrodes, which is not beneficial to ensure the system stability and reach low-energy consumption (Zhang et al., 2024b). Note that the continuous operation (i.e., 48 bed volumes) when powered on confirms the good stability of this system (Fig. S5). Fig. 1a illustrates the normalized concentration decays of SMX, CIP, OTC and AMX across a range of *j* values from 0.1 to 2.5 mA cm<sup>-2</sup>. Notably, AMX already undergoes direct degradation in the presence of the PAA solution, obscuring its degradation behavior during electrolysis. Upon current supply, a significant acceleration in the removal of SMX, CIP and OTC was observed (Fig. 1a). At j = 2.5 mA cm<sup>-2</sup>, the effluent concentrations of these antibiotics fell below the detection limit of HPLC (< 3.18 ppb).

Typically, high *i* accelerate charge transfer but may trigger mass transport limitations (e.g., bubbles covering the electrode surface), so the electro-oxidation flux  $(J_{EO})$  is utilized to couple reaction kinetics and mass transport. The  $J_{EO}$  for the removal of the three drugs that required the application of current (SMX, CIP, and OTC), depicted in Fig. 1b, exhibited a positive linear correlation with the applied *j* value. This suggests that the flow-through system is likely to have high efficiency with low energy consumption. Worth noting, even after current is cut off, residual HClO flowing within the system continued to react with active components in the PAA solution, generating <sup>1</sup>O<sub>2</sub> and maintaining a degree of antibiotic removal during the final stage of operation (OC<sub>final</sub> stage in Fig. 1a). The extent of antibiotic concentration rebound following current shutdown correlated well with the ease of degradation within the PAA-mediated electrochlorination treatment. For instance, CIP, being the most recalcitrant to degradation, exhibited the most rapid concentration increase.

#### 3.1.2. Hydraulic retention time

The variation observed in OC<sub>final</sub> across different HRT values underscores the significance of time available for reaction between residual HClO and antibiotics, which eventually modulated the effluent concentrations (Fig. S6), a phenomenon influenced by the inherent resistance of each antibiotic to degradation. Specifically, reducing the HRT from 10 min to 2.5 min markedly impacted CIP removal, decreasing the efficiency from 99.9 % to 67.2 %, while SMX removal decreased to 90.6 %. Conversely, OTC, being the most susceptible to degradation among these three drugs, remained largely unaffected (Fig. 1c). Complete degradation of CIP in the effluent at an HRT of 2.5 min proved challenging, highlighting its recalcitrant nature in this system. Therefore, to ensure concurrent degradation of multiple pollutants within the mixed contamination scenario, an HRT of 5 min was established as optimal.

#### 3.1.3. Solution pH

Given the short HRT, minimal pH variation was observed between influent and effluent. At pH values of 3.0, 5.0 and 9.0, antibiotic removal performance was excellent (Fig. 1d). However, a notable decline in antibiotic removal efficiency was evident at pH values exceeding 9 (Fig. S7 and Fig. 1d). Since the interactions between antibiotics and the reactor components were deemed insignificant, the effect of pH on removal was primarily attributed to alterations in protonation/deprotonation states. For PAA, with a  $pK_a$  value of 8.2, PAA<sup>-</sup> form became dominant at pH > 9.0. The electrostatic repulsion between the



Fig. 1. Optimization of the PAA-mediated electrochlorination treatment in the flow-through system. (a) Removal of SMX, CIP, OTC and AMX at different current densities. (b) Electroxidation fluxes ( $J_{EO}$ ) of target contaminants. Removal of SMX, CIP, and OTC at different (c) HRTs and (d) pH values. (e) Different contributions to degradation (except AMX, which is readily degraded), and calculation of (f) specific energy consumption. (g) Degradation of the four antibiotics when they are mixed, under optimal conditions. Experimental conditions, unless stated otherwise in each graph:  $[NaCI]_0 = [Na_2SO_4]_0 = 20 \text{ mM}$ ,  $[PAA]_0 = 50 \mu\text{M}$ ,  $[AMX]_0 = [SMX]_0 = [OTC]_0 = 25 \mu\text{M}$ ,  $j = 2.5 \text{ mA cm}^{-2}$ , HRT = 5 min, pH 3.0. For the mixture:  $[PAA]_0 = 4 \times 50 \mu\text{M}$ ,  $[AMX]_0 + [SMX]_0 + [CIP]_0 + [OTC]_0 = 4 \times 25 \mu\text{M}$ , HRT = 5 min, pH 3.0.

negatively charged graphene–based cathode and PAA<sup>-</sup>, governed by Coulomb's Law, hindered PAA electroactivation. More importantly, PAA<sup>-</sup> interacted with neutral PAA molecules to form reactive intermediates that subsequently decomposed into acetate anions,  $O_2$  and  $H^+$  (reaction (4)) (Kim and Huang, 2021).

enhanced micropollutants removal at pH  $< pK_a$  during PAA–based processes, a finding corroborated in our study, where system performance deteriorated significantly as pH rising from 9.0 to 12.0 (Fig. 1d).

3.1.4. Feasibility of PAA-mediated treatment of mixed antibiotics

 $CH_3C(0)OO^- + CH_3C(0)OOH \rightleftharpoons CH_3COOOHOO(0)CCH_3^- \rightarrow 2CH_3C(0)O^- + O_2 + H^+$ 

Considering the antibiotics structures (Table S2), SMX exhibits two  $pK_a$  values ( $pK_{a1} = 1.6$ ,  $pK_{a2} = 5.7$ ), CIP possesses two  $pK_a$  values ( $pK_{a1} = 6.2$ ,  $pK_{a2} = 8.6$ ), and OTC has three  $pK_a$  values ( $pK_{a1} = 3.6$ ,  $pK_{a2} = 7.5$ ,  $pK_{a3} = 9.4$ ). Kong et al. previously reported (Kong et al., 2022)

To assess the system effectiveness against mixed antibiotics, a cocktail of the four target molecules containing a consistent [PAA]<sub>0</sub>-to-[Antibiotics]<sub>0</sub> ratio (2:1) was employed. Results indicate that mixed antibiotics degradation in the simulated water matrix mirrored that of

(4)

individual antibiotics. Under the optimized parameters, the concentration of the mixed antibiotics in the effluent was lower than the detection limit of HPLC, and operated in a stable manner for 10 cycles (Fig. 1 g). With adsorption, electrosorption, and PAA-mediated chemical oxidation deemed negligible (discussed above), the contributions of direct electrochemical oxidation and synergistic effects were examined (Fig. S8 and Fig. 1e). Direct electrochemical oxidation at BDD surface, attributed to its high oxidation power to generate BDD(<sup>•</sup>OH), accounted for 43.3 %-47.7 % of both single and mixed antibiotic removal. Notably, when the electrolysis was made in Cl<sup>-</sup>-containing medium the removals were not significantly enhanced (Fig. S8). In contrast, PAA addition substantially improved antibiotics removal, attributed to the synergistic interaction between PAA and HClO (Fig. 1 g), aligning with previous findings (Lu et al., 2024b). Moreover, the specific energy consumption for mixed antibiotics degradation (5.3 Wh mmol<sup>-1</sup>) was lower than for individual antibiotics ( $\sim 21$  Wh mmol<sup>-1</sup>) (Fig. 1f). Worth comparing, in

EAOPs without PAA, the specific energy consumption for removing

target organic pollutants was 39–54 Wh mmol<sup>-1</sup> (Xie et al., 2021), and when using a flow-through electrochemical system, it was 16.3–58.7 Wh mmol<sup>-1</sup> (Wei et al., 2023). These results suggest the great potential of this system for efficiently treating more complex realistic matrices with reduced energy consumption.

# 3.2. Degradation mechanism for the treatment of mixed antibiotics and monitoring of typical TPs

Aiming to emulate more realistic scenarios, an actual groundwater (GW1) was collected from the Barcelona metropolitan area. Table S3 presents the water quality parameters after supplementing this water with the aforementioned four antibiotics and adjusting the chloride ion content to 20 mM to be comparable to trials performed in simulated water matrices. Notably, the removal of mixed antibiotics in actual groundwater was comparable to that observed in simulated matrices (Fig. S9 and Table S3). The short HRT resulted in a minimal pH variation



**Fig. 2. DFT calculations for the mechanistic study.** Chemical structure and surface electron density (calculated from Fukui indices) of (a) SMX, (b) CIP, (c) OTC, and (d) AMX. (e, f) Molecular orbital energies of Cl<sup>•</sup>, CIO<sup>•</sup>, <sup>•</sup>OH, <sup>1</sup>O<sub>2</sub>, SMX, CIP, OTC, and AMX. Blue and red lines account for HOMO and LUMO energy levels, respectively.

in the treated water (6.8  $\pm$  0.1  $\rightarrow$  6.3  $\pm$  0.2). Furthermore, nitrogen pollutants were effectively eliminated by the active chlorine generated at the anode.

Using DFT calculations and the Fukui function, the susceptible sites on SMX, CIP, OTC, and AMX molecules that are vulnerable to attacks by reactive species have been accurately identified (Fig. 2). This analysis has enabled us to propose a pathway for the generation of Cl-TPs in both the Cl<sup>-</sup> and PAA/Cl<sup>-</sup> systems. Fig. 2a-d showcase isosurface plots depicting the surface electron density of SMX, CIP, OTC, and AMX molecules based on the Fukui function. In these plots, green and blue, respectively, denote positive and negative values, with the size of the colored electron cloud denoting the magnitude. Regions exhibiting higher positive values are more likely to serve as active sites for attack of reactive species. While the isosurface mapping of electron density provides a visual understanding, it does not facilitate itself a detailed quantitative analysis of the Fukui function values. The condensed Fukui function theory suggests that larger values of  $f^-$ ,  $f^+$ , and  $f^0$  account for atoms that are more susceptible to attack by electrophilic, nucleophilic, and radical species, respectively (Table S4-S7). Notably, the benzene amine group in SMX (Chen et al., 2023), the piperazine moiety of CIP (Chen et al., 2024), the amine group (via demethylation) as well as the ring (via decarbonylation and deamidation) in OTC (Thomas et al., 2024), and the  $\beta$ -lactam ring (via hydrolysis) in AMX (Lu et al., 2023) are particularly vulnerable to such attacks.

Thermodynamically,  $Cl^{\bullet}(0.60 \text{ eV})$  and  $ClO^{\bullet}(1.51 \text{ eV})$ , characterized by smaller average HOMO–LUMO gaps, are more favorable for Cl–addition reaction with the four antibiotics under study, as compared to <sup>•</sup>OH (1.91 eV), in the absence of PAA (Fig. 2e, Table S8). This fact introduces a well-documented challenge in EAOPs, namely the facile accumulation of Cl-TPs during the treatment of chloride-containing actual water (Norra et al., 2022; Radjenovic and Sedlak, 2015; Shah et al., 2015). As elaborated in Text S11, our prior research revealed that the spontaneous reaction between PAA and reactive Cl species generates  ${}^{1}O_{2}$  (Lu et al., 2024b), and calculations indicate a narrow gap of only 0.13 eV between <sup>1</sup>O<sub>2</sub> HOMO and Cl<sup>•</sup> LUMO (Table S8). This implies that reactive chlorine-based species, especially Cl<sup>•</sup>, which is most reactive towards the target antibiotics, can be efficiently scavenged in PAA-mediated treatments, thereby attenuating the Cl-addition reaction. Moreover, the primary ROS in PAA-based systems, <sup>1</sup>O<sub>2</sub> and <sup>•</sup>OH, also exhibit favorable electrophilic attack capabilities due to their narrow HOMO-LUMO gaps (Fig. 2f), resulting in reduced Cl-TP yield. This conclusion is tentatively supported by our liquid chromatography-mass spectrometry (LC-MS) results (Fig. S10) and the monitoring of 15 toxic TPs in both simulated and actual groundwater (Text S4).

TPs were further analyzed using spectroscopy and GC–MS. As shown in Fig. S11 and S12, a pronounced reduction in DOM fluorescence intensity was observed in both simulated and GW1 samples treated in the presence of added PAA. The UV–vis spectra (Fig. S13 and S14) and UV indicators (Fig. 3a) were obtained for pre– and post–treatment samples. The results reveal that the  $E_{250}/E_{365}$  ratio, which inversely correlates with molecular weight (Chen et al., 2003), increased during the PAA–mediated electrochlorination. This increase was accompanied by the disruption of macromolecular antibiotic structures, leading to a rise in the concentration of aromatic hydrocarbons and cyclic compounds (SUVA<sub>254</sub> and A<sub>200–300</sub>) (Teng et al., 2020). Additionally, there was a concurrent rise in the abundance of C=O and C=C functional groups, as



Fig. 3. Toxic TPs detection in simulated and actual groundwater (GW1). (a) Changes of UV indicators during the different electrochlorination treatments. X-TPs generation during the treatments in the flow-through system in (b) simulated water and (c) GW1. Experimental conditions:  $[PAA]_0 = 4 \times 50 \ \mu\text{M}$ ,  $[AMX]_0 + [SMX]_0 + [CIP]_0 + [OTC]_0 = 4 \times 25 \ \mu\text{M}$ ,  $j = 2.5 \ \text{mA} \ \text{cm}^{-2}$ , HRT = 5 min, pH 3.0. (d) Acute toxicity of TPs as predicted by T.E.S.T. The EPA T.E.S.T. model3 was used to get toxicity data. T.E.S.T. uses quantitative structure activity relationship (QSAR) methodologies.

evidenced by an increase in the  $E_{265}/E_{465}$  ratio (Deng et al., 2019).

Regarding the GC-MS results shown in Fig. 3b and 3c and Fig. S15, only chloroform (m/z 82.93) was detected in simulated water, while 5 TPs were identified in the more complex actual groundwater. Notably, the yields of all detected TPs were reduced to varying degrees in the presence of PAA. In simulated water, chloroform was decreased by 26.9 %. In actual groundwater, the reductions for chloroform, dichlorobromoform (m/z 128.89), dibromochloroform (m/z 128.88) and 126.87), 2-chlorotoluene (*m*/*z* 126.01 and 91.04), and bromoform (*m*/*z* 251.78 and 172.82) were 80.8 %, 72.2 %, 31.9 %, 50.7 %, 99.9 %, respectively. This can be attributed to the favorable reaction between PAA and HXO (X = Cl or Br), which makes subsequent X-addition reaction less favorable. Indeed, the detected TPs exhibited toxicity levels comparable to the parent antibiotic and had higher bioaccumulation factors (Fig. 3d). In the absence of PAA, the yields of chloroform (limit of  $60 \mu g$  $L^{-1})$  and bromoform (limit of 100  $\mu g \ L^{-1})$  exceeded regulatory limits. In contrast, in actual groundwater, the yields of trihalomethanes (THMs) with PAA were all within the Chinese drinking water quality standards for 2022. In another reported Cl-TPs control strategy, the chlorination reaction was avoided by reducing the anode potential, and the dechlorination of Cl-TPs was addressed by using H\* produced on a Pd cathode (Wei et al., 2023). However, this strategy cannot accelerate the reaction by increasing the potential, whereas the addition of parallel electrode arrangements would be restricted by the electrode cost, not being advantageous in terms of specific energy consumption (16.3-58.7 Wh mmol<sup>-1</sup>). These findings further validate the potential of PAA–mediated EAOPs in mitigating the accumulation of toxic TPs in significant amounts. The discussion on the advantages of PAA compared with other processes is found in Text S12.

#### 3.3. Profiling of TPs at molecular level

Groundwater (GW2) sampled from a contaminated well adjacent to a farm in China served as the subject for investigating the impact of PAA dosing on TPs. To assess this, two [PAA]/[Antibiotics]<sub>0</sub> ratios were selected: 2:1, employed in the tested described above and commonly utilized in our previous research (Lu et al., 2024a, 2024b), and 10:1, employed in other contemporary studies (Cheng et al., 2024; Dong et al., 2024; Kim et al., 2020; Meng et al., 2023). For comparative purposes, an equal amount of acetic acid was administered to the control group devoid of PAA.

FT-ICR MS analysis revealed a marked reduction in both the total count and abundance of assigned formulae, correlating with a

significant decline in CHOX (X = Cl or Br) compounds following PAA-mediated electrochlorination treatment (Fig. 4a). This dehalogenation effect in response to PAA addition has been anticipated in earlier studies, although without offering detailed analysis and product monitoring (Lu et al., 2024a, 2024b; Shah et al., 2015). Specifically, the raw sample exhibited a total of 4420 assigned formulae (Table S9 and Fig. S16a), with CHOCl and CHOBr compounds constituting approximately one-tenth of the CHO compounds (Fig. S16b). After the PAA/Cl<sup>-</sup> and Cl<sup>-</sup> treatments, the total number and MW of all formulae remained relatively unchanged; however, CHOCl and CHOBr formulae with MWs exceeding 400 Da were predominantly eliminated in the PAA-mediated treatment. As detailed in Table S9, the halogen-containing formulae were predominantly CHOCl, with Br being a minor constituent in terms of both intensity and formula count, likely due to the additional Clintroduced. At the optimal PAA dosage ([PAA]/[Micropollutants] ratio = 2:1), the number of CHOCl formulae decreased by 59 % ( $n = 180 \rightarrow 83$ ) when comparing with pure electrochlorination. Only 117 CHOX (CHOCl and CHOBr) formulae were detected in final samples, halving the amount as compared to 253 formulae in the PAA-free electrochlorinated sample. Upon increasing the PAA dosage ([PAA]/[Micropollutants] ratio = 10:1), the average molecular mass remained relatively stable, indicating the absence of new polymerisation products. Notably, increasing PAA dosage did not cause a significant CHOX increase (to 148) in the PAA/Cl<sup>-</sup> process, contrasting with the 43.9 % enhancement observed when equal amounts of acetic acid were added in PAA-free electrochlorination (reaching 264).

The van Krevelen plot of CHOX formulae is shown in Fig. S17. The formulae clustering in lipid– and protein–like regions originate from organic matter leaching into groundwater from nearby landfills. Lignin, abundant in terrestrial ecosystems, is known to produce X-TPs, particularly haloacetic acids. In this study, the treatment without PAA produced more lignin–like substances when only an equal amount of acetic acid was added, implying increased production of halogen–containing formulae potentially due to the conversion of organic matter into lignin–like compounds. In contrast, PAA–mediated electrochlorination effectively removed highly unsaturated heavy formulae (O/C < 0.3, MW > 400 Da).

Fig. S18 illustrates five indices characterizing the formulae contained in the raw groundwater:  $AI_{mod}$ , O/C, H/C, NOSC, and DBE–O, along with their changes during treatments. The PAA–based processes gave rise to a higher proportion of formulae with low NOSC values, indicating potentially lower Gibbs free energy and susceptibility to oxidation. Principal component analysis (PCA) analysis of organic transformation



**Fig. 4.** Molecular profiling of TPs during electrochlorination treatments of GW2. (a) Changes in number and abundance of halogens–containing formulae during PAA/Cl<sup>-</sup> and Cl<sup>-</sup> treatments based on the data acquired by FT–ICR MS. In trials without PAA, equal amounts of acetic acid were added. Same experimental conditions of Fig. 3 were employed. (b) Susceptibility of CHOX transformation at the molecular level based on PCA analysis. 95 % confidence interval was introduced by confidence ellipses and shaded with color.

results, depicted in Fig. 4b, revealed that PC1 and PC2 accounted for 52.7 % and 24.9 % of the total variance, with eigenvalues of 3.16 and 1.50, respectively. PCA confirms that  $AI_{mod}$  values positively correlated with DBE–O, followed by NOSC and O/C in descending order. In the absence of PAA during the electrochlorination treatment of actual groundwater, CHOX formulae tended to exhibit higher H/C and MW values and were less oxidized. Consistent with the findings in Fig. S19 and Text S13, PAA–mediated treatment products were more unsaturated. Formulae characterized by higher  $AI_{mod}$  and lower H/C values, indicating greater unsaturation, were more likely to be reduced or eliminated during electrochlorination in the presence of PAA.

# 3.4. Reactivity changes and transformation pathways in PAA-mediated electrochlorination using the flow-through system

The degrees of saturation and oxidation of the TPs accumulated during the electrochlorination treatments were assessed using (DBE–O)/C and NOSC values, respectively, enabling the classification of molecules into four distinct categories: (1) Unsaturated and oxidized, (2) unsaturated and reduced, (3) saturated and oxidized, and (4) saturated and reduced (Li et al., 2024b; Yang et al., 2024; Zhang et al., 2021). As illustrated in Fig. 5a–f, PAA-mediated treatment resulted in the generation of fewer halogenated products and yielded lower average MWs of 451.94 Da and 441.24 Da at [PAA]/[Antibiotics]<sub>0</sub> ratios of 2:1 and 10:1, respectively, as compared to PAA-free process. The majority of CHOCI and CHOBr formulae in samples without PAA possessed positive



**Fig. 5.** Reactivity changes and transformation pathways during electrochlorination treatments of GW2 in the flow-through system. (DBE–O)/NOSC plots of DOM before and after treatment: (a) Raw sample, (b) [PAA]/[micropollutants] = 2:1 and (c) equal amounts of acetic acid without PAA, (d) [PAA]/[micropollutants] = 10:1 and (e) equal amounts of acetic acid without PAA. The symbol sizes represent relative abundance. (f) Percentage of formulae found for the four types of saturation and oxidation states. (g, h) The number of possible precursor-product pairs: mapping of transformation pathways undergone by compounds containing chlorine and bromine in PAA-mediated and PAA-free electrochlorination treatments. Pathways correspond to halogenation/dehalogenation reactions, and are non-repetitive to each other. Same experimental conditions of Fig. 3.

(DBE-O)/C values, whereas they displayed negative values following PAA-mediated treatment. Specifically, compared to pure electrochlorination, the number of unsaturated molecules among the halogenated products decreased by 44.8 % and 45.1 % when treated with  $[PAA]/[Antibiotics]_0$  ratios = 2:1 and 10:1, respectively (Fig. 5f). This reduction can be attributed to addition, oxidation reactions, or the elimination of unsaturated groups during PAA-mediated treatment. For instance, unsaturated formulas containing -COOH, -CH-CH2 or -S-O groups preferentially undergo decarboxylation, dealkylation and desulphurization reactions mediated by •OH and <sup>1</sup>O<sub>2</sub>, leading to an increase in saturation degree. Consequently, the values of DBE-O and AImod decreased during the PAA-mediated treatment (Fig. S18). Notably, the saturated and oxidized molecules remained virtually unchanged, indicating that addition and oxidation reactions were less significant than decarboxylation and dealkylation reactions. This finding aligns with the analysis of transformation pathways. As shown in Fig. S20, the number of potential precursor-product pairs for decarboxylation and dealkylation reactions was the highest among all reactions, and the presence or absence of PAA had minimal impact on this result, suggesting that the target pollutant tended to be converted into low-carbon formulae via decarboxylation and dealkylation routes, subsequently being removed from the water samples. Decarboxylation commonly occurred within and between chlorinated acid compounds, which also implies that CHOCl formulae contained abundant carboxyl groups.

Possible transformation pathways of TPs in water are outlined in Table S10. Fig. 5 g and h present the potential precursor-product pairs of CHOCl and CHOBr formulae identified through mass difference analysis based on transformation pathways. The total number of potential precursor-product pairs for PAA-mediated treatment was consistently the lowest (Table S11). Although the proportion (i.e., percentage) of halogenation reactions exceeded that of dehalogenation reactions in all electrochlorination treatments (Table S11 and Fig. S21), the total number of halogenation reactions decreased in the presence of PAA. Notably, the number of halogenation reactions decreased significantly by 77.9 % (Table S11, from 208 to 46) (i.e., compare PAA:MPs = 2:1 with its control group); however, this trend weakened with increasing PAA dosage (22.3 % decrease, from 672 to 522). At PAA:MPs = 2:1 (Fig. 5 g), the frequency of reaction types was as follows: decarbonylation (-O+HCl/HBr), dihydroxylation (-OH+Cl/Br), hydrogenation (+HCl/HBr), hydration (+HClO/HBrO), and then hydroxylation (-H+OCl/OBr), carboxylation -H+CO<sub>2</sub>Cl/ CO<sub>2</sub>Br), and dehydration (-OH<sub>3</sub>+Cl/Br). The Cl/Br-addition reaction was not detected, suggesting that there are almost no olefins or alkynes in CHOCl and CHOBr formulae.

# 4. Conclusions

The generation, transformation and mitigation of Cl-TPs constitute a pivotal focus in the realm of actual water treatment by powerful methods such as EAOPs. Considering the ubiquity of chloride ions in water streams, the propensity of commonly employed anodes to oxidize such active ions at low chlorine evolution potentials often leads to the accumulation of toxic halogenated compounds. In light of the widespread occurrence of X-TPs during EAOPs, this study has discussed the design of a flow-through electrochemical system based on PAA to achieve rapid removal of mixed antibiotics, while depicting the fundamental transformation mechanisms of Cl-TPs at the molecular level, which allows to address a critical research gap. Under optimal conditions ([PAA]<sub>0</sub>:[Antibiotics]<sub>0</sub> = 2:1, j = 2.5 mA cm<sup>-2</sup>, HRT = 5 min, and pH 3.0), PAA-mediated electrochlorination in the flow-through electrochemical system effectively removes four mixed antibiotics with a notably low specific energy consumption of 5.3 Wh mmol<sup>-1</sup>. Furthermore, reductions in TPs, including but not limited to chloroform (< 60  $\mu$ g L<sup>-1</sup>), are achieved in both simulated and actual groundwater, meeting the Chinese drinking water quality standards set out in 2022. FT-ICR MS

analysis reveals that the PAA-mediated treatment preferentially removes highly unsaturated, heavy molecular formulae (O/C < 0.3, MW >400 Da), with the number of CHOCl formulae decreasing by 59 % ( $n = 180 \rightarrow 83$ ) as compared to pure electrochlorination process. The primary transformation pathways of TPs have been identified as decarbonylation, dihydroxylation, and hydrogenation. Moreover, a significant reduction of 77.9 % (from 208 to 46) was observed in the number of possible halogenation reactions. The FT–ICR MS results provide a coherent and complementary explanation to the DFT calculations and experimental observations, acute toxicity predictions, spectroscopy, and FT-ICR MS enhances our understanding of the mechanisms underlying TPs transformations in the PAA-mediated EAOPs.

The reduced yield of toxic TPs is poised to facilitate the broader adoption of this technology in future. Future research should address the structural upgrade of flow-through reactors, adding rapid monitoring ports to achieve in-situ/operando capture and monitoring of ROS in flow-through mode. Note that this research has application potential within the pH range of 3.0 to 9.0, but further specialized optimization is needed to refine the technical applicability boundaries. Furthermore, a stratified toxicity testing framework should also be carried out, including further conducting zebrafish embryo development tests and *Daphnia magna* breeding tests after using the ISO 11348 standardized Microtox acute toxicity test.

#### Associated content

Supporting Information (SI) contains Text S1-S13, Tables S1-S11, and Figures S1-S21. This information is available free of charge on the Elsevier Publications website.

# CRediT authorship contribution statement

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

# 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.

# Acknowledgments

The authors acknowledge financial support from project No 42277041 (National Natural Science Foundation of China, NSFC). I.S. is grateful to project PID2022–1403780B-I00, funded by MICIU/AEI/ 10.13039/501100011033 (Spain) and by ERDF/EU. Help from the *Centres Científics i Tecnològics de la UB* (CCiT-UB) to carry out the SPME/ GC/MS and LC-MS/MS analysis is also acknowledged.

### Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2025.124013.

# Data availability

Data will be made available on request.

#### References

- Arulkumaran, N., Routledge, M., Schlebusch, S., Lipman, J., Conway Morris, A., 2020. Antimicrobial-associated harm in critical care: a narrative review. Intensive Care Med. 46, 225–235. https://doi.org/10.1007/s00134-020-05929-3.
- Baptista-Pires, L., Norra, G.-F., Radjenovic, J., 2021. Graphene-based sponges for electrochemical degradation of persistent organic contaminants. Water. Res. 203, 117492. https://doi.org/10.1016/j.watres.2021.117492.
- Ben, Y., Hu, M., Zhang, X., Wu, S., Wong, M.H., Wang, M., Andrews, C.B., Zheng, C., 2020. Efficient detection and assessment of human exposure to trace antibiotic residues in drinking water. Water. Res. 175, 115699. https://doi.org/10.1016/j. watres.2020.115699.
- Brillas, E., Sirés, I., Oturan, M.A., 2009. Electro-Fenton process and related electrochemical technologies based on Fenton's reaction chemistry. Chem. Rev. 109, 6570–6631. https://doi.org/10.1021/cr900136g.
- Chen, F., Liu, L., Wu, J., Rui, X., Chen, J., Yu, Y., 2022. Single-atom iron anchored tubular g-C<sub>3</sub>N<sub>4</sub> catalysts for ultrafast fenton-like reaction: roles of high-valency ironoxo species and organic radicals. Adv. Mater., 2202891 https://doi.org/10.1002/ adma.202202891.
- Chen, M., Yang, T., Zhao, L., Shi, X., Li, R., Ma, L., Huang, Y., Wang, Y., Lee, S., 2024. Manganese oxide on activated carbon with peroxymonosulfate activation for enhanced ciprofloxacin degradation: activation mechanism and degradation pathway. Appl. Surf. Sci. 645, 158835. https://doi.org/10.1016/j. apsusc.2023.158835.
- Chen, W., Westerhoff, P., Leenheer, J.A., Booksh, K., 2003a. Fluorescence excitation-emission matrix regional integration to quantify spectra for dissolved organic matter. Env. Sci. Technol. 37, 5701–5710. https://doi.org/10.1021/ es034354c.
- Chen, X.-J., Bai, C.-W., Sun, Y.-J., Huang, X.-T., Zhang, B.-B., Zhang, Y.-S., Yang, Q., Wu, J.-H., Chen, F., 2023. pH-driven efficacy of the ferrate(VI)–peracetic acid system in swift sulfonamide antibiotic degradation: a deep dive into active species evolution and mechanistic insights. Env. Sci. Technol. 57, 20206–20218. https://doi.org/ 10.1021/acs.est.3c06370.
- Cheng, Y., Wang, Z., Cao, L., Chen, Z., Chen, Y., Liu, Z., Ma, J., Xie, P., 2024. Tailorable morphology control of Prussian blue analogues toward efficient peracetic acid activation for sulfonamides removal. Appl. Catal. B: Env. 342, 123409. https://doi. org/10.1016/j.apcatb.2023.123409.
- Choi, S., Choi, W.I., Lee, J., Lee, C.H., Balamurugan, M., Schwarz, A.D., Choi, Z.S., Randriamahazaka, H., Nam, K.T., 2023. A reflection on sustainable anode materials for electrochemical chloride oxidation. Adv. Mater., 2300429 https://doi.org/ 10.1002/adma.202300429.
- Cuervo Lumbaque, E., Baptista-Pires, L., Radjenovic, J., 2022. Functionalization of graphene sponge electrodes with two-dimensional materials for tailored electrocatalytic activity towards specific contaminants of emerging concern. Chem. Eng. J. 446, 137057. https://doi.org/10.1016/j.cej.2022.137057.
- Deng, F., Olvera-Vargas, H., Zhou, M., Qiu, S., Sirés, I., Brillas, E., 2023. Critical review on the mechanisms of Fe<sup>2+</sup> regeneration in the electro-fenton process: fundamentals and boosting strategies. Chem. Rev. 123, 4635–4662. https://doi.org/10.1021/acs. chemrev.2c00684.
- Deng, Y., Chen, N., Feng, C., Chen, F., Wang, H., Feng, Z., Zheng, Y., Kuang, P., Hu, W., 2019. Research on complexation ability, aromaticity, mobility and cytotoxicity of humic-like substances during degradation process by electrochemical oxidation. Env. Pollut. 251, 811–820. https://doi.org/10.1016/j.envpol.2019.05.047.
- Dong, Y., He, C.-S., Sun, S., Liu, J., Xie, Z.-H., Li, J.-Y., Zhou, P., Zhang, H., Dong, F., Lai, B., 2024. Mechanically treated Mn<sub>2</sub>O<sub>3</sub> triggers peracetic acid activation for superior non-radical oxidation of micropollutants: identification of reactive complexes. Water. Res. 255, 121486. https://doi.org/10.1016/j. watres.2024.121486.
- Fu, C., Xu, B., Chen, H., Zhao, X., Li, G., Zheng, Y., Qiu, W., Zheng, C., Duan, L., Wang, W., 2022. Occurrence and distribution of antibiotics in groundwater, surface water, and sediment in Xiong'an New Area, China, and their relationship with antibiotic resistance genes. Sci. Total Env. 807, 151011. https://doi.org/10.1016/j. scitotenv.2021.151011.
- Jiang, W., Duan, Y., Bandaru, S.R.S., Radjenovic, J., Sedlak, D.L., Mi, B., 2024. Inhibition of chlorinated byproducts formation by boron-doped rGO electrodes during electrooxidation of trace organic contaminants. Appl. Catal. B: Env. Energy 357, 124303. https://doi.org/10.1016/j.apcatb.2024.124303.
- Kim, J., Du, P., Liu, W., Luo, C., Zhao, H., Huang, C.-H., 2020. Cobalt/peracetic acid: advanced oxidation of aromatic organic compounds by acetylperoxyl radicals. Env. Sci. Technol. 54, 5268–5278. https://doi.org/10.1021/acs.est.0c00356.
- Kim, J., Huang, C.-H., 2021. Reactivity of peracetic aid with organic compounds: a critical review. ACS EST Water 1, 15–33. https://doi.org/10.1021/ acsestwater.0c00029.
- Kong, D., Zhao, Y., Fan, X., Wang, Xianshi, Li, J., Wang, Xiaoxiong, Nan, J., Ma, J., 2022. Reduced graphene oxide triggers peracetic acid activation for robust removal of micropollutants: the role of electron transfer. Env. Sci. Technol. 56, 11707–11717. https://doi.org/10.1021/acs.est.2c02636.
- Li, S., Fu, X., Nørskov, J.K., Chorkendorff, I., 2024a. Towards sustainable metal-mediated ammonia electrosynthesis. Nat. Energy. https://doi.org/10.1038/s41560-024-01622-7.
- Li, J., Qin, W., Zhu, B., Ruan, T., Hua, Z., Du, H., Dong, S., Fang, J., 2024b. Insights into the transformation of natural organic matter during UV/peroxydisulfate treatment by FT-ICR MS and machine learning: non-negligible formation of organosulfates. Water. Res. 256, 121564. https://doi.org/10.1016/j.watres.2024.121564.
- Liu, X., Wang, Y., Crittenden, J., Su, Q., Mo, H., 2024. Enhanced treatment of high chloride organic wastewater under lower peroxymonosulfate consumption: a

pathway for the formation of Fe(IV)=O excited by chloride ions. Appl. Catal. B: Env. Energy 359, 124471. https://doi.org/10.1016/j.apcatb.2024.124471.

- Lu, J., Wang, Y., Li, H., Hu, W., Zhou, G., Sun, B., Gu, S., 2023. Bi<sub>2</sub>MoS<sub>x</sub>O<sub>6-x/a</sub>-CoS Crystalline/amorphous S-scheme heterojunction for visible light-driven targeted photo-decomposition of amoxicillin. Chem. Eng. J. 470, 144294. https://doi.org/ 10.1016/j.cej.2023.144294.
- Lu, W., Chen, N., Feng, C., An, N., Dong, Y., 2024a. Peracetic acid-based electrochemical treatment of sulfamethoxazole and real antibiotic wastewater: different role of anode and cathode. J. Hazard. Mater. 463, 132819. https://doi.org/10.1016/j. ihazmat.2023.132819.
- Lu, W., Chen, N., Feng, C., Sirés, I., An, N., Mu, H., 2024b. Exploring the viability of peracetic acid-mediated antibiotic degradation in wastewater through activation with electrogenerated HCIO. Water. Res. 261, 122007. https://doi.org/10.1016/j. watres.2024.122007.
- Lu, Y., Song, Z.-M., Wang, C., Liang, J.-K., Hu, Q., Wu, Q.-Y., 2021. Combining high resolution mass spectrometry with a halogen extraction code to characterize and identify brominated disinfection byproducts formed during ozonation. Sci. Total Env. 796, 149016. https://doi.org/10.1016/j.scitotenv.2021.149016.
- Meng, L., Dong, J., Chen, J., Li, L., Huang, Q., Lu, J., 2023. Activation of peracetic acid by spinel FeCo<sub>2</sub>O<sub>4</sub> nanoparticles for the degradation of sulfamethoxazole. Chem. Eng. J. 456, 141084. https://doi.org/10.1016/j.cej.2022.141084.
- Norra, G.-F., Baptista-Pires, L., Cuervo Lumbaque, E., Borrego, C.M., Radjenovic, J., 2022. Chlorine-free electrochemical disinfection using graphene sponge electrodes. Chem. Eng. J. 430, 132772. https://doi.org/10.1016/j.cej.2021.132772.
- Norra, G.-F., Radjenovic, J., 2021. Removal of persistent organic contaminants from wastewater using a hybrid electrochemical-granular activated carbon (GAC) system. J. Hazard. Mater. 415, 125557. https://doi.org/10.1016/j.jhazmat.2021.125557.
- Qian, Y., Huang, J., Chen, J., Xue, G., Zhou, Z., Gao, P., 2022. Activation of peracetic acid by RuO<sub>2</sub>/MWCNTs to degrade sulfamethoxazole at neutral condition. Chem. Eng. J. 431, 134217. https://doi.org/10.1016/j.cej.2021.134217.
- Radjenović, J., Farré, M.J., Mu, Y., Gernjak, W., Keller, J., 2012. Reductive electrochemical remediation of emerging and regulated disinfection byproducts. Water. Res. 46, 1705–1714. https://doi.org/10.1016/j.watres.2011.12.042.
- Radjenovic, J., Sedlak, D.L., 2015. Challenges and opportunities for electrochemical processes as next-generation technologies for the treatment of contaminated water. Env. Sci. Technol. 49, 11292–11302. https://doi.org/10.1021/acs.est.5b02414.
- Shah, A.D., Liu, Z.-Q., Salhi, E., Höfer, T., von Gunten, U., 2015. Peracetic acid oxidation of saline waters in the absence and presence of H<sub>2</sub>O<sub>2</sub>: secondary oxidant and disinfection byproduct formation. Env. Sci. Technol. 49, 1698–1705. https://doi. org/10.1021/es503920n.
- Teng, C., Zhou, K., Zhang, Z., Peng, C., Chen, W., 2020. Elucidating the structural variation of membrane concentrated landfill leachate during Fenton oxidation process using spectroscopic analyses. Env. Pollut. 256, 113467. https://doi.org/ 10.1016/j.envpol.2019.113467.
- Thomas, M., Nałęcz-Jawecki, G., Giebułtowicz, J., Drzewicz, P., 2024. Degradation of oxytetracycline by ferrate(VI): treatment optimization, UHPLC-MS/MS and toxicological studies of the degradation products, and impact of urea and creatinine on the removal. Chem. Eng. J. 485, 149802. https://doi.org/10.1016/j. cei.2024.149802.
- Wang, Z., Du, Y., Liu, T., Li, J., He, C., Liu, Y., Xiong, Z., Lai, B., 2024. How should we activate ferrate(VI)? Fe(IV) and Fe(V) tell different stories about fluoroquinolone transformation and toxicity changes. Env. Sci. Technol. 58, 4812–4823. https://doi. org/10.1021/acs.est.3c10800.
- Wei, R., Pei, S., Yu, Y., Zhang, J., Liu, Y., You, S., 2023. Water flow-driven coupling process of anodic oxygen evolution and cathodic oxygen activation for water decontamination and prevention of chlorinated byproducts. Env. Sci. Technol. 57, 17404–17414. https://doi.org/10.1021/acs.est.3c02256.
- Wu, D.-X., Lu, Y., Ye, B., Liang, J.-K., Wang, W.-L., Du, Y., Wu, Q.-Y., 2024. Phototransformation of brominated disinfection byproducts and toxicity elimination in sunlit-ozonated reclaimed water. Env. Sci. Technol. 58, 1700–1708. https://doi. org/10.1021/acs.est.3c06972.
- Wu, S., Hua, P., Gui, D., Zhang, J., Ying, G., Krebs, P., 2022. Occurrences, transport drivers, and risk assessments of antibiotics in typical oasis surface and groundwater. Water. Res. 225, 119138. https://doi.org/10.1016/j.watres.2022.119138.
- Xie, J., Ma, J., Zhao, S., Waite, T.D., 2021. Flow anodic oxidation: towards highefficiency removal of aqueous contaminants by adsorbed hydroxyl radicals at 1.5 V vs SHE. Water. Res. 200, 117259. https://doi.org/10.1016/j.watres.2021.117259.
- Xie, L., Wang, P., Zheng, W., Zhan, S., Xia, Y., Liu, Y., Yang, W., Li, Y., 2023. The strong metal-support interactions induced electrocatalytic three-electron oxygen reduction to hydroxyl radicals for water treatment. In: Proc. Natl. Acad. Sci. 120, e2307989120. https://doi.org/10.1073/pnas.2307989120.
- Yang, C., Sun, R., Cui, J., Yao, B., Guo, Y., 2024. Analysis of dissolved organic matter characteristics in pharmaceutical wastewater via spectroscopy combined with Fourier-transform ion cyclotron resonance mass spectrometry. J. Hazard. Mater. 479, 135706. https://doi.org/10.1016/j.jhazmat.2024.135706.
- Yuan, D., Yang, K., Pan, S., Xiang, Y., Tang, S., Huang, L., Sun, M., Zhang, X., Jiao, T., Zhang, Q., Li, B., 2021. Peracetic acid enhanced electrochemical advanced oxidation for organic pollutant elimination. Sep. Purif. Technol. 276, 119317. https://doi.org/ 10.1016/j.seppur.2021.119317.
- Zhang, B., Shan, C., Wang, S., Fang, Z., Pan, B., 2021. Unveiling the transformation of dissolved organic matter during ozonation of municipal secondary effluent based on FT-ICR-MS and spectral analysis. Water. Res. 188, 116484. https://doi.org/10.1016/ j.watres.2020.116484.

Zhang, Z., Cui, X., Qu, X., Fu, H., Tao, S., Zhu, D., 2024a. Revealing molecular structures of nitrogen-containing compounds in dissolved black carbon using ultrahighW. Lu et al.

resolution mass spectrometry combined with thermodynamic calculations. Env. Sci. Technol. 58, 11998–12007. https://doi.org/10.1021/acs.est.4c01829.

- Zhang, G., Li, Y., Zhao, C., Gu, J., Zhou, G., Shi, Y., Zhou, Q., Xiao, F., Fu, W., Chen, Q., Ji, Q., Qu, J., Liu, H., 2024b. Redox-neutral electrochemical decontamination of hypersaline wastewater with high technology readiness level. Nat. Nanotechnol. 19, 1130–1140. https://doi.org/10.1038/s41565-024-01669-3.
- Zhang, P., Xu, L., Su, J., Zeng, Y., Liu, Y., Li, X., 2024c. Simultaneous removal of nitrate, oxytetracycline and copper by ferrous-manganese co-driven immobilized bioreactor. J. Hazard. Mater. 466, 133621. https://doi.org/10.1016/j.jhazmat.2024.133621.
- Zhang, Q., Ying, G., Pan, C., Liu, Y., Zhao, J., 2015. Comprehensive evaluation of antibiotics emission and fate in the river basins of China: source analysis, multimedia modeling, and linkage to bacterial resistance. Env. Sci. Technol. 49, 6772–6782. https://doi.org/10.1021/acs.est.5b00729.
- Zhang, J., Zhang, Y., Lv, N., Li, F., Li, Y., Guo, Z., 2024d. Electrochemistry promotion of Fe(III)/Fe(II) cycle for continuous activation of PAA for sludge disintegration: performance and mechanism. Env. Res. 256, 119268. https://doi.org/10.1016/j. envres.2024.119268.
- Zou, R., Yang, W., Rezaei, B., Tang, K., Guo, K., Zhang, P., Keller, S.S., Andersen, H.R., Zhang, Y., 2024. Activation of peracetic acid by electrodes using biogenic electrons: a novel energy- and catalyst-free process to eliminate pharmaceuticals. Water. Res. 261, 122065. https://doi.org/10.1016/j.watres.2024.122065.
- Zuo, K., Garcia-Segura, S., Cerrón-Calle, G.A., Chen, F.-Y., Tian, X., Wang, X., Huang, X., Wang, H., Alvarez, P.J.J., Lou, J., Elimelech, M., Li, Q., 2023. Electrified water treatment: fundamentals and roles of electrode materials. Nat. Rev. Mater. 8, 472–490. https://doi.org/10.1038/s41578-023-00564-y.