



A review of anodic oxidation, electro-Fenton and electrochemical nitrate reduction: A decade of advances and future directions

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ABSTRACT

Electrochemical water treatment has advanced considerably over the past decade and is increasingly recognized as an effective and versatile approach for the removal of organic and inorganic contaminants. This review provides an integrated assessment of progress from 2015 to 2025 in anodic oxidation, electro-Fenton, and electrochemical nitrate reduction. Advances in electrode materials, reaction mechanisms, reactor engineering, and energy performance metrics are critically evaluated, with particular emphasis on operation in realistic water matrices and the transition from batch laboratory systems to flow-based and semi-autonomous configurations. Beyond materials development, this review demonstrates that reactor configuration, operating mode, and energy management increasingly govern process stability and scalability. The role of normalized energy metrics is evaluated within an engineering framework to support meaningful performance comparison. Persistent challenges are identified, including unrealistic contaminant concentrations, electrode durability limitations, and techno-economic constraints. Finally, emerging trends toward modular, adaptive, and decentralized systems, integration with renewable energy sources, hybridization with biological and membrane processes, and selective transformation or valorization of by-products are identified as key directions for future research.

1. Introduction

Electrochemical water treatment technologies have re-emerged over the last decade as a versatile class of advanced processes for water and wastewater remediation. Their appeal stems from distinctive attributes that directly align with current engineering needs such as operation under ambient conditions, modularity, compatibility with renewable electricity, and the ability to treat chemically diverse contaminants

without the continuous addition of hazardous reagents [1–3]. In these systems, the anode and cathode play complementary roles. Anodic reactions can generate ROS that drive the transformation of organic contaminants, whereas cathodic reactions enable the reduction of inorganic pollutants and/or the electrogeneration of key reagents such as H_2O_2 for EF. This combination allows electrochemical systems to address both organic and inorganic water quality challenges within a single treatment platform [4–7].

Abbreviations: ACE, Average current efficiency; BDD, Boron-doped diamond; BOD, Biochemical oxygen demand; CAPEX, Capital expenditure; CBZ, Carbamazepine; CPC, Compound parabolic collector; COD, Chemical oxygen demand; CNT, Carbon nanotubes; DMPO, 5,5-Dimethyl-1-pyrroline-N-oxide; DSA, Dimensionally stable anode; EAOP, Electrochemical advanced oxidation process; EC, Specific energy consumption; EC_{COD} , Specific energy consumption per unit COD removed; EC_{TOC} , Specific energy consumption per unit TOC removed; EE/O, Electric energy per order; EF, Electro-Fenton; EO, Electrochemical oxidation; ENR, Electrochemical nitrate reduction; EPR, Electron paramagnetic resonance; E_{cell} , Cell potential; E_{cat} , Cathodic potential; FE, Faradaic efficiency; FM01-LC, Filter-press flow reactor (FM01-LC type); GDE, Gas diffusion electrode; GE, Graphite electrode; HA, Humic acid; HEF, Heterogeneous electro-Fenton; HFCVD, Hot filament chemical vapor deposition; I , Applied current; j , Current density; MAD, Modular, adapted, and decentralized; MBs, Macrobubbles; MCE, Mineralization current efficiency; MF, Microfiltration; MOF, Metal-organic framework; NOM, Natural organic matter; NBs, Nanobubbles; NF, Nanofiltration; OEP, Oxygen evolution potential; ORR, Oxygen reduction reaction; OTC, Oxytetracycline; PEF, Photoelectro-Fenton; PFHxA, Perfluorohexanoic acid; PFOS, Perfluorooctanesulfonate; POE, Point of entry; POU, Point of use; PMS, Peroxymonosulfate; RO, Reverse osmosis; ROS, Reactive oxygen species; SAC, Single-atom catalyst; SEC-RPR, Solar electrochemical raceway pond reactor; SHE, Standard hydrogen electrode; SDS, Sodium dodecyl sulfate; SPEF, Solar photoelectro-Fenton; SS, Stainless steel; TOC, Total organic carbon; TRL, Technology readiness level; US, Ultrasound; UV, Ultraviolet; WHO, World Health Organization.

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Table 1
Standard reduction potential (E°) of common oxidizing species.

Oxidizing agent	E° (V vs. SHE)
Hypochlorite (ClO^-)	0.89
Superoxide ($\text{O}_2^{\bullet -}$)	0.93
Oxygen (molecular)	1.23
Chlorine	1.36
Hypochlorous acid (HClO)	1.63
H_2O_2	1.76
Ozone (O_3)	2.08
Singlet oxygen ($^1\text{O}_2$)	2.23
Oxygen (atomic)	2.42
Sulfate radical ($\text{SO}_4^{\bullet -}$)	2.6–3.1
Hydroxyl-radical ($\bullet\text{OH}$)	2.73
Fluorine	3.06

Among the different approaches, three technology families have received particularly intense attention, namely EO, EF, and ENR [8–11]. EO and EF have demonstrated high removal efficiencies for diverse emerging contaminants, such as pharmaceuticals, personal care products, pesticides, dyes, antibiotics, and endocrine-disruption compounds [12–14]. In parallel, nitrate and other nitrogen oxyanions have become a major target due to their widespread occurrence in drinking-water sources and their associated health and ecological risks, making ENR a rapidly expanding topic [15–17]. Importantly, the combined oxidative and reductive capabilities of electrochemical systems enable treatment strategies that go beyond single-contaminant studies, supporting emerging needs in potable water production, reuse, and decentralized sanitation.

Between 2015 and 2025, the field has expanded in both breadth and maturity. Progress has been achieved in the development of more stable and selective electrode materials, in the understanding of radical and non-radical reaction pathways, and in reactor design beyond conventional batch laboratory cells [15–21]. Notably, reactor configurations have progressed from small, stirred laboratory cells toward flow-based and modular designs and autonomous units compatible with renewable power [22,23]. This period therefore marks a transition from mainly laboratory demonstrations toward more integrated and application-oriented electrochemical treatment systems.

Despite these advances, electrochemical water treatment is not yet widely deployed on a commercial scale. Challenges include electrode cost and durability, maintenance requirements, energy consumption under realistic water conditions, and the scarcity of long-term field validation. In addition, many experimental studies still use pollutant concentrations significantly higher than those typically found in real waters. While such conditions facilitate mechanistic studies and materials screening, they may not fully reflect matrix effects such as scaling, fouling, or competitive reactions. As a result, energy efficiency and long-term performance can be overestimated.

Several reviews published in the past decade have examined EO, EF, and ENR individually. Although these contributions have provided valuable insights, the three technologies are often discussed separately despite sharing common electrochemical foundations, reactor concepts, and operational challenges. In this review, we present an integrated and comparative assessment of EO, EF, and ENR over the period 2015–2025. We focus on converging trends in materials development, mechanistic understanding, reactor engineering, and energy evaluation and the progression toward MAD systems integrated with renewable energy.

2. Fundamentals of electrochemical water treatment

This section briefly explains the fundamentals of the main electrochemical water treatment technologies that have received great attention over the last ten years. EO, also called anodic oxidation, EF and its related PEF, and ENR are detailed. Operating considerations and energetic parameters are finally presented as tools to understand the power of such technologies for water remediation.

2.1. Electrochemical oxidation

EO is the most used EAOP due to its conceptual simplicity and versatility. Its performance is primarily governed by the nature of the anode material that determines the oxidation power of the oxidants electrogenerated. Table 1 collects the standard reduction potentials (E°) of common oxidizing agents that are electrogenerated not only during EO but also in EF systems. In EO, organic contaminants in the aqueous solution can be degraded either by direct electron transfer at the anode surface or by mediated oxidation involving reactive species generated from water discharge or electrolyte oxidation. The former pathway typically results in limited organic removal, whereas the latter can lead to partial or even complete mineralization, particularly when operating at high current intensities (I). In this case, the anode (M) promotes water oxidation to O_2 with $E^\circ = 1.23 \text{ V/SHE}$ from reaction (1), forming surface-bound hydroxyl radicals $\text{M}(\bullet\text{OH})$, the key oxidizing species in EO [24]:



This reaction occurs in two extreme ideal anodes, so-called active and non-active anodes: Active anodes such as graphite, DSA like RuO_2 and IrO_2 , and Pt leads oxidize the organics to selective biodegradable intermediates like carboxylic acids. This low oxidation ability is ascribed to the oxidation of $\text{M}(\bullet\text{OH})$ to a chemisorbed “active oxygen” MO with low oxidation power. In contrast, non-active anodes such as BDD, Ti_4O_7 , PbO_2 , and doped SnO_2 favor complete mineralization of organics owing to their ability to generate higher concentrations of physisorbed $\text{M}(\bullet\text{OH})$. Among these, BDD is recognized as the most powerful anode, mainly due to its higher OEP, outstanding chemical and electrochemical stability, and low surface adsorption affinity.

Note that the oxidizing power of $\text{M}(\bullet\text{OH})$ decays by its parasitic non-oxidant reactions including its oxidation to O_2 by reaction (2), dimerization to H_2O_2 by reaction (3), or the formation of the hydroperoxyl radical ($\text{M}(\text{HO}_2^\bullet)$) from reaction (4). Additionally, ozone can be generated from reaction (5). Despite these competing reactions $\text{M}(\bullet\text{OH})$ remains the most potent ROS generated in EO [25].



In sulfate medium, the BDD anode can also promote the formation of additional oxidizing agents such as persulfate ($\text{S}_2\text{O}_8^{2-}$) and sulfate radical ($\text{SO}_4^{\bullet -}$) as follows [24,25]:



$\text{SO}_4^{\bullet -}$ is a strong oxidant whose E° value varies between +2.6 and +3.1 V/SHE (see Table 1), raising from pH 0 to 12. When the EO process is performed in chloride medium, active chlorine species ($\text{Cl}_2/\text{HClO}/\text{ClO}^-$) are generated via reactions (7)–(9), competing with $\text{M}(\bullet\text{OH})$ for organic oxidation. The anodic oxidation of Cl^- to $\text{Cl}_{2(\text{aq})}$ (7) is followed by its hydrolysis to HClO (8), which is in equilibrium with ClO^- (9). These species predominate in the medium in the order: $\text{Cl}_{2(\text{aq})}$ up to pH 3.0, HClO in the range 3.0–8.0, and ClO^- at pH > 8.0. Table 1 makes evident that HClO is the most potent oxidant under acidic medium. However, its reactivity is limited by parasitic reactions leading to toxic and undesirable chlorite, chlorate and perchlorate from reactions (10)–(12). These by-products are of regulatory concern. According to World Health Organization guidelines, chlorate and perchlorate limits in drinking water are $700 \mu\text{g L}^{-1}$ and $70 \mu\text{g L}^{-1}$, respectively. In undivided cells, partial cathodic reduction of ClO^- may also occur by reaction (13) [26].



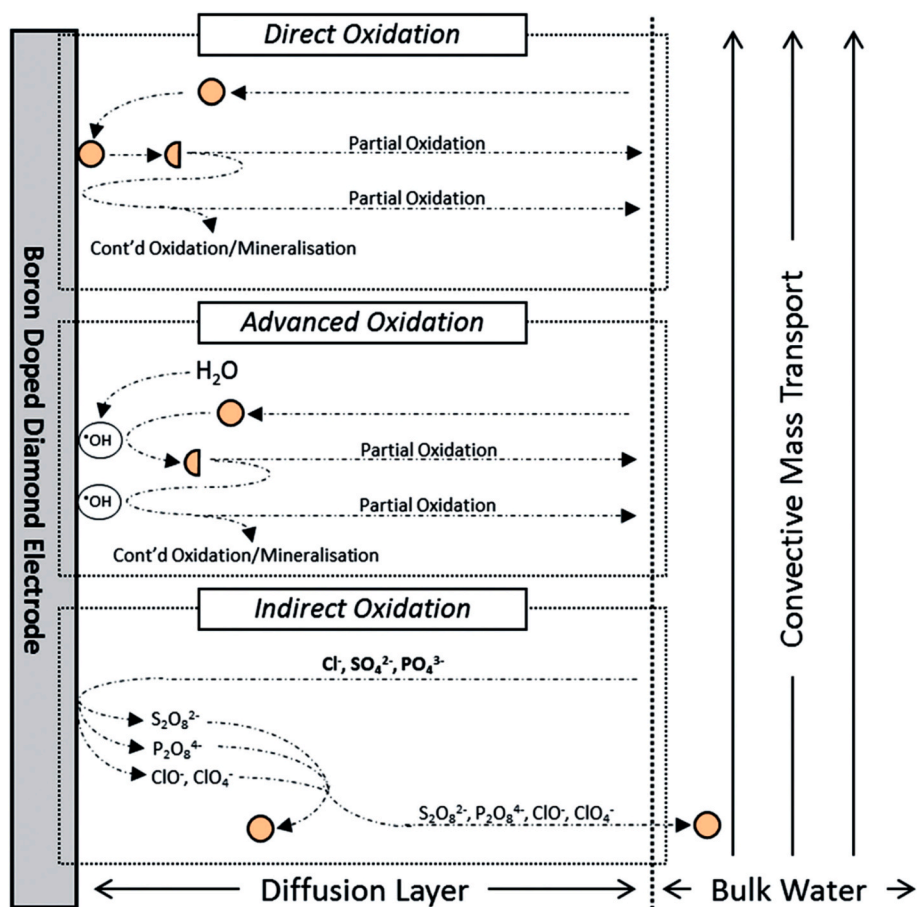
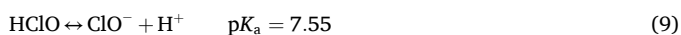


Fig. 1. Schematic mechanism of the direct electron transfer, advanced oxidation, and indirect oxidation processes at a BDD anode in EO. Adapted from ref. [27] with permission of Royal Society of Chemistry.



Since industrial and urban wastewaters typically contain high Cl^- concentrations, evaluating EO performance in chloride media is crucial. Under such conditions, RuO_2 anodes ($\text{DSA}-\text{Cl}_2$) give the largest amounts of active chlorine. However, highly recalcitrant chloroderivatives are formed, thus limiting the mineralization process of EO. Fig. 1 schematizes a mechanism of the processes taking place at the BDD surface to remove organics by direct electron transfer and/or mediated oxidation with $\text{M}(\cdot\text{OH})$ and generated oxidants such as active chlorine [27].

2.2. Electro-Fenton and related processes

Homogeneous EF, simply known as EF, is based on the in-situ production of H_2O_2 by reaction (14) with $E^\circ = 0.68$ V vs. SHE in acidic medium involving the two-electron reduction of O_2 gas preferentially at carbonaceous cathodes [28]:



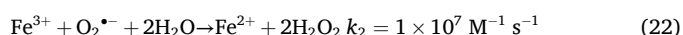
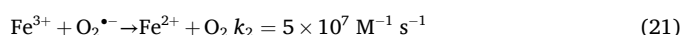
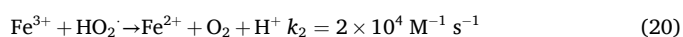
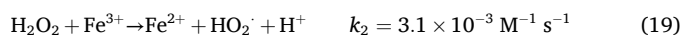
This reaction is easier than reduction of O_2 to water via 4-electrons with $E^\circ = 1.23$ V vs. SHE. However, parasitic reactions such as cathodic H_2O_2 reduction (15) and its spontaneous disproportion from Eq. (16) can occur, reducing the process efficiency. Additionally, in undivided cell, the anodic oxidation of electrogenerated H_2O_2 may form hydroperoxyl radicals ($\text{HO}_2^\cdot$) by reaction (17).



H_2O_2 is a weak oxidant (see Table 1) and its oxidation power can be strongly enhanced in EF by adding a small amount of Fe^{2+} to the acidic solutions. The Fenton reactions of Eq. (18) produces homogeneous $\cdot\text{OH}$, the main oxidizing species in EF, with an absolute rate constant $k_2 = 76 \text{ M}^{-1} \text{ s}^{-1}$ at optimum pH near 3.0 [25,28]:



The process operates catalytically through the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple, which is sustained by a network of reactions involving $\text{HO}_2^\cdot$ and $\text{O}_2^\cdot$ (Eqs. 19–22) [29,30]:



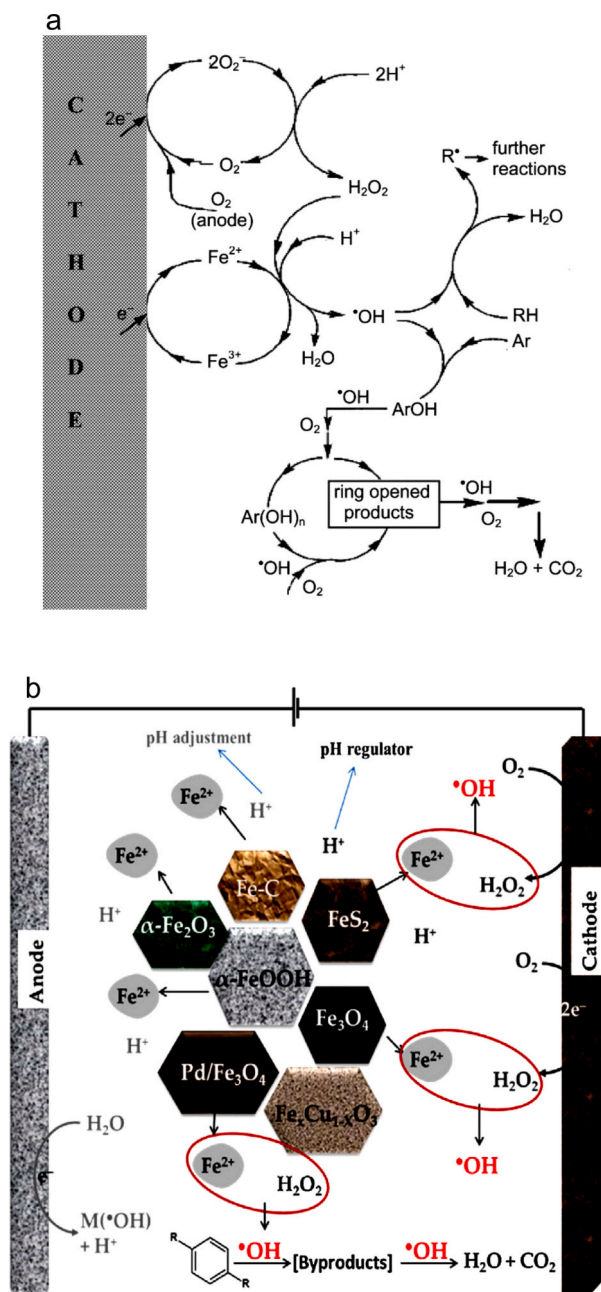
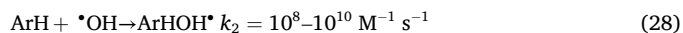
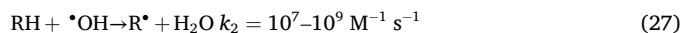
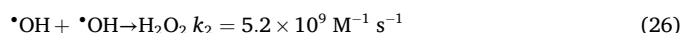
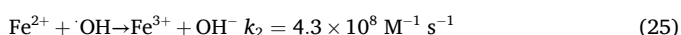
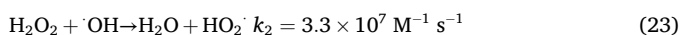


Fig. 2. (a) Schematic illustration of the main reactions involved in the EF process in a divided cell. RH is an unsaturated compound that is dehydrogenated and Ar is an aroma pollutant that is hydroxylated. (b) Schematic mechanism of the heterogeneous EF (HEF) process in an undivided cell with several solid catalysts, with reaction between electrogenerated H_2O_2 and their surface $\equiv\text{Fe}^{2+}$ ions. Adapted from ref. [30] with permission of Elsevier.

Inhibition reactions involve $\text{HO}_2^{\cdot}$ generation by reaction (23) with further superoxide ($\text{O}_2^{\cdot -}$) conversion by reaction (24), and removal of $\text{OH}^{\cdot}$ with Fe^{2+} by reaction (25) and its dimerization to H_2O_2 by reaction (26). So, this radical can attack saturated (RH) or aromatic (ArH) organics to give dehydrogenated or hydroxylated by-products by reactions (27) or (28), respectively [30].



Moreover, Fe^{2+} can be regenerated from Fe^{3+} reduction by reaction (29), with $E^\circ = 0.77 \text{ V}$ vs. SHE. In an undivided electrolytic cell, a slow oxidation of Fe^{3+} to Fe^{2+} occurs by reaction (30) [29]:

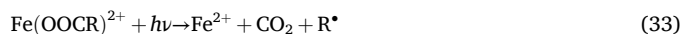


HEF extends EF applicability to near-neutral pH by employing solid iron catalyst or modified cathodes. In this case, H_2O_2 reacts with the surface $\equiv\text{Fe}^{2+}$ of such materials through heterogeneous Fenton reaction (31) [30]:



In an undivided cell, $\text{M}(\text{OH})$ formed from reaction (1) and $\text{OH}^{\cdot}$ generated from reactions (18) or (31) are the main oxidants in homogeneous or heterogeneous EF. Fig. 2a and b illustrate the mechanisms of both processes [30].

The PEF process is an advanced EF variant in which the acidic treated effluent is illuminated with UV light. Depending on the light source, UVA ($\lambda = 315\text{--}400 \text{ nm}$), UVB ($\lambda = 285\text{--}315 \text{ nm}$), or UVC ($\lambda < 285 \text{ nm}$) may be used. If sunlight is used as energy source, the process is called SPEF with $\lambda > 300 \text{ nm}$, which can be mimicked with a Xe lamp. The light irradiation causes: (i) the quick photoreduction of $\text{Fe}(\text{OH})^{2+}$, the preferent Fe^{3+} species at pH 2.8–3.5, according to photo-Fenton reaction (32) originating Fe^{2+} and more $\text{OH}^{\cdot}$ and (ii) the photolysis of $\text{Fe}(\text{III})$ -carboxylate complexes with Fe^{2+} regeneration from the general reaction (33) [28].

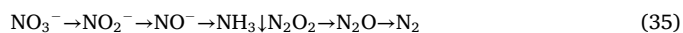


Recalcitrant carboxylic acids that form $\text{Fe}(\text{III})$ complexes are the main final by-products in EF. In PEF, these derivatives can be photolyzed, enhancing the mineralization process. When UVC light is applied, some organics can be photodegraded and H_2O_2 can be homolytically photolyzed to $\text{OH}^{\cdot}$ from reaction (34) increasing the oxidation power of the PEF system [28,30]:



2.3. Electrocatalytic reduction of nitrogen-oxyanions

ENR has emerged as a key electrified technology for addressing nitrate contamination in drinking water and groundwater. Its performance strongly depends on the choice of the cathode material, cell configuration, applied current density (j), and the composition and pH of the solution. The reduction proceeds through a multistep pathway involving consecutive transformation into NO_2^- , NO^- , N_2O_2 , NH_3 , and N_2 [31]:

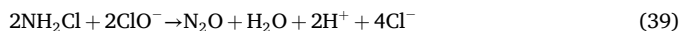


In non-chloride media, the process evolves from reactions (36)–(37) [32]:



However, in an undivided cell and in the presence of Cl^- , active chlorine is generated from reactions (7)–(9), which can react with NH_3

to form chloramines such as NH_2Cl that can yield N_2O by reaction (39) [33]. According to WHO guidelines, the recommended limit for monochloramine in drinking water is 3 mg L^{-1} (as total chlorine), making chloramine formation a relevant consideration in chloride-containing systems.



In real waters, ENR is particularly sensitive to hardness, carbonate alkalinity and NOM, which can promote inorganic scaling and surface fouling. These effects highlight the importance of coupling material development with water chemistry considerations and pre-treatment strategies when designing practical ENR systems [34].

2.4. Operating considerations and energetic parameters

The applied I , j , or applied cell (E_{cell}) determine the efficiency of the degradation and mineralization of a given organic pollutant in aqueous matrices. The degradation progress is commonly monitored by the decay of absorbance (A) at the maximum λ of the target pollutant in the solution or by measuring its concentration (c), whereas the mineralization evolution is measured from the abatement of the COD and/or TOC.

The percent of discoloration and that of degradation removal are calculated as follows [35]:

$$\% \text{Discoloration} = \frac{A_0 - A}{A_0} \times 100 \quad (40)$$

$$\% \text{Degradation removal} = \frac{c_0 - c}{c_0} \times 100 \quad (41)$$

where A_0 and c_0 are the initial values and A and c those values at electrolysis time t . Pseudo-first-order kinetics are commonly obeyed for these parameters, from which the apparent rate constants for discoloration (k_d) and degradation (k_1) are determined as the corresponding slopes of $\ln(A_0/A)-t$ and $\ln(c_0/c)-t$ plots, respectively.

From the COD (in $\text{mg O}_2 \text{ L}^{-1}$) or TOC (in mg C L^{-1}) abatement determined at constant I (in A), in batch mode, the percent of COD or TOC removal can be calculated as follows [30]:

$$\% \text{COD removal} = \frac{\Delta \text{COD}}{\text{COD}_0} \times 100 \quad (42)$$

$$\% \text{TOC removal} = \frac{\Delta \text{TOC}}{\text{TOC}_0} \times 100 \quad (43)$$

where ΔCOD and ΔTOC represent the decay of these parameters, and COD_0 and TOC_0 their initial values before treatment. From these parameters, the ACE at time t (in s) or the MCE at time t (in h) can be obtained from Eq. (44) and (45):

$$\% \text{ACE} = \frac{(\Delta \text{COD}) F V}{8 I t} \times 100 \quad (44)$$

$$\% \text{MCE} = \frac{n F V (\Delta \text{TOC})}{4.32 \times 10^7 m I t} \times 100 \quad (45)$$

where F is the Faraday constant ($96,487 \text{ C mol}^{-1}$), V is the solution volume (in L), the constant 8 mean the oxygen equivalent mass (g eq^{-1}), n is the theoretical number of electrons exchanged in the mineralization process of the organic pollutant, 4.32×10^7 is a conversion factor, and m is the number of carbon atoms of the pure organic pollutant tested.

To evaluate energy performance, additional figures of merit are commonly reported. These include EE/O, EC, EC_{COD} and EC_{TOC} . EE/O represents the amount of electrical energy required to reduce the concentration of a pollutant by one order of magnitude (90% removal) in a unit volume of water. It is widely used to compare different water treatment technologies, particularly when degradation follows pseudo-first-order kinetics. In contrast, EC, EC_{COD} , and EC_{TOC} relate the

Table 2

Relevant results for the advances of EO and cathode materials for EF and HEF.

Pollutant	System	Experimental conditions	Best results	Ref.
BDD 2,4-D	Undivided flow reactor, BDD with 165–323 sp^3/sp^2 ratio anode, BDD ₁₇₆ cathode	600 mL of 100 mg L^{-1} pollutant in pure water, 0.05 M NaCl, pH = 3.5, room temperature, liquid flow rate = 26.4 L h^{-1} , $j = 100 \text{ mA cm}^{-2}$, $Q^a = 32.5 \text{ Ah L}^{-1}$	Total removal between Q from 25 to 32.5 Ah L^{-1} . Fast decay for BDD ₁₇₆ . Overall TOC reduction between the same Q values, more rapid with raising sp^3/sp^2 ratio. Evolution of 5 aromatic by-products and ClO^- , ClO_3^- , and ClO_4^-	[38]
Aniline	Stirred undivided tank reactor, BDD with 154–303 sp^3/sp^2 ratio anode, SS ^b cathode	100 mL of 130 mg L^{-1} pollutant in pure water, 0.05 M NaCl, pH = 6.0, 25 °C, $j = 20 \text{ mA cm}^{-2}$, 360 min	Quicker and complete pollutant degradation at 40 min for BDD ₃₀₃ . At 360 min, 98% COD and 58% TOC decay, respectively. Increasing NO_3^- formation up to 23% N conversion with raising sp^3/sp^2 ratio. $\text{M}(\text{*OH})$ and active chlorine as oxidants. Detection of by-products by LC-MS and HPLC	[40]
Ciprofloxacin	Stirred undivided tank reactor, micro-BDD or nano-BDD anode, SS cathode	100 mL of 15 mg L^{-1} pollutant in pure water with 50 mM Na_2SO_4 , and 1 mM NaCl +25 mM Na_2SO_4 , WWTP, and urine, pH = 7.0, 25 °C, $j = 10\text{--}80 \text{ mA cm}^{-2}$, 60 min	In sulfate medium at $j = 80 \text{ mA cm}^{-2}$, overall decay (k_1 (min^{-1})) = 20 min (0.1991) for nano-BDD < 60 min (0.0759) for micro-BDD. TOC decay at 60 min = 63% for nano-BDD > 41% for micro-BDD. For nano-BDD at $j = 40 \text{ mA cm}^{-2}$, total degradation, TOC decay, and E_{EO} ($\text{kWh m}^{-3} \text{ order}^{-1}$) = 100%, 37%, and 4.7, 100%, 22%, and 12.8, and 90%, 28%, and 22.9 for 1 mM NaCl +25 mM Na_2SO_4 , WWTP, and urine	[41]
Reactive Blue 19	Stirred undivided tank reactor, 2D-BDD or 3D-BDD anode, SS cathode	500 mL of 100–300 mg L^{-1} pollutant in pure water, 0.1 M Na_2SO_4 ,	Better performance with 3D-BDD anode. For 100 mg L^{-1} pollutant, 100%	[45]

(continued on next page)

Table 2 (continued)

Pollutant	System	Experimental conditions	Best results	Ref.
		natural pH, room temperature, $I = 300$ mA, 180 min	discoloration in 60 min and 90% TOC reduction in 180 min	
PbO_2 Chloramphenicol	Stirred undivided tank reactor, PbO_2 and 1% Al- PbO_2 anodes, Ti cathode	250 mL of 500 mg L ⁻¹ pollutant in pure water, 0.1 M Na_2SO_4 , pH = 3.0–11.0, room temperature. $j = 50$ mA cm ⁻² , 150 min	Degradation at pH = 6.0 = 70% for $PbO_2 < 92\%$ for 1% Al- PbO_2 . At pH = 3.0, 97% removal with $k_1 = 0.0235$ min ⁻¹ and 58% TOC reduction. Good reproducibility after 8 successive steps. 18 by-products detected by GC-MS and ion chromatography	[47]
Acetamidiprid	Stirred undivided tank reactor, PbO_2 and Yb- PbO_2 anodes, Ti cathode	500 mL of 20 mg L ⁻¹ pollutant in pure water, 0.05 M Na_2SO_4 , pH = 3.0, room temperature $j = 150$ mA cm ⁻² , 120 min	Degradation = 80% for $PbO_2 < 96\%$ for Yb- PbO_2 with $k_1 = 0.02353$ min ⁻¹ . For the latter anode, 68% COD decay. Detection of 19 intermediates by LC-MS	[49]
<i>p</i> -Nitrophenol	Stirred undivided tank reactor, PbO_2 /SS, PDMS- PbO_2 /SS, Ce- PbO_2 /SS, and Ce-PDMS- PbO_2 /SS anodes, Ti cathode	50 mg L ⁻¹ pollutant in pure water, 0.3 M Na_2SO_4 , pH = 3.0, room temperature, $j = 30$ mA cm ⁻² , 120 min	Degradation, TOC removal, MCE, and k_1 (min ⁻¹) = 92%, 59%, 18%, and 0.02095 for PbO_2 /SS < 93%, 67%, 20%, and 0.02301 for PDMS- PbO_2 /SS < 95%, 70%, 21%, and 0.02349 for Ce- PbO_2 /SS < 97%, 75%, 18%, and 0.02703 for Ce-PDMS- PbO_2 /SS. •OH as main oxidant detected by EPR. Identification of 9 by-products by GC-MS	[54]
Ti_4O_7 Amoxicillin	Stirred undivided tank reactor, Ti_4O_7 or BDD anode, SS or carbon felt (for H_2O_2 generation) cathode	250 mL of 0.10 mM pollutant in pure water, 0.050 M Na_2SO_4 , pH = 5.7, room temperature, $I = 120$ mA, 480 min	Complete removal = 120 min for Ti_4O_7 -SS > 80 min for BDD-SS > 60 min for BDD-carbon felt > 40 min for Ti_4O_7 -carbon felt. TOC decay and MCE at 480 min = 66% and 4.5% for Ti_4O_7 -carbon felt < 96% and 5.8% for BDD-carbon	[58]

Table 2 (continued)

Pollutant	System	Experimental conditions	Best results	Ref.
PFOS ^c	Flow-by reactor, Ti_4O_7 or $(Ti_{1-x}Ce_x)_2O_7$ (x = 3%) anode, SS cathode	100 mL of 20 μM pollutant in pure water and river water, 10 mM Na_2SO_4 , natural pH, room temperature, liquid flow rate = 80 mL min ⁻¹ , $j = 20$ mA cm ⁻² , 240 min	felt. M(•OH) and M($HO_2^•$) as oxidants. Detection of intermediates by HPLC and NH_4^+ , NO_3^- , and SO_4^{2-} . In pure water, degradation at 120 min = 86% for $Ti_4O_7 < 99\%$ for $(Ti_{1-x}Ce_x)_2O_7$ (x = 3%). Practically all fluoride released as F^- . With river water, total degradation in 60 min, with excellent reusability after 20 runs	[60]
Carbamazepine	Stirred undivided tank reactor, $CeCo_{0.5}Fe_{0.5}O_3$ / Ti_4O_7 anode, carbon felt cathode	100 mL of 1–20 mg L ⁻¹ pollutant in pure water and real wastewaters, 1 mM PMS ^d , pH = 7.0, room temperature, $j = 1$ mA cm ⁻² , 30 min	In pure water, faster degradation at lower content of pollutant, Total degradation in 2 min with $k_1 = 5.466$ min ⁻¹ for 1 mg L ⁻¹ pollutant. No influence of common co-existing ions. Excellent reusability after 30 cycles of 30 min. Quicker degradation in aquaculture wastewater. Detection of oxidants $SO_4^{\bullet-}$, •OH, $O_2^{\bullet-}$, and 1O_2 by specific scavengers and EPR. Identification of heteroaromatic by-products by LC-MS/MS	[61]
Cathode materials for EF and HEF	Stirred undivided tank reactor, Ti/IrO ₂ anode, carbon felt cathode	100 mL of 12.5 mM Na_2SO_4 , pH = 6.5, 25 °C, $j = 22.2$ mA cm ⁻² , use of NBs ^e and MBs ^f , 60 min	Gas efficiency = 60% for NBs > 0.19% for MBs. H_2O_2 accumulation as function of dissolved oxygen = 30 mg L ⁻¹ for NBs > 16 mg L ⁻¹ for MBs at 28 mg O ₂ L ⁻¹ . NBs approaches to theoretical value	[63]
Rhodamine B	Stirred undivided tank reactor, Ti anode, G-GDE ^g , GDE ^h , or GE ⁱ cathode	50 mL of 20 mg L ⁻¹ dye in pure water, 0.05 M Na_2SO_4 , 0.3 M Fe^{2+} , pH = 3.0, room	H_2O_2 accumulated without pollutant (mg L ⁻¹) = 60 for G-GDE > 49 for GDE > 25 for	[68]

(continued on next page)

Table 2 (continued)

Pollutant	System	Experimental conditions	Best results	Ref.
Tetracycline	Stirred undivided tank reactor, Pt or BDD anode, carbon felt cathode	temperature, $j = 20$ mA cm^{-2} , 60 min	GE. Discoloration, k_d (min^{-1}), COD removal, and EC_{COD} ($\text{kWh} (\text{kg COD})^{-1}$) = 97%, 0.31, 79%, and 80 for G-GDE, 94%, 0.28, 77%, and 94 for GDE, and 86%, 0.24, 69%, and 122 for GE	[72]
		230 mL of 0.20 mM drug in pure water, 0.050 M Na_2SO_4 , 1.0 g L^{-1} chalcopryrite, 0.20 mM Fe^{2+} , pH = 5.94, room temperature, $I = 300$ mA, 480 min	Total removal: 7 min with BDD/chalcopryrite <12 min with Pt/chalcopryrite. Total TOC decay for BDD/chalcopryrite in 480 min, 94% for BDD/ Fe^{2+} . Detection of 10 aromatic derivatives by GC-MS. Evolution of oxalic, acetic, oxamic, malic, succinic, and malonic acids by HPLC, as well as NH_4^+ and NO_3^-	
Oxytetracycline	Stirred undivided tank reactor, Ti/Ir-Ru anode, FeNi_3 /carbon/carbon paper cathode	200 mL of 10 mg L^{-1} drug in pure water, 0.1 M Na_2SO_4 , pH = 3.0, room temperature, $I = 60$ mA, 90 min	97% abatement with 0.1 M Na_2SO_4 , total removal in 0.05 M $\text{NaCl} + 0.05$ M Na_2SO_4 . About 0.3 mg L^{-1} of Fe and Ni released. Good reusability after 4 successive cycles. $\cdot\text{OH}$ as main oxidant, minor role of $\text{O}_2^{\cdot-}$ and $^1\text{O}_2$, as found by specific scavengers. Identification of 13 derivatives by LC-MS	[75]
Rhodamine B	Stirred undivided tank reactor, anode not-specified, rGO ¹ /MIL-88 A/carbon felt cathode	10 mg L^{-1} dye in pure water, 0.1 M Na_2SO_4 , pH = 3.0, room temperature, $E_{\text{cat}} = -0.4$ V/Ag AgCl, 120 min	13.5 mg L^{-1} of H_2O_2 accumulated without pollutant. 93% discoloration in 120 min. Oxidant $\cdot\text{OH}$ detected by specific scavengers and EPR. Good reusability after 4 consecutive steps.	[76]
2,4-Dichlorophenol	Stirred undivided tank reactor, Ti/IrO ₂ or BDD anode,	160 mL of 10 mg C L^{-1} chemical in pure water	In pure water, total degradation in 20 min and 6.18	[77]

Table 2 (continued)

Pollutant	System	Experimental conditions	Best results	Ref.
	GDE cathode, N-porous carbon/ FeNi_4 catalyst	and real wastewaters, 0.10 g L^{-1} catalyst, pH = 4.0, room temperature, $I = 50$ mA, 240 min	mg L^{-1} Fe leaching without Na_2SO_4 and 60 min with 0.050 M Na_2SO_4 . In urban wastewater, 97% removal in 90 min. TOC reduction in pure water: 68% with BDD > 47% with Ti/IrO ₂ . Moderate reusability after 5 successive runs	

^a Q: Electric charge. ^b SS: Stainless steel. ^c PFOS: Perfluorooctanesulfonate. ^d PMS: Peroxymonosulfate. ^e NBs: Nanobubbles. ^f MBs: Macrobubbles. ^g G-GDE: graphite-graphene gas-diffusion electrode. ^h GDE: Graphite gas-diffusion electrode. ⁱ GE: Graphite sheet electrode. ^j rGO: Reduced graphene oxide.

applied electrical energy to the treated volume or to the amount of mineralized organic matter. These parameters can be calculated according to Eqs. (46)–(49) [30].

$$\text{EE} / \text{O} \left(\text{kWh m}^{-3} \text{order}^{-1} \right) = \frac{E_{\text{cell}} I t}{V \log \left(\frac{c_0}{c} \right)} \quad (46)$$

$$\text{EC} \left(\text{kWh m}^{-3} \right) = \frac{E_{\text{cell}} I t}{V} \quad (47)$$

$$\text{EC}_{\text{COD}} \left(\text{kWh} (\text{g COD})^{-1} \right) = \frac{E_{\text{cell}} I t}{V(\Delta \text{COD})} \quad (48)$$

$$\text{EC}_{\text{TOC}} \left(\text{kWh} (\text{g TOC})^{-1} \right) = \frac{E_{\text{cell}} I t}{V(\Delta \text{TOC})} \quad (49)$$

3. Advances in the last decade (2015–2025)

The literature analyzed in this section was selected through a structured search conducted in the Scopus database. The search strategy was based on the keyword's EO, EF, and ENR with the publication period restricted to 2015–2025. Only peer-reviewed articles written in English were considered. The retrieved studies were screened based on their relevance to advances in electrode materials, mechanistic understanding, reactor configurations, performance metrics, and applications in realistic water matrices related to EO, EF, and ENR.

3.1. Materials developments and mechanistic insights

3.1.1. Materials developments for EO

Between 2015 and 2025, significant efforts focused on improving electrode materials for EO, particularly anodes for organic pollutant degradation. Classical electrodes such as BDD, PbO_2 , and Ti/IrO₂, although extensively studied, underwent renewed optimization, while novel materials such as Ti_4O_7 and architectures continued emerging to enhance performance. Among these, BDD has established itself as the gold standard due to its exceptional properties. The sp^3 -hybridized tetrahedral lattice of diamond provides extreme hardness, high thermal conductivity, and low intrinsic electrical conductivity, whereas boron doping introduces high electronic conductivity, enabling efficient electron transfer, and making BDD ideally suited for EO applications [36].

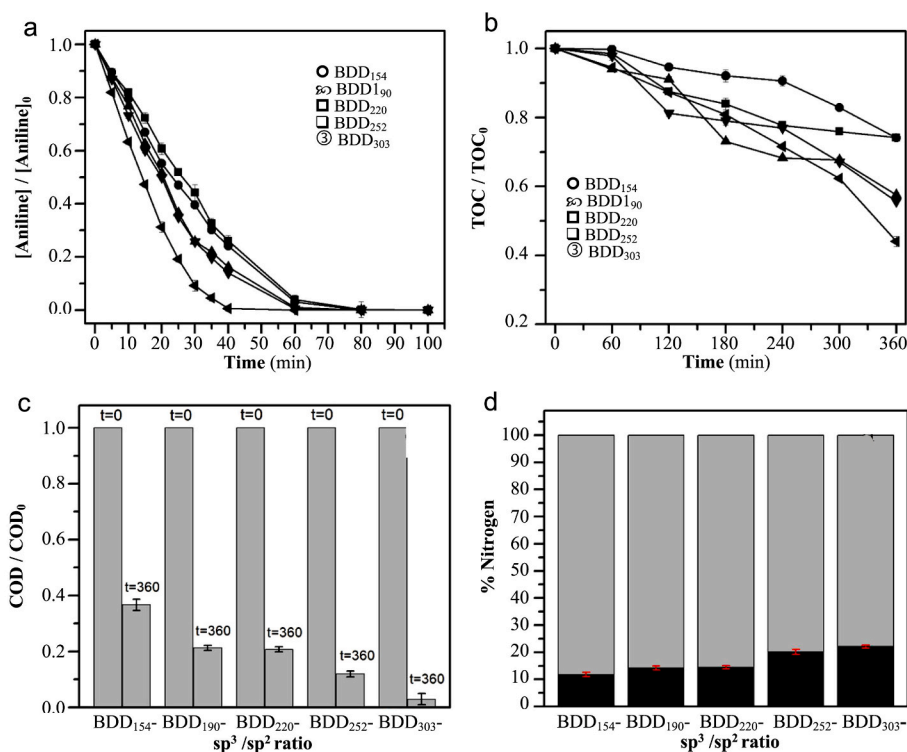


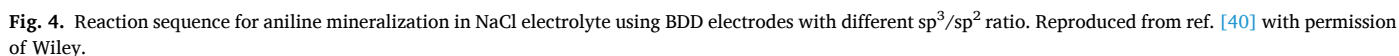
Fig. 3. Normalized (a) aniline concentration and (b) TOC vs. time for the EO process of 130 mg L⁻¹ of the chemical (100 mg C L⁻¹ TOC₀) in pure water with 0.05 M NaCl at pH = 6.0 and 25 °C using a stirred undivided tank reactor equipped with BDD anodes with 500 ppm of B and different sp³/sp² ratio and stainless steel (SS) cathode at j = 20 mA cm⁻². (c) Normalized COD at the beginning and the end of the above assays. (d) (■) Initial percent of the treated aniline solution and (■) percent of NO₃⁻ determined in the above trials. Adapted from ref. [40] with permission of Wiley.

During this period, the influence of the sp³/sp² ratio on BDD performance became an important focus. This ratio governs electron-transfer kinetics, adsorption, and potential window, and also dictates degradation pathways and oxidant production during EO [37–40]. For instance, Souza et al. [38] described the EO process of 100 mg L⁻¹ of 2,4-dichlorophenoxyacetic acid (2,4-D) in pure water with 0.05 M NaCl at pH = 3.5 using an undivided flow reactor with different BDD₁₆₅–BDD₃₂₃ anodes (the subindex means its sp³/sp² ratio) and BDD₁₇₆ cathode at j = 100 mA cm⁻². While a similar total removal of the herbicide was determined for electric charge (Q) from 25 to 32.5 Ah L⁻¹ slightly faster with BDD₁₇₆, TOC was completely reduced in the same Q range, more rapidly with increasing the sp³/sp² ratio, then being BDD₃₂₃ the more powerful anode (see Table 2). The authors also followed the evolution of 5 aromatic by-products and ClO⁻, ClO₂⁻, and ClO₄⁻, thus demonstrating the formation of active chlorine and related by-products from reactions (7)–(13), in parallel to BDD(·OH) produced by reaction (1). The rise of sp³/sp² ratio caused the reduction of aromatic by-products and enhanced chloro-anions generation. Similar trends were observed by Espinoza et al. [40] when electrolyzed 130 mg L⁻¹ of aniline in pure water with 0.05 M NaCl at pH = 6.0 and 25 °C using a stirred undivided tank reactor with a BDD₁₅₄–BDD₃₀₃ anode and stainless steel (SS) cathode at j = 20 mA cm⁻², Fig. 3a highlights the quicker and total decay in 40 min of the pollutant with the higher sp³/sp² ratio of BDD₃₀₃. This anode yielded the higher 98% COD and 58% TOC removal at 360 min, as can be seen in Fig. 3b and c, respectively (see Table 2 as well). Fig. 3d reveals an increasing release of NO₃⁻ with raising sp³/sp² ratio up to a maximum of 23% of N conversion for BDD₃₀₃. From the by-products detected by LC-MS and HPLC, the reaction sequence of Fig. 4 was proposed for aniline mineralization with oxidation by M(·OH) and chlorine species such as active chlorine. Different oligomers with 6 lateral groups (R₁ to R₆) were initially generated depending on the anode used, which evolved to several monomeric derivatives. These compounds led to 6 short-linear carboxylic acids with NO₃⁻ loss, regardless of the anode used, to be

finally mineralized to CO₂.

On the other hand, some BDD synthesized variants have been increasingly explored [41–45]. dos Santos et al. [41] showed that nanocrystalline BDD (nano-BDD) improved charge transfer compared to microcrystalline BDD (micro-BDD). These materials were synthesized by hot filament chemical vapor deposition (HFCVD) technique with 2 and 8 vol% of CH₄ vapor for micro- and nano-BDD, respectively, and their different uniform morphology can be observed in the field emission gun-scanning electron microscopy (FEG-SEM) images of Fig. 5a and b. The antibiotic ciprofloxacin was taken as model molecule and 15 mg L⁻¹ of it in pure water with 50 mM Na₂SO₄ at pH = 7.0 and 25 °C was electrolyzed in a stirred undivided tank reactor with a SS cathode at j = 10–80 mA cm⁻². Fig. 5c shows that for the best performance at j = 80 mA cm⁻², the pollutant was completely removed in 20 and 60 min for nano- and micro-BDD with k₁-values of 0.1991 and 0.0759 min⁻¹ (see Table 2), respectively. Fig. 5d depicts a maximum TOC reduction of 63% for nano-BDD > 41% for micro-BDD achieved at 60 min. The study was extended for the best nano-BDD to other media, namely 1 mM NaCl + 25 mM Na₂SO₄, WWTP, and urine. Fig. 5e and f reveal the best performance for the former medium leading to 100% degradation, 37% TOC removal, and E/EO = 4.7 kWh m⁻³ order⁻¹. Conversely, Li et al. [42] reported similar TOC reduction (> 95%) for artificial human urine by micro- and nano BDD at j = 100 mA cm⁻², but nano-BDD exhibited a 32.8% longer service life, attributed to nanoscale homogeneity reducing interfacial stress and delamination. Other recent innovations include BDD/graphene/Ti mesh composites [43], ultrananocrystalline BDD [44], and three-dimensional microporous BDD (3D-BDD) [45]. The latter work demonstrated a rise in electroactive surface area and mass transfer compared to conventional 2D-BDD, thereby improving degradation and mineralization efficiencies of 100 mg L⁻¹ of the anthraquinone dye Reactive Blue 19 in pure water with 0.1 M Na₂SO₄ at natural pH and I = 300 mA (see Table 2).

It is noticeable that many BDD materials have been successfully



In parallel, PbO_2 re-emerged as a competitive anode due to its high conductivity, tunable OEP, and facile electrodeposition routes. Historically, Pb^{2+} leaching and corrosion constrained applicability. However, these limitations have been substantially mitigated through targeted doping and surface engineering [46]. Metal (Al, Fe), rare-earth (Y, Yb, Ce, Sm, In), and polymeric dopants have been successfully incorporated to enhance both catalytic activity and structural integrity. For instance, Al-doped PbO_2 exhibited an OEP of 2.12 V/SCE and can be easily

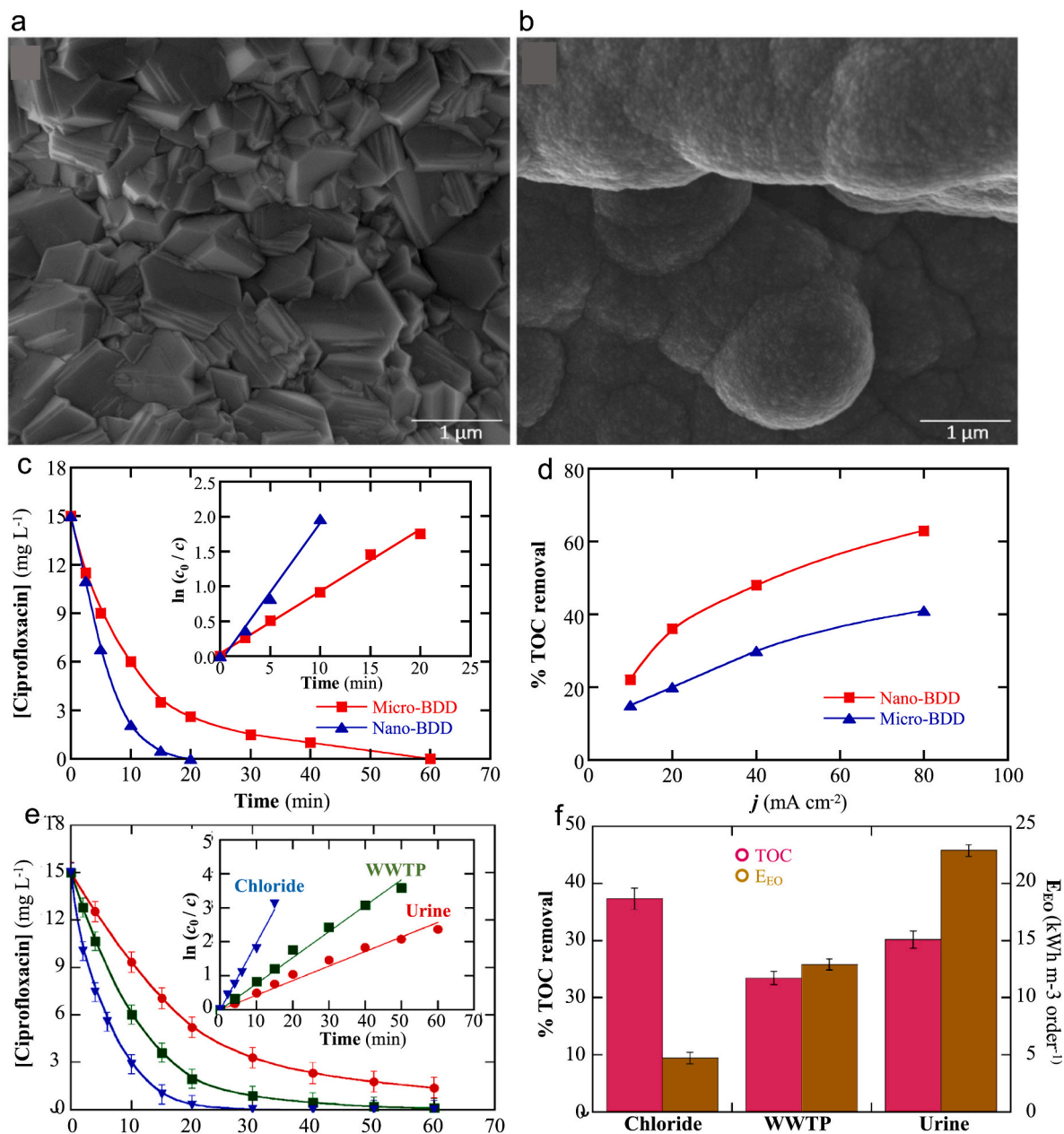


Fig. 5. Field emission gun-scanning electron microscopy (FEG-SEM) images of (a) micro-BDD and (b) nano-BDD films obtained by hot filament chemical vapor deposition (HFCVD) technique with 2 and 8 vol% of CH₄ vapor, respectively. (c) Time course of ciprofloxacin concentration for the EO process of 15 mg L⁻¹ drug in pure water with 50 mM Na₂SO₄ at pH = 7.0 and 25 °C using a stirred undivided tank reaction with a micro-BDD or nano-BDD anode and SS cathode at $j = 80$ mA cm⁻². (d) Percent of TOC removal in front of j after 60 min of electrolysis under the above conditions. (e) Decay of 15 mg L⁻¹ ciprofloxacin in 1 mM + 25 mM Na₂SO₄, WWTP, and urine at pH = 7.0 using a nano-BDD anode at $j = 40$ mA cm⁻². The inset panel shows the pseudo-first-order kinetic analysis. (f) Percent of TOC removal and E_{EO} for after 60 min of the above trials. Adapted from ref. [41] with permission of Elsevier.

constructed by electrodeposition of a mixture of Pb(NO₃)₂ and Al(NO₃)₃ in aqueous HNO₃ onto Ti/Sn-SbO_x [47]. Fig. 6a highlights the superiority of 1% Al-PbO₂ with 92% degradation compared to 70% for PbO₂ after 150 min of EO process of 500 mg L⁻¹ chloramphenicol in pure water with 0.1 M Na₂SO₄ at pH = 6.0 and room temperature at $j = 50$ mA cm⁻². For the modified anode, better results were found at pH = 3.0 with 97% removal with $k_1 = 0.0235$ min⁻¹ and 58% TOC reduction (see Table 2). Good reproducibility was obtained after 8 successive steps, and 18 by-products were detected by GC-MS and ion chromatography. Similarly, [Fe(CN)₆]³⁻-modified PbO₂ showed a compact morphology with extended lifetime of 287 h vs. 100 h for pristine PbO₂, and enhanced kinetics for lignin degradation [48]. Rare-earth doping was particularly effective in inducing oxygen vacancies via 4f orbital

interactions, promoting electron mobility and stability [49–51]. The work of Yao et al. [49] assessed the behavior of a Yb-PbO₂ anode, prepared by electrodeposition. As can be seen in Fig. 6b for 20 mg L⁻¹ acetamidrid in pure water with 0.05 M Na₂SO at pH = 3.0, this modified anode largely improved the performance of PbO₂. After 120 min at $j = 150$ mA cm⁻², the pollutant was degraded by 80% for PbO₂, much smaller than 96% determined for Yb-PbO₂ with $k_1 = 0.02353$ min⁻¹ leading to 68% COD reduction (see Table 2). For this anode, 19 by-products were detected by LC-MS.

Hydrophobic surface modification of PbO₂ using SDS [52], PTFE [53], or PDMS (a silicone polymer) [54] has limited •OH adsorption and increased OEP, improving oxidation selectivity and durability. Fig. 6c and data of Table 2 reveal quicker destruction of 50 mg L⁻¹ of *p*-

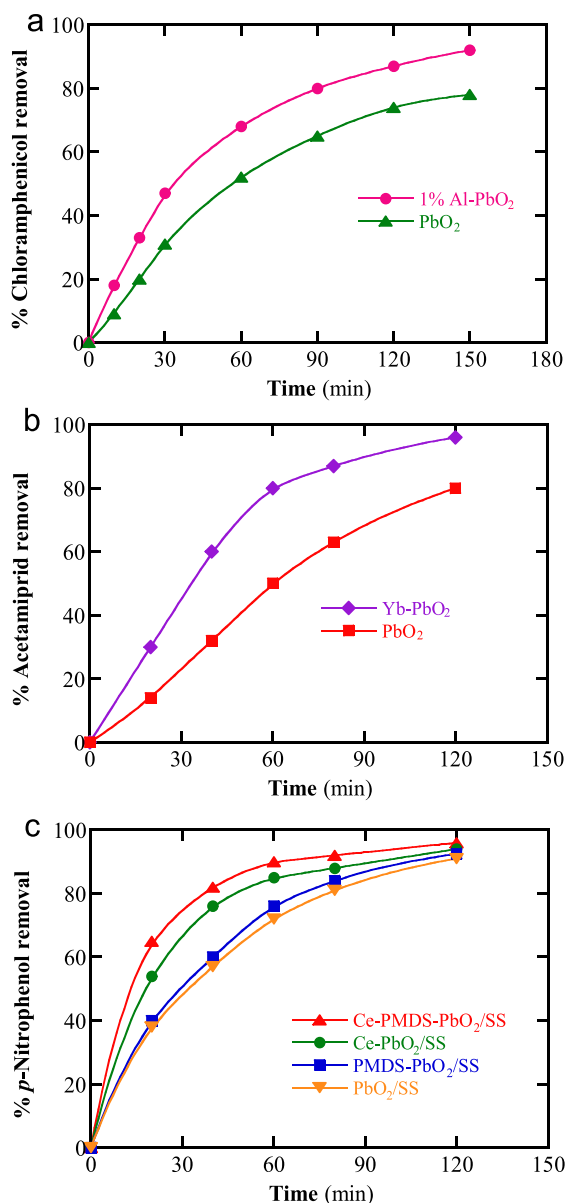


Fig. 6. Change of the percentage of pollutant removal with time for EO with modified PbO₂ anodes. (a) 500 mg L⁻¹ chloramphenicol in pure water with 0.1 M Na₂SO₄ at pH = 6.0 and room temperature using a stirred undivided tank reactor with PbO₂ and 1% Al-PbO₂ anodes and Ti cathode at $j = 50 \text{ mA cm}^{-2}$ (adapted from ref. [47] with permission of Elsevier). (b) 20 mg L⁻¹ acetamidiprid in pure water with 0.05 M Na₂SO₄ at pH = 3.0 and room temperature using a stirred undivided tank reactor with PbO₂ and Yb-PbO₂ anodes and Ti cathode at $j = 150 \text{ mA cm}^{-2}$ (adapted from ref. [49] with permission of Elsevier). (c) 50 mg L⁻¹ *p*-nitrophenol in pure water with 0.3 M Na₂SO₄ at pH = 3.0 and room temperature using a stirred undivided tank reactor with PbO₂/SS, PDMS (silicone polymer)-PbO₂/SS, Ce-PbO₂/SS, and Ce-PMDS-PbO₂/SS, anodes and SS cathode at $j = 30 \text{ mA cm}^{-2}$ (adapted from ref. [53] with permission of Elsevier).

p-nitrophenol in pure water with 0.3 M Na₂SO₄ at pH = 3.0, room temperature, and $j = 30 \text{ mA cm}^{-2}$ for anodes in the order: PbO₂/SS < PDMS-PbO₂/SS < Ce-PbO₂/SS < Ce-PMDS-PbO₂/SS in front of a SS cathode. The best Ce-PMDS-PbO₂/SS anode yielded 97% degradation with $k_1 = 0.02703 \text{ min}^{-1}$ and 75% TOC decay with 18% MCE [54]. EPR spectra recorded with DMPO of Fig. 7a yielded the expected 1:2:2:1 quadruplet of its adduct with $\cdot\text{OH}$, more intense with Ce-PMDS-PbO₂/SS. This is indicative of greater formation of $\text{M}(\cdot\text{OH})$ as main oxidant from reaction (1) by this anode, thus justifying its higher oxidation power. From the 9 intermediates identified by GC-MS, it was proposed the mechanism for

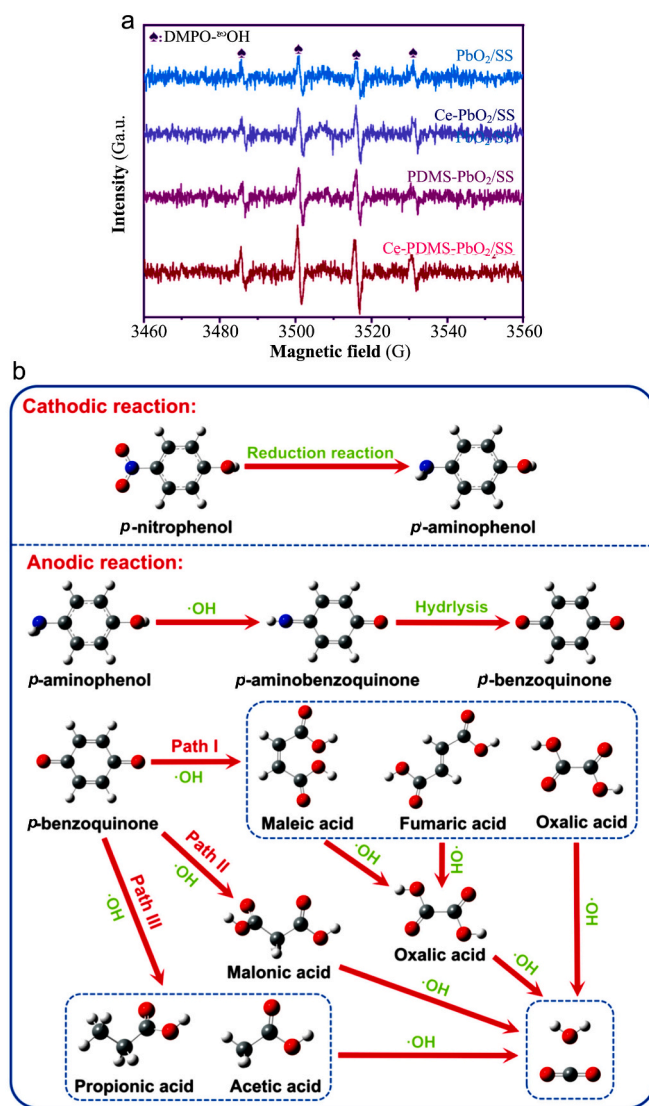


Fig. 7. (a) EPR spectra of the adduct 5,5-dimethyl-1-pyrroline-N-oxide (DMPO)- $\cdot\text{OH}$ obtained in 0.3 M Na₂SO₄ for different modified PbO₂ anodes. (b) Proposed reaction sequence for *p*-nitrophenol mineralization by EO in 0.3 M Na₂SO₄ using a Ce-PMDS-PbO₂/SS anode. Adapted from ref. [53] with permission of Elsevier.

p-nitrophenol mineralization shown in Fig. 7b. This pollutant was reduced at the cathode to *p*-aminophenol, which was subsequently oxidized at the anode by $\text{M}(\cdot\text{OH})$ up to CO₂ through the cleavage of the benzenic ring with generation of 6 short-linear carboxylic acids.

While most PbO₂ studies were conducted in synthetic media, recent works have extended these evaluations to complex effluents such as industrial and domestic wastewater, demonstrating improved stability and reusability [55–57]. These findings underscore the practical potential of modified PbO₂ and the importance of testing under real conditions.

Complementing these efforts, Magnéli-phase titanium suboxide (Ti_nO_{2n-1}) have gained increasing prominence as low-cost and robust ceramic electrodes. Ti₄O₇ combines excellent electrical conductivity, chemical inertness, and high OEP, providing a balance between performance and economic feasibility. Synthesized via thermal reduction of mixing TiO₂ with coke under controlled atmospheres [58]. Ti₄O₇-based materials have achieved competitive EO efficiency, but with slightly lower OEP value than BDD, thus expecting the generation of less amount of $\text{M}(\cdot\text{OH})$ from reaction (1). The interest of Ti₄O₇ for wastewater

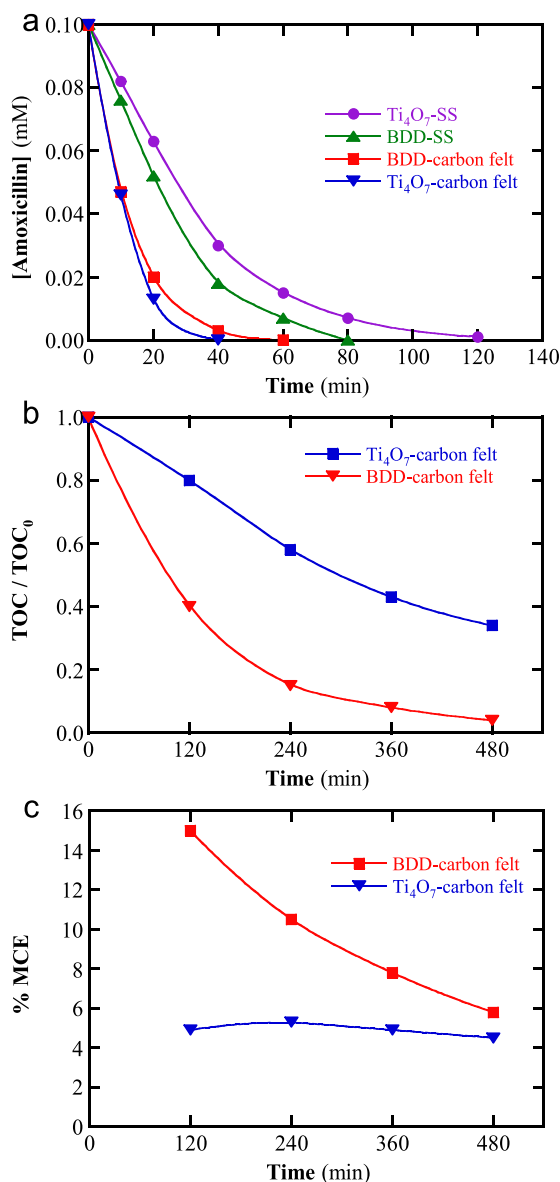
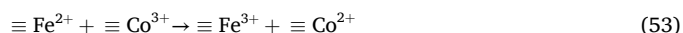
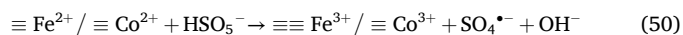


Fig. 8. (a) Change of amoxicillin concentration with time for the EO treatment of 0.10 mM drug in pure water with 0.050 M Na₂SO₄ at pH = 5.7 and room temperature using a stirred undivided tank reaction with a Ti₄O₇ or BDD anode and SS or carbon felt cathode at $I = 120$ mA. Time course of (b) normalized TOC and (c) percentage of mineralization of current efficiency for the above assays with carbon felt cathode. Adapted from ref. [58] with permission of Elsevier.

treatment has been reported by Ganiyu et al. [58] by studying the EO treatment of 0.10 mM amoxicillin in pure water with 0.050 M Na₂SO₄ at pH = 5.7 and room temperature using a stirred undivided tank reactor with Ti₄O₇ or BDD anode and SS or carbon felt cathode at $I = 120$ mA. Fig. 8a shows the effect of the electrodes over the degradation efficiency, reaching complete removal in 120 min for Ti₄O₇-SS > 80 min for BDD-SS > 60 min for BDD-carbon felt > 40 min for Ti₄O₇-carbon felt (see Table 2). For a SS cathode, M(OH) at the anode is the main oxidant and then, the more powerful BDD upgraded Ti₄O₇. In contrast, with carbon felt cathode, H₂O₂ is electrogenerated from reaction (14) giving additional anodic oxidant M(HO₂) from reaction (4), at larger extent for Ti₄O₇ that originated its higher degradation compared to BDD. However, the low oxidation ability of M(HO₂) did not accelerate the destruction of by-products and mineralization was marked by the action of M(OH), superior for BDD. This can be deduced from Fig. 8b and c where after 480 min of electrolysis, the BDD-carbon felt system yielded

96% TOC decay with 5.8% MCE, much greater than 66% TOC decay with 4.5% MCE for Ti₄O₇-carbon felt one. The authors completed the study by detecting the intermediates by HPLC and the release of NH₄⁺, NO₃⁻, and SO₄²⁻ from the heteroatoms of the pollutant.

The excellent performance of Ti₄O₇ for the remediation of wastewater has been confirmed in other works, e.g., for tetracycline [59], but more efforts have been centered in improving its oxidation power by doping with Ce³⁺ [60] and using composites with perovskite [61] and MOFs [62]. Lin et al. [60] immersed Ti₄O₇ in a CeCl₃ solution and the resulting loaded powder was treated by plasma sintering at 1100 °C and 5 MPa to yield (Ti_{1-x}Ce_x)O₇ anode, which was activated under cathodic polarization at -2.0 V /SCE. The best anode producing more oxidant M(OH) was found for $x = 3\%$. Under these conditions, the treatment of 20 μM of PFOS in pure water with 10 mM Na₂SO₄ at natural pH using a flow-by reactor with SS cathode at $j = 20$ mA cm⁻² for 120 min gave a degradation of 86% for pure Ti₄O₇, enhanced to 99% for the Ce³⁺-doped anode with almost overall defluorination of the pollutant (see Table 2). Surprisingly, complete degradation was obtained with river water with excellent reusability after 20 runs, suggesting that its components favored the complexation of PFOS for quicker destruction. It is interesting to remark the work of Jing et al. [61], who constructed a CeCo_{0.5}Fe_{0.5}O₃/Ti₄O₇ anode for the EO process of 1–20 mg L⁻¹ of carbamazepine (CBZ) in pure water with 1 mM PMS (HSO₅⁻) at pH = 7.0. Fig. 9a shows the proposed mechanism for the generation of oxidants SO₄^{•-}, OH[•], O₂^{•-}, and singlet oxygen (¹O₂) detected by specific scavengers and EPR. PMS is reduced to SO₄^{•-} by the oxidation of the surface ≡Fe²⁺ and ≡Co²⁺ of the anode to ≡Fe³⁺ and ≡Co³⁺ by reaction (50). OH[•] is then formed by hydrolysis of SO₄^{•-} by reaction (51). In parallel, M(OH) is produced at Ti₄O₇ from reaction (1). OH[•] dimerizes to H₂O₂ by reaction (26), which originated O₂^{•-} by reactions (23) and (24). This species led to ¹O₂ by reaction (52). Note the spontaneous reaction (53) at the anode involving the formation of ≡Fe³⁺ and ≡Co³⁺ from ≡Fe²⁺ and ≡Co²⁺. Fig. 9b highlights the very fast removal of CBZ with these oxidizing species under the EO conditions chosen, which decreased with raising pollutant content because of the attack of similar amounts of oxidants with gradual increase of organic load. The best results were found for the lower content of 1 mg L⁻¹ CBZ that attained total degradation in only 2 min with very high $k_1 = 5.466$ min⁻¹ (see Table 2). Fig. 9c shows the similar degradation efficiency obtained for several common pollutants at 0.05 mM content, whereas Fig. 9d makes evident the little influence of common inorganic ions and HA on the removal of CBZ. The study extended to other aqueous matrices like lake water, medical wastewater, and WWTP gave practically the same results as in pure water, as can be seen in Fig. 9e, although faster CBZ removal can be observed for aquaculture wastewater, probably by the formation of more easily oxidizable complexes with its components. All these findings indicate that CeCo_{0.5}Fe_{0.5}O₃/Ti₄O₇ can be useful as anode for this system in practice, which was confirmed by its excellent reusability obtained after 30 cycles of 10 mg L⁻¹ CBZ removal with 1 mM PMS of 30 min. All these advances clearly indicate that Ti₄O₇ represents a new generation of EO anodes capable of bridging the gap between high-performance and economically sustainable water treatment technologies.



3.1.2. Cathode material for EF and HEF

Progress in cathode materials has been equally decisive for EF and HEF, where performance depends on H₂O₂ electrogeneration rate, current and gas efficiencies, and catalyst utilization, and overall process performance, strongly depending on their behavior. A recent study [63

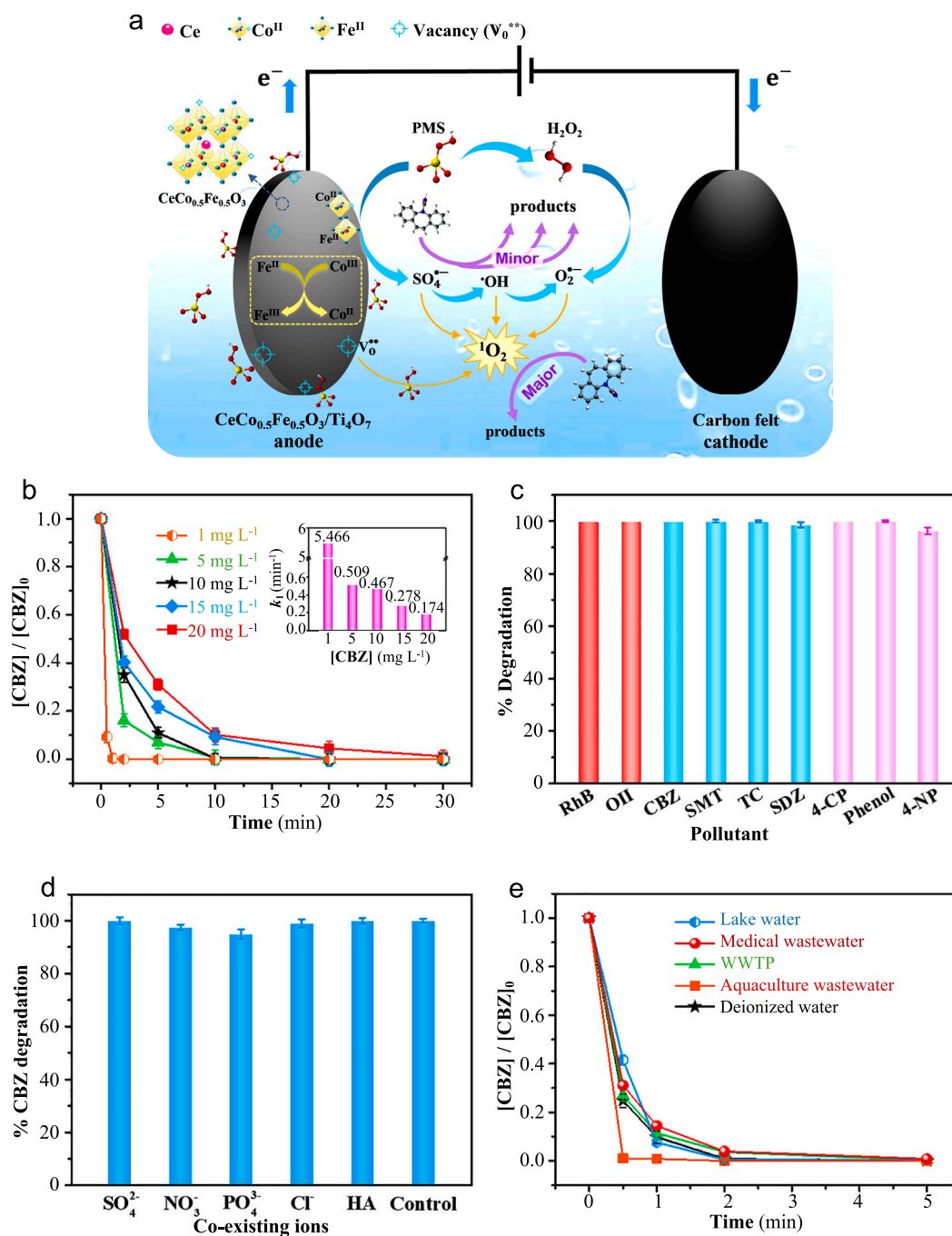


Fig. 9. (a) Proposed mechanism for the hybrid EO/peroxymonosulfate (PMS) process of carbamazepine (CBZ). (b) Effect of CBZ content on the variation of the normalized drug concentration with time for 1 mM PMS solutions in pure water at pH = 7.0 and room temperature using a stirred undivided tank photoreactor with a $\text{CeCo}_{0.5}\text{Fe}_{0.5}\text{O}_3/\text{Ti}_4\text{O}_7$ anode and carbon felt cathode at $j = 1 \text{ mA cm}^{-2}$. (c) Percent of degradation after 60 min of treatment of 0.05 mM of Rhodamine B (RhB), Orange II (OII), sulfamethazine (SMT), tetracycline (TC), sulfadiazine (SDZ), 4-chlorophenol (4-CP), phenol, and 4-nitrophenol (4-NP). (d) Effect of 10 mg L^{-1} inorganic ions and 10 mM humic acid (HA) over the percent of 1 mg L^{-1} CBZ degradation. (e) Effect of several aqueous matrices upon the above conditions. Adapted from ref. [61] with permission of Elsevier.

[has shown the significant influence of the size of the O_2 bubbles injected to the solution over H_2O_2 accumulation for 100 mL of 12.5 mM Na_2SO_4 at pH = 6.5 and 25 °C using a stirred undivided tank reactor with a Ti/IrO₂ anode and carbon felt cathode at $j = 22.2 \text{ mA cm}^{-2}$. Fig. 10a highlights that 60% of gas efficiency, i.e., the percent of H_2O_2 produced from dissolved oxygen with 5 min of aeration, was achieved after 60 min of electrolysis NBs, whereas only 0.19% was obtained with MBs. This was reflected in Fig. 10b by the much quicker H_2O_2 accumulation with NBs compared to MBs (30 vs. 16 mg L⁻¹) at 28 mg O₂ L⁻¹

(see Table 2) and in Fig. 10c by the best approaching to the theoretical value with NBs. This behavior can be ascribed to the enhancement of the mass transfer of O_2 toward the cathode by the greater total area with smaller size of injected NBs.

Carbon-based materials have long been recognized as promising cathodes due to their high electrical conductivity, chemical stability, porosity, low cost, and limited reactivity toward H_2O_2 decomposition [64]. Classical carbonaceous materials such as graphite, carbon felt, and carbon sponge have been widely employed in EF and HEF with solid

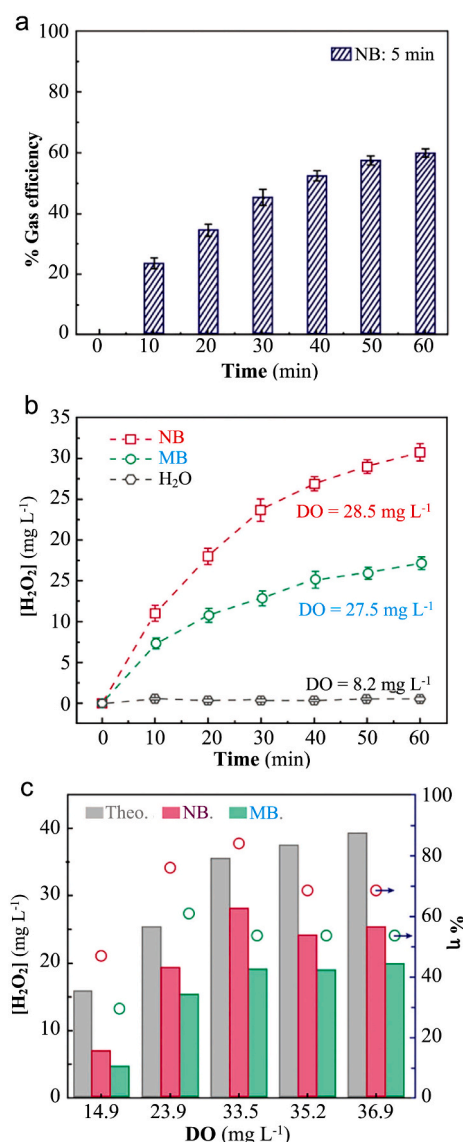
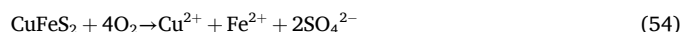


Fig. 10. Accumulated H₂O₂ during the electrolysis of 100 mL of 12.5 mM Na₂SO₄ at pH = 6.5 and 25 °C using a stirred undivided tank reactor with a Ti/IrO₂ anode and carbon felt cathode at $j = 22.2 \text{ mA cm}^{-2}$. (a) Gas efficiency calculated from the initial dissolved oxygen and the H₂O₂ produced using nanobubbles (NBs). (b) H₂O₂ content attained under non-aerated conditions (8.3 mg O₂ L⁻¹) and after aeration with macrobubbles (MBs) (27.5 mg O₂ L⁻¹) and NBs (28.5 mg O₂ L⁻¹) of oxygen. (c) H₂O₂ concentration and reaction yield at different dissolved oxygen (DO) levels considering theoretical, NBs, and MBs. Adapted from ref. [63] with permission of Wiley.

catalysts [65]. Recent efforts have focused on engineering carbon cathodes to favor the two-electron oxygen reduction reaction ($2e^-$ ORR) to H₂O₂ by reaction (14) while suppressing the competing four-electron pathway to H₂O. Heteroatom doping, particularly nitrogen, has proven high effectiveness for EF. For instance, nitrogen-doped graphene supported on carbon nanotubes (N-G/CNT) introduces defect sites and charge delocalization, enhancing O₂ adsorption and H₂O₂ selectivity [66]. Other advanced configurations include GDEs based on WO₃ [67], and graphene/graphite (G-GDE) composites [68], which exhibit high stability and electrocatalytic efficiency. Fig. 11a depicts the EF mechanism proposed for G-GDE cathode, which presented micropores and channels to favor the O₂ reduction to H₂O₂ from reaction (14) and the reduction of Fe³⁺ to Fe²⁺ from reaction (29), thus accelerating [•]OH generation from Fenton reaction (18) [68]. This is confirmed in Fig. 11b

by the greater content of accumulated H₂O₂ of 60 mg L⁻¹ obtained with G-GDE in front of 49 mg L⁻¹ with graphite GDE and 25 mg L⁻¹ GE after 60 min of electrolysis of 50 mL of 0.05 M Na₂SO₄ at pH = 3.0, room temperature at $j = 20 \text{ mA cm}^{-2}$ (see Table 2). This better behavior of G-GDE enhances the EF process of 20 mg L⁻¹ Rhodamine B in the above solution by adding 0.3 M Fe²⁺, as shown in Fig. 11c to Fig. 11f. So, it was found a 97% of discoloration, $k_d = 0.31 \text{ min}^{-1}$, 79% of COD removal, and $EC_{\text{COD}} = 80 \text{ kWh (kg COD)}^{-1}$.

Noble-metal-based cathodes also deliver excellent H₂O₂ selectivity and stability. Pd- and Au-based GDEs have shown superior performance, achieving high H₂O₂ concentrations and efficient degradation of target organic pollutants under EF conditions [69,70]. Despite these advances, the scarcity and high cost of noble metals, along with the need for strongly acidic conditions (pH ~3.0), limit their large-scale application. Consequently, research has shifted toward HEF that operate stably across wider pH ranges. Strategies include dispersing solid catalysts directly in solution, using natural minerals such as pyrite [71], chalcopyrite [72], or vermiculite [73]. While effective in neutral electrolytes, challenges remain regarding catalyst recovery and stability. For instance, Fig. 12a depicts the change of tetracycline concentration with time for the HEF treatment of 230 mL of 0.20 mM drug in 0.050 M Na₂SO₄ with 1.0 g L⁻¹ chalcopyrite (CuFeS₂) as solid catalyst at pH = 5.94 and room temperature using a stirred undivided tank reactor with a Pt or BDD anode and carbon felt cathode at $I = 300 \text{ mA}$. Chalcopyrite is partly dissolved to Cu²⁺ and Fe²⁺ via reaction (54) and both ions originated [•]OH via reactions (18) and (31) with Fe³⁺/Fe²⁺ pair and the corresponding like processes with Cu²⁺/Cu⁺ one. Fig. 12a makes evident the superiority of BDD over Pt for drug removal (see Table 2), which can be ascribed to the greater BDD([•]OH) production from reaction (1) in oxidative competence with the above produced [•]OH. Fig. 12b reveals that the BDD/chalcopyrite process is slightly more powerful than the BDD/Fe²⁺ one, indicating the little [•]OH production from the Cu²⁺/Cu⁺ pair. GC-MS analysis of the treated BDD/chalcopyrite solution allowed identifying 10 derivatives, whereas HPLC detected 6 final carboxylic acids such as oxalic, acetic, oxamic, succinic, malic, and malonic acids. Fig. 12c shows the evolution of these acids with electrolysis time and Fig. 12d highlights the greater release of NH₄⁺ in front NO₃⁻ released from the N contained in the drug. From these by-products, the reaction sequence of Fig. 13 for tetracycline mineralization was proposed in which [•]OH is the main oxidant and final carboxylic acids are formed from the cleavage of precedent cyclic derivatives, then being mineralized to CO₂.



Immobilization of catalytic materials onto cathode surfaces yielding functionalized materials has gained increasing attention, improving reusability, stability, and scalability for practical applications. In recent years, MOFs have emerged as state-of-the-art materials as cathodes for HEF systems. Fe₂O₃/N-C composites derived from Fe-based MOFs exhibit excellent activity and stability for HEF degradation of bisphenol A, with low Fe leaching and high recyclability [74]. Similar findings were found by constructing cathodes with FeNi₃ marigold-like nano-sheets synthesized from Fe-Ni MOFs that were mixed with carbon to be printed onto carbon paper [75]. This cathode was used to treat 200 mL of 10 mg L⁻¹ OTC in pure water with 0.1 M Na₂SO₄ at pH = 3.0 and room temperature, confronted with a Ti/IrO₂ anode at $I = 60 \text{ mA}$. Fig. 14a shows the mechanism proposed for this cathode, where H₂O₂ formed from reaction (14) was directly decomposed by surface $\equiv\text{Fe}^{2+}$ via reaction (31) and $\equiv\text{Ni}^{2+}$ by analogous like reaction, generating [•]OH. O₂^{•-} and ¹O₂, which were detected by specific scavengers. Under these conditions, 97% of the drug was abated in 90 min with release of about 0.3 mg L⁻¹ of Fe and Ni and good reusability was obtained after 4 consecutive steps (see Table 2). 13 derivatives were identified by LC-MS and a more rapid total abatement in 90 min with 0.05 M NaCl + 0.05 M Na₂SO₄ was found by the additional action of active chlorine formed

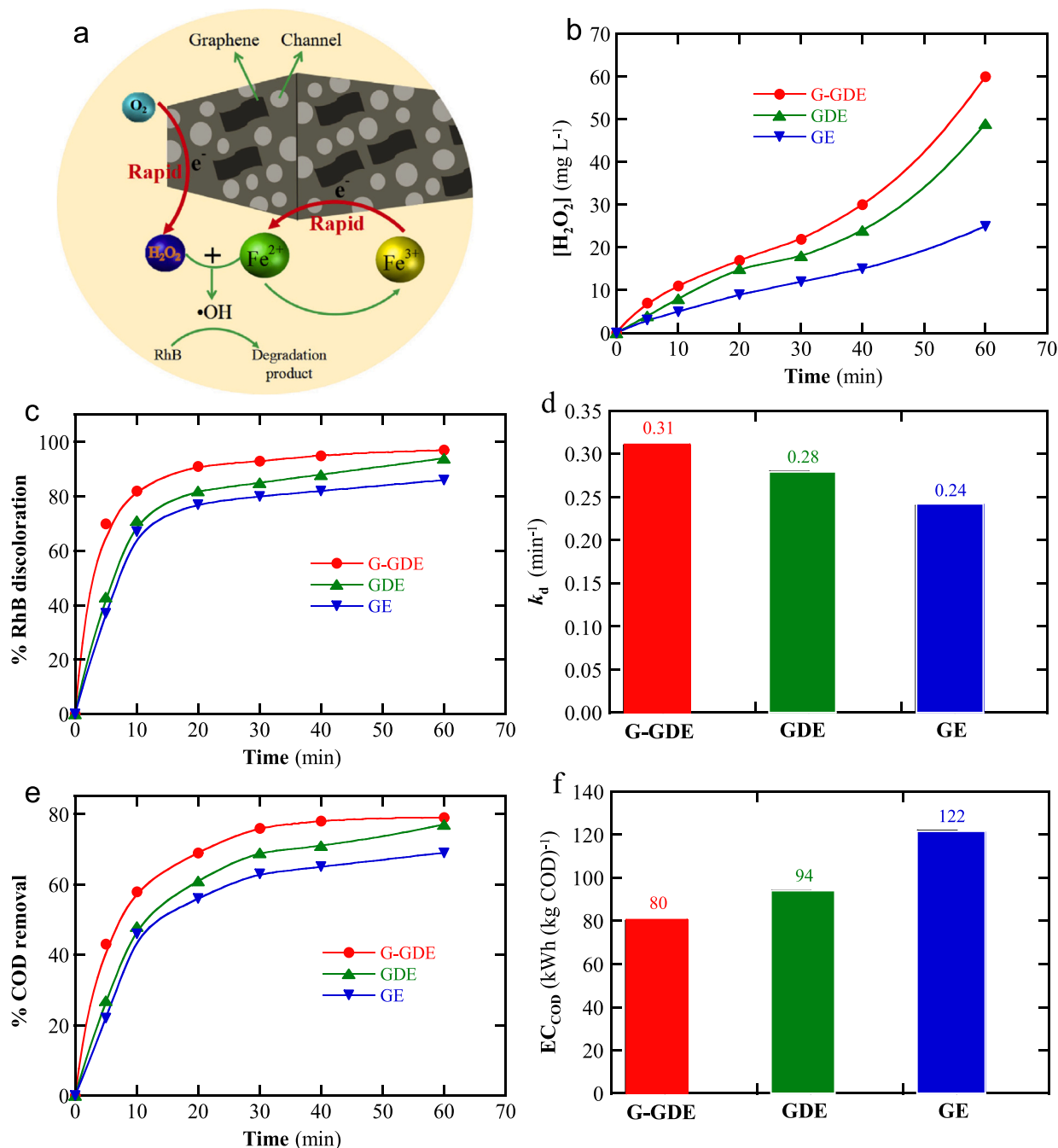


Fig. 11. (a) Proposed mechanism for the EF process with graphite/graphene gas-diffusion electrode (G-GDE) cathode. (b) Variation of accumulated H_2O_2 with time during the electrolysis of 50 mL of 0.05 M Na_2SO_4 at pH = 3.0 and room temperature using a stirred undivided tank reactor with a Ti anode and cathode of G-GDE, graphite gas-diffusion electrode (GDE), or graphite sheet electrode (GE) at $j = 20\ mA\ cm^{-2}$ under bubbling $60\ mL\ O_2\ min^{-1}$. (c) Percentage of Rhodamine B discoloration vs. time and (d) pseudo-first order rate constant for discoloration obtained for the EF process of $20\ mg\ L^{-1}$ dye under the above conditions by adding $0.3\ M\ Fe^{2+}$. (e) Time course of the percentage of COD removal for the same assays and (f) the corresponding energy consumption per unit COD mass at the end of such trials. Adapted from ref. [68] with permission of Elsevier.

from reactions (7) and (8). Other interesting bifunctional reduced graphene oxide (rGO)/MIL-88 A/carbon felt enable simultaneous in situ H_2O_2 generation and activation. It produced $\bullet OH$, as detected by specific scavengers and EPR, following the mechanism of Fig. 14b [76]. This cathode gave $13.5\ mg\ L^{-1}\ H_2O_2$ after 120 min of electrolyzing $0.1\ M\ Na_2SO_4$ at pH = 3.0 and room temperature by applying a cathodic potential (E_{cat}) of $-0.4\ V/Ag|AgCl$. After adding $10\ mg\ L^{-1}$ of Rhodamine B, 93% of discoloration was attained in 120 min with good reusability after 4 consecutive runs (see Table 2),

SACs have recently attracted attention due to their well-defined

active sites, high atomic utilization, and tunable electronic structures for HEF with solid catalyst or functionalized cathodes. In the former case, it is noticeable the work of Xia et al. [77] considering a catalyst like FeN_4 on N-doped carbon to efficiently remove 2,4-dichlorophenol. Fig. 14c schematizes the mechanism proposed for $\bullet OH$ production at the surface of this catalyst by heterogeneous Fenton reaction (31). The assays were made with 160 mL of $10\ mg\ C\ L^{-1}$ of 2,4-dichlorophenol in pure water and real wastewaters with $0.10\ g\ L^{-1}$ catalyst at pH = 4.0 and room temperature using a stirred undivided tank reactor with a GDE cathode at $I = 50\ mA$. The treatment with BDD anode in pure water

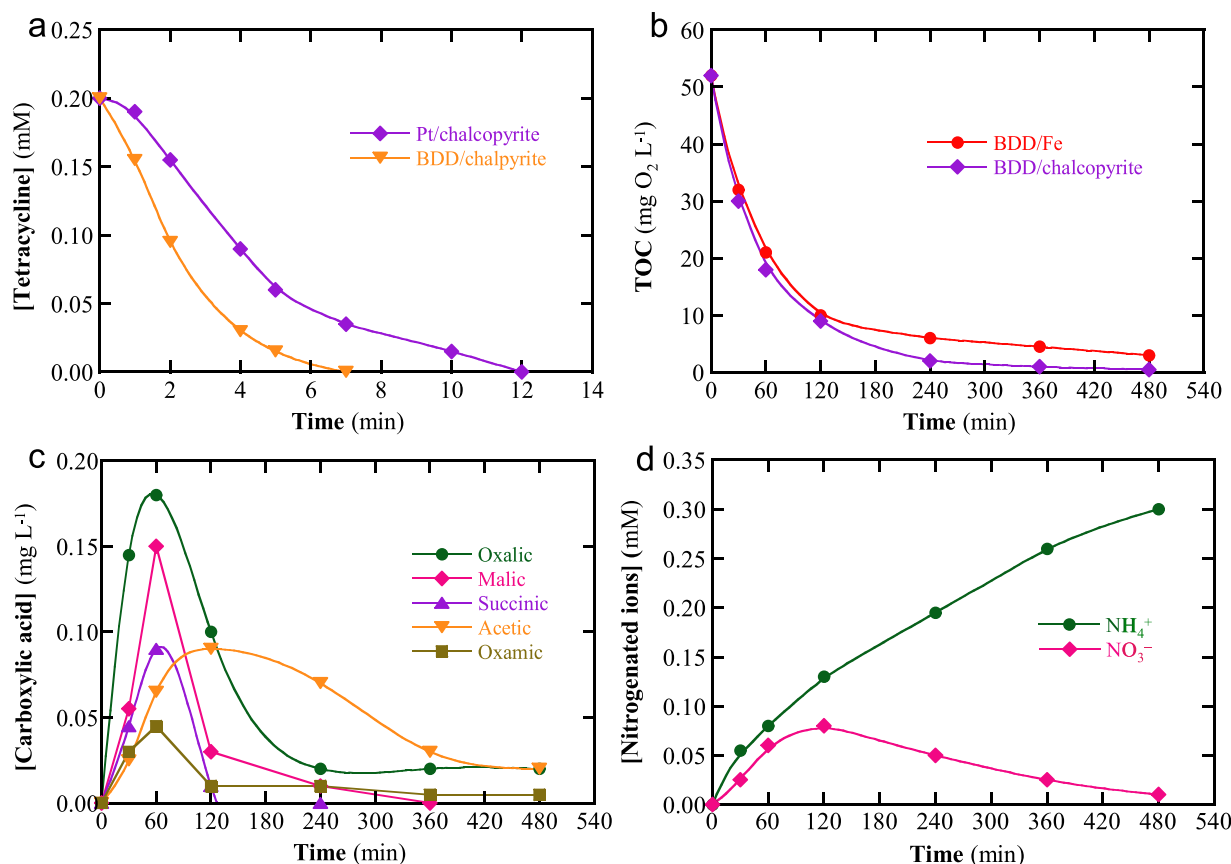


Fig. 12. (a) Change of tetracycline concentration with time for the HEF treatment of 230 mL of 0.20 mM drug in 0.050 M Na₂SO₄ with 1.0 g L⁻¹ chalcopyrite as solid catalyst at pH = 5.94 and room temperature using a stirred undivided tank reactor with a Pt or BDD anode and carbon felt cathode at $I = 300$ mA. (b) TOC vs. time for the above assay with BDD anode and with 0.20 mM Fe²⁺ (EF process). (c) Evolution of carboxylic acids and (d) nitrogenated ions detected during the above HEF process with BDD/chalcopyrite. Adapted from ref. [72] with permission of Elsevier.

yielded total degradation in 20 min and 6.18 mg L⁻¹ Fe leaching without Na₂SO₄ and much longer time of 60 min was required with 0.050 M Na₂SO₄ as electrolyte, indicating a scavenging effect of adsorbed SO₄²⁻ onto the catalyst (see Table 2). This caused a moderate reusability of the catalysts after 5 successive steps. It was also found after 240 min in pure water without Na₂SO₄ that TOC was reduced by 68% with BDD, much higher than 47% determined with Ti/IrO₂, related to the greater parallel oxidation with BD(*OH), as stated above. The study was extended to an urban wastewater to find 97% removal of 2,4-dichlorophenol in a long time of 90 min, due to the adsorption and oxidation of its components.

Bimetallic SACs such as NiCo alloys on graphene aerogels act as sustainable cathodes for in situ H₂O₂ generation. Co sites preferentially adsorbed O₂ for H₂O₂ production, while Ni sites activated H₂O₂ for *OH formation, enabling efficient degradation of ibuprofen with low energy input [78]. More recently, cobalt SACs have been modified with epoxy groups to enhance O₂ transport and Co–N stability, generating H₂O₂ onsite for direct dye removal under acidic conditions [79].

3.1.3. Cathode material for electrochemical nitrate reduction

Beyond H₂O₂ generation, cathodes also play a central role in ENR, an emerging route for sustainable nitrogen management. This process enables the conversion of NO₃⁻ pollutant into ammonia (NH₃) following reactions (36) and (37), a valuable chemical feedstock, or nitrogen gas (N₂) from reaction (38), an environmentally benign product. Over the past decade, substantial advances have been made in tailoring catalytic materials for nitrate electroreduction to NH₃ with optimized electronic structures, abundant active sites, and tunable selectivity.

Transition-metal-based catalysts such as Cu, Co, and Ni have long been considered the foundation of nitrate electroreduction due to their

favorable adsorption energies for nitrate and reaction intermediates [80]. Among them, Cu-based catalysts have shown the highest activity toward NH₃ production. For instance, Fig. 15a shows that single-site Cu atoms in Cu/Th-BPYDC achieved an NH₃ yield of 225.3 μmol h⁻¹ cm⁻² with Faradaic efficiency of 92.5% at $E_{\text{cat}} = 0.0$ V/RHE [81]. Theoretical analyses revealed that Cu sites acted as Lewis's acid centers, facilitating NH₃ desorption and improving catalytic turnover. Better performance has been reported for Cu–cis-N₂O₂ single-atom catalyst, which demonstrated exceptional polarity and strong NO₃⁻ adsorption, enabling efficient formation of intermediate *ONH to yield NH₃ [82]. Fig. 15b depicts that this cathode yielded a maximum NH₃ yield of 27.5 mg h⁻¹ cm⁻² at $E_{\text{cat}} = -1.2$ V/RHE with maximum 93.19% FE after 480 min at $E_{\text{cat}} = -2.0$ V/RHE. In this last case, a remarkable durability over 2000 h was obtained.

Bimetallic systems, particularly Cu–Pt electrodes synthesized via controlled electrodeposition, have demonstrated the potential of synergistic electronic effects between Cu and Pt sites to reduce NO₃⁻. Moderate Pt loadings optimized nitrate-to-ammonia conversion, reaching 94% nitrate reduction, 84% NH₃ selectivity, and low 22% Faradaic efficiency using a stirred undivided tank reactor [83]. However, high FE are often achieved under potentiostatic control in divided cells, where anodic oxidation of produced ammonia is suppressed. Under more practical conditions (galvanostatic operation, undivided reactors, and complex water matrices) selectivity frequently decreases due to competing pathways and parasitic reactions. From an implementation perspective, selectivity remains the main bottleneck for ENR. Nitrite accumulation is particularly concerning, as NO₂⁻ is strictly regulated in drinking water. Therefore, FE alone is insufficient to assess process viability; it must be evaluated alongside by-product formation,

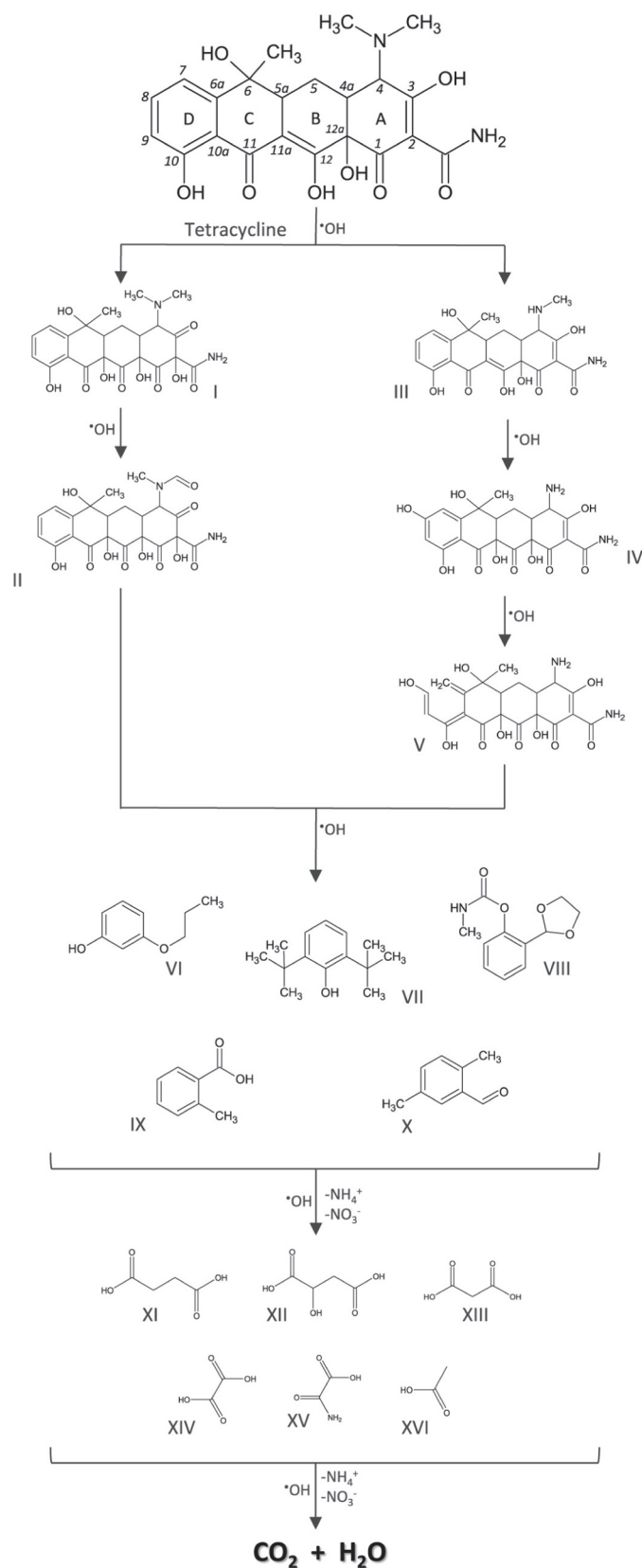


Fig. 13. Proposed reaction sequence for tetracycline mineralization by HEF using chalcocopyrite as solid catalyst. Adapted from ref. [72] with permission of Elsevier.

operating mode, and reactor configuration.

Additional systems such as Co_3O_4 /graphene nanoribbons [84], WSe_{2-x} [85], and B-doped MoS_2 [86] have also exhibited strong activity and stability toward NH_3 formation. Fig. 15c reveals that the WSe_{2-x} cathode gave a maximum NH_3 yield of about $3.7 \text{ mg h}^{-1} \text{ cm}^{-2}$ at $E_{\text{cat}} = -1.0 \text{ V/RHE}$ with 90% faradaic efficiency. A good stability of this cathode was obtained during 30 h at $E_{\text{cat}} = -0.8 \text{ V/RHE}$. Beyond traditional metals and alloys, new classes of materials including doped carbon nanostructures with earth-abundant elements [87], perovskite oxides [88], and Co-based MOFs [89] have emerged due to their tunable surface chemistry, structural versatility, and potential for targeted active-site design. For the Co^{2+} -MOF cathode at $E_{\text{cat}} = -0.6 \text{ V/RHE}$, $31.6 \text{ mg h}^{-1} \text{ cm}^{-2}$ of NH_3 yield with 93% of faradaic efficiency was determined, which remained stable during 96 h.

3.2. Coupling electrified processes with UV, ultrasound, membranes, or biological treatment

Over the past decade, research in water and wastewater treatment has increasingly shifted toward the integration of hybrid and sequential processes to improve the removal of refractory and persistent pollutants. In this context, growing attention has been devoted to electrochemical technologies coupled with complementary physical, chemical, or biological processes, as such systems can substantially enhance pollutant degradation, mineralization efficiency, and overall energy performance. By combining electrochemical oxidation with auxiliary techniques such as irradiation, ultrasonic agitation, membrane-based separation, or biological treatment, these integrated systems exploit synergistic effects that cannot be achieved by standalone electrochemical processes.

The SPEF process exemplifies the potential of this strategy. SPEF achieves rapid degradation kinetics and high MCE values ($> 50\%$) while maintaining lower EC_{TOC} values than conventional PEF systems. This improvement is largely due to free solar irradiation, which promotes photoreduction of $\text{Fe}(\text{OH})^{2+}$ complexes with continuous Fe^{2+} regeneration from reaction (12) and photolysis of final $\text{Fe}(\text{III})$ -carboxylate species from reaction (13) without additional energy input [90–92]. These assays were typically performed with an incident UV irradiance between 30 and 40 W m^{-2} and highlighted the importance of reactor design and solar collection efficiency. For instance, Fig. 16a schematizes a solar flow plant with solar CPC photoreactor used for the treatment of tetracycline solution in sulfate medium at $\text{pH} = 3.0$ during 360 min of electrolysis at $j = 50 \text{ mA cm}^{-2}$ [90]. Fig. 16b shows that the herbicide mineralization was enhanced in the order: EO with electrogenerated H_2O_2 ($\text{EO}/\text{H}_2\text{O}_2$) $< \text{EF} < \text{SPEF}$, with 0.50 mM Fe^{2+} added for both Fenton processes. Nevertheless, SPEF only reduced 65% of TOC, demonstrating the high recalcitrance of by-products formed. In contrast, Fig. 16c reveals that a mixture of 3 dyes with near 5-fold higher TOC_0 was completely mineralized with a high $\text{MEC} = 23.2\%$ and low $\text{EC}_{\text{TOC}} = 0.66 \text{ kWh (g TOC)}^{-1}$ in 300 min at $j = 100 \text{ mA cm}^{-2}$ [91].

Despite its environmental and energetic advantages, SPEF remains investigated by relatively few research groups. Its limited dissemination arises mainly from dependence on natural sunlight, which restricts consistent operation to favorable geographic and climatic conditions. Furthermore, practical issues such as operation under cloudy conditions, at night, or during seasons with limited solar irradiance remain unresolved. When solar radiation is unavailable, artificial UVA or UVC sources are commonly employed in PEF systems to maintain continuous operation. Mechanistically, EF, PEF and SPEF share a Fenton-based homogeneous pathway, with irradiation introducing additional photochemical steps. UVA or solar light accel the catalytic cycle, whereas UVC light further promotes direct H_2O_2 photolysis, increasing $\cdot\text{OH}$ formation and overall oxidation efficiency. Although PEF systems can achieve excellent results, lamp operation dominates their energy consumption. To reduce energy demand, Barazorda-Ccahuana et al. [93] proposed a staged EF + UVA/UVC configuration, in which a short irradiation period follows an initial EC stage, lowering EC_{TOC} from 2.4 to 1.2 kWh

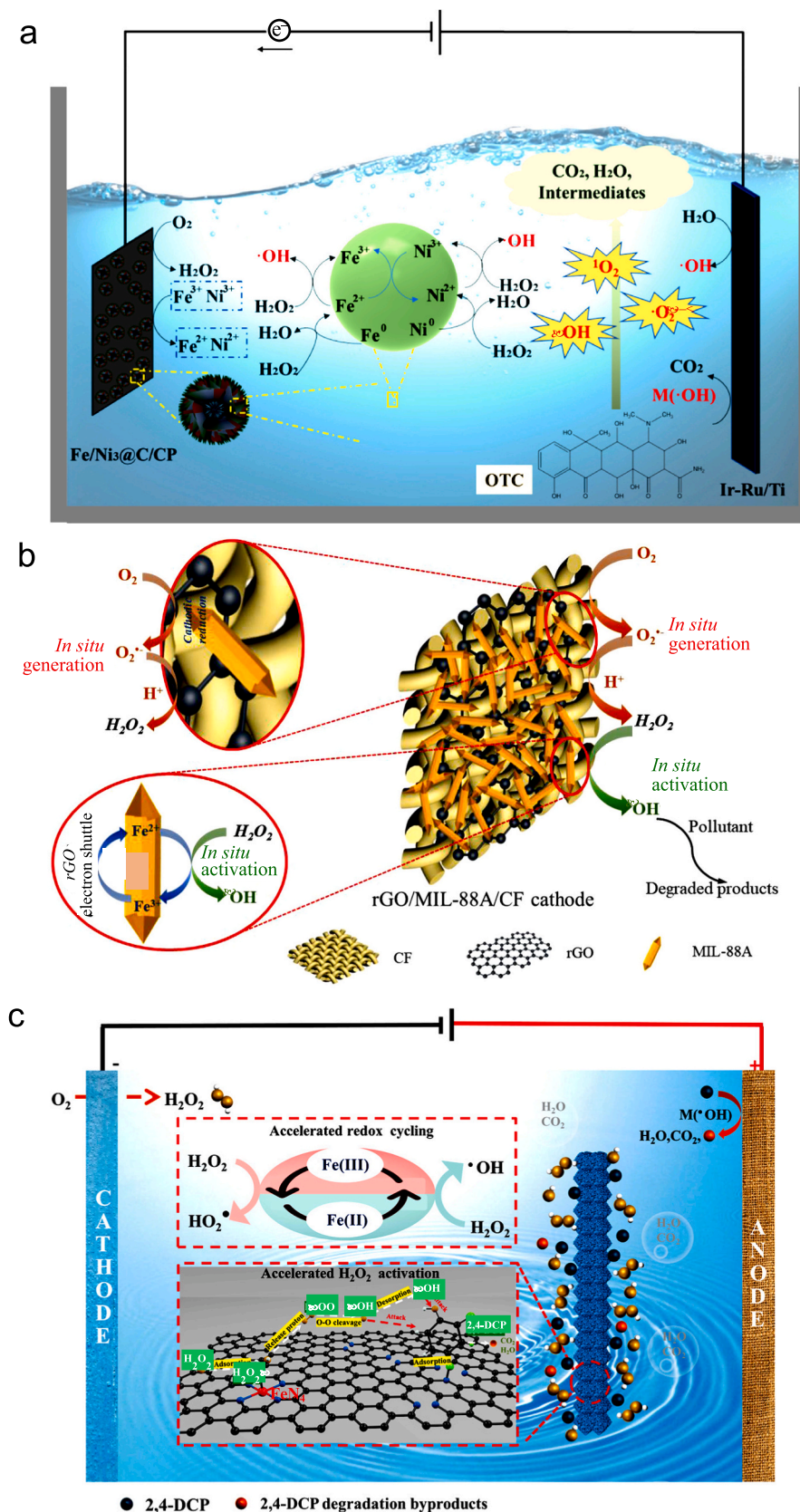


Fig. 14. Proposed mechanisms for HEF processes. (a) Oxytetracycline (OTC) removal with FeNi₃/carbon/carbon paper cathode (adapted from ref. [75] with permission of Elsevier). (b) Rhodamine B with reduced graphene oxide (rGO)/MIL-88 A/carbon felt cathode (adapted from ref. [76] with permission of Elsevier). (c) 2,4-Dichlorophenol with N-porous carbon/FeNi₄ catalyst (adapted from ref. [77] with permission of Elsevier).

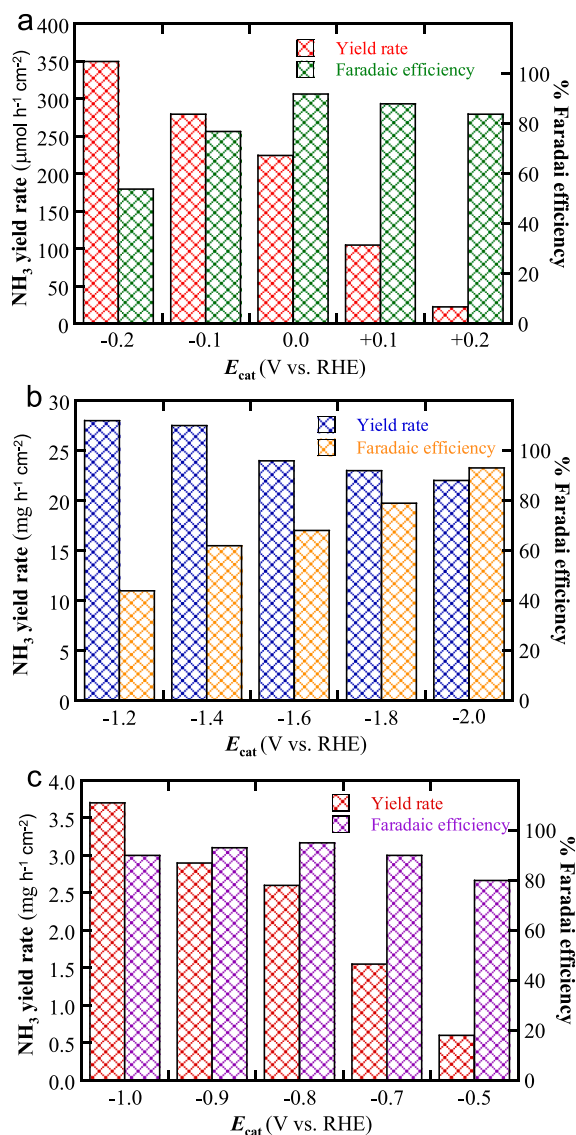


Fig. 15. Effect of cathodic potential on ammonia yield rate and percent of faradaic efficiency for NO_3^- electroreduction. Cathode: (a) Cu/Th-2,2'-bipyridine-5,5'-dicarboxylic acid (BPYDC) (adapted from ref. [81] with permission of American Chemical Society), (b) Cu-cis-N₂O₄ (adapted from ref. [82] with permission of Wiley), and (c) WSe_{2-x} (adapted from ref. [85] with permission of Elsevier).

(gTOC)⁻¹. Extending this concept, Sánchez-Montes et al. [94] introduced an intermittent EO/H₂O₂/UVC strategy, in which electrolysis is first applied to generate H₂O₂, followed by UVC irradiation with the current switched off. This decoupled operation avoids residual H₂O₂ accumulation while maximizing oxidant utilization.

Coupling EO with US has also demonstrated significant improvements in pollutant degradation [95]. Acoustic cavitation, produced by ultrasonic waves (20 kHz–2 MHz), generates localized hotspots (~5000 K, >1000 atm), producing $\bullet OH$ radicals from H₂O cleavage and inducing intense micro-mixing [96]. These effects continuously clean electrode surfaces, enhance mass transfer, and promote ROS formation, resulting in faster and more energy-efficient oxidation. Llanos et al. [97] demonstrated this synergy for real wastewater disinfection, increasing *Escherichia coli* inactivation rate from 0.0242 min⁻¹ (EO alone) to 0.1428 min⁻¹ under 200 W US. The main oxidants also electrogenerated active chlorine species from reactions (12) to (14), whose activity was enhanced by ultrasonic dispersion. Similarly, Yang et al. [98] applied a coupled EO/US system with nanostructured electrodes to treat

biologically pretreated cephalosporin pharmaceutical wastewater. Fig. 17a highlights a sketch of the experimental set up used with a cell equipped with a Ti/RuO₂-IrO₂ anode and SS cathode placed in a US generator. Fig. 17b makes evident that 94% COD removal was obtained by EO/US after 30 min under optimum conditions at $j = 8\ mA\ cm^{-2}$ and 45 kHz US. It showed synergism with respect to the sum of EO and US processes, giving 50% and 3% COD decay, respectively. Apart from active chlorine generation, the authors suggested the US-induced Cl₂ homolysis oxidant to generate Cl $\bullet$ radical, so promoting mineralization. Comparable enhancements of these processes have been reported for hospital effluent treatment [99].

Another powerful intensification route involves coupling electrified processes with membrane-based separation. Pressure-driven membrane technologies such as MF, NF, and RO are commercially mature and widely implemented, particularly in point-of-use and water reuse applications, with RO dominating the global market. Nevertheless, membranes give purely physical separation processes and therefore, they are incapable of degrading contaminants, leading to the accumulation of organic micropollutants in the retentate. In addition, membrane fouling caused by organic matter, inorganic salts, and microorganisms progressively reduces permeability and increases energy [100]. Coupling membrane filtration with electrochemical technologies provides an effective process-intensification strategy. Electrochemical treatments can be applied either as a post-treatment step for retentate degradation or integrated into hybrid/one-pot systems, where separation and electrochemical reactions occur simultaneously. In both configurations, membranes enhance pollutant concentration and alleviate mass-transfer limitations, whereas electrochemical reactions may also contribute to in situ membrane cleaning and performance recovery, mitigating fouling effects [101].

Experimental studies highlight both the benefits and trade-offs of membrane-electrochemical coupling. Ultrafiltration used as a pre-concentration step prior to BDD-based electrochemical oxidation enabled high rejection and permeate fluxes. However, the electrochemical treatment of the resulting concentrate required higher specific energy consumption from 590 to 882 kWh kg⁻¹, indicating that pre-concentration alone does not guarantee improved electrochemical efficiency [102]. In contrast, NF coupled with BDD-based EO proved highly effective for the treatment of PFHxA [103]. Fig. 18a schematizes the setup for the nanofiltration system of 204 mg L⁻¹ PFHxA with a NF270 membrane, yielding 96.6–99.4% rejection. The resulting retentate of 780 mg L⁻¹ of this pollutant was further treated by EO with a flow-by cell with p-Si/BDD anode and cathode. Fig. 18b and c show a fast degradation up to ~98% PFHxA removal for 360, 120, and 60 min and > 95% TOC abatement for 360, 180, and 120 min reached at j -values of 20, 50, and 100 mA cm⁻². These results demonstrate the effectiveness of the sequential NF-EO process and underline the critical role of membrane selectivity and retentate chemistry in determining overall process performance.

More integrated configurations, such as EF catalytic membranes, further strengthen membrane-electrochemical coupling by integrating separation and oxidation within a hybrid and single functional unit. In the case of a graphene-modified EF catalytic membrane [104], Fig. 19a presents the proposed mechanism for $\bullet OH$ production from reactions (14) and (30). Fig. 19b reveals that This architecture led to 90% removal and 60% mineralization of 1 mM florfenicol during filtration + EF with Pt anode at $E_{cat} = -0.6\ V/SCE$, markedly outperforming 50% and 4% for filtration + EO, and only 27% and 25% for standalone membrane filtration. The system also exhibited stable operation with effective antifouling behavior, indicating enhanced mass transfer and local oxidant utilization. The low 4% mineralization for filtration + EO was ascribed to the high recalcitrance of reduction by-products formed at the cathode. Nevertheless, challenges related to long-term electrochemical stability, material durability, and scale-up remain to be addressed before practical implementation [104,105]. Applications to inorganic contaminants such as nitrate are comparatively scarce, despite promising

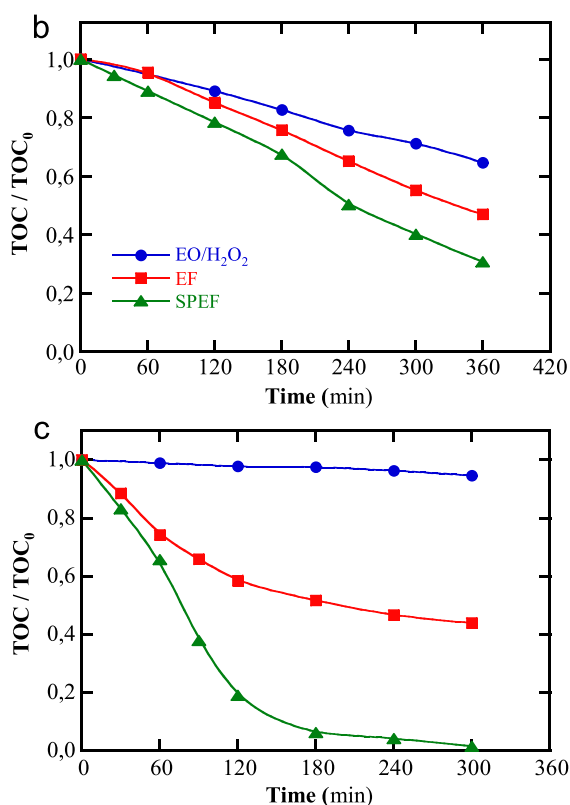
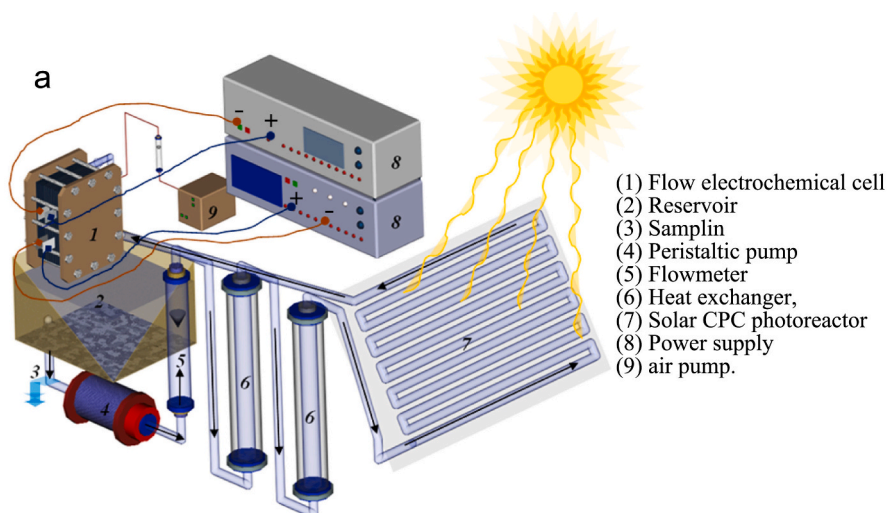


Fig. 16. (a) Schematic illustration of a 2.5 L solar flow plant with a solar compound parabolic collector (CPC) photoreactor designed for wastewater treatment by SPEF. EO with electrogenerated H_2O_2 (EO/ H_2O_2), EF, and SPEF processes, both with 0.50 mM Fe^{2+} , for: (b) herbicide tebuthiuron solution of $\text{TOC}_0 = 20 \text{ mg C L}^{-1}$ with $0.05 \text{ M Na}_2\text{SO}_4$ at $\text{pH} = 3.0$ and 35°C using the above flow plant with a BDD/air-diffusion cell at $j = 50 \text{ mA cm}^{-2}$ and liquid flow rate $= 200 \text{ L h}^{-1}$ (adapted from ref. [90] with permission of Elsevier), and (c) mixture of $0.136 \text{ mM Tartrazine} + 0.154 \text{ mM Ponceau SS} + 0.080 \text{ mM Direct Blue 71}$ ($\text{TOC}_0 = 105 \text{ mg C L}^{-1}$) in $0.050 \text{ M Na}_2\text{SO}_4$ at $\text{pH} = 3.0$ and 35°C using the same plant with a Pt/air-diffusion press cell and a solar planar photoreactor at $j = 100 \text{ mA cm}^{-2}$ and liquid flow rate $= 180 \text{ L h}^{-1}$ (adapted from ref. [91] with permission of Elsevier), (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

results obtained using membrane-enabled preconcentration coupled with electroreduction [106].

Finally, coupling electrified processes with biological treatment represents a highly complementary and energy-efficient strategy. Electrochemical pre-treatment can selectively convert recalcitrant compounds into more biodegradable intermediates, increasing BOD_5/COD ratio and reducing toxicity, thereby enhancing downstream biological degradation. Given that biological processes are well established, inexpensive, and highly effective for biodegradable substrates, complete

electrochemical mineralization is often unnecessary and energetically unfavorable. This concept has been demonstrated by short EO or EF pre-treatments that substantially increased biodegradability, enabling overall COD removals of 80–90% after subsequent biological treatment while minimizing electrical energy input [107,108].

At more advanced level, integrated bioelectrochemical systems, such as microbial EF cells, further intensify this synergy by enabling simultaneous electrochemical oxidation and microbial degradation these systems. Electroactive microorganisms can also utilize biodegradable

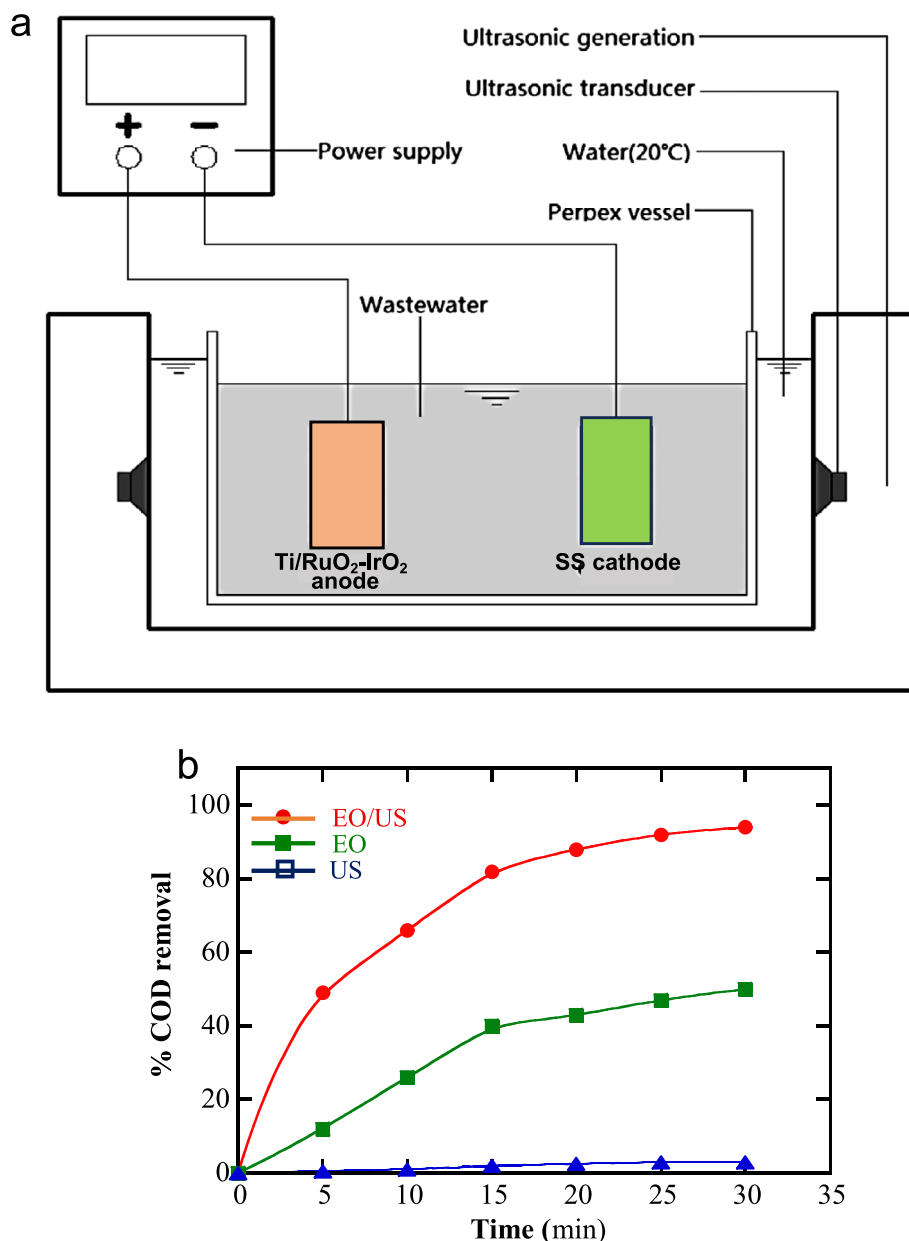


Fig. 17. (a) Sketch of the EO/ultrasounds (US) system for the treatment of biologically treated cephalosporin pharmaceutical wastewater. (b) Variation of the percent of COD with time for different processes of 500 mL of the above wastewater with $\text{COD}_0 = 323 \text{ mg O}_2 \text{ L}^{-1}$ at $\text{pH} = 6.3$ and room temperature operating at the optimum values of $j = 8 \text{ mA cm}^{-2}$ and 45 kHz US. Adapted from ref. [98] with permission of Elsevier.

organic matter as a fuel for bio-electricity cogeneration from biofilms at the anode, enhancing both treatment efficiency and energy utilization [109]. As an example, Fig. 20a shows the diagram with proposed mechanism for $\cdot\text{OH}$ generation involving reactions (14) and (31) for a microbial heterogeneous EF cell [110]. An anode biofilm of *Shewanella decolorationis* S12 was fed with lactate as carbon source to give electrons to the anode to pass to the CNT/ γ -FeOOH cathode through an external resistance. Fig. 20b highlights the slow oxidation of 0.1 mM Orange II in 100 mM phosphate buffer solution at $\text{pH} = 7.0$, giving 98% discoloration in 13 d and 97% TOC reduction in 43d due to the low catalytic activity of γ -FeOOH by the small generated I . However, the high k_d -value decay from 0.21 to 0.12 h^{-1} after 10 steps, probably by cathodic deposition on the cathode, as shown in Fig. 20c, revealed an unstable behavior. Fig. 20d depicts the accumulation of H_2O_2 and Fe^{2+} in the catholyte up to 265 and 1.7 mg L^{-1} , respectively, at 53 h, consequence of the slow reaction (18) at $\text{pH} = 7.0$, whereas Fig. 20e presents the power density generated vs. current density plot, with maximum of 320 mW

m^{-2} at $j = 1.0 \text{ A m}^{-2}$. Similarly, enhanced carbamazepine removal compared with conventional EF and biological treatments has also been reported due to the combined action of $\cdot\text{OH}$ oxidant and electroactive microbial communities [111]. Overall, biologically integrated electrified processes offer a pragmatic and sustainable pathway for wastewater treatment, particularly when electrochemical intervention is strategically used to enhance biodegradability rather than to pursue complete mineralization.

3.3. Reactors, technology readiness, and decentralized treatment scenarios

Environmental electrochemistry has progressed from laboratory demonstrations to increasingly mature, engineered solutions. This maturation stems from three converging advances: (i) more efficient and selective electrodes tailored to specific functions (oxidation, H_2O_2 generation, ENR), (ii) expanded mechanistic understanding of radical and

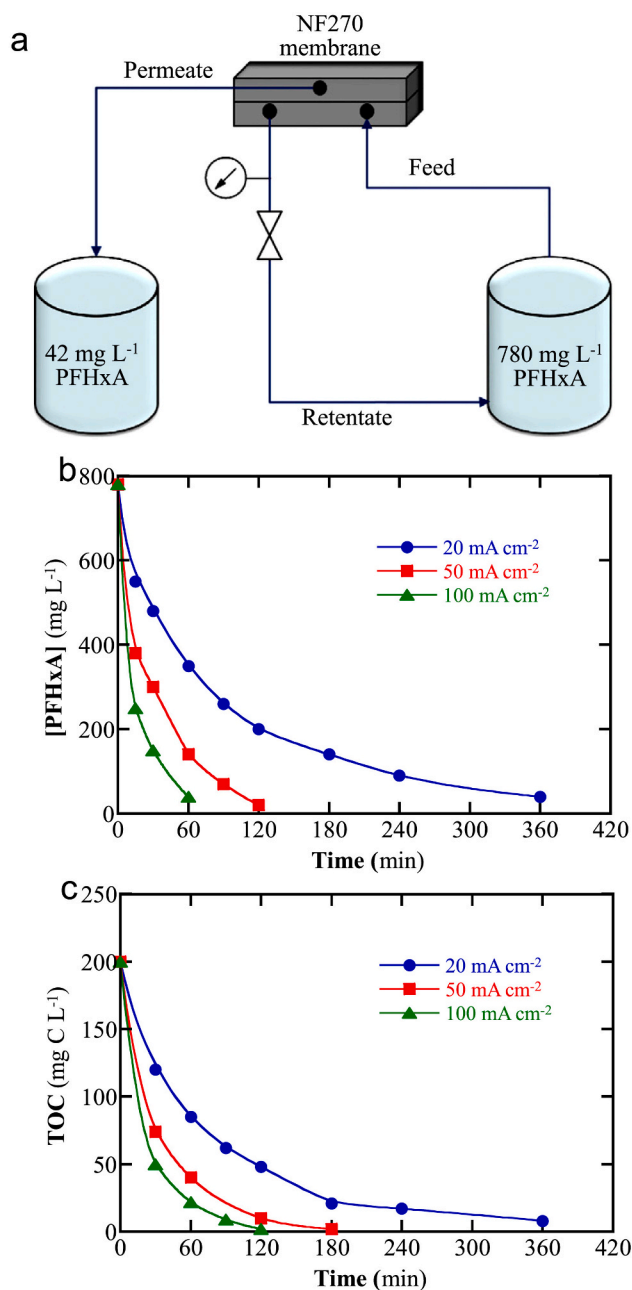


Fig. 18. (a) Scheme of nanofiltration set-up in concentration mode of an industrial wastewater containing 204 mg L⁻¹ perfluorohexanoic acid (PFHxA) showing the permeate and retentate concentrations obtained using a NF270 membrane. Change of (b) PFHxA and (c) TOC of 1 L retentate with time for the EO process with a flow-by cell equipped with p-Si/BDD anode and cathode at different j values. Adapted from ref. [103] with permission of Elsevier.

non-radical pathways, and (iii) reactor engineering enabling stable operation in complex real matrices. In practice, these developments have reduced historical barriers such as limited selectivity, high energy demand, and poor transferability from synthetic waters to real effluents [112]. Reactor architecture dictates current distribution, energy efficiency, and operational stability, and therefore controls whether a promising material or mechanism becomes deployable technology. Accordingly, electrochemical treatment has then shifted from undivided bench-scale batch cells to engineered reactors operated in flow modes and validated with real effluents. An example of stirred two-electrode undivided tank reactor with a jacket for external thermostatisation for EO and EF processes is given in Fig. 21a. Examples of filter-press flow

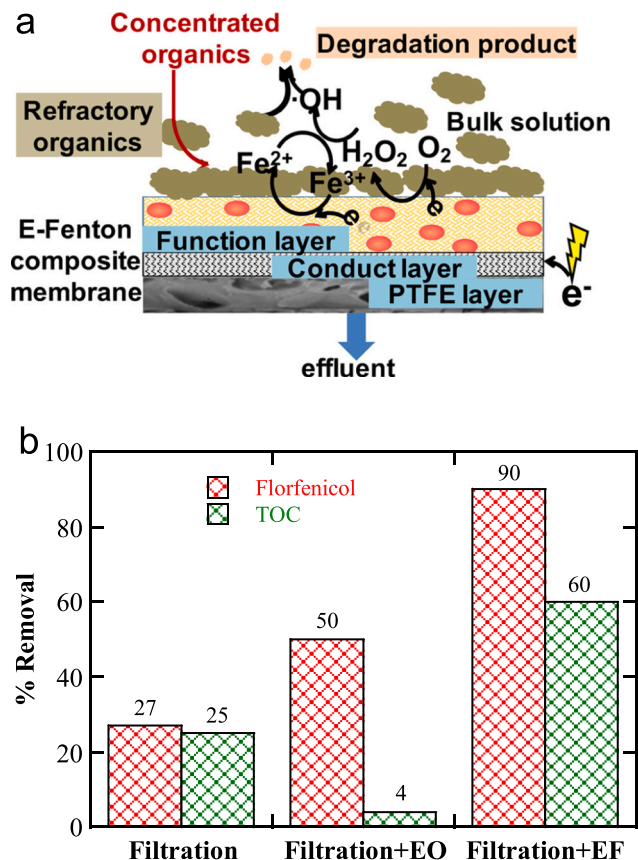


Fig. 19. (a) Proposed mechanism for •OH generation in the EF process in a graphene-modified membrane. Percentage of removal of (b) florfenicol concentration and (b) TOC during the continuous filtration, filtration + EO (with N₂ feeding), and filtration + EF (with O₂ feeding) processes of 1 mg L⁻¹ drug in 100 mM Na₂SO₄ using a cell with a Pt anode and graphene-modified membrane at $E_{cat} = -0.6$ V/SCE and membrane flux of 101.5 L m⁻² h⁻¹ MPa⁻¹ at 25 °C. Adapted from ref. [104] with permission of American Chemical Society.

cell (FM01-LC reactor and bench-scaled flow plants with /electrochemical divided reactor and undivided cell with parallel plate electrodes are shown in Fig. 21b to 21d [112]. Under the Technology Readiness Level (TRL) framework, this corresponds to a transition from TRL 3–4 toward flow-based and semi-autonomous systems reaching TRL 5–7, supported by hydrodynamic optimization, numerical modeling, and prototype demonstrations [113].

Autonomous reactor configurations represent a clear milestone in this evolution. Extensive work by the Brillas group has demonstrated that electrochemical systems can operate without continuous chemical dosing while maintaining high treatment efficiency. In particular, solar autonomous plants, with treatment capacities of up to 10 L, have proven effective for the degradation and mineralization of dyes using SPEF technology [114]. This study then illustrates how coupling reactor autonomy with renewable energy sources enhances robustness and scalability. Further advances in reactor design have enabled high performance under realistic conditions. Pre-pilot batch reactors of 2 L equipped with BDD anodes achieved complete degradation of 10 mg L⁻¹ ciprofloxacin in ultrapure water and in more complex matrices such as tap water and synthetic urine [115]. These results highlight the importance of rational hydrodynamic design and current distribution control in sustaining performance when treating chemically complex effluents

Open solar electrochemical raceway pond reactors (SEC-RPRs) further exemplify the integration of reactor engineering and process intensification (see scheme in Fig. 22a [116]). Their shallow geometry maximizes contact between wastewater and natural UV radiation while

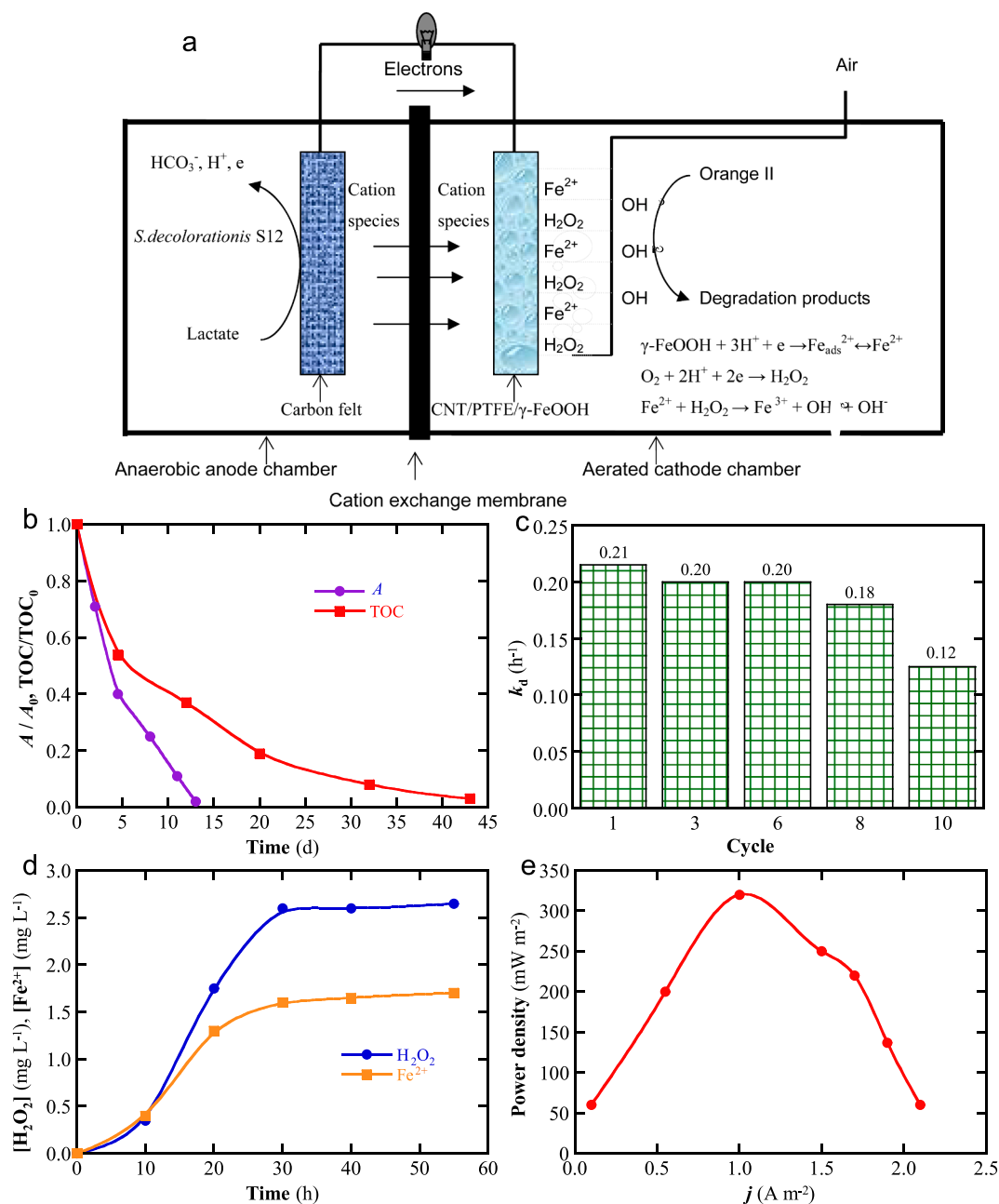


Fig. 20. (a) Schematic diagram of a microbial heterogeneous EF cell designed for Orange II removal. The anode chamber contained a carbon felt anode with *Shewanella decolorationis* S12 fed with lactate. The cathode chamber was equipped with a carbon nanotube (CNT)/ γ -FeOOH cathode and contained 0.1 mM dye and 100 mM phosphate buffer solution at pH = 7.0. (b) Normalized absorbance and TOC vs. time. (c) Change of rate constant for discoloration in consecutive cycles. (d) Evolution of generated H_2O_2 and Fe^{2+} . (e) Power density as function of produced current density. Adapted from ref. [110] with permission of ACS.

enabling continuous and homogeneous H_2O_2 electrogeneration. Application of the SPEF process in SEC-RPRs resulted in complete removal of several contaminants of emerging concern and substantial COD removal in secondary municipal effluents, achieving compliance with Chilean discharge standards within short treatment times [116]. Similarly, compact multifunctional flow reactors of 1 L integrating electro-generated oxidants with UVC irradiation achieved more than 99% degradation of tetracycline and 63.2% TOC removal with relatively low EC_{TOC} of 1.54 kWh (g TOC)⁻¹, while operating at neutral pH [117], as can be seen in Fig. 23 that includes a sketch of the flow-by plant used. The best result was obtained when both H_2O_2 from reaction (14) and active chlorine from reactions (7)–(9) were produced in 45 mM K_2SO_4 and 15 mM NaCl upon 9 W UVC light.

Beyond technological maturity, these reactor developments are

particularly relevant for regions with limited or no access to centralized wastewater treatment infrastructure. In such contexts, decentralized electrochemical reactors enable the local treatment of domestic effluents, including greywater and sanitary wastewater, reducing dependence on sewer networks and allowing on-site water reuse. Their modular, compact, and electrified design makes them suitable for deployment in remote or resource-limited areas, where conventional treatment plants are economically or logistically unfeasible. Importantly, these concepts have already been validated under real operating conditions. Self-contained sanitation systems based on electrochemical oxidation of feces and urine have been designed as containerized units capable of treating wastewater from approximately 25 users per day while enabling water recycling. These systems were successfully deployed in public-use settings in the United States, India, and China,

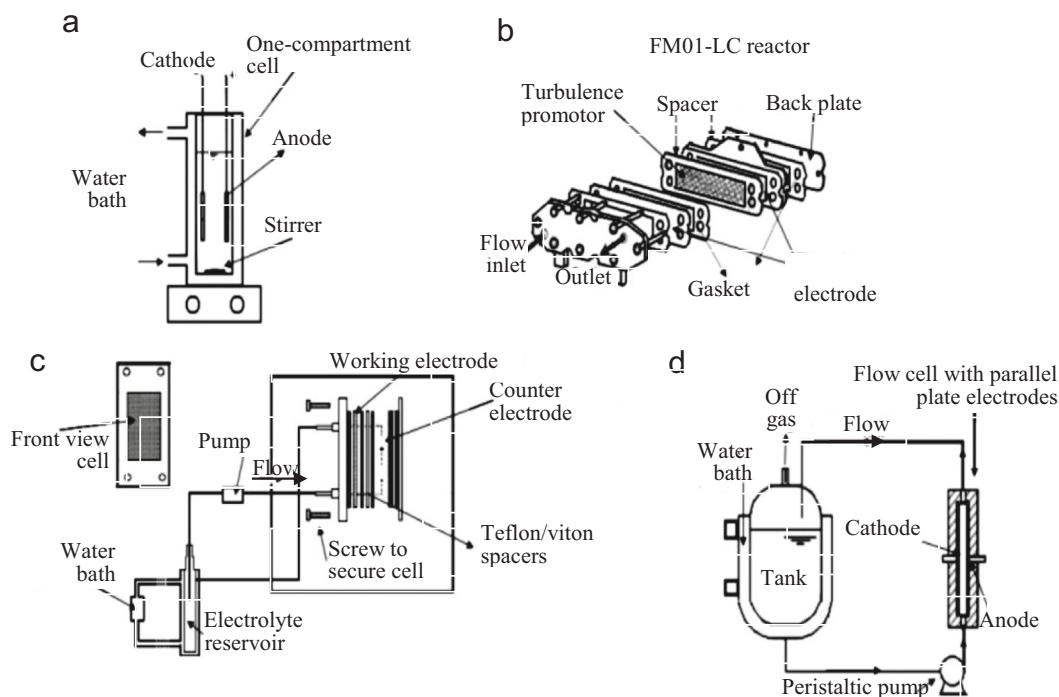


Fig. 21. Electrochemical plants and reactors used in EO and EF processes in batch operation. (a) Stirred two-electrode undivided tank reactor with a jacket for external thermostatzation, (b) filter-press flow cell (FM01-LC reactor) used in bench-scaled flow plants with (c) /electrochemical divided reactor and (d) undivided cell with parallel plate electrodes, Adapted from ref. [112] with permission of American Chemocal Society.

demonstrating effective organic matter removal and pathogen inactivation [118]. Complementarily, solar-powered, off-grid electrochemical Fenton-based reactors evaluated as tertiary treatment units for real sanitary wastewater following biological pre-treatment produced effluents compliant with regulatory limits for organic matter, suspended solids, and pathogen indicators. This confirms the feasibility of on-site treatment and local reuse without connection to centralized infrastructure. Fig. 22b schematizes a biological/EF plant designed for sanitary wastewater treatment, and Fig. 22c to 22e present photos of the plant and EF reactor [119].

Finally, the maturation of environmental electrochemistry also extends beyond oxidation. In nitrate removal, ENR has advanced primarily through the POE and POU reactor systems, supported by improved cathode materials and system-level optimization. Recent techno-economic benchmarking against RO and ion exchange shows that electrochemical nitrate reduction can be competitive for POE/POU applications when reactor configuration, electrode area ratios, and energy demand are carefully optimized. In particular, the cathode-to-anode area ratio emerges as a key design lever, as oversized anodes composed of costly materials can disproportionately increase capital costs. These findings highlight that reactor design, rather than materials alone, governs feasibility at the POE/POU scale, confirming that electrochemical water treatment has reached a mature, engineering-driven stage suitable for decentralized nitrate removal [120]. Overall, 2015–2025 consolidated environmental electrochemistry as a mature and versatile platform for water and wastewater treatment. Advances in materials, mechanistic understanding, and reactor engineering have enabled reliable operation in complex matrices and opened practical routes toward decentralized and local water treatment.

4. Challenges, future directions and research needs

Over the past decade, electrified water treatment has evolved into a technically robust and increasingly mature field. Nevertheless, its commercial implementation remains constrained by interconnected

challenges related to energy demand, material cost, reactor design, and technology translation. At the same time, emerging trends toward decentralized, renewable-powered, and modular systems are redefining the role of electrified technologies within future water infrastructure. This section consolidates the main research gaps, priority topics, and standardization needs that must be addressed to accelerate the transition from laboratory research to practical deployment.

4.1. Key research gaps

One persistent gap in literature is the widespread misconception regarding the energy consumption and operating costs of electrified processes. The feasibility of autonomous, solar-powered electrochemical reactors has been demonstrated, with reported energy demands on the order of $\sim 1 \text{ kWh d}^{-1}$, corresponding to the electricity generated by a single photovoltaic panel. These findings highlight the strong compatibility of electrified water treatment with renewable energy sources, particularly solar energy. This is especially relevant for regions with high solar availability and urgent needs for water treatment and reuse solutions to meet the United Nations Sustainable Development Goal 6 [121]. Another major research gap concerns the frequent use of pollutant concentrations far above environmentally relevant levels. In real waters, most organic micropollutants, such as pharmaceuticals, pesticides, and endocrine-disrupting compounds are typically present at ng L^{-1} to low $\mu\text{g L}^{-1}$ concentration, whereas nitrate levels in contaminated groundwater usually range from 10 to 150 mg L^{-1} as $\text{NO}_3^- \text{--N}$. In contrast, many laboratory studies rely on synthetic solutions with organic pollutant concentrations in the mg L^{-1} range, often exceeding environmental levels by two to four orders of magnitude. This discrepancy can significantly distort process interpretation and scalability. At elevated concentrations, diffusion-controlled mass transport and the ratio between target compounds and electrogenerated oxidants differ substantially from those encountered under realistic conditions, leading to overestimated degradation kinetics, faradaic efficiencies, and engineering figures of merit such as EE/O [122].

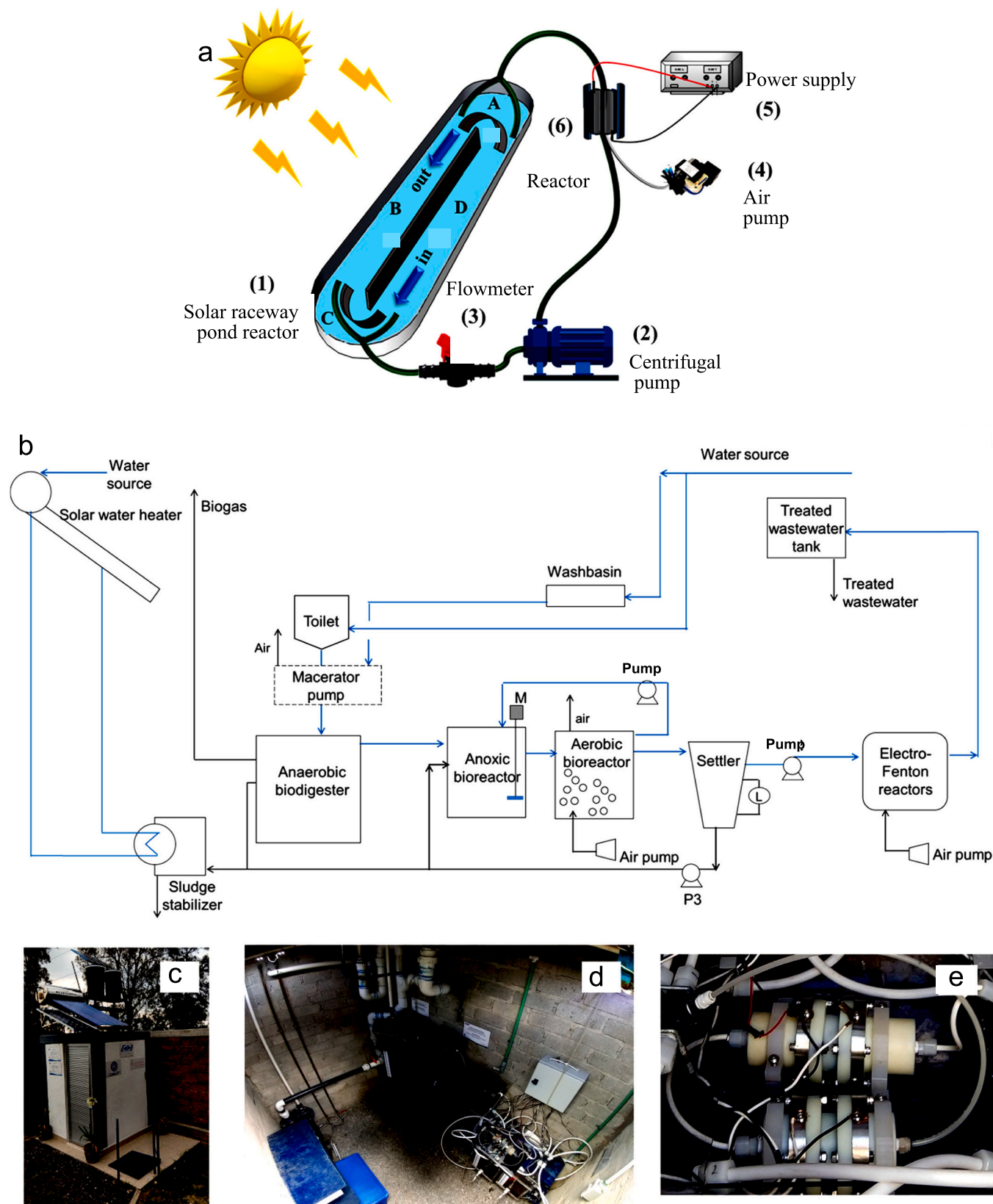


Fig. 22. (a) Sketch of a flow plant with a solar raceway pond reactor (adapted from ref. [116] with permission of Elsevier). (b) Schematic diagram of the hybrid biological/EF plant used for sanitary wastewater treatment. Photographs of (c) and (d) the plant, and (e) the EF reactor (adapted from ref. [119] with permission of Elsevier).

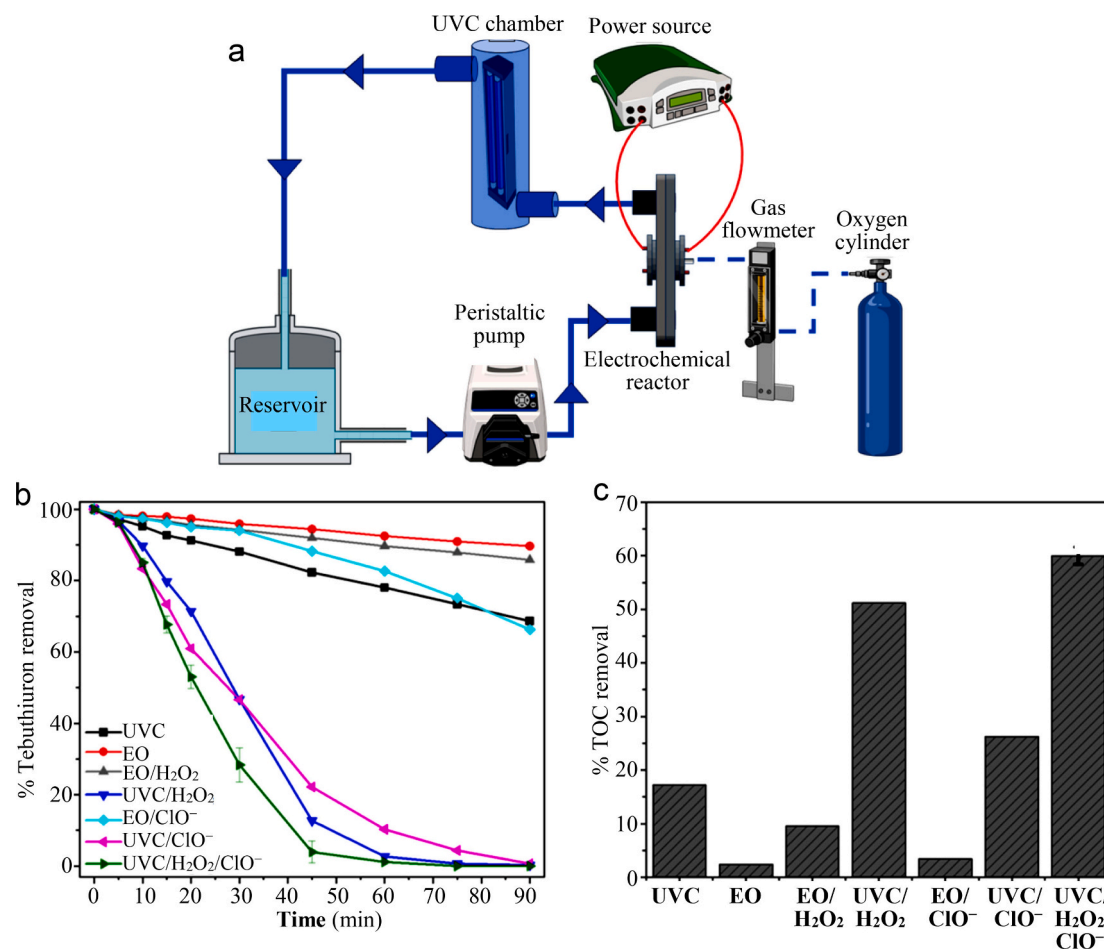


Fig. 23. (a) Scheme of the flow-by undivided reactor connected to a 9 W UVC chamber for tebuthiuron wastewater remediation. (b) Variation of the percentage of pesticide removal with time and (c) percent of TOC removal at 120 min for several treatments of 1 L of 0.1 mM tebuthiuron in 45 mM K₂SO₄ and/or 15 mM Cl⁻ at pH = 7.0, 22 °C, and liquid flow rate = 30 L h⁻¹ using a DSA anode and a GDE cathode at $j = 10 \text{ mA cm}^{-2}$. Adapted from ref. [117] with permission of Elsevier.

4.2. Priority research topics

Future research should increasingly focus on evaluating electrochemical treatments under environmentally relevant conditions, including the identification and toxicity assessment of transformation products, which are critical for regulatory compliance and environmental safety. In parallel, there is a growing need to move beyond the conventional objective of complete mineralization. In many cases, partial electrochemical transformation can generate less toxic and more biodegradable intermediates, achieving treatment goals with lower energy demand and enabling effective coupling with biological treatment or resource recovery strategies. However, working at environmentally relevant concentrations often requires advanced and costly analytical instrumentation, which may limit accessibility. The transition toward more realistic experimental conditions should therefore be conducted in a balanced and coherent manner. This has to ensure that methodological advances do not inadvertently concentrate research leadership within a small number of highly funded groups but instead support broad and inclusive progress across the field.

From an implementation perspective, priority challenges differ between organic contaminant removal and nitrate treatment. For organic pollutants, electrode cost and long-term durability remain dominant constraints. In contrast, electrochemical nitrate reduction has advanced rapidly through the development of bimetallic cathodes with enhanced activity and selectivity. Importantly, the economic feasibility of electrified technologies cannot be evaluated solely on the basis of degradation efficiency or laboratory-scale kinetic performance. A realistic

assessment must consider CAPEX, OPEX, maintenance requirements, electrode lifetime, and system integration within specific application contexts [123]. This highlights the need for robust techno-economic studies that go beyond laboratory-scale performance metrics.

Validation in complex real effluents represents another priority topic. Industrial, municipal, agricultural, and domestic wastewaters contain diverse inorganic ions and natural organic matter that strongly influence electrochemical performance. For example, water hardness can interfere with electro-Fenton reactions through the formation of stable complexes [124], while water matrix composition plays a decisive yet still underexplored role in ENR [125].

4.3. Integration, standardization, and implementation pathways

A major opportunity for the next stage of development lies in the integration of electrochemical processes with complementary technologies, particularly membrane separation and biological treatment. While batch experiments in synthetic matrices provide valuable mechanistic insights, they often overlook critical aspects such as membrane fouling, ionic competition, variable hydraulic regimes, and the formation of biodegradable intermediates under realistic conditions. Hybrid configurations allow electrochemical systems to operate as selective transformation or pre-treatment steps, while membranes enable separation and concentration, and biological processes provide low-cost mineralization of biodegradable intermediates. Such coupling represents an effective process-intensification strategy that can reduce overall energy demand and enhance system sustainability under real operating

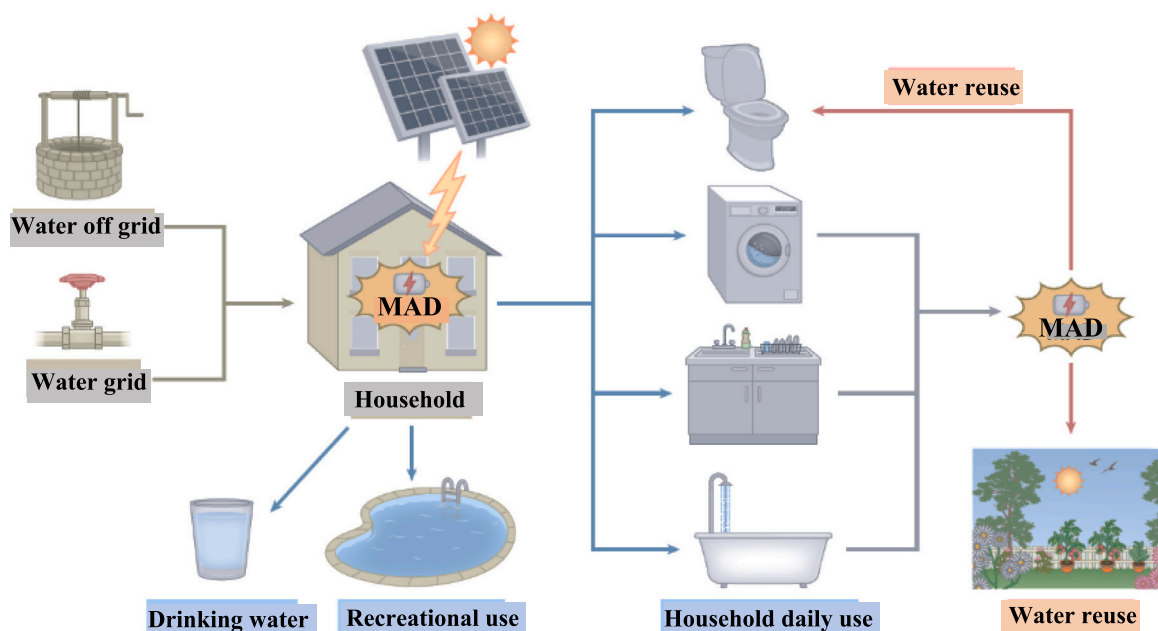


Fig. 24. Conceptual framework of a household-scale modular, adaptive, and decentralized (MAD) electrified water treatment system. The scheme illustrates the integration of grid-connected or off-grid water sources with renewable-energy-driven electrochemical treatment units installed at the point of use. The treated water is redistributed for multiple domestic applications, while greywater streams are locally reprocessed within the same MAD platform to support on-site reuse and circular water management. Adapted from Ref. [129] with permission from Nature.

conditions. Beyond pollutant removal, the valorization of electrochemical transformation products is emerging as a promising direction, leading to the concept of electro-refineries [126]. In this framework, electrified processes are designed not only to destroy contaminants but also to recover value-added products within the same integrated system. Proof-of-concept studies using real industrial effluents collected from a cashew nut processing facility have demonstrated that coupling anodic oxidation with electrochemically assisted separation enables the selective conversion of pollutants into recoverable carboxylates with low environmental footprints [127]. Although still at an early stage, this approach highlights the potential of electrified water treatment to align remediation with resource recovery and circular economy principles rather than conventional end-of-pipe mineralization strategies.

The need for standardized energy assessment becomes evident. EE/O should be consistently adopted as a unifying performance metric across electrified technologies. Given that pollutant degradation often follows pseudo-first-order kinetics, EE/O enables meaningful comparison between systems and supports the definition of realistic performance targets, particularly when partial transformation rather than complete mineralization is sufficient. However, although EE/O improves comparability, reported energy values remain strongly dependent on reactor configuration, operating mode, and water matrix composition. Therefore, direct comparisons must be interpreted with caution. Looking forward, MAD systems represent a key direction for future development. These systems are particularly suited for POU and POE applications, as well as for communities lacking centralized infrastructure [128]. Accordingly, techno-economic analyses should increasingly accompany technical performance evaluations. MAD systems should be designed to address specific treatment objectives rather than aiming for universal solutions. For example, dos Santos et al. [129] discussed the potential of decentralized electrified systems for domestic wastewater treatment and proposed the use of the MAD system of Fig. 24.

Finally, the emergence of startups dedicated to electrochemical water treatment reflects the increasing technological maturity of the field and represents an important pathway for translation. However, successful commercialization requires moving beyond optimized batch demonstrations in synthetic waters toward robust validation under

realistic operational conditions. Companies developing compact and deployable electrochemical solutions therefore play a key role in forcing this transition, as market viability depends not only on peak laboratory performance but also on stability, maintenance requirements, and cost-effectiveness under real-world scenarios.

5. Conclusions

This review synthesizes the decade 2015–2025 of advances in electrified water treatment technologies, covering developments in electrode materials, reaction mechanisms, reactor design, and application scenarios. Collectively, the literature demonstrates that environmental electrochemistry has evolved from predominantly laboratory-scale studies into an increasingly engineering-driven and application-oriented discipline. Progress in EO, EF-based processes, and ERN has been enabled by more selective and durable electrodes, improved control of reactive species generation, and the transition from batch operation toward flow-based and modular reactor configurations. These advances have expanded the applicability of electrified technologies to both. Organic and inorganic contaminants and enabled reliable operation in increasingly complex water matrices. Beyond individual processes, a central conclusion emerging from this review is that the feasibility of electrified water treatment no longer depends solely on material performance, but rather on the integrated optimization of electrodes, reactor configuration, energy metrics, and treatment objectives. This shift marks a clear transition from proof-of-concept studies toward system-level engineering and deployment-oriented research. Looking ahead, the next decade is expected to be defined not by incremental material improvements alone, but by the translation of electrified water treatment technologies into scalable, modular, and economically viable systems. Continued progress will depend on aligning technological development with realistic operating conditions, robust performance metrics, and practical implementation pathway. This positions electrified processes as a core component of future water treatment infrastructure.

CRediT authorship contribution statement

Alessandro J. dos Santos: Writing – review & editing, Writing – original draft, Visualization, Validation, Project administration, Conceptualization. **Enric Brillas:** Writing – review & editing, Writing – original draft, Visualization, Validation, 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.

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Data availability

No data was used for the research described in the article.

References

- [1] A. Serrano Mora, S.T. McBeath, C.A. Cid, M.R. Hoffmann, N.J.D. Graham, Diamond electrode facilitated electrosynthesis of water and wastewater treatment oxidants, *Curr. Opin. Electrochem.* 32 (2022) 100899, <https://doi.org/10.1016/j.coelec.2021.100899>.
- [2] A.P.R.A. Ferreira, R.C.P. Oliveira, M.M. Mateus, D.M.F. Santos, A review of the use of electrolytic cells for energy and environmental applications, *Energies* 16 (2023) 1593, <https://doi.org/10.3390/en16041593>.
- [3] N.G. Yasri, E.P.L. Roberts, Electrochemical regeneration of adsorbents: an electrochemist's perspective, *Curr. Opin. Electrochem.* 46 (2024) 101504, <https://doi.org/10.1016/j.coelec.2024.101504>.
- [4] K. Yang, Z. He, Integrating oxidation and reduction processes in electrochemical wastewater treatment for contaminant removal with byproduct control, *Water Res.* 282 (2025) 123632, <https://doi.org/10.1016/j.watres.2025.123632>.
- [5] M.C. Santos, V.S. Antonin, F.M. Souza, L.R. Aveiro, V.S. Pinheiro, T.C. Gentil, T. S. Lima, J.P.C. Moura, C.R. Silva, L.E.B. Lucchetti, L. Codognoto, I. Robles, M.R. V. Lanza, Decontamination of wastewater containing contaminants of emerging concern by electrooxidation and Fenton-based processes - a review on the relevance of materials and methods, *Chemosphere* 307 (2022) 135763, <https://doi.org/10.1016/j.chemosphere.2022.135763>.
- [6] L. Zhang, W. Peng, W. Wang, Y. Cao, G. Fan, Y. Huang, M.Q. Mengyao, A comprehensive review of the electrochemical advanced oxidation processes: detection of free radical, electrode materials and application, *J. Environ. Chem. Eng.* 12 (2024) 113778, <https://doi.org/10.1016/j.jece.2024.113778>.
- [7] E. Brillas, J.M. Peralta-Hernandez, Fluoroquinolone ciprofloxacin removal from synthetic and real wastewaters by single and combined electrochemical advanced oxidation processes. A review, *Chemosphere* 380 (2025) 144457, <https://doi.org/10.1016/j.chemosphere.2025.144457>.
- [8] R. Fu, P.-S. Zhang, Y.-X. Jiang, L. Sun, X.-H. Sun, Wastewater treatment by anodic oxidation in electrochemical advanced oxidation process: advance in mechanism, direct and indirect oxidation detection methods, *Chemosphere* 311 (2023) 136993, <https://doi.org/10.1016/j.chemosphere.2022.136993>.
- [9] D. Chen, D. Yin, Di.S. Zhang, S. Yip, J.C. Ho, Nitrate electroreduction: recent development in mechanistic understanding and electrocatalyst design, *Mater. Today Energy* 44 (2024) 101610, <https://doi.org/10.1016/j.mtener.2024.101610>.
- [10] U. Razzag, T.-B. Nguyen, M.U. Saleem, V.-R. Le, C.-W. Chen, X.-T. Bui, C.-D. Dong, Recent progress in electro-Fenton technology for the remediation of pharmaceutical compounds in aqueous environments, *Sci. Total Environ.* 946 (2024) 174253, <https://doi.org/10.1016/j.scitotenv.2024.174253>.
- [11] M. Jiang, X. Huang, D. Luo, C. Tian, Z. Jin, Recent breakthroughs in electrocatalytic reduction of nitrogen-oxyanions for environmentally benign ammonia synthesis, *Nano Energy* 135 (2025) 110683, <https://doi.org/10.1016/j.nanoen.2025.110683>.
- [12] A.J. dos Santos, G.V. Fortunato, M.R.V. Lanza, Recent advances in electrochemical water technologies for the treatment of antibiotics: a short review, *Curr. Opin. Electrochem.* 26 (2021) 100674, <https://doi.org/10.1016/j.coelec.2020.100674>.
- [13] A.B.B. Isaev, N.S.S. Shabanov, A.G.G. Magomedova, P.V. Nidheesh, M.A. Oturan, Electrochemical oxidation of azo dyes in water: a review, *Environ. Chem. Lett.* 21 (2023) 2863–2891, <https://doi.org/10.1007/s10311-023-01610-5>.
- [14] I. Lozano, P. Cervantes-Aviles, A. Keller, C. Lopez Aguilar, Removal of pharmaceuticals and personal care products from wastewater via anodic oxidation and electro-Fenton processes: current status and needs regarding their application, *Water Sci. Technol.* 88 (2023) 1143–1154, <https://doi.org/10.2166/wst.2023.266>.
- [15] J. Choi, H.-L. Du, C.K. Nguyen, B.H.R. Suryanto, A.N. Simonov, D.R. MacFarlane, Electroreduction of nitrates, nitrites, and gaseous nitrogen oxides: a potential source of ammonia in dinitrogen reduction studies, *ACS Energy Lett.* 5 (2020) 2095–2097, <https://doi.org/10.1021/acsenenergylett.0c00924>.
- [16] Y. Chen, B. Xu, K. Laszlo, Y. Wang, Electrocatalytic nitrate reduction: the synthesis, recovery and upgradation of ammonia, *J. Environ. Chem. Eng.* 12 (2024) 112348, <https://doi.org/10.1016/j.jece.2024.112348>.
- [17] J. Bai, Z. Dong, X. Jiang, Q. Zhou, J. Zhao, J. Mei, Z. Tan, T. Liao, Z. Sun, Advancing nitrate-to-ammonia electrocatalysis: strategies in catalyst design, electrolyte engineering, and performance evaluation, *Adv. Sci.* 12 (2025), <https://doi.org/10.1002/adv.202508614>.
- [18] Z. Hu, J. Cai, G. Song, Y. Tian, M. Zhou, Anodic oxidation of organic pollutants: anode fabrication, process hybrid and environmental applications, *Curr. Opin. Electrochem.* 26 (2021) 100659, <https://doi.org/10.1016/j.coelec.2020.100659>.
- [19] X. Zhang, X. Wang, X. Zhang, H. Wu, R. Liang, M. Zhou, Minghua bifunctional metallic composite catalyst cathode in heterogeneous electro-Fenton process: classification, preparation and reactive species, *Electrochim. Acta* 472 (2023) 143437, <https://doi.org/10.1016/j.electacta.2023.143437>.
- [20] S. Yin, Z. Guan, Y. Zhu, D. Guo, X. Chen, S. Wang, Highly efficient electrocatalytic nitrate reduction to ammonia: group VIII-based catalysts, *ACS Nano* 18 (2024) 27833–27852, <https://doi.org/10.1021/acsnano.4c09247>.
- [21] S.B. Ramesh, N. Nippatlapalli, Current trends and future directions in novel electrochemical innovations for wastewater treatment: a multidimensional critique on financial viability, life cycle sustainability, and circular economical benefits, *J. Water Process Eng.* 74 (2025) 107799, <https://doi.org/10.1016/j.jwpe.2025.107799>.
- [22] J. Radjenovic, D.L. Sedlak, Challenges and opportunities for electrochemical processes as next-generation technologies for the treatment of contaminated water, *Environ. Sci. Technol.* 49 (2015) 11292–11302, <https://doi.org/10.1021/acs.est.5b02414>.
- [23] S.O. Ganiyu, C.A. Martínez-Huitle, M.A. Rodrigo, Renewable energies driven electrochemical wastewater/soil decontamination technologies: a critical review of fundamental concepts and applications, *Appl. Catal. B Environ.* 270 (2020) 118857, <https://doi.org/10.1016/j.apcatb.2020.118857>.
- [24] C.A. Martínez-Huitle, M. Panizza, Electrochemical oxidation of organic pollutants for wastewater treatment, *Curr. Opin. Electrochem.* 11 (2018) 62–71, <https://doi.org/10.1016/j.coelec.2018.07.010>.
- [25] I. Sirés, E. Brillas, M.A. Oturan, M.A. Rodrigo, M. Panizza, Electrochemical advanced oxidation processes: today and tomorrow. A review, *Environ. Sci. Pollut. Res.* 21 (2014) 8336–8367, <https://doi.org/10.1007/s11356-014-2783-1>.
- [26] F. Souza, S. Quijorna, M.R.V. Lanza, C. Sáez, P. Cañizares, M.A. Rodrigo, Applicability of electrochemical oxidation using diamond anodes to the treatment of a sulfonyleurea herbicide, *Catal. Today* 280 (2017) 192–198, <https://doi.org/10.1016/j.cattod.2016.04.030>.
- [27] S.T. McBeath, D.P. Wilkinson, N.J.D. Graham, Application of boron-doped diamond electrodes for the anodic oxidation of pesticide micropollutants in a water treatment process: a critical review, *Environ. Sci.: Water Res. Technol.* 5 (2019) 2090–2107, <https://doi.org/10.1039/c9ew00589g>.
- [28] E. Brillas, Solar photoelectro-Fenton: a very effective and cost-efficient electrochemical advanced oxidation process for the removal of organic pollutants from synthetic and real wastewaters, *Chemosphere* 327 (2023) 138532, <https://doi.org/10.1016/j.chemosphere.2023.138532>.
- [29] M. Murati, N. Oturan, J.J. Aaron, A. Dirany, B. Tassin, Z. Zdravkovski, M. A. Oturan, Degradation and mineralization of sulcotriene and mesotriene in aqueous medium by the electro-Fenton process: a kinetic study, *Environ. Sci. Pollut. Res.* 19 (2012) 1563–1573, <https://doi.org/10.1007/s11356-011-0667-1>.
- [30] E. Brillas, Recent development of electrochemical advanced oxidation of herbicides. A review on its application to wastewater treatment and soil remediation, *J. Clean. Prod.* 290 (2021) 125841, <https://doi.org/10.1016/j.jclepro.2021.125841>.
- [31] M. Duca, M.T.M. Koper, Powering denitrification: the perspectives of electrocatalytic nitrate reduction, *Energy Environ. Sci.* 5 (2012) 9726–9742, <https://doi.org/10.1039/c2ee23062c>.
- [32] L. Wang, M. Li, X. Liu, C. Feng, N. Chen, W. Hu, Design and applications of Ti nano-electrode for denitrification of groundwater, *Environ. Technol.* 38 (2017) 3055–3063, <https://doi.org/10.1080/09593330.2017.1287223>.
- [33] E. Lacasa, J. Llanos, P. Cañizares, M.A. Rodrigo, Electrochemical denitrification with chlorides using DSA and BDD anodes, *Chem. Eng. J.* 184 (2012) 66–71, <https://doi.org/10.1016/j.cej.2011.12.090>.
- [34] J. Martínez, A. Ortiz, I. Ortiz, State-of-the-art and perspectives of the catalytic and electrocatalytic reduction of aqueous nitrates, *Appl. Catal. B Environ.* 207 (2017) 42–59, <https://doi.org/10.1016/j.apcatb.2017.02.016>.
- [35] F. Souza, C. Sáez, M. Lanza, P. Cañizares, M.A. Rodrigo, Towards the scale-up of electrolysis with diamond anodes: effect of stacking on the electrochemical oxidation of 2,4 D, *J. Chem. Technol. Biotechnol.* 91 (2016) 742–747, <https://doi.org/10.1002/jctb.4639>.
- [36] J.V. Macpherson, A practical guide to using boron doped diamond in electrochemical research, *Phys. Chem. Chem. Phys.* 17 (2015) 2935, <https://doi.org/10.1039/c4cp04022h>.
- [37] S. Garcia-Segura, E.S. dos Santos, C.A. Martínez-Huitle, Role of sp³/sp² ratio on the electrocatalytic properties of boron-doped diamond electrodes: a mini review, *Electrochem. Commun.* 59 (2015) 52–55, <https://doi.org/10.1016/j.elecom.2015.07.002>.

- [38] F.L. Souza, C. Saez, M.R.V. Lanza, P. Cañizares, M.A. Rodrigo, The effect of the sp^3/sp^2 carbon ratio on the electrochemical oxidation of 2,4-D with p-Si BDD anodes, *Electrochim. Acta* 187 (2016) 119–124, <https://doi.org/10.1016/j.electacta.2015.11.031>.
- [39] S.M.L.O. Marcionilio, D.M. Araujo, T.D.V. Nascimento, C.A. Martínez-Huitle, J. Linares, Evaluation of the toxicity reduction of an ionic liquid solution electrochemically treated using BDD films with different sp^3/sp^2 ratios, *Electrochem. Commun.* 118 (2020) 106792, <https://doi.org/10.1016/j.elecom.2020.106792>.
- [40] L.C. Espinoza, M. Aranda, D. Contreras, A. Henríquez, R. Salazar, Effect of the sp^3/sp^2 ratio in boron-doped diamond electrodes on the degradation pathway of aniline by anodic oxidation, *ChemElectroChem* 6 (2019) 4801–4810, <https://doi.org/10.1002/celec.201901218>.
- [41] A.J. dos Santos, G.V. Fortunato, M.S. Kronka, L.G. Vernasqui, N.G. Ferreira, M.R. V. Lanza, Electrochemical oxidation of ciprofloxacin in different aqueous matrices using synthesized boron-doped micro and nano-diamond anodes, *Environ. Res.* 204 (2022) 112027, <https://doi.org/10.1016/j.envres.2021.112027>.
- [42] Z. Li, G. Zhao, H. Li, C. Sun, J. Li, C. Xie, Y. Shi, X. Zhao, Z. Li, L. Lei, B. Yang, Synergistically optimized boron-doped nanocrystalline diamond anodes for enhanced durability in electrochemical wastewater oxidation, *Sep. Purif. Technol.* 379 (2025) 134846, <https://doi.org/10.1016/j.seppur.2025.134846>.
- [43] B. Wang, M. Li, C. Li, X. Xuan, H. Li, Boron-doped diamond/graphene/Ti mesh array-based anode and boron-doped graphene/Ti mesh array-based cathode for the rapid degradation of organic dyes, *J. Environ. Chem. Eng.* 12 (2024) 113254, <https://doi.org/10.1016/j.jece.2024.113254>.
- [44] L.G. Vernasqui, A.J. dos Santos, G.V. Fortunato, M.S. Kronka, H.L. Barazorda-Cachua, A.S. Fajardo, N.G. Ferreira, M.R.V. Lanza, Highly porous seeding-free boron-doped ultrananocrystalline diamond used as high-performance anode for electrochemical removal of carbaryl from water, *Chemosphere* 305 (2022) 135497, <https://doi.org/10.1016/j.chemosphere.2022.135497>.
- [45] R. Mei, Q. Wei, C. Zhu, W. Ye, B. Zhou, L. Ma, Z. Yua, K. Zhou, 3D macroporous boron-doped diamond electrode with interconnected liquid flow channels: a high-efficiency electrochemical degradation of RB-19 dye wastewater under low current, *Appl. Catal. B Environ.* 245 (2019) 420–427, <https://doi.org/10.1016/j.apcatb.2018.12.074>.
- [46] W. Liu, X. Su, Y. Wu, G. Yi, X. Guo, S. Shi, C. Zhang, Y. Zhang, A comprehensive review of PbO_2 electrodes in electrocatalytic degradation of organic pollutants, *Environ. Res.* 279 (2025) 121885, <https://doi.org/10.1016/j.envres.2025.121885>.
- [47] J. Chen, Y. Xia, Q. Dai, Electrochemical degradation of chloramphenicol with a novel Al doped PbO_2 electrode: performance, kinetics and degradation mechanism, *Electrochim. Acta* 165 (2015) 277–287, <https://doi.org/10.1016/j.electacta.2015.02.029>.
- [48] X. Hao, Y. Quansheng, S. Dan, Y. Honghui, L. Jidong, F. Jiangtao, Y. Wei, Fabrication and characterization of PbO_2 electrode modified with $[Fe(CN)_6]^{3-}$ and its application on electrochemical degradation of alkali lignin, *J. Hazard. Mater.* 286 (2015) 509–516, <https://doi.org/10.1016/j.jhazmat.2014.12.065>.
- [49] Y. Yao, G. Teng, Y. Yang, C. Huang, B. Liu, L. Guo, Electrochemical oxidation of acetaminophen using Yb-doped PbO_2 electrodes: electrode characterization, influencing factors and degradation pathways, *Sep. Purif. Technol.* 211 (2019) 456–466, <https://doi.org/10.1016/j.seppur.2018.10.021>.
- [50] Y. Yao, B. Ren, Y. Yang, C. Huang, M. Li, Preparation and electrochemical treatment application of Ce- PbO_2 /ZrO₂ composite electrode in the degradation of acridine orange by electrochemical advanced oxidation process, *J. Hazard. Mater.* 361 (2019) 141–151, <https://doi.org/10.1016/j.jhazmat.2018.08.081>.
- [51] Y. Xia, X. Bian, Y. Xia, W. Zhou, L. Wang, S. Fan, P. Xiong, T. Zhan, Q. Dai, J. Chen, Effect of indium doping on the PbO_2 electrode for the enhanced electrochemical oxidation of aspirin: an electrode comparative study, *Sep. Purif. Technol.* 237 (2020) 116321, <https://doi.org/10.1016/j.seppur.2019.116321>.
- [52] X. Li, H. Xu, W. Yan, Effects of twelve sodium dodecyl sulfate (SDS) on electrocatalytic performance and stability of PbO_2 electrode, *J. Alloys Compd.* 718 (2017) 386–395, <https://doi.org/10.1016/j.jallcom.2017.05.147>.
- [53] T. Su, Z. Li, X. Liu, Y. Ren, R. Yang, Z. Zhao, H. Wang, Q. Yan, S. Man, Degradation of microplastics by PTFE doped PbO_2 anode: effects of surface wettability, *Sep. Purif. Technol.* 379 (2025) 135092, <https://doi.org/10.1016/j.seppur.2025.135092>.
- [54] H. Li, H. Wu, L. Li, W. Zhu, S. Li, Q. Yu, L. Han, Z. Chen, Ultrasonic-electrodeposition construction of high hydrophobic Ce-PDMS- PbO_2 /SS electrode for p-nitrophenol degradation: catalytic, kinetics and mechanism, *Appl. Catal. B Environ.* 335 (2023) 122884, <https://doi.org/10.1016/j.apcatb.2023.122884>.
- [55] M.M. Emamjomeh, A. Shabanloo, A. Ansari, M. Esfandiari, M. Mousazadeh, K. Tari, Anodic oxidation of ciprofloxacin antibiotic and real pharmaceutical wastewater with Ti/ PbO_2 electrocatalyst: influencing factors and degradation pathways, *J. Water Process Eng.* 57 (2024) 104662, <https://doi.org/10.1016/j.jwpe.2023.104662>.
- [56] C. Wang, Y. Li, J. Wan, Y. Hu, Y. Huang, Electrochemical degradation of textile effluent using PbO_2 electrode in tube electrolyzer, *J. Electrochem. Sci. Technol.* 15 (2024) 190–197, <https://doi.org/10.33961/jecst.2023.00731>.
- [57] C. Yang, W. Zhao, Z. Wang, R. Guo, D. Shao, H. Xu, W. Yan, H. Song, New hierarchical Ti/SnO₂- PbO_2 /CNT electrode: enhanced electrochemical properties and improved electrochemical oxidation towards various real wastewaters, *J. Water Process Eng.* 58 (2024) 104899, <https://doi.org/10.1016/j.jwpe.2024.104899>.
- [58] S.O. Ganiyu, N. Oturan, S. Raffy, M. Cretin, R. Esmilaire, E. van Hullebusch, G. Esposito, M.A. Oturan, Sub-stoichiometric titanium oxide (Ti_4O_7) as a suitable ceramic anode for electrooxidation of organic pollutants: a case study of kinetics, mineralization and toxicity assessment of amoxicillin, *Water Res.* 106 (2016) 171–182, <https://doi.org/10.1016/j.watres.2016.09.056>.
- [59] J. Wang, D. Zhi, H. Zhou, X. He, D. Zhang, Evaluating tetracycline degradation pathway and intermediate toxicity during the electrochemical oxidation over a Ti/ Ti_4O_7 anode, *Water Res.* 137 (2018) 324–334, <https://doi.org/10.1016/j.watres.2018.03.030>.
- [60] H. Lin, R. Xiao, R. Xie, L. Yang, C. Tang, R. Wang, J. Chen, S. Lv, Q. Huang, Defect engineering on a Ti_4O_7 electrode by Ce^{3+} doping for the efficient electrooxidation of perfluorooctanesulfonate, *Environ. Sci. Technol.* 55 (2021) 2597–2607, <https://doi.org/10.1021/acs.est.0c06881>.
- [61] J. Jing, X. Wang, M. Zhou, Electro-enhanced activation of peroxymonosulfate by a novel perovskite- Ti_4O_7 composite anode with ultra-high efficiency and low energy consumption: the generation and dominant role of singlet oxygen, *Water Res.* 232 (2023) 119682, <https://doi.org/10.1016/j.watres.2023.119682>.
- [62] W. Leng, J. Lai, C. Yang, Y. Liu, J. Wang, L. Yang, S. Lv, Interface engineering on Magnéli Ti_4O_7 electrodes by doping with waste MOF-recycled N-doped carbon polyhedrons toward efficient electrooxidation of tetracycline, *J. Environ. Chem. Eng.* 12 (2024) 114359, <https://doi.org/10.1016/j.jece.2024.114359>.
- [63] A.L. Magdaleno, G.A. Cerrón-Calle, A.J. dos Santos, M.R.V. Lanza, O.G. Apul, S. García-Segura, Unlocking the potential of nanobubbles: achieving exceptional gas efficiency in electrogeneration of hydrogen peroxide, *Small* 20 (2024), <https://doi.org/10.1002/sml.202304547>.
- [64] J. Wang, C. Li, M. Rauf, H. Luo, X. Sun, Y. Jiang, Gas diffusion electrodes for H_2O_2 production and their applications for electrochemical degradation of organic pollutants in water: a review, *Sci. Total Environ.* 759 (2021) 143459, <https://doi.org/10.1016/j.scitotenv.2020.143459>.
- [65] H. He, Z. Zhou, Electro-Fenton process for water and wastewater treatment, *Crit. Rev. Environ. Sci. Technol.* 47 (2017) 2100–2131, <https://doi.org/10.1080/10643389.2017.1405673>.
- [66] T. Liu, K. Wang, S. Song, A. Brouzgou, P. Tsiakaras, Y. Wang, New electro-Fenton gas diffusion cathode based on nitrogen-doped graphene@carbon nanotube composite materials, *Electrochim. Acta* 194 (2016) 228–238, <https://doi.org/10.1016/j.electacta.2015.12.185>.
- [67] E.C. Paz, L.R. Aveiro, V.S. Pinheiro, F.M. Souza, V.B. Lima, F.L. Silva, P. Hammer, M.R.V. Lanza, M.C. Santos, Evaluation of H_2O_2 electrogeneration and decolorization of Orange II azo dye using tungsten oxide nanoparticle-modified carbon, *Appl. Catal. B Environ.* 232 (2018) 436–445, <https://doi.org/10.1016/j.apcatb.2018.03.082>.
- [68] Z. Zhang, H. Meng, Y. Wang, L. Shi, X. Wang, S. Chai, Fabrication of graphene@graphite-based gas diffusion electrode for improving H_2O_2 generation in electro-Fenton process, *Electrochim. Acta* 260 (2018) 112–120, <https://doi.org/10.1016/j.electacta.2017.11.048>.
- [69] G.V. Fortunato, M.S. Kronka, A.J. dos Santos, M. Ledendecker, M.R.V. Lanza, Low pH loadings onto Printex L6: synthesis, characterization and performance towards H_2O_2 generation for electrochemical water treatment technologies, *Chemosphere* 259 (2020) 127523, <https://doi.org/10.1016/j.chemosphere.2020.127523>.
- [70] M.S. Kronka, G.V. Fortunato, L. Mira, A.J. dos Santos, M.R.V. Lanza, Using Au NPs anchored on ZrO_2 /carbon black toward more efficient H_2O_2 electrogeneration in flow-by reactor for carbaryl removal in real wastewater, *Chem. Eng. J.* 452 (2023) 139598, <https://doi.org/10.1016/j.cej.2022.139598>.
- [71] N. Barhoumi, N. Oturan, H. Olvera-Vargas, E. Brillás, A. Gadri, S. Ammar, M. A. Oturan, Pyrite as a sustainable catalyst in electro-Fenton process for improving oxidation of sulfamethazine. Kinetics, mechanism and toxicity assessment, *Water Res.* 94 (2016) 52–61, <https://doi.org/10.1016/j.watres.2016.02.042>.
- [72] N. Barhoumi, H. Olvera-Vargas, N. Oturan, D. Huguenot, A. Gadri, S. Ammar, E. Brillás, M.A. Oturan, Kinetics of oxidative degradation/mineralization pathways of the antibiotic tetracycline by the novel heterogeneous electro-Fenton process with solid catalyst chalcopirite, *Appl. Catal. B Environ.* 209 (2017) 637–647, <https://doi.org/10.1016/j.apcatb.2017.03.034>.
- [73] A.J. dos Santos, I. Sirés, A.P.M. Alves, C.A. Martínez-Huitle, E. Brillás, Vermiculite as heterogeneous catalyst in electrochemical fenton-based processes: application to the oxidation of ponceau SS dye, *Chemosphere* 240 (2020), <https://doi.org/10.1016/j.chemosphere.2019.124838>.
- [74] J.-Y. Lu, Y.-R. Yuan, X. Hu, W.-J. Liu, C.-X. Li, H.-Q. Liu, W.-W. Li, MOF-derived Fe_2O_3 /nitrogen/carbon composite as a stable heterogeneous electro-Fenton catalyst, *Ind. Eng. Chem. Res.* 59 (2020) 1800–1808, <https://doi.org/10.1021/acs.iecr.9b04428>.
- [75] E. Liu, T. Hu, N.A. Al-Dhabi, T.-O. Soyol-Erdene, O. Bayanjargal, Y. Zuo, J. Wang, W. Tang, MOF-derived Fe/Ni@C marigold-like nanosheets as heterogeneous electro-Fenton cathode for efficient antibiotic oxytetracycline degradation, *Environ. Res.* 247 (2024) 118357, <https://doi.org/10.1016/j.envres.2024.118357>.
- [76] F. Xie, Y. Gao, J. Zhang, H. Bai, J. Zhang, Z. Li, W. Zhu, A novel bifunctional cathode for the generation and activation of H_2O_2 in electro-Fenton: characteristics and mechanism, *Electrochim. Acta* 430 (2022) 141099, <https://doi.org/10.1016/j.electacta.2022.141099>.
- [77] P. Xia, Z. Ye, L. Zhao, Q. Xue, S. Lanzalaco, Q. He, X. Qi, I. Sirés, Tailoring single-atom FeN_4 moieties as a robust heterogeneous catalyst for high-performance electro-Fenton treatment of organic pollutants, *Appl. Catal. B Environ.* 322 (2023) 122116, <https://doi.org/10.1016/j.apcatb.2022.122116>.
- [78] C. Dong, Y. Chen, C. Yang, P. Li, Y. Zhang, P. Wang, Y. Wang, W. Fang, L. Lin, X. Li, Pinning-effect single-atom NiCo alloy embedded graphene-aerogel in electro-Fenton process for rapid degradation of emerging contaminants, *Appl. Catal. B Environ. Energy* 357 (2024) 124286, <https://doi.org/10.1016/j.apcatb.2024.124286>.

- [79] T. Lu, Y. Liu, Y. Li, J. Chen, S. Chen, X. Liao, W. Xia, T. Zhou, W. Wang, Z. Chen, R. Huang, H. Wang, Identifying catalytic sites in oxygen-modified cobalt single atoms for H_2O_2 electrosynthesis and in situ realizing electro-Fenton process in acid, *Appl. Catal. B Environ. Energy* 365 (2025) 124949, <https://doi.org/10.1016/j.apcatb.2024.124949>.
- [80] Y. Zhou, L. Zhang, Z. Zhu, M. Wang, N. Li, T. Qian, C. Yan, J. Lu, Optimizing intermediate adsorption over PdM (M=Fe, Co, Ni, Cu) bimetallic for boosted nitrate electroreduction to ammonia, *Angew. Chem. Int. Ed.* 63 (2024), <https://doi.org/10.1002/anie.202319029>.
- [81] Z. Gao, Y. Lai, Y. Tao, L. Xiao, L. Zhang, F. Luo, Constructing well-defined and robust Th-MOF-supported single-site copper for production and storage of ammonia from electroreduction of nitrate, *ACS Cent. Sci.* 7 (2021) 1066–1072, <https://doi.org/10.1021/acscentsci.1c00370>.
- [82] X. Cheng, J. He, H. Ji, H. Zhang, Q. Cao, W. Sun, C. Yan, J. Lu, Coordination symmetry breaking of single-atom catalysts for robust and efficient nitrate electroreduction to ammonia, *Adv. Mater.* 34 (2022), <https://doi.org/10.1002/adma.202205767>.
- [83] G.A. Cerrón-Calle, A.S. Fajardo, C.M. Sánchez-Sánchez, S. García-Segura, Highly reactive Cu-PT bimetallic 3D-electrocatalyst for selective nitrate reduction to ammonia, *Appl. Catal. B Environ.* 302 (2022) 120844, <https://doi.org/10.1016/j.apcatb.2021.120844>.
- [84] M.K.R. Souza, E.S.F. Cardoso, L.M.C. Pinto, I.S.C. Crivelli, C.D. Rodrigues, R. S. Souto, A.T. Rezende-Filho, M.R.V. Lanza, G. Maia, Effective nitrate Electroconversion to Ammonia using an entangled co 3 O 4 /graphene nanoribbon catalyst, *ACS Appl. Mater. Interfaces* 17 (2025) 1295–1310, <https://doi.org/10.1021/acsmi.4c18269>.
- [85] P. Shen, G. Wang, K. Chen, J. Kang, D. Ma, K. Chu, Selenium-vacancy-rich WSe_2 for nitrate electroreduction to ammonia, *J. Colloid Interface Sci.* 629 (2023) 563–570, <https://doi.org/10.1016/j.jcis.2022.09.012>.
- [86] Y. Luo, K. Chen, P. Shen, X. Li, X. Li, Y. Li, K. Chu, B-doped MoS_2 for nitrate electroreduction to ammonia, *J. Colloid Interface Sci.* 629 (2023) 950–957, <https://doi.org/10.1016/j.jcis.2022.09.049>.
- [87] A.S. Fajardo, P. Westerhoff, C.M. Sanchez-Sanchez, S. Garcia-Segura, Earth-abundant elements a sustainable solution for electrocatalytic reduction of nitrate, *Appl. Catal. B Environ.* 281 (2021) 119465, <https://doi.org/10.1016/j.apcatb.2020.119465>.
- [88] K. Chu, W. Zong, G. Xue, H. Guo, J. Qin, H. Zhu, N. Zhang, Z. Tian, H. Dong, Y.-E. Miao, M.B.J. Roeffaers, J. Hofkens, F. Lai, T. Liu, Cation substitution strategy for developing perovskite oxide with rich oxygen vacancy-mediated charge redistribution enables highly efficient nitrate electroreduction to ammonia, *J. Am. Chem. Soc.* 145 (2023) 21387–21396, <https://doi.org/10.1021/jacs.3c06402>.
- [89] P. Muthukumar, Z. Ullah, X. Zhang, H. Ullah, Y. Liu, L. Li, S. Tian, X. Zhou, S. P. Anthony, Y. Zuo, C. Lv, X. Wang, C. Wang, Unlocking a water coordination environment in co-based metal-organic frameworks for advanced nitrate-to-ammonia electroreduction, *J. Am. Chem. Soc.* 147 (2025) 29949–29960, <https://doi.org/10.1021/jacs.5c07066>.
- [90] F. Gozzi, I. Sirés, A. Thiam, S.C. de Oliveira, A. Machulek Jr., E. Brillas, Treatment of single and mixed pesticide formulations by solar photoelectro-Fenton using a flow plant, *Chem. Eng. J.* 310 (2017) 503–513, <https://doi.org/10.1016/j.cej.2016.02.026>.
- [91] A.J. dos Santos, I. Sirés, C.A. Martínez-Huitle, E. Brillas, Total mineralization of mixtures of tartrazine, ponceau SS and direct blue 71 azo dyes by solar photoelectro-Fenton in pre-pilot plant, *Chemosphere* 210 (2018) 1137–1144, <https://doi.org/10.1016/j.chemosphere.2018.07.116>.
- [92] D.R.V. Guelfi, E. Brillas, F. Gozzi, A. Machulek Jr., S.C. de Oliveira, I. Sirés, Influence of electrolysis conditions on the treatment of herbicide bentazon using artificial UVA radiation and sunlight. Identification of oxidation products, *J. Environ. Manag.* 231 (2019) 213–221, <https://doi.org/10.1016/j.jenvman.2018.10.029>.
- [93] H.L. Barazorda-Ccahuana, A.S. Fajardo, A.J. dos Santos, M.R.V. Lanza, Decentralized approach toward organic pollutants removal using UV radiation in combination with H_2O_2 -based electrochemical water technologies, *Chemosphere* 342 (2023) 140079, <https://doi.org/10.1016/j.chemosphere.2023.140079>.
- [94] I. Sánchez-Montes, G.O.S. Santos, T.O. Silva, R. Colombo, M.R.V. Lanza, An innovative approach to the application of electrochemical processes based on the *in-situ* generation of H_2O_2 for water treatment, *J. Clean. Prod.* 392 (2023) 136242, <https://doi.org/10.1016/j.jclepro.2023.136242>.
- [95] J. Theerthagiri, J. Madhavan, S.J. Lee, M.Y. Choi, M. Ashokkumar, B.G. Pollet, Sono-electrochemistry for energy and environmental applications, *Ultrason. Sonochem.* 63 (2020) 104960, <https://doi.org/10.1016/j.ultrasonch.2020.104960>.
- [96] R. Patidar, V.C. Srivastava, Understanding of ultrasound enhanced electrochemical oxidation of persistent organic pollutants, *J. Water Process Eng.* 37 (2020) 101378, <https://doi.org/10.1016/j.jwpe.2020.101378>.
- [97] J. Llanos, S. Cotillas, P. Cañizares, M.A. Rodrigo, Conductive diamond sono-electrochemical disinfection (CDS) for municipal wastewater reclamation, *Ultrason. Sonochem.* 22 (2015) 493–498, <https://doi.org/10.1016/j.ultrasonch.2014.05.009>.
- [98] B. Yang, J. Zuo, P. Li, K. Wang, X. Yu, M. Zhang, Effective ultrasound electrochemical degradation of biological toxicity and refractory cephalosporin pharmaceutical wastewater, *Chem. Eng. J.* 287 (2016) 30–37, <https://doi.org/10.1016/j.cej.2015.11.033>.
- [99] S. Cotillas, E. Lacasa, C. Sáez, P. Cañizares, M.A. Rodrigo, Electrolytic and electro-irradiated technologies for the removal of chloramphenicol in synthetic urine with diamond anodes, *Water Res.* 128 (2018) 383–392, <https://doi.org/10.1016/j.watres.2017.10.072>.
- [100] E.O. Ezugbe, S. Rathilal, Membrane technologies in wastewater treatment: a review, *Membranes* 10 (2020) 89, <https://doi.org/10.3390/membranes10050089>.
- [101] S.O. Ganiyu, E.D. van Hullebusch, M. Cretin, G. Esposito, M.A. Oturan, Coupling of membrane filtration and advanced oxidation processes for removal of pharmaceutical residues: a critical review, *Sep. Purif. Technol.* 156 (2015) 891–914, <https://doi.org/10.1016/j.seppur.2015.09.059>.
- [102] G. Acosta-Santoyo, J. Llanos, A. Raschitor, E. Bustos, P. Canizares, M.A. Rodrigo, Performance of ultrafiltration as a pre-concentration stage for the treatment of oxyfluorfen by electrochemical BDD oxidation, *Sep. Purif. Technol.* 237 (2020) 116366, <https://doi.org/10.1016/j.seppur.2019.116366>.
- [103] Á. Soriano, D. Gorri, A. Urtiaga, Efficient treatment of perfluorohexanoic acid by nanofiltration followed by electrochemical degradation of the NF concentrate, *Water Res.* 112 (2017) 147–156, <https://doi.org/10.1016/j.watres.2017.01.043>.
- [104] W.-L. Jiang, X. Xia, J.-L. Han, Y.-C. Ding, M.R. Haider, A.-J. Wang, Graphene modified electro-Fenton catalytic membrane for in situ degradation of antibiotic florfenicol, *Environ. Sci. Technol.* 52 (2018) 9972–9982, <https://doi.org/10.1021/acs.est.8b01894>.
- [105] L. Guo, Y. Jing, B.P. Chaplin, Development and characterization of ultrafiltration tio2 magneli phase reactive electrochemical membranes, *Environ. Sci. Technol.* 50 (2016) 1428–1436, <https://doi.org/10.1021/acs.est.5b04366>.
- [106] W. Xu, Z. Yin, X. Feng, B. Yu, N. Li, C. Liu, Effective removal of nitrate from chloride-rich wastewater via bipolar membrane electrolysis, *Sep. Purif. Technol.* 377 (2025) 1334515, <https://doi.org/10.1016/j.seppur.2025.134515>.
- [107] C. Trellu, O. Ganzenko, S. Papirio, Y. Pechaud, N. Oturan, E.D. van Hullebusch, G. Esposito, M.A. Oturan, Combination of anodic oxidation and biological treatment for the removal of phenanthrene and tween 80 from soil washing solution, *Chem. Eng. J.* 306 (2016) 588–596, <https://doi.org/10.1016/j.cej.2016.07.108>.
- [108] A. Aboudalle, H. Djelal, F. Fourcade, L. Domergue, A.A. Assadi, T. Lendormie, S. Taha, A. Amrane, Metronidazole removal by means of a combined system coupling an electro-Fenton process and a conventional biological treatment: by-products monitoring and performance enhancement, *J. Hazard. Mater.* 359 (2018) 85–95, <https://doi.org/10.1016/j.jhazmat.2018.07.006>.
- [109] H. Zhao, Q. Zhang, Performance of electro-Fenton process coupling with microbial fuel cell for simultaneous removal of herbicide mesotrione, *Bioresour. Technol.* 319 (2021) 124244, <https://doi.org/10.1016/j.biortech.2020.124244>.
- [110] C.-H. Feng, F.-B. Li, H.-J. Mai, X.-Z. Li, Bio-electro-Fenton process driven by microbial fuel cell for wastewater treatment, *Environ. Sci. Technol.* 44 (2010) 1875–1880, <https://doi.org/10.1021/es9032925>.
- [111] W. Wang, Y. Lu, H. Luo, G. Liu, R. Zhang, S. Jin, A microbial electro-Fenton cell for removing carbamazepine in wastewater with electricity output, *Water Res.* 139 (2018) 58–65, <https://doi.org/10.1016/j.watres.2018.03.066>.
- [112] C.A. Martínez-Huitle, M.A. Rodrigo, I. Sirés, O. Scialdone, Single and coupled electrochemical processes and reactors for the abatement of organic water pollutants: a critical review, *Chem. Rev.* 115 (2015) 13362–13407, <https://doi.org/10.1021/acs.chemrev.5b00361>.
- [113] B. Belsa, L. Xia, F.P. García de Arquer, CO_2 electrolysis technologies: bridging the gap toward scale-up and commercialization, *ACS Energy Lett.* 9 (2024) 4293–4305, <https://doi.org/10.1021/acsenenergylett.4c00955>.
- [114] S. García-Segura, E. Brillas, Combustion of textile monoazo, diazo and triazo dyes by solar photoelectro-Fenton: decolorization, kinetics and degradation routes, *Appl. Catal. B Environ.* 181 (2016) 681–691, <https://doi.org/10.1016/j.apcatb.2015.08.042>.
- [115] R. Montenegro-Ayo, T. Pérez, M.R.V. Lanza, E. Brillas, S. García-Segura, A.J. dos Santos, New electrochemical reactor design for emergent pollutants removal by electrochemical oxidation, *Electrochim. Acta* 458 (2023) 142551, <https://doi.org/10.1016/j.electacta.2023.142551>.
- [116] S. Campos, J. Lorca, J. Vidal, W. Calzadilla, C. Toledo-Neira, M. Aranda, S. Miralles-Cuevas, A. Cabrera-Reina, R. Salazar, Removal of contaminants of emerging concern by solar photo electro-Fenton process in a solar electrochemical raceway pond reactor, *Process. Saf. Environ. Prot.* 169 (2023) 660–670, <https://doi.org/10.1016/j.psep.2022.11.033>.
- [117] R.S. Souto, I. Sánchez-Montes, G.O.S. Santos, P.J.M. Cordeiro-Junior, R. Colombo, M.C. Santos, M.R.V. Lanza, Electrochemical degradation of tebutiuron pesticide using a flow reactor: insights into the co-generation of oxidants and ecotoxicological risks, *J. Environ. Chem. Eng.* 13 (2025) 115528, <https://doi.org/10.1016/j.jece.2025.115528>.
- [118] C.A. Cid, Y. Qu, M.R. Hoffmann, Design and preliminary implementation of onsite electrochemical wastewater treatment and recycling toilets for the developing world, *Environ. Sci.: Water Res. Technol.* 4 (2018) 1439–1450, <https://doi.org/10.1039/c8ew00209f>.
- [119] J.D. García-Espinoza, I. Robles, F.J. Rodríguez-Valadez, A. Rodríguez-García, J. A. Ramírez, M. Hernández-Iturriga, L.A. Godínez, Electro-Fenton systems for “on-site” sanitary wastewater treatment: towards an off-grid technology for developing countries, *J. Environ. Chem. Eng.* 10 (2022) 107954, <https://doi.org/10.1016/j.jece.2022.107954>.
- [120] G.A. Cerrón-Calle, A.S. Fajardo, R. Stirling, P. Westerhoff, S. García-Segura, Techno-economic analysis of electrochemical reduction of nitrate for point-of-entry and point-of-use drinking water treatment, *Appl. Catal. B Environ. Energy* 382 (2026) 125984, <https://doi.org/10.1016/j.apcatb.2025.125984>.
- [121] G. Schmidt-Traub, C. Kroll, K. Teksoz, D. Durand-Delacré, J.D. Sachs, National baselines for the sustainable development goals assessed in the SDG index and dashboards, *Nat. Geosci.* 10 (2017) 547–557, <https://doi.org/10.1038/NGEO2985>.

- [122] S. García-Segura, A.B. Nienhauser, A.S. Fajardo, R. Bansal, C.L. Conrad, J. D. Fortner, M. Marcos-Hernández, T. Rogers, D. Villagran, M.S. Wong, P. Westerhoff, Disparities between experimental and environmental conditions: research steps toward making electrochemical water treatment a reality, *Curr. Opin. Electrochem.* 22 (2020) 9–16, <https://doi.org/10.1016/j.coelec.2020.03.001>.
- [123] B.P. Chaplin, The prospect of electrochemical technologies advancing worldwide water treatment, *Acc. Chem. Res.* 52 (2019) 596–604, <https://doi.org/10.1021/acs.accounts.8b00611>.
- [124] A.J. dos Santos, M.D. de Lima, D.R. da Silva, S. García-Segura, C.A. Martínez-Huitle, Influence of the water hardness on the performance of electro-Fenton approach: decolorization and mineralization of Eriochrome black T, *Electrochim. Acta* 208 (2016) 156–163, <https://doi.org/10.1016/j.electacta.2016.05.015>.
- [125] A. Atrashkevich, A.S. Fajardo, P. Westerhoff, W.S. Walker, C.M. Sánchez-Sánchez, S. García-Segura, Overcoming barriers for nitrate electrochemical reduction: bypassing water hardness, *Water Res.* 225 (2022) 119118, <https://doi.org/10.1016/j.watres.2022.119118>.
- [126] R.S.S. Castro, G.O.S. Santos, M.R.V. Lanza, G.R. Salazar-Banda, K.I.B. Eguiluz, C. Sáez, M.A. Rodrigo, Towards an electrochemically-based circular economy: electro-refinery for valorizing phenolic wastewater, *Sep. Purif. Technol.* 354 (2025) 128828, <https://doi.org/10.1016/j.seppur.2024.128828>.
- [127] J. Parrilla, I.D.B. Segundo, C.M.F. Marchante, E.V. Santos, J. Lobato, S.S.L. Castro, C.A. Martínez-Huitle, M.A. Rodrigo, Proof of concept for the organic electrefinery technology with actual effluents, *Ind. Eng. Chem. Res.* 63 (2024) 18734–18745, <https://doi.org/10.1021/acs.iecr.4c02235>.
- [128] J. Stoler, W. Jepson, A. Wutich, C.A. Velasco, P. Thomson, C. Staddon, P. Westerhoff, Modular, adaptive, and decentralised water infrastructure: promises and perils for water justice, *Curr. Opin. Electrochem. Sustain.* 57 (2022) 101202, <https://doi.org/10.1016/j.cosust.2022.101202>.
- [129] A.J. dos Santos, H.L. Barazorda-Cahuana, G. Caballero-Manrique, Y. Chérémond, P.J. Espinoza-Montero, J.R. González-Rodríguez, U.J. Jáuregui-Haza, M.R. V. Lanza, A. Nájera, C. Oporto, A. Pérez Parada, T. Pérez, V. Delgado Quezada, V. Rojas, V. Sosa, A. Thiam, R.A. Torres-Palma, R. Vargas, S. García-Segura, Accelerating innovative water treatment in Latin America, *Nature Sustain.* 6 (2023) 349–351, <https://doi.org/10.1038/s418>.