INSIGHTIA JOURNAL OF RESEARCH AND INNOVATION
OPEN-ACCESS JOURNAL | ISSN (ONLINE): [XXXX]

Review

Volume 1, Issue 1 (May-June) 2026
Article No. 05, Pages 01-20
https://doi.org/10.33/IJRI11.05

Electrochemical Degradation of Toxic Industrial Chemicals: Mechanistic Insights, Electrode Materials, and Practical Challenges

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Received: 12 April 2026 | Accepted: 16 June 2026 | Published online: 14 July 2026

Abstract: Electrochemical degradation has emerged as an effective and environmentally sustainable strategy for removing persistent toxic industrial chemicals from contaminated water. This mini-review summarizes recent advances in electrochemical advanced oxidation and reduction processes for degrading aromatic amines, nitroaromatics, phenols, chlorophenols, dyes, pesticides, volatile organic compounds, heterocyclic pollutants, and per- and polyfluoroalkyl substances (PFAS). The review discusses the fundamental degradation mechanisms involving direct electron transfer and indirect oxidation through reactive oxygen species, including hydroxyl, sulfate, and chlorine radicals, alongside cathodic reduction pathways. Particular emphasis is placed on the influence of electrode materials, including boron-doped diamond, PbO_2, SnO_2–Sb, mixed metal oxides, and carbon-based electrodes, as well as reactor configurations that determine treatment efficiency and energy consumption. Critical operational parameters, analytical techniques for identifying transformation products, environmental safety concerns, and hybrid treatment strategies are also examined. Finally, current challenges related to electrode durability, energy demand, by-product toxicity, and industrial-scale implementation are discussed, highlighting future opportunities for developing cost-effective, energy-efficient, and sustainable electrochemical wastewater treatment technologies.

Keywords: Electrochemical degradation; Advanced oxidation processes; Toxic industrial chemicals; Electrode materials; Wastewater treatment; Reactive oxygen species.

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1. Introduction

Rapid industrialization and urban expansion have substantially increased the discharge of persistent toxic organic pollutants into aquatic environments. Industrial effluents generated from pharmaceutical, petrochemical, textile, dye, pesticide, leather, and chemical manufacturing sectors contain diverse classes of hazardous contaminants, including aromatic amines, nitroaromatic compounds, phenols, chlorophenols, azo dyes, pesticides, volatile organic compounds (VOCs), nitrogen-containing heterocycles, and per- and polyfluoroalkyl substances (PFAS) [1–4]. Many of these pollutants exhibit high chemical stability, low biodegradability, bioaccumulative potential, and significant toxicity, posing severe risks to aquatic ecosystems and human health. Their prolonged environmental persistence has been associated with carcinogenicity, mutagenicity, endocrine disruption, neurotoxicity, and developmental disorders, making their effective removal a global environmental priority [2,5].

Conventional wastewater treatment technologies, including biological degradation, adsorption, coagulation–flocculation, membrane filtration, and thermal oxidation, often show

limited effectiveness toward these refractory organic contaminants [1,6]. Biological treatment processes are particularly ineffective for compounds containing stable aromatic structures or strong carbon–fluorine bonds, while adsorption and membrane-based technologies merely transfer contaminants from one phase to another, generating secondary waste that requires additional management [6,7]. Similarly, thermal and chemical oxidation methods generally demand high energy consumption, expensive reagents, or harsh operating conditions, thereby limiting their practical and economic feasibility for large-scale wastewater treatment [6].

Electrochemical advanced oxidation processes (EAOPs) have emerged as promising and environmentally sustainable alternatives for the degradation of recalcitrant industrial pollutants because of their high oxidation efficiency, operational simplicity, and compatibility with renewable electricity sources [1,8]. Unlike conventional chemical oxidation methods, EAOPs generate highly reactive oxidizing species directly within the electrochemical reactor through the application of electrical current, thereby minimizing the need for external chemical oxidants [8,9]. Depending on the electrode material, electrolyte composition, and operating conditions, anodic oxidation can produce hydroxyl radicals (•OH), sulfate radicals ($SO_4^{\bullet-}$), reactive chlorine species (Cl•, HOCl/OCl^-), singlet oxygen ($^1O_2$), ozone (O_3), and hydrogen peroxide, all of which contribute to the rapid degradation and eventual mineralization of complex organic molecules into carbon dioxide, water, and inorganic ions [9–11]. In parallel, cathodic reduction processes enable selective transformation of reducible contaminants such as nitroaromatic compounds, halogenated organics, and nitrate-containing pollutants, thereby expanding the applicability of electrochemical remediation technologies [1].

The efficiency of electrochemical degradation is strongly governed by electrode materials and reactor configuration. High oxygen evolution overpotential electrodes such as boron-doped diamond (BDD), PbO_2, and Sb-doped SnO_2 favor the production of physisorbed hydroxyl radicals capable of achieving near-complete mineralization of persistent pollutants, whereas active anodes such as IrO_2 and RuO_2 primarily promote mediated oxidation through surface-bound oxygen species [9,12]. Recent advances in nanostructured electrodes, flow-through electrochemical reactors, electro-Fenton systems, and photoelectrocatalytic processes have further improved pollutant degradation kinetics, current efficiency, and energy utilization while facilitating scale-up for industrial wastewater treatment [3,10].

This mini-review critically summarizes recent developments in the electrochemical degradation of toxic industrial chemicals, emphasizing degradation mechanisms, electrode materials, reactor configurations, analytical methods, operational parameters, environmental challenges, and future research directions. Particular attention is given to the mechanistic understanding of electrochemical oxidation and reduction pathways, the identification of transformation products, and engineering strategies required for the practical implementation of sustainable electrochemical wastewater treatment technologies.

2. Classes of Toxic Industrial Chemicals

Industrial wastewater contains a broad spectrum of toxic organic contaminants that differ in their chemical structures, physicochemical properties, persistence, and degradation behavior. These pollutants originate from diverse industrial activities, including petrochemical processing, textile manufacturing, pharmaceutical production, agriculture, metallurgy, pulp and paper industries, and chemical synthesis. Many of these compounds exhibit high chemical stability because of aromatic rings, halogen substitutions, or strong carbon–fluorine bonds, rendering them resistant to conventional biological treatment. Their persistence in aquatic environments leads to bioaccumulation, ecotoxicity, and long-term human health risks, thereby

necessitating the development of efficient remediation technologies such as electrochemical advanced oxidation processes (EAOPs) [13–16].

2.1 *Aromatic Amines*

Aromatic amines, including aniline, toluidines, phenylenediamines, and nitroaniline derivatives, are extensively used as intermediates in the manufacture of dyes, rubber chemicals, pharmaceuticals, pesticides, and polymers. These compounds are also generated during the reductive degradation of azo dyes in wastewater treatment systems. Owing to their aromatic amino groups, aromatic amines exhibit high toxicity, mutagenicity, and carcinogenicity, while their resistance to biodegradation enables prolonged environmental persistence. Their oxidation generally proceeds through hydroxylation, deamination, and aromatic ring-opening reactions before complete mineralization [13,17].

2.2 *Nitroaromatic Compounds*

Nitroaromatic compounds, such as nitrobenzene, nitrophenols, dinitrotoluene, and nitrochlorobenzenes, are widely employed in the production of explosives, dyes, pharmaceuticals, pesticides, and synthetic intermediates. The electron-withdrawing nitro group imparts exceptional chemical stability, making these compounds recalcitrant toward biological degradation. Many nitroaromatics exhibit acute toxicity, carcinogenicity, and mutagenicity, while their degradation frequently involves sequential reduction to nitroso, hydroxylamine, and amino intermediates prior to complete oxidation [13,18].

2.3 *Phenols and Chlorophenols*

Phenolic compounds are common pollutants originating from petroleum refining, coal conversion, resin manufacturing, pharmaceuticals, pesticides, and coking industries. Chlorophenols, particularly 2,4-dichlorophenol and pentachlorophenol, possess even greater persistence because chlorine substitution enhances resistance toward microbial degradation. These compounds are highly toxic to aquatic organisms and humans, exhibiting endocrine-disrupting and carcinogenic effects. Electrochemical oxidation effectively converts phenolic compounds into hydroxylated intermediates followed by aromatic ring cleavage and mineralization [13,19].

2.4 *Synthetic Dyes and Pigments*

Synthetic dyes represent one of the largest classes of industrial water pollutants released primarily from textile, leather, printing, cosmetics, and paper industries. Azo dyes account for nearly 70% of global dye production, whereas anthraquinone, triarylmethane, and indigo dyes constitute other major classes. Their complex aromatic structures, high molecular weight, and chromophoric functional groups impart exceptional stability against light, heat, and microbial degradation. Besides aesthetic pollution, dye-containing wastewater reduces light penetration and dissolved oxygen levels, adversely affecting aquatic ecosystems [16,20].

2.5 *Pesticides and Agrochemicals*

Agricultural runoff and agrochemical manufacturing release diverse pesticide residues into surface and groundwater. Common pollutants include phenoxy herbicides (2,4-D), atrazine, glyphosate, carbamates, organophosphates, and organochlorine pesticides. Many pesticides contain heterocyclic, halogenated, or aromatic structures that exhibit remarkable environmental persistence and bioaccumulative potential. Chronic exposure has been associated with neurotoxicity, endocrine disruption, reproductive toxicity, and ecological damage [15,21].

2.6 *Volatile Organic Compounds (VOCs)*

Volatile organic compounds such as benzene, toluene, ethylbenzene, xylene (BTEX), trichloroethylene, perchloroethylene, and chlorinated methanes are extensively used as industrial solvents, degreasing agents, fuel additives, and paint components. Because of their high volatility and mobility, VOCs contaminate both groundwater and the atmosphere, posing serious occupational and environmental hazards. Several VOCs, particularly benzene and chlorinated solvents, are recognized human carcinogens and are difficult to remove completely using conventional treatment methods [14,22].

2.7 *Nitrogen- and Sulfur-Containing Heterocyclic Compounds*

Nitrogen- and sulfur-containing heterocyclic compounds, including pyridine, quinoline, pyrimidine, indole, thiophene, and benzothiazole derivatives, are frequently encountered in pharmaceutical manufacturing, petroleum refining, coal tar processing, pesticides, and dye industries. Their aromatic heterocyclic structures confer exceptional chemical stability and resistance toward microbial degradation. Many heterocyclic compounds exhibit significant toxicity and persist in wastewater unless subjected to advanced oxidation or electrochemical treatment [13,23].

2.8 *Per- and Polyfluoroalkyl Substances (PFAS)*

PFAS comprise a large family of fluorinated surfactants and specialty chemicals widely used in firefighting foams, non-stick cookware, waterproof textiles, food packaging, semiconductor manufacturing, and electroplating. Representative compounds such as perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) are commonly referred to as "forever chemicals" because of the extraordinary strength of the carbon–fluorine bond. Their persistence, bioaccumulation, long-range transport, and potential adverse health effects—including developmental toxicity, immune dysfunction, and carcinogenicity—have made PFAS one of the most challenging classes of emerging contaminants for environmental remediation [14,24].

2.9 *Emerging Organic Contaminants*

Beyond conventional industrial pollutants, increasing attention has been directed toward emerging contaminants such as endocrine-disrupting chemicals (bisphenol A, phthalates), benzotriazoles used as anticorrosion agents, pharmaceuticals, personal care products, flame retardants, and plastic additives. These contaminants are frequently detected at trace concentrations but may induce chronic toxicity, endocrine disruption, antibiotic resistance, and ecological imbalance. Their continuous release into aquatic environments has stimulated considerable interest in advanced electrochemical treatment technologies capable of complete mineralization or detoxification [14,15].

Collectively, these diverse classes of toxic industrial chemicals significantly impair water quality, threaten aquatic biodiversity, and increase risks to human health through bioaccumulation and food-chain transfer. Their chemical diversity and persistence necessitate versatile treatment technologies capable of achieving efficient degradation while minimizing secondary pollution. Consequently, electrochemical degradation has emerged as a promising strategy for the remediation of complex industrial wastewaters containing both conventional and emerging organic contaminants [13–16].

3. Electrochemical Principles

Electrochemical degradation is based on the conversion of electrical energy into chemical energy to generate highly reactive oxidizing or reducing species capable of transforming persistent organic pollutants into less toxic or completely mineralized products. Depending on the electrode material, electrolyte composition, and operating conditions,

pollutant degradation proceeds through **direct electrochemical reactions** at the electrode surface or **indirect reactions** mediated by electrogenerated reactive species [24–26].

In **direct anodic oxidation**, pollutant molecules are first adsorbed onto the anode surface, where they undergo electron transfer to form highly reactive radical cations. These intermediates subsequently experience bond cleavage, hydroxylation, dealkylation, dechlorination, or ring-opening reactions, depending on their molecular structure and the catalytic properties of the electrode [24,27]. The degradation efficiency of this pathway largely depends on the adsorption affinity of pollutants and the electrochemical activity of the electrode material.

In contrast, **indirect anodic oxidation** is the predominant degradation mechanism in most electrochemical advanced oxidation processes (EAOPs). During water electrolysis, oxidation of water at the anode generates adsorbed hydroxyl radicals (M–OH•), which can either react directly with organic contaminants or desorb as free hydroxyl radicals (•OH) in solution. These radicals possess an oxidation potential of approximately 2.8 V versus the standard hydrogen electrode (SHE), enabling rapid and non-selective oxidation of a wide range of refractory organic compounds [25,28]. High oxygen evolution overpotential (OEP) electrodes, including boron-doped diamond (BDD), PbO_2, and Sb-doped SnO_2, promote the formation of physisorbed hydroxyl radicals that exhibit superior mineralization efficiency compared with active electrodes such as IrO_2 and RuO_2, where chemisorbed oxygen species predominantly participate in partial oxidation reactions [25,29].

The nature of the supporting electrolyte also significantly influences degradation pathways by generating additional reactive oxidants. Chloride-containing electrolytes produce active chlorine species such as chlorine radicals (Cl•), chlorine gas (Cl_2), hypochlorous acid (HOCl), and hypochlorite ions (OCl^-), which contribute to indirect oxidation of pollutants but may also promote the formation of chlorinated by-products under certain conditions [30]. Similarly, sulfate-based electrolytes can generate sulfate radicals ($SO_4^{\bullet-}$) through electrochemical activation of persulfate or peroxydisulfate. Sulfate radicals possess high oxidation potentials (2.5–3.1 V) and longer lifetimes than hydroxyl radicals, making them particularly effective for degrading highly stable aromatic and fluorinated contaminants [31].

Besides anodic oxidation, **cathodic reduction** provides complementary pathways for the treatment of reducible pollutants. Nitroaromatic compounds are sequentially reduced through nitroso and hydroxylamine intermediates to form aromatic amines, while halogenated organic compounds undergo reductive dechlorination, resulting in detoxification and enhanced biodegradability [24,32]. Electrochemical reduction has also been successfully employed for nitrate removal, converting nitrate into nitrite, ammonia, or nitrogen gas depending on the cathode material and applied potential [33].

Among hybrid electrochemical technologies, the **electro-Fenton process** has attracted considerable attention because of its exceptionally high oxidation efficiency. In this process, dissolved oxygen is electrochemically reduced at the cathode to generate hydrogen peroxide ($O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$), which subsequently reacts with ferrous ions to produce hydroxyl radicals through the classical Fenton reaction ($Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^-$). Continuous in situ regeneration of Fe^{2+} at the cathode sustains radical production and significantly enhances pollutant mineralization [34,35]. Furthermore, photoelectrocatalytic and sonoelectrochemical systems integrate ultraviolet irradiation or ultrasonic cavitation with electrochemical oxidation, thereby increasing reactive oxygen species generation, reducing electrode fouling, and accelerating degradation kinetics [35,36].

Overall, electrochemical advanced oxidation processes involve sequential oxidation or reduction reactions in which complex organic molecules are progressively transformed into oxygenated intermediates, low-molecular-weight carboxylic acids, and finally mineralized into carbon dioxide, water, and inorganic ions. The relative contribution of direct electron transfer, hydroxyl radical oxidation, sulfate radical oxidation, active chlorine chemistry, and cathodic reduction depends on pollutant chemistry, electrode characteristics, electrolyte composition, and reactor operating conditions [24–36]. These mechanistic principles form the basis for designing efficient electrochemical systems capable of treating diverse industrial wastewaters containing persistent organic contaminants (Figure 1).

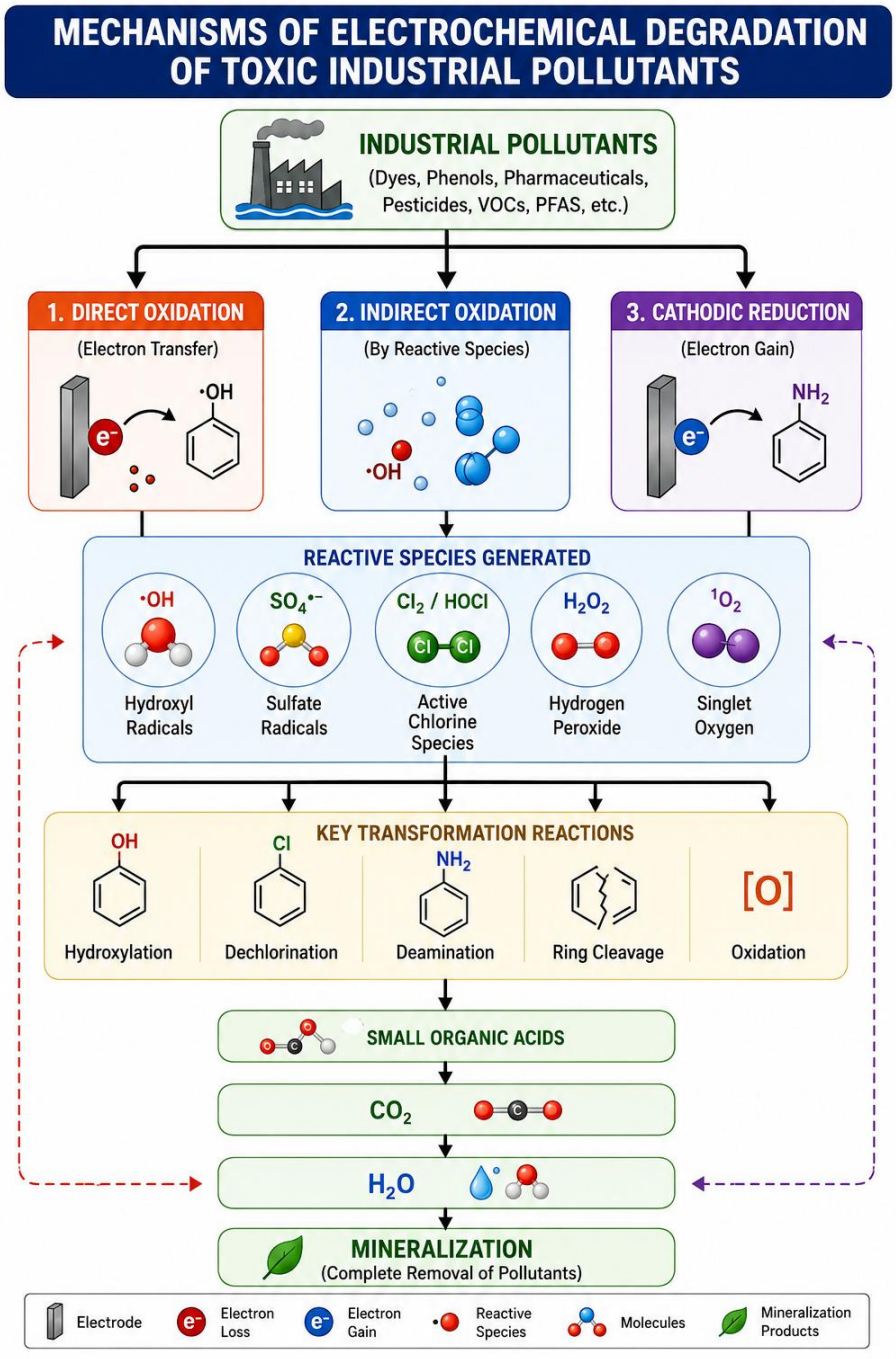


Figure 1. Mechanism of electrochemical degradation.

This flowchart shows the broad pathway: pollutants → radical/oxidised intermediates → lower-molecular-weight organics → mineralisation. Intermediate steps (hydroxylation, dechlorination, decarboxylation, coupling, etc.) depend on chemical structure.

4. Electrode Materials and Reactor Configurations

The efficiency of electrochemical degradation processes is primarily governed by electrode material, reactor architecture, and operating conditions. Electrode properties determine the generation of reactive oxygen species (ROS), electron-transfer kinetics, pollutant adsorption, current efficiency, and long-term operational stability. Likewise, reactor configuration directly influences mass transport, energy consumption, and process scalability. Consequently, selecting appropriate electrode materials and reactor designs is essential for maximizing pollutant mineralization while minimizing operational costs and secondary pollution [37–39].

4.1 Anode Materials

Anodes are the active sites for pollutant oxidation and reactive radical generation in electrochemical advanced oxidation processes (EAOPs). Based on their oxygen evolution behavior, anodes are broadly classified as **inactive** (non-active) and **active** electrodes. Inactive anodes generate weakly adsorbed hydroxyl radicals (•OH), enabling complete mineralization of organic pollutants, whereas active anodes favor the formation of chemisorbed oxygen species that generally promote selective oxidation rather than complete degradation [37,40].

4.1.1 Boron-Doped Diamond (BDD)

BDD is widely recognized as the benchmark anode for wastewater treatment because of its exceptional chemical inertness, broad electrochemical potential window, high oxygen evolution overpotential, and remarkable resistance to corrosion. These characteristics facilitate the generation of large quantities of physisorbed hydroxyl radicals with minimal parasitic oxygen evolution, allowing efficient degradation of highly recalcitrant pollutants including pharmaceuticals, dyes, pesticides, PFAS, and heterocyclic compounds [38,41]. Numerous studies have reported near-complete mineralization efficiencies using BDD electrodes; however, their widespread industrial application remains constrained by high fabrication costs associated with chemical vapor deposition (CVD) technology [38,42].

4.1.2 Lead Dioxide (PbO_2)

PbO_2 electrodes are attractive because of their high electrocatalytic activity, relatively low production cost, and ease of fabrication. They generate abundant hydroxyl radicals and exhibit excellent oxidation capability toward phenols, aromatic amines, azo dyes, and pharmaceutical contaminants [39]. Nevertheless, concerns regarding Pb^{2+} leaching, gradual electrode degradation, and environmental toxicity have limited their long-term application despite recent advances in doped PbO_2 coatings that improve stability and catalytic performance [39,43].

4.1.3 Antimony-Doped Tin Oxide (SnO_2–Sb)

Sb-doped SnO_2 electrodes are another class of inactive anodes characterized by high oxygen evolution potential and strong oxidation capability. They efficiently produce hydroxyl radicals and are particularly suitable for treating low- to medium-strength industrial wastewater containing dyes, pharmaceuticals, and phenolic compounds [37]. However, their relatively low electrical conductivity and limited mechanical stability often result in shorter operational lifetimes compared with BDD electrodes [39].

4.1.4 Mixed Metal Oxides (MMO)

Mixed metal oxide electrodes, particularly Ti/IrO_2 and Ti/RuO_2 dimensionally stable anodes (DSAs), are widely employed in industrial electrochemical systems owing to their excellent mechanical durability, high conductivity, and resistance to corrosion [37,44]. Unlike BDD, MMO electrodes mainly generate chemisorbed oxygen species and active chlorine in

chloride-containing electrolytes, making them particularly effective for electrochlorination processes and oxidation of cyanides and ammonia. However, their relatively lower hydroxyl radical production limits complete mineralization of highly persistent organic contaminants [44].

4.1.5 Carbon-Based and Nanostructured Electrodes

Graphite, glassy carbon, carbon nanotubes (CNTs), graphene, carbon felt, and carbon cloth have gained increasing attention because of their high conductivity, chemical stability, and low cost. These materials are frequently employed as cathodes for hydrogen peroxide production in electro-Fenton systems, although modified carbon anodes have also demonstrated promising oxidation performance [45]. Recent advances in nanostructured electrodes incorporating graphene, metal oxides, transition metals (Ni, Co, Ce), and noble metals (Pt, Pd) have significantly enhanced electron transfer, catalytic activity, and resistance to fouling. Hybrid electrodes such as Ti/Ta_2O_5–SnO_2, graphene/TiO_2, and CNT-based composites have exhibited superior degradation efficiencies toward phenolic compounds and pharmaceutical pollutants compared with conventional electrode materials [38,46], (Table 1).

Table 1. Comparison of commonly used anode materials for electrochemical degradation of industrial pollutants.

Anode material	Oxidation mechanism	Advantages	Limitations	Typical applications
Boron-doped diamond (BDD)	Free •OH radicals	Highest mineralization efficiency; excellent stability	High fabrication cost	PFAS, pharmaceuticals, dyes, pesticides
PbO_2	•OH and active oxygen species	High activity; inexpensive	Pb leaching; moderate stability	Phenols, aromatic amines, dyes
SnO_2–Sb	•OH radicals	High oxidation potential	Poor conductivity; limited lifetime	Textile and pharmaceutical wastewater
Ti/IrO_2, Ti/RuO_2 (MMO)	Active oxygen/chlorine species	Industrial durability; corrosion resistant	Lower mineralization efficiency	Chloride-containing wastewater
Pt/TiO_2	Direct oxidation	High conductivity	Expensive; oxygen evolution	Laboratory and specialized applications
Carbon-based electrodes	Adsorption + electron transfer	Low cost; electro-Fenton compatibility	Moderate oxidation activity	Electro-Fenton, biosystems

4.2 Cathode Materials

Cathodes play a central role in electrochemical reduction and electro-Fenton processes by facilitating oxygen reduction to hydrogen peroxide and promoting reductive transformation of contaminants. Carbon-based materials, including graphite felt, carbon cloth, reticulated vitreous carbon, and carbon nanotubes, are the most widely employed cathodes because of their high conductivity, large specific surface area, and excellent catalytic activity toward the two-electron oxygen reduction reaction (ORR) [45,47]. Gas-diffusion electrodes (GDEs) further enhance oxygen transport, enabling continuous in situ H_2O_2 production and improving hydroxyl radical generation in electro-Fenton systems. Recent modifications using transition metals, heteroatom doping, and nanostructured carbon have substantially increased hydrogen peroxide yield while reducing energy consumption [45,48].

4.3 Reactor Configurations

Beyond electrode selection, reactor configuration strongly influences pollutant transport, current distribution, hydraulic efficiency, and energy utilization. Conventional batch reactors remain valuable for mechanistic investigations but are often limited by concentration

polarization and low mass-transfer rates during scale-up [49]. Continuous flow-by reactors improve hydraulic performance but still rely primarily on diffusion-controlled transport.

Flow-through electrochemical reactors employing porous electrodes or packed-bed architectures significantly enhance convective mass transfer by forcing wastewater through the electrode matrix, thereby improving pollutant-electrode contact and current efficiency [49,50]. Three-dimensional (3D) electrochemical reactors further increase the active surface area through conductive particle electrodes such as granular activated carbon or graphite granules, resulting in higher degradation rates and lower energy consumption than conventional two-dimensional systems [45].

Membrane-divided electrochemical cells utilize cation- or anion-exchange membranes to separate anodic and cathodic compartments, thereby minimizing undesirable side reactions and preventing product recombination. Although membrane reactors improve selectivity and product recovery, they also increase electrical resistance and operational cost [37]. More recently, electrochemical membrane reactors integrating filtration with electrocatalysis have attracted considerable attention because they simultaneously remove suspended solids and degrade dissolved organic pollutants [50].

Gas-diffusion electrode reactors constitute another important advancement, particularly for electro-Fenton technology, where continuous oxygen supply promotes efficient hydrogen peroxide generation and enhanced pollutant mineralization [48]. These reactors exhibit excellent potential for pilot-scale wastewater treatment owing to their relatively low energy demand and high current efficiency.

Table 2. Representative electrochemical reactor configurations for wastewater treatment.

Reactor type	Configuration	Major advantages	Limitations
Batch reactor	Undivided cell	Simple laboratory operation	Low mass transfer
Flow-by reactor	Parallel electrodes	Continuous operation	Diffusion limitations
Flow-through reactor	Porous electrodes	High current efficiency; scalable	Higher fabrication complexity
Divided cell	Ion-exchange membrane	Reduced side reactions	Increased electrical resistance
3D electrochemical reactor	Particle electrodes	Large active surface area	Electrode fouling
Gas diffusion electrode reactor	Oxygen-fed cathode	High H_2O_2 generation	Gas management required

Overall, recent developments in electrode engineering and reactor design have significantly improved the efficiency and sustainability of electrochemical wastewater treatment. Future research should focus on developing low-cost, environmentally benign electrode materials, optimizing continuous-flow reactor systems, and integrating electrochemical technologies with complementary advanced oxidation processes to facilitate industrial-scale implementation [38,49,50].

5. Mechanistic Pathways

The degradation mechanisms involved in electrochemical advanced oxidation processes (EAOPs) are largely governed by the nature of the pollutant, electrode material, and reactive oxygen species (ROS) generated during electrolysis. Oxidation generally proceeds through **direct electron transfer** at the anode surface or **indirect oxidation** mediated by highly reactive species such as hydroxyl radicals (•OH), sulfate radicals ($SO_4^{\bullet -}$), active chlorine species, and singlet oxygen. Among these, physisorbed hydroxyl radicals generated on non-active anodes (e.g., BDD) possess the highest oxidation potential, enabling rapid mineralization of a broad range of persistent organic pollutants [51–53].

For **aromatic hydrocarbons and phenolic compounds**, hydroxyl radicals initially attack the aromatic ring to form hydroxylated intermediates such as catechol and hydroquinone, followed by successive oxidation to quinones and ring-opening products including short-chain carboxylic acids, which are ultimately mineralized into CO_2 and H_2O [52,54]. In chlorinated phenols, oxidative dechlorination frequently precedes aromatic ring cleavage, thereby reducing the toxicity and persistence of chlorinated intermediates [55].

The electrochemical degradation of **aromatic amines and nitroaromatic compounds** involves both oxidative and reductive pathways. Aromatic amines undergo anodic oxidation via radical cation formation, producing intermediates such as phenylhydroxylamine, nitrosobenzene, and azo compounds before complete ring cleavage. Conversely, nitroaromatic pollutants are preferentially reduced at the cathode through sequential electron-transfer reactions (nitro → nitroso → hydroxylamine → amine), after which the resulting aromatic amines are further oxidized and mineralized [51,56].

Azo dyes are primarily degraded through cleavage of the azo (–N=N–) linkage, resulting in rapid decolorization followed by oxidation of the released aromatic fragments into low-molecular-weight organic acids [57]. Similarly, **nitrogen- and sulfur-containing heterocyclic compounds**, including pyridine and thiophene derivatives, undergo electrophilic attack at heteroatom-containing sites, leading to hydroxylation, deamination or desulfurization, ring opening, and eventual mineralization [53,58].

The degradation of highly persistent **per- and polyfluoroalkyl substances (PFAS)** represents one of the most challenging applications of electrochemical treatment. On boron-doped diamond electrodes, PFAS degradation proceeds via direct electron transfer and decarboxylation, followed by sequential cleavage of carbon–carbon and carbon–fluorine bonds, resulting in progressive shortening of perfluoroalkyl chains before complete mineralization to fluoride ions and carbon dioxide [59]. Identification of transformation products using LC–MS/MS, GC–MS, and high-resolution mass spectrometry has greatly improved mechanistic understanding and enables evaluation of detoxification pathways and environmental safety [52,59,60].

6. Kinetics, Current Efficiency, and Energy Consumption

The kinetics of electrochemical degradation are generally described by a **pseudo-first-order model**, where the degradation rate depends on pollutant concentration, electrode material, current density, and mass-transfer conditions [61,62]. High oxygen evolution overpotential anodes, such as boron-doped diamond (BDD) and PbO_2, typically exhibit faster degradation kinetics owing to their enhanced generation of hydroxyl radicals and reduced competition from oxygen evolution reactions [62,63]. Current efficiency (CE) is an important performance indicator that reflects the fraction of electrical charge effectively utilized for pollutant oxidation rather than parasitic reactions, including oxygen and hydrogen evolution [61]. Energy consumption, commonly expressed as **kWh kg^{-1} COD removed** or **kWh m^{-3} treated**, remains a critical parameter for industrial implementation. It is influenced by cell voltage, current density, wastewater conductivity, and reactor design [64]. Strategies such as optimizing current density, improving mass transfer through flow-through reactors, and integrating electrochemical systems with electro-Fenton or catalytic oxidation processes have been shown to substantially reduce energy demand while maintaining high degradation efficiencies [63–65].

7. Analytical Methods and Identification of Transformation Products

Reliable assessment of electrochemical degradation requires comprehensive identification of both parent pollutants and their transformation products. High-performance liquid chromatography (HPLC), gas chromatography–mass spectrometry (GC–MS), liquid chromatography–mass spectrometry (LC–MS/MS), and high-resolution mass spectrometry (HRMS) are widely employed to quantify contaminant removal and elucidate degradation pathways [66,67]. Mineralization efficiency is commonly evaluated using total organic carbon (TOC) and chemical oxygen demand (COD) analyses, while UV–Vis spectroscopy provides rapid monitoring of chromophore degradation, particularly for dyes and aromatic compounds [66]. Reactive oxygen species are frequently detected using electron paramagnetic resonance (EPR) spectroscopy with spin-trapping agents such as DMPO, alongside fluorescence probes and radical scavenger experiments [62]. Electrochemical impedance spectroscopy (EIS) is additionally used to evaluate electrode stability, charge-transfer characteristics, and surface fouling during prolonged operation [68]. Identification of intermediate products is essential for assessing detoxification because partial oxidation may generate transient compounds with greater toxicity than the parent pollutant. Advanced LC–MS/MS and HRMS analyses have revealed sequential hydroxylation, dechlorination, deamination, and ring-opening reactions for phenols, aromatic amines, pesticides, pharmaceuticals, and PFAS, enabling the proposal of detailed degradation pathways and confirmation of complete mineralization [67–70].

8. Factors Affecting Electrochemical Degradation Performance

The efficiency of electrochemical degradation is strongly influenced by operational parameters, including **solution pH, electrolyte composition, conductivity, current density, temperature, and mass-transfer conditions**. Among these, pH plays a crucial role by regulating pollutant speciation, electrode surface chemistry, and reactive oxygen species (ROS) generation. Electro-Fenton processes typically exhibit maximum efficiency under acidic conditions (pH ≈ 3), whereas anodic oxidation can operate over a broader pH range depending on the electrode material [71,72]. The supporting electrolyte also significantly affects degradation pathways. Sulfate-based electrolytes (Na_2SO_4, H_2SO_4) promote sulfate radical formation, while chloride-containing electrolytes enhance conductivity and generate active chlorine species (Cl_2, HOCl, ClO^-), which accelerate oxidation but may also produce undesirable chlorinated by-products [72,73]. Low wastewater conductivity increases cell resistance and energy consumption, necessitating the addition of supporting electrolytes in many practical applications [74]. Furthermore, natural organic matter (NOM), bicarbonate, carbonate, and other inorganic ions can scavenge hydroxyl radicals, thereby decreasing oxidation efficiency [71]. Reactor hydrodynamics, flow rate, and electrode geometry determine mass-transfer rates and current utilization, while elevated temperatures generally enhance reaction kinetics but may simultaneously increase competing oxygen evolution reactions [74,75]. Therefore, systematic optimization of these parameters is essential to maximize pollutant removal while minimizing energy consumption and secondary reactions.

9. Environmental, Toxicity, and Safety Considerations

Although electrochemical advanced oxidation processes are regarded as environmentally friendly technologies, several environmental and safety challenges must be carefully addressed before large-scale implementation. Incomplete oxidation may generate potentially toxic transformation products, including chlorinated organics, aldehydes, quinones, and low-molecular-weight carboxylic acids, necessitating comprehensive identification and toxicity assessment of intermediates [76,77]. The use of chloride-containing electrolytes may further promote the formation of chlorate and perchlorate during prolonged electrolysis,

requiring optimization of operating conditions or post-treatment polishing steps [72]. Electrode stability also remains an important concern, particularly for PbO_2 and metal oxide electrodes that may release trace metal ions during long-term operation [73]. In addition, anodic and cathodic reactions produce oxygen, chlorine, and hydrogen gases, requiring appropriate ventilation and gas management to ensure operational safety [74]. Despite these limitations, electrochemical technologies generate minimal sludge compared with conventional chemical oxidation methods and can be readily coupled with renewable electricity, reducing greenhouse gas emissions and improving overall sustainability [75,78]. Future industrial deployment should therefore integrate life-cycle assessment, techno-economic analysis, and regulatory compliance to ensure environmentally safe and economically viable wastewater treatment, particularly for highly persistent contaminants such as PFAS and pharmaceutical residues [78–80].

10. Integration with Complementary Technologies

Electrochemical advanced oxidation processes (EAOPs) are increasingly integrated with complementary treatment technologies to enhance degradation efficiency, reduce energy consumption, and achieve complete mineralization of complex industrial effluents. Among these, **adsorption–electrochemical systems** employing granular activated carbon (GAC) or biochar effectively concentrate pollutants before electrochemical oxidation, thereby improving removal efficiency and extending electrode lifetime [81]. **Electro-Fenton** and **bio-electrochemical systems** combine in situ hydroxyl radical generation with biological degradation, enabling efficient treatment of refractory organic pollutants while reducing operational costs [82]. Similarly, **photoelectrocatalysis**, utilizing UV or solar irradiation with semiconductor electrodes such as TiO_2 or BDD, enhances reactive oxygen species (ROS) production and accelerates pollutant mineralization [83]. Emerging hybrid technologies, including **sono-electrochemical oxidation**, **electrochemical membrane reactors**, and **membrane bioreactor–electrochemical systems**, further improve mass transfer, mitigate electrode fouling, and facilitate continuous wastewater treatment, (Figure 2). These integrated approaches have demonstrated superior performance compared with standalone electrochemical processes and represent promising strategies for treating complex industrial wastewater containing multiple contaminant classes [84–86].

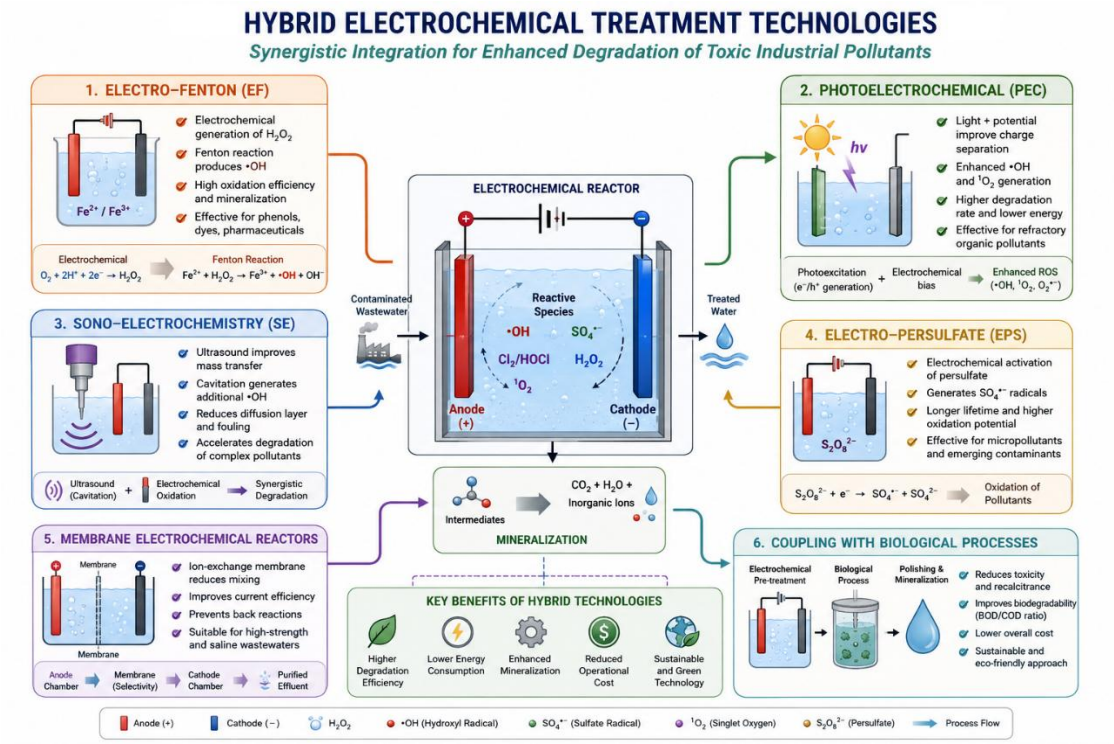


Figure 2. Hybrid electrochemical treatment technologies.

11. Scale-Up and Reactor Engineering

Despite remarkable laboratory-scale success, the industrial implementation of electrochemical wastewater treatment remains challenging due to limitations associated with reactor design, electrode cost, and energy consumption. Scale-up requires optimization of electrode surface area, current distribution, hydraulic flow patterns, and mass-transfer characteristics to ensure uniform oxidation and minimize energy losses [87]. Continuous-flow electrochemical reactors, flow-through porous electrodes, three-dimensional particle-electrode systems, and multi-electrode stack configurations have demonstrated improved treatment capacity and current efficiency under pilot-scale conditions [84,88]. However, the high capital cost of advanced electrode materials, particularly boron-doped diamond, continues to restrict widespread commercialization. Future scale-up efforts should prioritize long-term validation using real industrial effluents, coupled with techno-economic analysis, life-cycle assessment, and process intensification strategies to establish economically viable and environmentally sustainable treatment systems [83,87,89], (Figure 3).

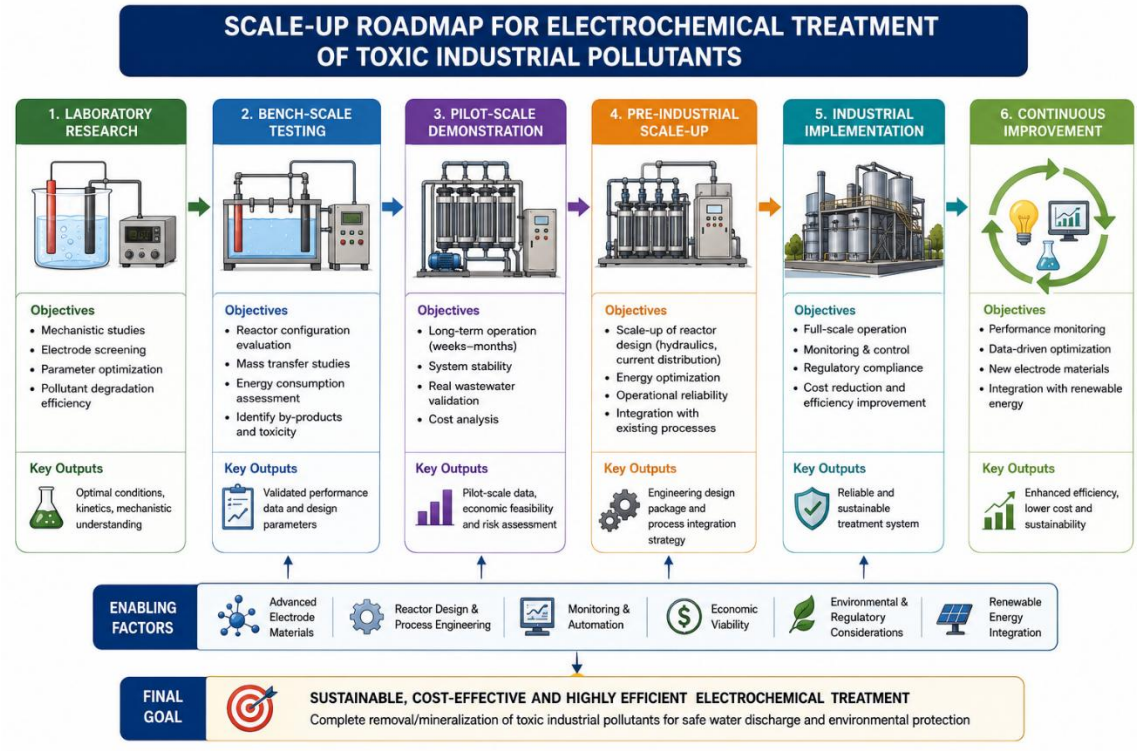


Figure 3. Scale-up roadmap.

12. Future Perspectives and Research Gaps

Although electrochemical technologies have demonstrated outstanding potential for degrading persistent industrial pollutants, several scientific and engineering challenges remain before large-scale commercialization can be achieved. Future research should focus on the development of **low-cost, highly durable electrode materials**, including doped boron-doped diamond, Magnéli-phase titanium oxides, graphene-based composites, and other nanostructured electrocatalysts with enhanced radical generation and resistance to deactivation [90,91]. Advanced mechanistic investigations combining high-resolution analytical techniques, density functional theory (DFT), and machine learning are expected to improve understanding of degradation pathways and facilitate prediction of transformation products [92]. Greater emphasis should also be placed on integrating electrochemical oxidation with biological, photocatalytic, membrane, and renewable energy technologies to improve energy efficiency and achieve complete pollutant mineralization [84,85]. Furthermore, future studies should incorporate real-time process monitoring, digital process control, standardized toxicity assessment of transformation products, and comprehensive techno-economic and life-cycle analyses to support regulatory acceptance and industrial deployment. Addressing these challenges will accelerate the transition of electrochemical advanced oxidation processes from laboratory research to sustainable full-scale wastewater treatment technologies for emerging contaminants, including PFAS, pharmaceuticals, and industrial chemicals [89–93].

13. Conclusions

Electrochemical oxidation and reduction present versatile methods for degrading a broad spectrum of toxic industrial chemicals. By selecting appropriate electrode materials (Table 1) and reactor configurations (Table 2), and by understanding mechanistic pathways, practitioners can optimize removal efficiency and energy use. Advanced analytical tools enable tracking of pollutants and by-products, ensuring complete detoxification. Key challenges remain in electrode longevity, scale-up, and minimizing secondary pollution. Continued interdisciplinary research – spanning electrochemistry, materials science, environmental

engineering, and analytics – is essential to translate laboratory success into practical treatment systems. With ongoing innovation, electrochemical degradation could become a mainstream technology for sustainable wastewater remediation of even highly recalcitrant contaminants.

Author Contributions

Neha Choudhary: Conceptualization, Methodology, Investigation, Data Curation, Formal Analysis, Visualization, Writing Original Draft, Writing Review & Editing, Validation, Supervision, and Final Approval of the Manuscript.

Institutional Review Board Statement

Not applicable

Informed Consent Statement

Not applicable.

Data Availability Statement

No new data were created or analyzed in this study. Data sharing is not applicable.

Funding

This research received no external funding.

Acknowledgments

The author sincerely expresses heartfelt gratitude to the management and I.F.T.M University, Moradabad, U.P., India, for providing continuous encouragement, academic guidance, and an inspiring research environment during the preparation of this review.

Conflicts of Interest

The authors declare no conflict of interest.

Abbreviations

The following abbreviations are used in this manuscript:

Abbreviation	Definition
AO	Anodic Oxidation
AOPs	Advanced Oxidation Processes
BDD	Boron-Doped Diamond
BTEX	Benzene, Toluene, Ethylbenzene, and Xylene
CE	Current Efficiency
COD	Chemical Oxygen Demand
CNTs	Carbon Nanotubes
CO_2	Carbon Dioxide
CVD	Chemical Vapor Deposition
DSA	Dimensionally Stable Anode

EAOPs	Electrochemical Advanced Oxidation Processes
EIS	Electrochemical Impedance Spectroscopy
EPR	Electron Paramagnetic Resonance
GC–MS	Gas Chromatography–Mass Spectrometry
GAC	Granular Activated Carbon
GDE	Gas Diffusion Electrode
H_2O_2	Hydrogen Peroxide
HPLC	High-Performance Liquid Chromatography
HOCl	Hypochlorous Acid
HRMS	High-Resolution Mass Spectrometry
LC–MS/MS	Liquid Chromatography–Tandem Mass Spectrometry
MMO	Mixed Metal Oxide
Na_2SO_4	Sodium Sulfate
NOM	Natural Organic Matter
OCl^-	Hypochlorite Ion
OEP	Oxygen Evolution Overpotential
ORR	Oxygen Reduction Reaction
PFOA	Perfluorooctanoic Acid
PFAS	Per- and Polyfluoroalkyl Substances
PFOS	Perfluorooctane Sulfonate
PbO_2	Lead Dioxide
ROS	Reactive Oxygen Species
RuO_2	Ruthenium Dioxide
Sb	Antimony
SHE	Standard Hydrogen Electrode
SnO_2–Sb	Antimony-Doped Tin Oxide
$SO_4^{\bullet-}$	Sulfate Radical
TiO_2	Titanium Dioxide
TOC	Total Organic Carbon
UV–Vis	Ultraviolet–Visible Spectroscopy
VOCs	Volatile Organic Compounds
•OH	Hydroxyl Radical
$^1O_2$	Singlet Oxygen

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