

Review

Advances and Prospects in Electrocatalytic Processes for Wastewater Treatment

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Abstract: Wastewater pollution is severe, with various refractory compounds extensively used and discharged into sewage, posing risks to the environment and human health. Electrocatalytic technologies including direct and indirect electrocatalytic oxidation, electrocatalytic reduction, and electro-Fenton processes offer advantages such as high efficiency, ease of control, and minimal secondary pollution. This review aims to systematically introduce the principles, current research status, advantages, and disadvantages of various electrocatalytic processes used for wastewater treatment, with a focus on the electrode materials, operational parameters, and cost analysis of various electrocatalytic technologies. It also provides new insights into efficient electrode materials for future electrocatalytic technologies in treating refractory wastewater.

Keywords: wastewater pollution; direct electrocatalytic oxidation; indirect electrocatalytic oxidation; electrocatalytic reduction; electro-Fenton processes



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1. Introduction

Freshwater, a vital resource for life and human civilization, constitutes only a minor fraction of the Earth's total water resources. The total volume of usable freshwater for humans and ecological processes reaches approximately 200,000 cubic kilometers, representing just 1% of the freshwater resources. Currently, global freshwater reserves are rapidly depleting, significantly impacting many densely populated areas. With the rapid development of technology and human society, water resources essential for daily life and agricultural and industrial production are increasingly contaminated by chemical pollutants from human activities. Over 100,000 chemical substances are detected in the water environment, raising widespread concern among the environmental science community and the public. The main types of wastewaters include domestic, industrial, agricultural, and medical wastewater [1]. Chemical substances and excessive nutrients in wastewater lead to ecosystem degradation, affecting soil, freshwater, and marine environments, resulting in food insecurity and other social issues.

Refractory pollutants, including antibiotics, personal care products, dyes, endocrine disruptors, and heavy metals are currently widely used and discharged into the environment [2]. The sources and hazards of these pollutants are shown in Table 1. These pollutants are characterized by persistence, long-range transport, bioaccumulation, and high toxicity. They can travel over long distances, and accumulate in the food chain, affecting organisms at higher trophic levels. These substances can cause carcinogenic, teratogenic, and mutagenic effects. Emerging pollutants like perfluorooctanoic acid pose serious threats to natural ecosystems and biological health, with significant impacts on tissues and organs [3]. Antibiotics such as penicillin and streptomycin can induce hypersensitivity reactions, ranging from mild rashes and fever to hematopoietic suppression and even neurological damage [4]. Endocrine disruptors harm reproductive, developmental,

and immune systems in organisms [5]. For example, consumption of fish contaminated with polychlorinated biphenyls by pregnant women may lead to shortened gestation, low birth weight, intelligence deficits, memory issues, and delayed neurodevelopment. Heavy metals such as mercury have led to neurological disorders, exemplified by Minamata disease in Japan. Excessive lead exposure can cause anemia, neurological damage, and memory decline, and, in pregnant women, high levels of lead can result in hearing loss or reduced intelligence in infants.

Table 1. Refractory pollutants and their adverse effects.

Type of Pollutants	Sources	Adverse Effects
Antibiotics	Medical wastewater	Allergic reactions, immune system damage, impact on children's development
Personal care products	Municipal wastewater	Endocrine disruption, neurological damage, liver and kidney damage, respiratory system effects
Dyes	Printing and dyeing textiles, rubber, leather, papermaking industries	Carcinogenicity, mutagenicity, and teratogenicity; skin and mucous membrane irritation; neurological damage
Endocrine disruptors	Pesticides, plastics, food additives	Endocrine system disruption, neurological damage, increased cancer risk, developmental effects
Heavy metals	Industrial wastewater	Neurological damage, reproductive system damage, increased risk of cancer, cardiovascular diseases

Common methods for treating refractory pollutants in wastewater include physical, chemical, and biological approaches, and their advantages and disadvantages are shown in Table 2. Physical methods, such as coagulation–precipitation, activated carbon adsorption, and membrane filtration, are highly efficient and widely applicable. Researchers have made a lot of efforts to improve the effectiveness of these methods. For instance, activated carbon fiber composites are developed by introducing new materials into the pores or on the surface of activated carbon to improve adsorption capacity. When activated carbon fibers are catalytically activated with iron and magnesium oxides, π -bonds form between chlorine and metal atoms, significantly increasing the adsorption of dichloroethylene, with equilibrium adsorption reaching up to 7 mmol g^{-1} [6]. However, physical methods primarily transfer pollutants rather than degrade them completely. In comparison, chemical treatment involves chemical reactions to separate, transform, destroy, or recycle refractory pollutants in wastewater, including neutralization, chemical precipitation, redox reactions, ion exchange, and electrolysis. For example, adding ozone can oxidize and remove phenols and cyanides, while hydroxides or barium salts can precipitate and remove heavy metals and cyanides. Chemical methods offer high degradation efficiency and allow for selective treatment of pollutants. However, they usually require chemical reagents, resulting in high costs and strict operational requirements, often necessitating the combination with other techniques. Recently, photothermal catalysis has emerged as a promising technology for wastewater treatment in recent years. This approach integrates photochemical and thermocatalytic processes, enabling the efficient utilization of the full solar spectrum to drive various chemical reactions for environmental remediation and energy conversion [7]. This integration offers several advantages over traditional methods, potentially leading to significant advancements in wastewater treatment. Biological treatments, such as activated sludge and biofilm processes, provide effective degradation of complex wastewater with various pollutants. For example, the bacterium *Pseudomonas aeruginosa* NY3 can continuously produce hydrogen peroxide, hydroxyl ($\bullet\text{OH}$) radicals, and superoxide radicals under aerobic conditions, oxidizing phenanthrene in aqueous solutions [8]. However, biological methods have limitations, including long processing times, sensitivity to environmental conditions, and the need for extended periods and sophisticated equipment to effectively remove toxic and non-biodegradable organic pollutants.

Table 2. The advantages and disadvantages of methods for treating refractory wastewater.

Treatment Methods	Advantages	Disadvantages
Physical methods	High treatment efficiency, simple process, and low treatment costs	Unable to completely degrade pollutants
Chemical methods	Easy to operate, strong adaptability, broad treatment range	High costs, potential for secondary pollution
Biological methods	Environmentally friendly, low cost, capable of degrading a variety of pollutants	Long treatment time, sensitive to the environment, difficult to treat high-concentration pollutants
Electrocatalytic processes	Low secondary pollution, mild reaction conditions, high efficiency	High energy consumption, electrode materials may need to be replaced regularly

In recent years, electrocatalysis has garnered increasing attention as an advanced oxidation process. Electrocatalysis is characterized by its eco-friendliness, lack of secondary pollution, ease of control, and high efficiency. Under an applied electric field, refractory organic pollutants undergo direct or indirect redox reactions on the electrode surface or in the water, leading to their decomposition and water purification. Electrocatalysis typically requires only the addition of electrolyte solutions or specific activators, such as chloride ions for hypochlorous acid generation. This significantly reduces the amount of chemical reagents needed compared to traditional methods. As a result, electrocatalysis minimizes the potential for secondary pollutant formation, contributing to a more environmentally friendly treatment approach. The main techniques include direct electrocatalytic oxidation (DEO), indirect electrocatalytic oxidation (IEO), electrocatalytic reduction (ER), and the electro-Fenton process (EFP). A comparison of the advantages and disadvantages of four electrocatalytic technologies is presented in Table 3. Significant progress has been made in wastewater treatment using electrocatalysis over the past decade [9].

Table 3. The advantages and disadvantages of electrocatalytic technologies.

Treatment Methods	Advantages	Disadvantages
DEO	Easy to operate, minimal secondary pollution	Low mass transfer efficiency.
IEO	High treatment efficiency, wide applicability	High energy consumption.
ER	High treatment efficiency, environmentally friendly	Requires highly selective catalysts to avoid side reactions
EFP	High treatment efficiency	Requires maintaining an acidic environment

This review aims to provide a systematic overview of electrocatalytic processes for wastewater treatment. It delves into the fundamental principles behind these processes, the current state of research, and the inherent advantages and limitations of various electrocatalytic techniques. The discussion encompasses critical aspects such as the selection of suitable electrode materials, the impact of operational parameters, and a cost analysis of different electrocatalytic technologies. The review also explores promising future directions for the development and implementation of this technology.

2. DEO

DEO includes two pathways, namely, electrocatalytic conversion and electrocatalytic combustion, as illustrated in Figure 1a. In DEO, H_2O is electrolyzed on the anode surface to generate adsorbed $\bullet OH$ radicals. When using an active electrode, these $\bullet OH$ interacts with the oxide layer on the anode, transferring oxygen into the oxide lattice to form higher-valent oxides (MO_{x+1}) (Equation (1)). MO_{x+1} are highly oxidative, selectively oxidizing organic compounds on the electrode surface, primarily resulting in electrochemical conversion where organic pollutants are not fully oxidized. This process degrades adsorbed organic pollutants into smaller, non-toxic, or biodegradable molecules, suitable for further biological treatment, such as oxidizing aromatic compounds to fatty acids. Common active electrodes

include Ti/IrO₂, Ti/RuO₂, and Pt electrodes. Xu et al. studied the oxidation of formic acid on a platinum electrode using cyclic voltammetry, finding that it undergoes direct oxidation without forming formate as an intermediate [10]. Li et al. used Ti/Sb-SnO₂, Ti/Sb-SnO₂-PbO₂, and Ti/Sb-SnO₂-PbO₂ for the direct electrocatalytic oxidation of aniline. [10] After 5 h of electrolysis in 5 g L⁻² Na₂SO₄ solution, the removal rates of aniline were 95.9%, 90.5%, and 88.4%, respectively.

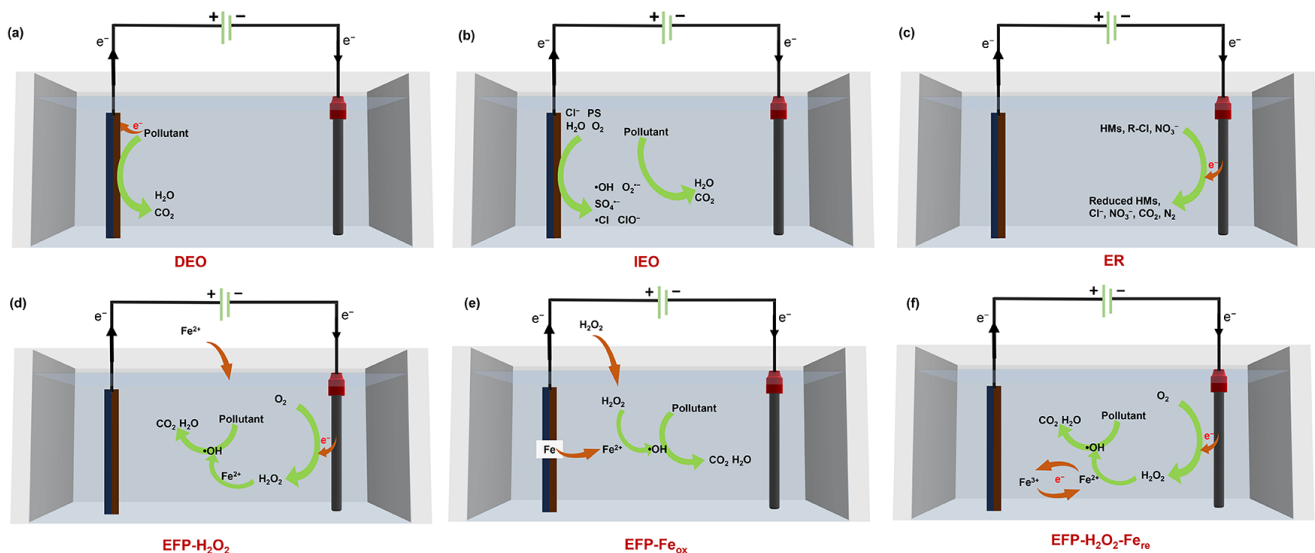
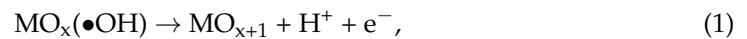


Figure 1. The scheme of electrocatalytic processes for wastewater treatment: (a) DEO, (b) IEO, (c) ER, (d) cathodic EFP with oxygen reduction, (e) sacrificial anode EFP, and (f) Fe²⁺ recycling EFP with cathodic oxygen reduction.

When the anode is a non-active electrode, •OH is physically adsorbed on the electrode surface (Equation (2)). The •OH directly reacts with organic compounds, with no selectivity, primarily leading to electrochemical combustion, which deeply oxidizes organic pollutants into stable inorganic substances such as CO₂ and H₂O. Common non-active electrodes include PbO₂, boron-doped diamond (BDD), and SnO₂ electrodes. Kapalka et al. studied the oxidation of ammonia on BDD electrodes at high pH (>8) through radical oxidation and found that chlorine radicals enhance ammonia oxidation under low pH conditions [11]. In an electrolytic solution of 0.1 M NaCl with 0.05 M ammonia at pH 5.5 and a current density of 30 mA cm⁻², ammonia concentration decreased linearly, and residual active chlorine was very low, indicating that all generated active chlorine reacted with ammonia. Recent progress of DEO has been summarized in Table 4.

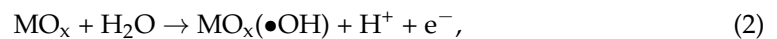


Table 4. Recent progress of DEO.

Electrode Catalyst	Pollutants	Operating Parameters	Removal Rate
Cu/NF [12]	ammonia	1.1 V cell potential, 0.01 M ammonia, 100 mM Na ₂ SO ₄ , pH 11	61%
Ni ₂ P-s/NF [13]	ammonia	current density 17.8 mA cm ⁻² , 160 mM ammonia	70%
carboxylated multi-walled carbon nanotube-reduced graphene oxide [14]	enrofloxacin	/	/

3. IEO

IEO utilizes the addition of metal or non-metal ions to the electrolyte, forming a homogeneous electrocatalytic system. These ions undergo oxidation at the anode surface, generating a range of active species including hydroxyl radicals ($\bullet\text{OH}$), sulfate radicals ($\text{SO}_4\bullet^-$), superoxide radicals ($\bullet\text{O}_2^-$), and reactive chlorine species (RCS) [15]. These powerful oxidants then degrade organic pollutants due to their high reactivity. The generation of these active species is essential for the reaction (Figure 1b, Equations (3)–(5)). Notably, the presence of chloride ions during electrolysis can lead to the formation of hypochlorite, further accelerating the oxidation of organic contaminants (Equations (6)–(8)). IEO leverages a combination of intermediate oxidation and direct anodic oxidation, ultimately enhancing the overall efficiency of the degradation process. Importantly, these reactive species are short-lived, existing only during electrolysis. Once the current is interrupted, they are no longer generated and disappear from the solution. Recent progress of IEO for refractory pollutants is summarized in Table 5.

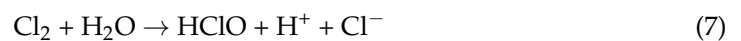
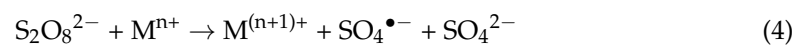


Table 5. Recent progress of IEO for refractory pollutants.

Electrode Catalyst	Pollutants	Operating Parameters	Active Species	Removal Rate
$\text{Ti}_3\text{C}_2\text{Tx}$ [16]	metformin	0.525 C g ⁻¹ , 0.005 mA cm ⁻² , pH 6 in absence of NaCl; or 26.25 C g ⁻¹ , 0.5 mA cm ⁻² in the presence of 2.5 w/v% NaCl	$\bullet\text{OH}$	99%
Polypyrrole (PPy) coated carbon (PPy@CCM) [17]	phenol	2.0 V potential, 2.50 g L ⁻¹ Na ₂ SO ₄ , 1.5 mL min ⁻¹ flow rate, 50 mg L ⁻¹ phenol, 0.5 kWh kgCOD ⁻¹ energy consumption	$\bullet\text{OH}$	Phenol 99.51%, COD 89.90%
GAC@Ni/Fe [18]	sulfamethylthiadiazole (SMT)	5 V cell voltage, 3 g particle electrode dosage, 2 cm electrode plate spacing, 1 mg L ⁻¹ SMT initial concentration	$\bullet\text{OH}$	90.89% in 30 min
NiO–TiO ₂ [19]	ammonia	200 mM NH ₄ OH, 100 mM NaNO ₃ , pH 9 with a current density of 30 mA cm ⁻²	$\bullet\text{OH}$	96.4% in 9 h
spinel Cu _x Co _{1-x} Mn ₂ O ₄ [20]	tetracycline	current density 20 mA cm ⁻² , pH = 3 and 20 mg L ⁻¹ tetracycline	$\bullet\text{OH}$	91.3% in 120 min
GAC-Co-Mn [21]	sulfanilamide	voltage 15 V, weak acid and weak base, aeration velocity 16 L h ⁻¹ , sulfanilamide 50 mg L ⁻¹	$\bullet\text{OH}$	Sulfanilamide 92.881% and TOC 82.335% in 90 min
Ti–Ag/γ-Al ₂ O ₃ [22]	pesticide wastewater	current density of 30 mA cm ⁻² , initial pH of 2.0, electrode distance of 3.0 cm, air flow of 3.0 L min ⁻¹	/	COD 82.50%

Table 5. Cont.

Electrode Catalyst	Pollutants	Operating Parameters	Active Species	Removal Rate
SnO ₂ -Sb NPA [23]	Bisphenol A	current density 20 mA cm ⁻² , neutral pH, 25 mg L ⁻¹ BPA and 0.1 M Na ₂ SO ₄	•OH and •O ₂ ⁻	Bisphenol A 100%, TOC 42.8% in 120 min
Ti/SnO ₂ -RuO ₂ [24]	cefotaxime sodium	current density 25 mA cm ⁻² , NaCl 5 mM, pH 7, cefotaxime 100 mg L ⁻¹	•OH and ClO ⁻	86.33% in 45 min
Sr _x La _{1-x} Mn _y Co _{1-y} O _{3-δ} [25]	ammonium nitrogen and methyl orange	T = 35 °C, current density = 20 mA cm ⁻² , pH = 9, C _{Cl⁻} = 2000 mg L ⁻¹	•OH, •O ₂ ⁻ and active chlorine	ammonium nitrogen 98.23%, methyl orange 99.61% and COD 88.16% in 60 min
SnOx/La-Sb [26]	moxifloxacin	10 mg L ⁻¹ moxifloxacin, current density 2.5 mA cm ⁻² in 0.05 M Na ₂ SO ₄ at neutral pH	•OH	nearly 100% and TOC 41% in 30 min
CuFe ₂ O ₄ /ACF cathode and RuO ₂ /Ti anodes [27]	phenol	1.00 mM PS, current density of 50 A m ⁻² , and initial pH of 7.0	•OH and SO ₄ ^{•-}	97% in 60 min
boron-doped diamond anode [28]	2,4-Dichlorophenoxyacetic acid	2 M sulfuric acid, current efficiency 5 mA cm ⁻²	SO ₄ ^{•-}	96%
Fe [29]	landfill leachate	pH 6.8, applied current of 200 mA, oxidant dosage of 6 mM	•OH and SO ₄ ^{•-}	TOC 73% in 80 min
DSA [30]	landfill leachate	current density of 12.5 mA cm ⁻² and NaOH dosage of 10 g/L	RCS and •OH	COD 50.94% NH ₄ ⁺ -N 38.11%
platinum-coated titanium [31]	Humic acids	10 mM NaCl, current efficiency 153 A m ⁻²	RCS and •OH	/
iron anode reactor and Ti/RuO ₂ anode reactor (TAR) [32]	landfill leachate	IAR: current density 70 mA/cm ² and initial pH value 6.5 TAR: current density 70 mA/cm ² and initial pH value 9.0	RCS and •OH	TN 98.3%, COD 94.6%

3.1. •OH-Based IEO

Hydroxyl radicals (•OH) are highly reactive oxygen species with strong oxidizing potential (2.8 V) and high electronegativity. These properties enable them to react rapidly with various biomolecules, organic pollutants, and even inorganic species like ammonia and nitrogen, resulting in a wide range of chemical reactions. These radicals can oxidize pollutants through addition or hydrogen abstraction, decomposing them into CO₂, H₂O, N₂, and other inorganic compounds [33]. However, their usefulness is limited by their short lifespan (less than 1 μs) and restricted diffusion distance. Cho et al. addressed these limitations by developing a three-dimensional electrode reactor (3DER) using granular activated carbon (GAC) in place of a traditional two-dimensional electrode reactor (2DER) [34]. The GAC particles function as microelectrodes, enhancing ibuprofen (IBP) degradation compared to a 2D system. This improvement is attributed to the increased surface area promoting earlier adsorption of IBP and facilitating its indirect oxidation by dissolved radicals. Additionally, the 3DER design catalyzes the formation of hydrogen peroxide (H₂O₂) from dissolved oxygen (O₂), which in turn reacts to generate •OH. This enhanced •OH production contributes to the impressive 98% IBP removal rate achieved by the 3DER within 4 h, exceeding the 2DER by a factor of 2.5. Arias et al. studied the anodic oxidation (AO) of volatile organic compounds (VOCs) at high current densities, showing that boron-doped diamond (BDD) electrodes produced sufficient reactive species, including •OH radicals, leading to an 80% mineralization rate of VOCs [35]. Yang et al. doped La³⁺ into

the SnO_2 crystal structure of the anode, employing it for a high-performance electrochemical wastewater treatment. The resultant $\text{SnO}_x/\text{La-Sb}$ anode significantly enhanced the ability to degrade moxifloxacin, achieving nearly 100% removal within 30 min of treatment. Notably, the process also exhibited low energy consumption, requiring only 0.09 kWh m^{-3} . The improved performance could be attributed to that the La^{3+} doping-induced oxygen vacancy activated the anode surface by boosting the interfacial electron transfer and $\bullet\text{OH}$ generation (Figure 2a) [26].

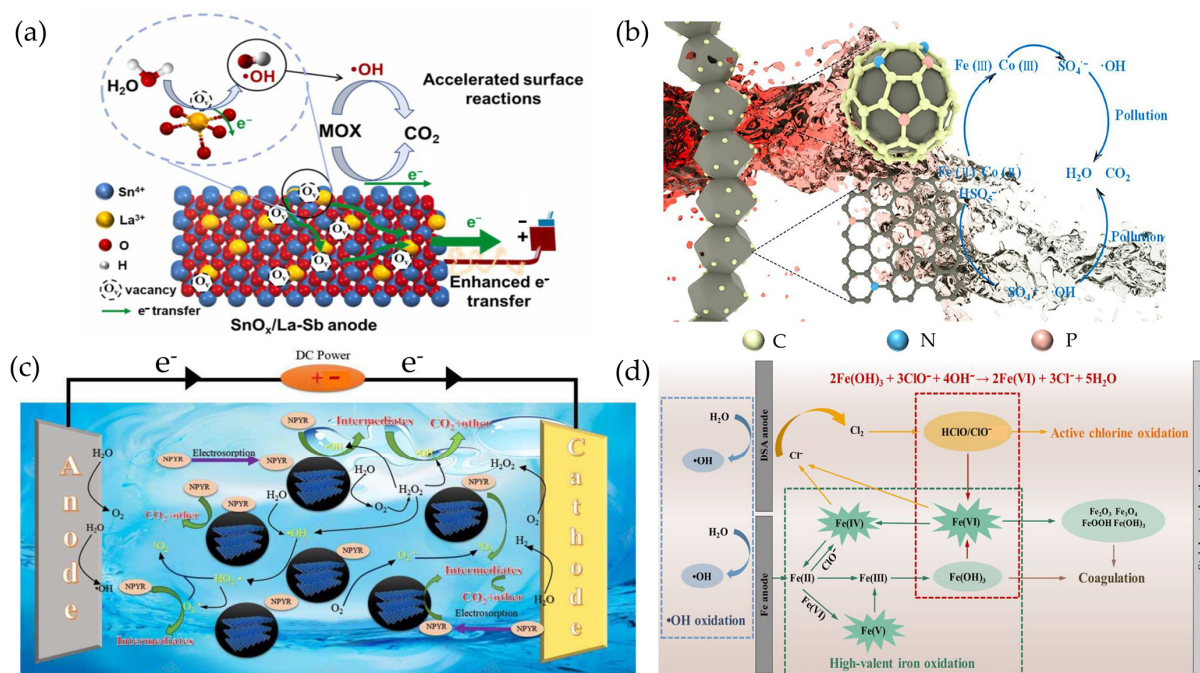


Figure 2. The schematic mechanism for pollution treatment by IEO: (a) MOX oxidation on the O_V -enriched $\text{SnO}_x/\text{La-Sb}$ anode, (b) pollution degradation by Fe/Co-N/P-9 carbon nanofiber, (c) the degradation NPYR in 3DER with ZnAl-LDH/AC system, (d) leachate pretreatment with Fe-DAS dual anode configuration.

The presence of $\bullet\text{OH}$ radicals in various systems can be confirmed through spectroscopic analysis. The basic principle involves the reaction of $\bullet\text{OH}$ with coumarin ($\text{C}_9\text{H}_6\text{O}_2$) to produce the highly fluorescent compound 7-hydroxycoumarin ($\text{C}_9\text{H}_6\text{O}_3$), which can be detected under fluorescence spectroscopy [36]. The fluorescence intensity is linearly related to the concentration of 7-HC, allowing for the construction of a standard curve. Experimental data show that the reaction yields 29% of total hydroxyl radicals as 7-HC. The generation of $\bullet\text{OH}$ radicals can be calculated based on the concentration of coumarin and fluorescence intensity. The $\bullet\text{OH}$ radicals can also be detected using electron spin resonance (ESR), a technique for qualitative analysis of radicals by transferring them into a magnetic field. However, due to the instability and rapid reaction of radicals in electrocatalytic oxidation, direct detection with a spectrometer is not feasible. A spin trap must be used to form stable adducts for analysis. DMPO is commonly used for detecting $\bullet\text{OH}$, with a characteristic peak ratio of 1:2:2:1 for the DMPO- OH adduct. Interestingly, Wang et al. investigated the sources of 5,5-dimethyl-1-pyrroline N-oxide (DMPO) adducts in systems containing Cu(II) , $\text{Cu(II)}/\text{H}_2\text{O}_2$, $\text{Cu(II)}/\text{peroxymonosulfate}$ (PMS), and $\text{Cu(II)}/\text{persulfate}$ (PDS), finding that DMPO- $\bullet\text{OH}$ signals could be observed in most Cu(II) systems even in the absence of peroxides, indicating alternative sources for these adducts beyond the intended spin trapping of $\bullet\text{OH}$ by DMPO [37].

3.2. $\text{SO}_4^{\bullet-}$ -Based IEO

Sulfate radicals ($\text{SO}_4^{\bullet-}$) possess a high oxidation potential of 2.5–3.1 V and a broad pH application range, with a lifespan of 30–40 μs in water. In AO processes utilizing sulfate electrolytes, $\text{SO}_4^{\bullet-}$ and $\text{S}_2\text{O}_8^{2-}$ are the primary active species generated. The dominant transformation pathways involve the direct oxidation of SO_4^{2-} at the anode surface to form $\text{S}_2\text{O}_8^{2-}$, which is subsequently activated into $\text{SO}_4^{\bullet-}$ through radical or non-radical mechanisms. Additionally, $\bullet\text{OH}$ produced from water oxidation also contribute to the formation of $\text{SO}_4^{\bullet-}$. Chen and Saha revealed that the strong oxidative ability of $\bullet\text{OH}$ facilitates the generation of $\text{SO}_4^{\bullet-}$, and the production rate of $\text{SO}_4^{\bullet-}$ is correlated to that of $\bullet\text{OH}$ [38,39].

However, it is crucial to note that while sulfate ions act as precursors for $\text{SO}_4^{\bullet-}$, they also compete with pollutants for $\bullet\text{OH}$. Consequently, increasing sulfate concentration does not always enhance pollutant removal. Moreover, excessive sulfate concentrations can hinder electrocatalytic performance by blocking active sites on the anode. To address these limitations, Wang et al. developed an Fe/Co-N/P-9 electrode (carbonized at 900 $^{\circ}\text{C}$), where graphite carbon nanofibers provided good conductivity (Figure 2b) [40]. Iron and cobalt served as catalytic centers, and heteroatoms influenced the electronegativity of neighboring carbon atoms, affecting PMS adsorption. This design offers a large surface area for efficient mass transfer and utilizes a graphitic carbon layer for enhanced stability. The catalyst showed remarkable performance in degrading Rhodamine B. The presence of both $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$ in the system was confirmed through radical quenching experiments and ESR spectroscopy. Additionally, Gao et al. employed the ESR secondary radical spin trapping method utilizing DMPO and dimethyl sulfoxide as a typical $\bullet\text{OH}$ scavenger. Their findings revealed the generation of $\bullet\text{OH}$ across a range of conditions, from weakly acidic (pH = 5.5) to strongly alkaline (optimal pH = 13.0). However, $\text{SO}_4^{\bullet-}$ was identified as the dominant radical species at pH < 5.5 [41].

3.3. $\bullet\text{O}_2^-$ -Based IEO

The $\bullet\text{O}_2^-$ exhibits lower reactivity compared to other reactive oxygen species. However, its advantages lie in its extended lifespan (around 1 ms in aqueous solutions) and ability to travel longer distances, allowing it to effectively reach and degrade target pollutants. Zhang et al. employed a three-dimensional reactor containing ZnAl-layered double hydroxide/activated carbon (ZnAl-LDH/AC) as particle electrodes for the electrocatalytic degradation of nitrosopyrrolidine (NPYR) in water, achieving an impressive removal rate of 83.78% under optimal conditions (Figure 2c) [42]. ESR measurements utilizing DMPO and TEMP as spin traps revealed the presence of both DMPO- $\bullet\text{OH}$ and DMPO- $\bullet\text{O}_2^-$ adducts. Subsequent radical quenching experiments confirmed that $\bullet\text{OH}$ and $\bullet\text{O}_2^-$ were the primary active species, while singlet oxygen ($^1\text{O}_2$) also contributed to the degradation of NPYR, albeit to a lesser extent. Notably, model optimization and DFT calculations indicated that the nitroso oxygen atom in NPYR is more susceptible to electrophilic and radical attacks compared to the nitrogen atom. Consequently, radical attack preferentially targets and breaks the N-N and N-O bonds within the NPYR molecule. A BDD anode achieved complete removal (100%) of acid orange 74 (AO74) and an 84.3% reduction in chemical oxygen demand (COD) within 2 h under specific operating conditions (40 mA cm^{-2} current density and 2.5 g L^{-1} Na_2SO_4 electrolyte) [43]. Interestingly, the removal efficiency of AO74 decreased by 7.94% when p-benzoquinone, a superoxide scavenger, was introduced. This observation suggests the involvement of $\bullet\text{O}_2^-$ produced during BDD anode oxidation. These superoxide radicals can further react to form H_2O_2 , which contributes to enhanced AO74 oxidation.

It is important to note that DMPO can also be used for ESR detection of $\bullet\text{O}_2^-$. The characteristic ESR spectrum of the DMPO- $\bullet\text{O}_2^-$ adduct exhibits four lines with an equal intensity ratio (1:1:1:1). Interestingly, Wang et al. investigated the sources of DMPO adducts in various systems containing Cu(II) ions with different oxidants (H_2O_2 , PMS, and PDS) [37]. They found that DMPO- $\bullet\text{O}_2^-$ adducts only appeared under highly alkaline conditions

within the Cu(II)/PDS system. This suggests that the formation of $\bullet\text{O}_2^-$ in this specific case might be linked to a unique reaction pathway.

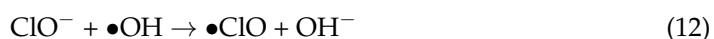
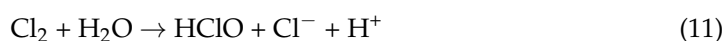
3.4. RCS-Based IEO

Chlorides are ubiquitous electrolytes in wastewater, significantly influencing the generation of active species during electrochemical oxidation processes. In chloride-containing media, the primary RCS includes Cl_2 , HClO , ClO^- , ClO_2 , $\bullet\text{Cl}$, and $\bullet\text{ClO}$. The specific composition of RCS depends on the prevailing pH and Cl^- concentration. Chloride ions undergo a two-electron transfer process to form Cl_2 , which subsequently reacts with H_2O to generate the weak acid HClO . Depending on the pH, HOCl reaches an equilibrium with the ClO^- . Additionally, under specific conditions, some AO systems can produce $\bullet\text{Cl}$ and $\bullet\text{ClO}$ [44–46]. Notably, the formation of chlorinated byproducts should be minimized in practical applications of electrochemical oxidation with Cl^- .

The speciation of RCS is heavily influenced by pH. At pH values below 1, Cl_2 and HClO coexist, with Cl_2 dominating. As the pH increases from 1 to 4, HClO becomes the predominant species. Between pH 4 and 7.5, both HClO and ClO^- exist, with HClO prevailing. Finally, at pH exceeding 7.5, ClO^- becomes the primary form, acting as a weaker oxidant compared to HClO [47]. Importantly, Zheng et al. demonstrated that the presence of Cl^- and HCO_3^- in electrochemical systems promotes the formation of ClO species, consequently facilitating the simultaneous removal of refractory organics and nitrogen from secondary coking wastewater [48]. Their study achieved an impressive 87.8% COD removal and 86.5% total nitrogen removal using a PbO_2/Ti anode and a Cu/Zn cathode at a current density of 37.5 mA cm^{-2} for 6 h.

Due to their strong oxidizing properties, RCS find applications in various fields. Wang et al. employed anodic oxidation in Cl^- -containing electrolytes to generate RCS [49]. The presence of these radicals was confirmed using probe experiments, and they demonstrated superior performance in self-cleaning ultrafiltration membranes compared to other reactive oxygen species systems. In the medical field, reactive radicals offer a promising approach to combating tumors without inducing drug resistance, a limitation associated with traditional therapies. However, the efficacy of existing ROS-based cancer treatments is hampered by their low production rates. Song et al. discovered that $\bullet\text{Cl}$ possessing strong nucleophilicity can effectively target and attack intracellular biomolecules, triggering apoptosis in cancer cells [50]. This approach offers advantages in terms of high efficiency and low cost. Photocatalysis provides another avenue for RCS utilization. Zhou et al. employed $\bullet\text{Cl}$ to rapidly convert amino groups in urine to N_2 , achieving selective urea denitrification [51]. Additionally, RCS also demonstrated its applications in sterilization [52]. The RCS was generated through photolysis and the presence was confirmed via quenching and kinetic simulations.

RCS plays a crucial role in electrochemical oxidation processes due to their unique combination of properties such as low oxidation potential, short lifespan, and strong oxidizing power. This combination makes them a cost-effective and efficient method for degrading pollutants in chloride-containing electrolytes [53]. The primary reactions leading to RCS formation involve the oxidation of Cl^- ions, generating $\bullet\text{Cl}$ radicals alongside Cl_2 and HClO (Equations (9)–(11)). Subsequently, ClO^- can further react to form $\bullet\text{ClO}$ (Equations (12) and (13)), and Cl^- can also produce $\bullet\text{Cl}_2^-$ radicals (Equations (14)–(16)).





Currently, chlorine radical detection methods primarily fall into two categories: qualitative detection and quantitative detection. Qualitative detection utilizes ESR technology, where DMPO is added as a radical trapping agent. The detection spectrum typically shows a seven-line pattern, corresponding to oxidized derivatives of DMPO-X [54]. For example, Wang et al. successfully utilized a mixed cobalt–nickel electrocatalytic system with NaCl as the electrolyte for selective methane conversion [55]. Employing EPR analysis, they detected strong signals corresponding to $\bullet\text{Cl}$ and $\bullet\text{ClO}$ radicals, confirming their role as the primary reactive species during the electrocatalytic process. A novel electrocatalytic oxidation process employing a Fe-DSA dual anode configuration had been established for leachate pretreatment. In this process, chloride in the leachate was converted to active chlorine by the DSA anode, while $\text{Fe}(\text{OH})_3$ was generated from the Fe anode. Consequently, $\text{Fe}(\text{VI})$ was formed in situ through the reactions between active chlorine and $\text{Fe}(\text{OH})_3$. The decomposition of $\text{Fe}(\text{VI})$ produced iron oxide, amorphous iron-oxygen hydroxide, and amorphous $\text{Fe}(\text{OH})_3$, which enhanced the removal performance through coagulation (Figure 2d) [30].

Quantitative detection involves free radical quenching experiments. Here, specific chemicals are used to scavenge and react with the radicals of interest. Table 6 provides details on commonly used RCS quenching agents, their types, and their corresponding rate constants. Li et al. constructed a CoFe_2O_4 anodic oxidation system, employing a heterogeneous electro-Fenton/Cl system for the degradation of norfloxacin (NOR) [56]. Through free radical quenching experiments using different scavengers like benzoic acid (BA), carbamazepine (CBZ), and 1-4Dioxomethylbenzene (DMOB), they were able to quantitatively determine the steady-state concentrations of $\bullet\text{Cl}$, $\bullet\text{ClO}$, and $\bullet\text{Cl}_2^-$ during the degradation process. These concentrations were found to be 2.50×10^{-12} M, 2.72×10^{-13} M, and 1.39×10^{-11} M, respectively.

Table 6. Commonly used RCS quenching agents, their types, and their corresponding rate constants.

Type of Quencher	Quenching of Free Radicals	Reaction Rate Constant
Benzoicacid (BA)	$\bullet\text{OH}$, $\bullet\text{Cl}$	$K_{\bullet\text{OH}} = 5.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, $K_{\text{Cl}\bullet} = 1.8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$
1-4Dioxomethylbenzene (DMOB)	$\bullet\text{OH}$, $\bullet\text{Cl}$, $\bullet\text{ClO}$	$K_{\bullet\text{OH}} = 7.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, $K_{\text{Cl}\bullet} = 1.8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, $K_{\text{ClO}\bullet} = 2.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$
Cassimarine (CBZ)	$\bullet\text{OH}$, $\bullet\text{Cl}$, $\bullet\text{ClO}$, $\bullet\text{Cl}_2^-$	$K_{\bullet\text{OH}} = 8.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, $K_{\text{Cl}\bullet} = 3.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, $K_{\text{ClO}\bullet} = 1.97 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, $K_{\text{ClO}_2\bullet} = 4.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$

4. ER

Electrocatalytic reduction offers a promising approach for treating oxyanions associated with heavy metals, halogens, nitrate ions, and other similar contaminants. This technology leverages an externally applied electric field to drive the reduction of high-valence cations present in these pollutants at the cathode surface. Through this electron gain, the reduction process transforms the pollutants into non-toxic elemental substances or into less toxic intermediates that are more readily biodegradable (Figure 1c). The recent research on electrocatalytic reduction for the degradation of pollutants is shown in Table 7.

Table 7. The recent research on electrocatalytic reduction for degradation of pollutants.

Electrode Catalyst	Pollutants	Operating Parameters	Removal Rate
conductive carbon fibers cloth cathode and Platinum-coated titanium panel anode [57]	Nickel Sulfate and Copper Sulfate (0.06 M)	low voltage supply energy of 10 V, and pH value of 6.8	97% in 20 h
IrO ₂ -Ta ₂ O ₅ /Ti anode and graphite cathode [58]	mixed heavy metal ions extracted from soils by citrate	current density 26 mA cm ⁻²	99.4% in 12 h
multi-hole stainless steel anode and multi-hole titanium cathode [59]	Cr and Cu ions	current density 0.40 mA cm ⁻²	COD 87.23%, TOC 80.42%, Cr 91.25% Cu 95.97%
PdNi/PPy-rGO/Ni [60]	diclofenac	20 mg L ⁻¹ diclofenac, current 7 mA	100% in 140 min
multi-walled carbon nanotubes MWCNT-Ti ₄ O ₇ [61]	dibromoacetic acid (DBAA)	1 mg L ⁻¹ DBAA in 10 mM KH ₂ PO ₄ /K ₂ HPO ₄ at −1.5 V SHE	96%
Pd ₇ Au ₃ ANs [62]	4-chlorophenol	50 mM potassium sulfate solution mixed with 50 mg L ⁻¹ 4-chlorophenol, −1.1 V (vs. SCE)	98.35% in 4 h
Cu ₃ P/CF [63]	nitrates	−1.2 V (vs. Ag/AgCl), 50 mM Na ₂ SO ₄	97.7%
Co/CoO NSAs [64]	nitrates	−1.6 V (vs. SCE), 0.1 M Na ₂ SO ₄	91.2%
Pd-TiO ₂ [65]	nitrates	−0.55 V (vs. RHE), 0.25 M NO ₃ [−]	99.6%

4.1. ER of Heavy Metals

Due to the non-degradability and bio-toxicity of heavy metals (HMs), as well as their threat to public health and ecosystems, these pollutants have recently become a global focus of concern. ER technology involves the transformation of high-valence HMs into low-valence or zero-valent states by accepting electrons. Therefore, in this method, active sites are released by converting HMs to their zero-valent state. This technology is categorized into two types: direct reduction, where HMs directly accept electrons from the cathode surface, and indirect reduction, where electrons are accepted through the help of a reducing agent and in-situ-generated active radicals. In the direct reduction of heavy metals, HMs directly accept electrons from the cathode surface, followed by nucleation to form metal oxides or elemental metals. In the indirect reduction of HMs, electrons are transferred through a mediator, such as a reducing agent or in-situ-generated reactive radicals (e.g., •H, e[−], H₂O₂), to achieve HM reduction [66].

ER can also address the challenge of heavy metal complexes. However, achieving high selectivity of complex reduction remains a significant challenge. Qin et al. used a molybdenum disulfide nanosheets/graphite felt (MoS₂/GF) cathode, achieving an average Faradaic efficiency of 29.6% for Cu-EDTA at −0.65 V (vs. SCE), with a specific removal rate (SRR) of 0.042 mol cm⁻² h⁻¹ [66]. Detoxification of metal complexes is crucial in the electrochemical reduction of HMs. Pan et al. designed BaTiO₃@graphene electrodes and fabricated them into three-dimensional millimeter-scale spheres [67]. They demonstrated that 100% of Cu-EDTA was in situ dissociated by the piezoelectric potential of barium titanate@graphene. The addition of graphene significantly enhanced the surface potential of barium titanate@graphene through its flexoelectric effect (increasing from 19.8 ± 0.97 to 96.8 ± 1.48 mV), effectively promoting piezoelectric catalysis. Additionally, Cu(II) released from Cu-EDTA dissociation was simultaneously recovered via interactions with graphene groups. Yang employed inert electrodes (IrO₂-Ta₂O₅/Ti anode and graphite cathode) to remove mixed heavy metal ions extracted from soils by citrate. This combined cathodic precipitation process decreased the concentrations of toxic heavy metals by over 99.4% after 12 h of electrolysis at a current density of 26 mA cm⁻². The low potential of the cathode facilitated the electrodeposition of Cd, while the local alkaline environment,

created by electro-mediated water reduction, led to the hydrolytic precipitation of Zn and Pb. Additionally, the precipitation of Fe from Fe-rich soil resulted in the coprecipitation of As on the cathode surface (Figure 3a) [58].

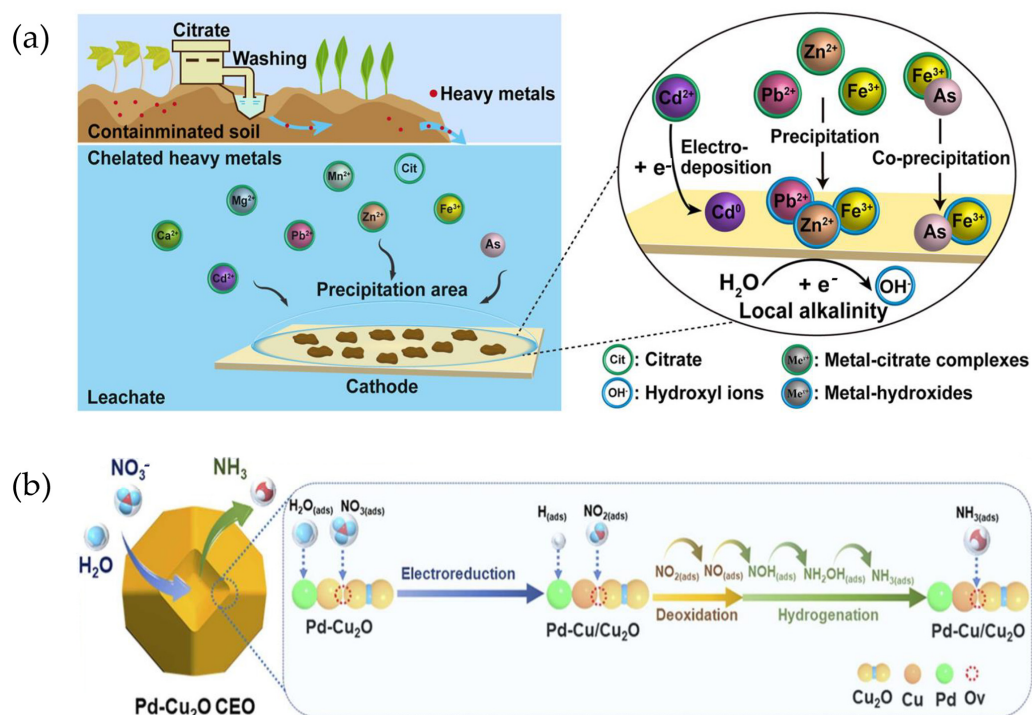
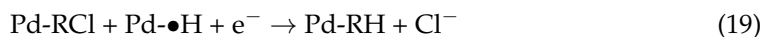
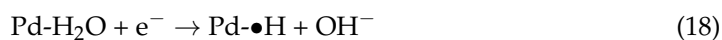
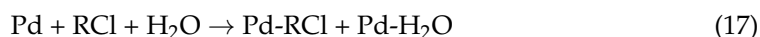


Figure 3. The mechanism of ER for pollutant treatment: (a) the high-efficiency removal of heavy metals from soil leachate, (b) the electrocatalytic nitrate reduction to ammonia.

4.2. ER for the Dehalogenation

ER of halogens involves utilizing hydrogen protons generated from the electrocatalytic water splitting process to produce $\bullet\text{H}$. $\bullet\text{H}$ can attack the carbon–halogen bonds, replacing the halogen atoms and hydrogenating the carbon–halogen bonds, thereby achieving halogen reduction. Taking the reduction of chlorinated organic compounds on metallic Pd as an example, the reduction process is illustrated by Equations (17)–(20).



Electrocatalytic reduction of halogens commonly employs cathode materials such as transition metals including Pd, Fe, Co, Ni, Ag, and Cu. These metals form M-H bonds that selectively absorb and store $\bullet\text{H}$, effectively preventing $\bullet\text{H}$ from escaping as H₂. They exhibit high activity in breaking carbon–halogen bonds. Jiang et al. utilized supermolecular coordination cages (SCCs) as templates and prepared Pd nanoparticle catalysts on carboxymethyl cellulose (CMC) hydrogel supports via the impregnation-reduction method [68]. Their study demonstrated that SCCs not only significantly reduced the aggregation tendency of Pd nanoparticles but also played a crucial role in adjusting their size and size distribution, providing guidance for the construction of electrode catalysts.

Transition metal phosphides are also common cathode materials where transition metal and phosphorus sites serve as proton acceptors and hydride acceptor centers, thereby enhancing electrocatalytic efficiency. Yao et al. reported a novel amorphous nickel phos-

phide catalyst (ANP) for removing trichloroacetic acid (TCAA) from water [69]. The superhydrophilic surface of ANP facilitated the contact between the electrocatalyst and the electrolyte, reducing impedance and promoting rapid electron transfer from the electrode to water, thereby enhancing atomic hydrogen production. ANP exhibited electrochemical dechlorination efficiency comparable to Pd-based catalysts, with an apparent reaction rate constant of 0.0283 min^{-1} . Liu et al. prepared crystalline cobalt phosphide nanosheets arrayed on titanium plates (C-CoP/Ti) for cathodic dechlorination of fluorophenylkone (FLO) [70]. Under -1.2 V conditions, the C-CoP/Ti electrode achieved a dehalogenation rate of 97.4% for 20 mg L^{-1} FLO within 30 min, with nearly complete degradation of Cl and 20% of F in 120 min.

Carbonaceous materials such as graphene electrodes, activated carbon electrodes, and graphite felt electrodes are also viable cathode materials. King et al. utilized activated carbon cathodes in 100 mM phosphate electrolyte for electrocatalytic reduction of halogenated alkanes, observing degradation consistent with first-order kinetics with degradation rates reaching 90% [71]. Higher substitution of halogen groups correlated with slower degradation rates. Carbon materials are also common electrode modification materials, enhancing the dispersion of catalytic metals and preparing efficient and stable composite electrodes. Lou et al. fabricated a novel Ag@Ni/GF electrode with silver nanoparticles deposited on nickel-coated graphite felt via the self-deposition method [72]. This electrode exhibited high silver content (13.7 mg cm^{-3}), large surface area ($26 \text{ m}^2 \text{ g}^{-1}$), and excellent electrocatalytic performance toward chloroacetanilide herbicides like metolachlor. It achieved a dechlorination conversion rate of 96%–99% for an initial concentration of 50 mg L^{-1} metolachlor, with a current efficiency of 36.6%, and selectively generated 76.1% dechlorinated metolachlor.

4.3. ER of Nitrate

ER technology has emerged as a promising approach for nitrate removal due to its efficiency and tunability. Non-metallic electrodes, particularly boron-doped diamond (BDD) electrodes, have garnered significant interest for their high wear and corrosion resistance. García et al. demonstrated complete nitrate removal from slaughterhouse wastewater within 180 min at 35.7 mA cm^{-2} using BDD electrodes without additional reagents, primarily converting nitrate to N_2 gas [73]. However, the high cost of chemical vapor deposition limits the widespread application of BDD electrodes. Other non-metallic electrodes often face limitations such as insufficient activity, slow kinetics, and low reduction efficiency.

Metal oxide electrodes, particularly those composed of transition metals like Cu, Co, Ag, Ti, Nb, Bi, and Ru, have become a major focus in ER research. These materials offer diverse interfaces, structures, defects, and oxygen vacancies, leading to high nitrate conversion efficiency, Faradaic efficiency, and selective ammonia formation. Wang et al. utilized CuO nanowire arrays, achieving a remarkable nitrate conversion efficiency of 97.0% and an ammonia yield of $0.2449 \text{ mmol h}^{-1} \text{ cm}^{-2}$ at an optimal potential of -0.85 V (vs. RHE). Their work also demonstrated a Faradaic efficiency of 95.8% and ammonia selectivity of 81.2% in a $0.5 \text{ M Na}_2\text{SO}_4$ electrolyte [74]. CoO_x nanosheets with abundant adsorbed oxygen effectively suppressed hydrogen evolution on the electrode. This approach yielded an ammonia production rate of $82.4 \pm 4.8 \text{ mg h}^{-1} \text{ mg}^{-1}$ and a Faradaic efficiency of $93.4 \pm 3.8\%$ at -0.85 V (vs. RHE) [75]. Jia et al. explored the role of oxygen vacancies in nitrate reduction by heating TiO_2 in an H_2 atmosphere, generating TiO_{2-x} [76]. These oxygen vacancies facilitated the incorporation of oxygen atoms from nitrate, weakening N-O bonds and minimizing byproduct formation. Their work achieved a nitrate conversion rate of 95.2%, ammonia selectivity of 87.1%, and a yield of $0.045 \text{ mmol h}^{-1} \text{ mg}^{-1}$ at -1.6 V (vs. SCE) in $0.5 \text{ M Na}_2\text{SO}_4$ electrolyte solution, with a Faradaic efficiency of 85%. Wan et al. pioneered the use of niobium oxides (NbO_x) with oxygen vacancies for nitrate electroreduction to NH_3 [77]. Prepared hydrothermally, the NbO_x catalyst achieved a Faradaic efficiency of 94.5% and an ammonia production rate of $55.0 \text{ } \mu\text{g h}^{-1} \text{ mg}^{-1}$ at -1.15 V (vs. RHE) in a $0.5 \text{ M K}_2\text{SO}_4$ electrolyte.

Recent advancements in ER technology highlight the potential of bimetallic alloy electrodes. These electrodes leverage synergistic effects between constituent metals to enhance performance. Xu et al. designed a low-palladium content alloy with Cu_2O using a layered defect method (Figure 4b) [78]. The combination of cavity defects and surface oxygen vacancies in this bimetallic catalyst synergistically promoted nitrate adsorption, weakened N-O bonds, and limited byproduct formation. Their work achieved an ammonia yield of $925.11 \mu\text{g h}^{-1} \text{mg}^{-1}$, Faradaic efficiency of 96.56%, and maximum ammonia selectivity of 95.31% at -1.3 V (vs. SCE) in a $0.5 \text{ M K}_2\text{SO}_4$ electrolyte solution. Similarly, Wang et al. electrochemically deposited $\text{Cu}_{50}\text{Ni}_{50}$ alloy nanoparticles, achieving a near-perfect Faradaic efficiency of $99 \pm 1\%$ at a low potential of -0.15 V (vs. RHE) in a 1.0 M KOH electrolyte [79]. This efficiency improvement was attributed to the d-band center shift of the $\text{Cu}_{50}\text{Ni}_{50}$ alloy catalyst toward the Fermi level, enhancing the adsorption of intermediate species. Wang et al. further explored Pt_xRu_y alloy nanoparticles prepared via NaBH_4 reduction, demonstrating a Faradaic efficiency exceeding 93% for nitrate reduction to ammonia in a $1.0 \text{ M H}_2\text{SO}_4$ electrolyte solution [80]. This ongoing research on ER technology suggests a promising future for nitrate removal, with bimetallic alloy electrodes offering particularly high efficiency and selectivity.

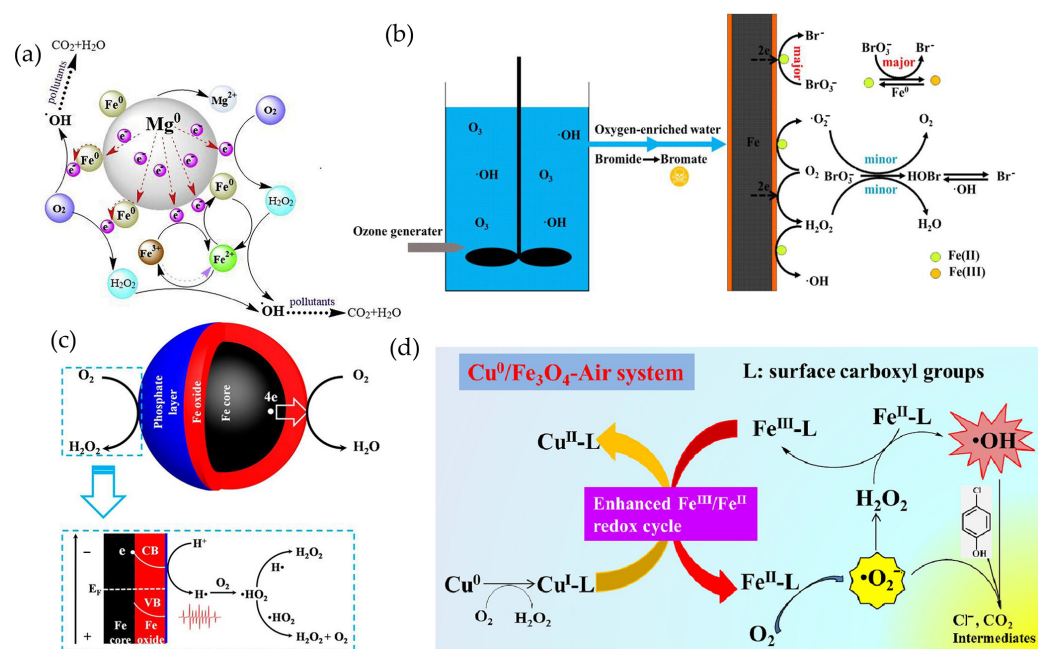
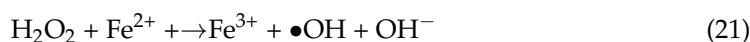


Figure 4. (a) The mechanism of degradation of 4-chlorophenol through EFP with the activation of ZVMs. (b) A possible mechanism of bromate removal through EFP activated by core-shell $\text{Fe@Fe}_2\text{O}_3$ nanowires. (c) Schematic illustration for enhanced H_2O_2 generation with $\text{Fe@Fe}_2\text{O}_3$ Core-Shell nanowires in the presence of phosphate. (d) Possible mechanism of EFP with the activation of O_2 on $\text{Cu}^0/\text{Fe}_3\text{O}_4$ composites.

5. EFP

In 1876, the use of a mixture of H_2O_2 and Fe^{2+} to degrade tartaric acid marked the beginning of the Fenton process and its related chemical reactions. Fenton reaction technology offers advantages such as rapid reaction rates, low toxicity, and environmental compatibility, playing a crucial role in water pollution treatment. However, traditional Fenton methods suffer from several notable drawbacks including a narrow effective pH range, substantial generation of hazardous iron sludge when pH exceeds four, significant safety risks associated with H_2O_2 storage and transportation, uncontrollable reaction rates [81]. These limitations have spurred the development of advanced Fenton technologies, such as the sono-Fenton process, photo-Fenton process, and electro-Fenton process (EFP) [82,83].

EF, gaining significant traction since the 2000s, offers a more controllable and cost-effective approach. EF processes address the limitations of traditional Fenton by generating H_2O_2 in situ at the cathode through a two-electron oxygen reduction reaction. This eliminates the need for external H_2O_2 addition, reducing handling complexity and costs. Moreover, EFP facilitates the continuous regeneration of Fe^{3+} back to Fe^{2+} through electrochemical processes, mitigating iron sludge production. The core principle of EFP relies on the generation of highly oxidizing hydroxyl radicals ($\bullet\text{OH}$) from H_2O_2 and Fe^{2+} , which degrade organic pollutants in wastewater to harmless products like CO_2 and H_2O (Equation (21)).



EF processes can be categorized into three types based on the source of Fe^{2+} and H_2O_2 : cathodic electro-Fenton process with oxygen reduction (EFP- H_2O_2), sacrificial anode electro-Fenton process (EFP- Fe_{ox}), and cathodic and Fe^{2+} recycling electro-Fenton process (EFP- H_2O_2 - Fe_{re}). In the EF- H_2O_2 process, H_2O_2 is generated at the cathode while Fe^{2+} needs to be added externally to react with H_2O_2 and produce $\bullet\text{OH}$ radicals (Equation (22), Figure 1d). Conversely, the EF- Fe_{ox} process utilizes a sacrificial anode to generate Fe^{2+} and requires external H_2O_2 (Equation (23), Figure 1e). Finally, the EF- H_2O_2 - Fe_{re} process offers a self-sustaining system where O_2 is reduced to H_2O_2 at the cathode, and Fe^{3+} is electrochemically regenerated to Fe^{2+} , eliminating the need for external addition of both reagents (Equation (24), Figure 1f).



The versatility of the EFP allows for its application in various scenarios, including treating soil-washing wastewater [84], oxidizing arsenite for safer drinking water [85], and reducing ammonia nitrogen in water [86]. Additionally, EFP effectively reduces organic loads in diverse industrial wastewaters like those from mixed industries [87], pharmaceuticals [88], and mining operations [89]. With its clean reaction mechanisms, environmental compatibility, and minimal secondary pollution, EFP holds immense promise for the future of wastewater treatment. Current research efforts by scientists worldwide are focused on optimizing electrode materials, and reactor configurations, and integrating EF with other treatment methods for even greater efficacy [90].

5.1. H_2O_2 Electrogeneration in EFP

The electrochemical generation of H_2O_2 at the cathode is a key factor influencing the efficiency of the EFP [91]. The rate and quantity of H_2O_2 generated during the reaction process are heavily influenced by the selected cathode material and its configuration within the reactor [92].

The cathode material is a critical factor for efficient electrogeneration of H_2O_2 in the EFP. It affects the H_2O_2 production rate, current efficiency, and parallel reactions. Moreover, the performance of the cathode determines the energy requirements and costs. Innovative reactor designs using gas pressure or turbulent conditions of the solution can achieve higher O_2 mass transfer and H_2O_2 generation rates. Innovations in cathode design include gas diffusion electrodes and rotating cylindrical electrodes, which pressurize the system and induce turbulence to enhance O_2 mass transfer. Li et al. utilized electrode aeration to provide gas directly within the electrode, facilitating easier gas transport within the electrode and enhancing gas–liquid–solid interfaces with higher O_2 mass transfer and utilization rates [93]. Recently, natural air diffusion electrodes with superhydrophobic three-phase interfaces were used to rapidly produce H_2O_2 ($101.67 \text{ mg h}^{-1} \text{ cm}^{-2}$) with high oxygen utilization rates (44.5–64.9%) [94]. Cathode substrates and diffusion layers enable natural air diffusion into the reduction reaction interface. Gas diffusion electrodes

(GDEs) facilitate the gas diffusion process and accelerate oxygen reduction [95]. However, gas diffusion in GDEs depends on O_2 supply (pure O_2 or air) and electrochemical reactor design. GDEs currently face challenges such as low H_2O_2 production rates, low oxygen utilization rates, and high energy consumption. Therefore, optimizing GDEs to become efficient and economical cathode O_2 supply methods remains a current challenge [96]. Additionally, pressurized reactors in EFP have emerged as a promising strategy to improve the removal efficiency of target compounds. Poza-Nogueiras et al. demonstrated this application by employing a pressurized jet aerator within an EFP system for the elimination of clofibric acid [96]. Their study utilized iron-containing alginate beads as the catalyst and investigated the impact of current intensity (0.12 A and 0.25 A) and pressure (atmospheric vs. 1 bar gauge). Notably, regardless of the applied current, increasing the pressure from atmospheric to 1 bar gauge significantly enhanced the removal of clofibric acid. This improvement was accompanied by a decrease in the specific energy consumption of the electrochemical cell, suggesting a more efficient treatment process under pressurized conditions [97].

To address these challenges, two approaches have been proposed: (i) improving the composition and performance of cathode materials, and (ii) passive diffusion of dissolved O_2 from air, present in wastewater. Significant progress has been made in the first approach using nanotechnology, which modifies, synthesizes, or enhances GDE performance through structural gas transport or accelerated O_2 conversion to H_2O_2 to improve production efficiency, such as catalyst morphology control and heteroatom doping. In the latter approach, passive O_2 diffusion from air to GDE is limited by the mass transfer of O_2 from solution to the cathode and its solubility in water. Research has shown that using natural air diffusion electrodes (NADEs) can enhance H_2O_2 production and utilization efficiency [98]. H_2O_2 production on NADEs reached 158% and 188% when currents of 0.2 A and 1.2 A were applied, respectively, with total energy consumption being only 7.2% and 25.4% of traditional GDEs. These results demonstrate the superiority of NADEs over conventional air electrodes due to their extremely high oxygen mass transfer efficiency and reduced energy consumption.

5.2. Activation of H_2O_2 to Produce $\bullet OH$

The second crucial stage in EFP involves the activation of generated H_2O_2 into highly reactive $\bullet OH$. The efficiency of H_2O_2 utilization in the $\bullet OH$ generation process depends on the chosen catalyst and reaction conditions. Catalytic decomposition of H_2O_2 can be achieved using either homogeneous or heterogeneous catalysts, distinguished by their physical state. Homogeneous catalysts typically use soluble iron salts, offering the advantage of simpler operation. In contrast, heterogeneous catalysts employ iron species or other metal species supported on solid carriers, which are advantageous for their ease of separation from the treated system, facilitating catalyst reusability and recyclability, and making them well-suited for industrial applications.

In homogeneous EFP, the activation of H_2O_2 primarily relies on externally added Fe^{2+} . For instance, researchers achieved a COD removal rate of 56.4% in municipal solid waste leachate (initial COD concentration $\sim 420 \text{ mg L}^{-1}$) after 4 h using Pd/Al_2O_3 and Fe^{2+} catalysts (pH = 3.0), while simultaneously introducing H_2 and O_2 [99].

Zero-valent metals (ZVMs) such as Fe, Al, Zn, Mg, and Cu have been utilized as heterogeneous catalysts in activating EFP [100]. However, for Fenton/Fenton-like processes using ZVMs, they can only convert O_2 into H_2O_2 , thus requiring Fenton/Fenton-like catalysts to decompose in situ generated H_2O_2 into $\bullet OH$. Consequently, various composite materials have been developed, such as Zn/Fe and Mg/Fe (Figure 4a) [101]. In the activation of O_2 by Fe^0 , in-situ-generated $Fe(II)$ can induce the decomposition of H_2O_2 . However, in an Al^0/O_2 system, since Al^{3+} is the only oxidation state accessible in the solution, the formation of $\bullet OH$ is attributed to the transfer of electrons from Al^0 to H_2O_2 [102].

Transition metal composite materials can also serve as heterogeneous catalysts. Due to their partially filled *d*-orbitals, transition metals exist in multiple oxidation states, enabling

them to catalyze the decomposition of H_2O_2 into $\bullet\text{OH}$ in Fenton/Fenton-like processes. Many transition metal ion complexes activate O_2 to degrade pollutants in Fenton/Fenton-like processes through similar reaction mechanisms. In aqueous solutions, dissolved O_2 is activated by washed-out Fe^{2+} to form $\bullet\text{O}_2^-$ intermediates, generating H_2O_2 , which then undergoes a Fenton reaction to produce $\bullet\text{OH}$ radicals for pollutant degradation. Similarly, surface-bound Fe^{2+} can activate O_2 in a heterogeneous manner to generate H_2O_2 and $\bullet\text{OH}$. Goethite and magnetite have also been explored as promising heterogeneous alternatives for EFP [103]. Meijide et al. synthesized a composite containing goethite as the iron source in polyvinyl alcohol–alginate beads. This composite catalyst effectively achieved around 94% TOC removal after 8 h of treatment under optimal conditions (catalyst dosage = 2 g L^{-1} and pH 3) for the mineralization of pyridinium-based ionic liquids via a heterogeneous EFP. Choe et al. developed an EFP system employing a magnetically coated stainless steel mesh as the cathode for methylene blue removal from wastewater [103]. Their findings demonstrated enhanced catalytic activation of in-situ-generated H_2O_2 when the steel meshes were coated with magnetite particles, highlighting the potential of magnetite as a cathode material in EFP systems [104].

Furthermore, composite materials composed of ZVM oxides and transition metal oxides have garnered special attention. The slow generation rate of Fe(II) is the rate-limiting step in heterogeneous Fenton reactions, where ZVM oxides can accelerate the reduction of Fe(III) to Fe(II) , thereby improving the efficiency of H_2O_2 utilization. For example, $\text{Fe@Fe}_2\text{O}_3$ composed of a Fe^0 core and Fe_2O_3 shell can activate O_2 through a two-electron reduction pathway to generate H_2O_2 , and has been employed for the degradation of bromates and 4-CP in engineering applications. The presence of $\text{Fe@Fe}_2\text{O}_3$ nanowires effectively promotes BrO_3^- removal, facilitating its reduction to bromide (Br^-) with the generation of HOBr intermediates. Bromide species analyses and characterizations of the nanowires suggested that surface-bound Fe^{2+} on core–shell $\text{Fe@Fe}_2\text{O}_3$ could effectively promote the EFP. Meanwhile, molecular oxygen competed for electrons from both Fe^{2+} and Fe^0 to generate reactive oxygen species of $\bullet\text{O}_2^-$, H_2O_2 , and $\bullet\text{OH}$ during the BrO_3^- removal process (Figure 4b) [105]. Mu investigated the effect of phosphate on the activation of molecular oxygen with $\text{Fe@Fe}_2\text{O}_3$ nanowires. The oxygen reduction pathway on $\text{Fe@Fe}_2\text{O}_3$ nanowires was gradually shifted from a four-electron reduction pathway to a sequential one-electron reduction one, along with increasing the phosphate concentration from 0 to 10 mmol L^{-1} . This change in ORR greatly enhanced the molecular oxygen activation and ROS generation performances of $\text{Fe@Fe}_2\text{O}_3$ nanowires, and thus increased their aerobic 4-chlorophenol degradation rate by tenfold (Figure 4c) [106]. Similarly, carboxylated $\text{Cu}^0/\text{Fe}_3\text{O}_4$ nanocomposites exploit the synergistic effect of surface carboxyl groups and Cu^0 to enhance $\text{Fe}^{3+}/\text{Fe}^{2+}$ conversion within Fe_3O_4 , ensuring a sustained supply of Fe^{2+} for H_2O_2 decomposition (Figure 4d) [107].

6. Electrocatalytic-Combined Treatment Technology

6.1. Photo-Electrocatalysis

Photo-electrocatalytic (PEC) technology offers a promising approach to environmental remediation by merging the advantages of electrochemical and photocatalytic processes. PEC utilizes a semiconductor photocatalyst to facilitate the separation of photogenerated electron-hole pairs, thereby significantly enhancing catalytic efficiency for various applications. Beyond its high efficiency, PEC technology boasts additional advantages such as low cost, non-toxicity, and remarkable chemical stability. Cerro-Lopez et al. investigated the synergistic effect of PEC technology for pollutant removal from water [108]. The mesostructured $\text{PbO}_2/\text{TiO}_2$ was synthesized and employed in electrocatalytic and photo-electrocatalytic degradation of diclofenac (DCF) with a concentration of 15 ppm in a 0.1 M NaSO_4 solution by applying a current of 30 mA cm^{-2} under different pH conditions. In the electrocatalytic process at pH 6.0, over 50% DCF removal was achieved. Notably, the introduction of UV irradiation during the photo-electrocatalytic experiment led to a significant synergistic effect, enhancing DCF removal efficiency by more than 20% compared to the

electrocatalytic process alone. This enhanced degradation was further confirmed by COD analysis, revealing a 76% reduction in COD under PEC conditions compared to a 42% reduction in the electrocatalytic process. Scavenging experiments identified the involvement of photogenerated holes (h^+), $\bullet OH$, and sulfate-based oxidants in the DCF degradation process. Similarly, Umukoro et al. explored the potential of PEC technology for degrading another pharmaceutical contaminant, ciprofloxacin [108]. A pn MoS_2 - SnO_2 heterojunction fixed on expanded graphite (EG) was employed as the photocathode, displaying a remarkable 78.5% PEC removal efficiency for ciprofloxacin, significantly higher than the 55.5% removal achieved by electrocatalysis alone under a current density of $0.010\text{ A}\cdot\text{cm}^{-2}$. The improvement was attributed to the formation of MoS_2 - SnO_2 p-n heterojunctions, which enhanced the light-harvesting capacity and consequently boosted PEC performance [109].

6.2. Microbial Fuel Cells

Electrocatalytic processes combined with microbial fuel cells (MFCs) present another promising strategy for wastewater treatment. MFCs harness the bioelectrochemical activity of microorganisms to decompose organic matter, generating electrical energy as a byproduct. Electrocatalytic components can be further incorporated within the system to facilitate the degradation of pollutants, leading to a synergistic treatment effect. This integrated approach offers several advantages, including enhanced pollutant removal efficiency and the potential for partial energy recovery through MFCs, reducing the overall energy consumption of the treatment process. Hu et al. explored this synergy by employing a Ni/MXene photoelectrochemical cathode within an MFC for chloramphenicol degradation (Figure 5a) [110]. Under optimized conditions ($pH = 2$), this system achieved a maximum degradation efficiency of 82.62% for an initial chloramphenicol concentration of 30 mg L^{-1} after 36 h. Yap et al. investigated the impact of aeration and catalysts on both caffeine removal and electricity generation within an MFC (Figure 5b) [111]. Their findings revealed that a CuO/C cathode under aerated conditions achieved a significantly higher caffeine removal rate (52.16%) within 24 h compared to a bare carbon plate (3.41%). Additionally, the CuO/C cathode exhibited superior power and current densities ($28.75\text{ mW}\cdot\text{m}^{-2}$ and $253.33\text{ mA}\cdot\text{m}^{-2}$, respectively) under aeration compared to the bare C cathode ($9.75\text{ mW}\cdot\text{m}^{-2}$ and $106.67\text{ mA}\cdot\text{m}^{-2}$). Interestingly, connecting the circuit under aerated conditions further enhanced COD removal in the anode chamber, suggesting a complex interplay between aeration, catalyst selection, and MFC operation. Guo et al. explored the method to enhance the electron transfer efficiency and power output of a microbial fuel cell (MFC) by decorating a commercial carbon paper (CP) anode with a composite material of Mo_2C/RGO (molybdenum carbide/reduced graphene oxide) [112]. This modification significantly increased the power output density ($1747 \pm 37.6\text{ mW m}^{-2}$) compared to the unmodified control ($926.8 \pm 6.3\text{ mW m}^{-2}$). The Mo_2C/RGO composite also facilitated the formation of a three-dimensional hybrid biofilm and effectively improved the interaction between bacteria and the electrode, leading to a substantial increase in Coulombic efficiency (13.2%) compared to the unmodified control (1.2%).

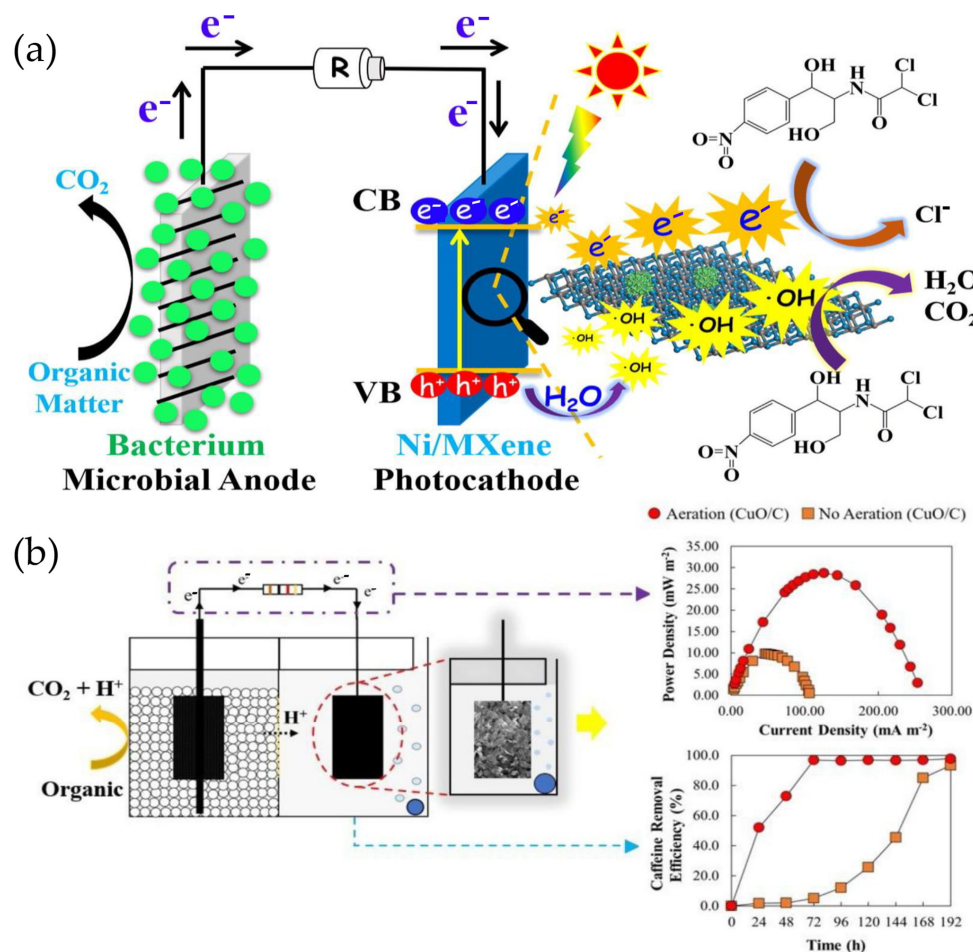


Figure 5. (a) The photo-electrocatalytic mechanism of degradation Chloramphenicol in photo-electrocatalytic microbial fuel cell over Ni/MXene photocathode. (b) The mechanism of caffeine removal and bioelectricity generation in CuO/C cathode-based microbial fuel cell.

7. Cost Analysis of Electrocatalytic Technology

The cost-effectiveness of electrocatalytic technology is paramount for its widespread adoption in practical applications. The total operating cost encompasses several factors including electrode preparation and maintenance, electrical energy consumption, electrolyte consumption, and labor costs.

Among these factors, electrical energy consumption is a major hurdle, particularly for processes like electrochemical combustion, hindering their large-scale implementation. In the context of wastewater treatment, the primary cost contributors are typically the electrical energy required for operation and the cost of the electrode materials themselves. Table 8 summarizes operating cost assessments from various studies. Kaur et al. investigated the economic feasibility of Ti/RuO₂ electrodes for degrading Ofloxacin (OFLX) antibiotic from synthetic wastewater using the IEO method. Under optimal conditions (pH 2, current 1 A, initial OFLX concentration 50 mg L⁻¹, and NaCl concentration 2 g L⁻¹), an impressive 88.6% degradation of OFLX was achieved within 30 min. The study reported a cost of ~USD 0.50 g⁻¹ of TOC removed for the Ti/RuO₂ electrodes. Additionally, the electrical energy consumption at optimal conditions was 541.92 Wh for removing 1 g of TOC in 1 h. Combining the electricity and electrode costs, the total operating cost for TOC removal reached ~USD 0.54 g⁻¹ of TOC removed [113]. Srivastava et al. explored the application of Ti/RuO₂ anodes and Fe cathodes for treating real wastewater containing high nitrate concentrations. This system achieved a maximum nitrate reduction efficiency of 46.18% under specific operating conditions (current density = 214.29 A m⁻², pH = 7.95, and treatment time = 180 min). Electrical energy consumption for this removal rate was calculated

as $108.04 \text{ kWh m}^{-3}$. The cost analysis revealed an electrode cost of $286.25 \text{ USD m}^{-3}$ for the combined anode and cathode setup [114].

Table 8. Total operating cost for different types of pollutants.

Electrode Catalyst	Electrolyte	Pollutants	Electrical Energy Consumed	Cost of Electrical Energy	Cost of Electrodes	Total Operating Cost
BDD, $\text{Ti}_n\text{O}_{2n-1}$, Ti/IrO ₂ -Ta ₂ O ₅	poly (methyl methacrylate)	perfluorooctane sulfonate [115]	4.0 kWh m^{-3}	0.45 EUR m^{-3}	/	0.45 EUR m^{-3}
Ti/RuO ₂	NaCl	pharmaceuticals wastewater	0.542 kWh m^{-3}	0.033 EUR m^{-3}	1.99 EUR m^{-3}	2.02 EUR m^{-3}
Ti/RuO ₂	NH ₄ Cl	nitrate [114]	$108.04 \text{ kWh m}^{-3}$	7.89 USD m^{-3}	$286.25 \text{ USD m}^{-3}$	294 USD m^{-3}
Ti/RuO ₂	/	highly acidic wastewater [116]	$735.72 \text{ kWh m}^{-3}$	36.7 USD m^{-3}	400 USD m^{-3}	436 USD m^{-3}
Al	/	sugar industry wastewater [117]	58 kWh m^{-3}	3.57 USD m^{-3}	2.65 USD m^{-3}	6.22 USD m^{-3}

In response to these economic challenges, researchers are actively exploring cost-reduction strategies, including choosing methods with low manufacturing costs to produce more efficient electrode catalyst materials, or considering the integration of electrocatalytic technology with biofuel cells and other systems to reduce the consumption of electrical energy.

8. Conclusions

This review focuses on elucidating the mechanisms of electrocatalytic technology for the treatment of refractory pollutants and the current research findings, including the preparation of efficient electrode materials, optimization of operational conditions, and cost analysis. Electrochemical water treatment technology has advanced significantly with the continuous development of electrocatalysis theory. However, it still faces shortcomings and challenges, primarily in two aspects. Firstly, the high cost of electrode materials, limited stability, short lifespan, and high energy consumption remain major concerns. Many new electrodes involve expensive materials such as rare earth elements, precious metals, carbon nanotubes, and graphene. The complex preparation methods restrict their widespread application, largely confining electrode development to the experimental research stage. Secondly, the electrocatalytic degradation mechanism remains imperfect. The degradation of organic pollutants in water via electrocatalysis is a complex process. Actual industrial wastewater contains various substances including organic compounds, heavy metal ions, and inorganic salts, complicating the electrocatalytic process. The generation and transformation processes of active radicals during reactions, as well as the reactions of organic chemical wastewater on electrode surfaces and in solution, are still unclear. These uncertainties limit the application of electrocatalytic technology in degrading organic chemical wastewater.

Considering current research and application trends, the future research directions of electrochemical water treatment technology will mainly focus on three aspects. (1) Design and development of electrode materials: Efficient and stable electrode materials are crucial for electrochemical oxidation water treatment technology. Developing electrodes based on optimized electron transfer and micro-interface regulation will directly impact the efficiency of electrochemical oxidation water treatment. Moreover, developing cost-effective electrodes that can be scaled up for practical engineering applications is a current and future research priority. (2) Optimization of operating parameters: To maximize the performance of anode materials, it is essential to explore key operational parameters during degradation processes. Factors such as supporting electrolytes, pH, properties of organic substances, and mass transfer kinetics within reactors are critical for understanding the dynamics of electrocatalytic oxidation processes. Additionally, establishing kinetic models of substance degradation processes will guide the targeted design of anode materials. (3) Recovery of resources and energy: Wastewater pollutants contain significant chemical

energy. Future directions in water pollution control technology involve recovering this chemical energy to simultaneously degrade pollutants and generate energy. By controlling electrode reactions and finely tuning micro-interfaces, efficient separation and targeted conversion of pollutants can be achieved, advancing toward resource recovery and energy utilization in water pollution control technologies.

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