

Review

Electrochemical Techniques for the Elimination of Pesticides from Wastewater: Challenges and Emerging Directions

Tanja P. Brdarić , Marija J. Ječmenica Dučić  and Danka D. Aćimović * 

Department of Physical Chemistry, VINČA Institute of Nuclear Sciences-National Institute of the Republic of Serbia, University of Belgrade, Mike Petrovića Alasa 12-14, 11000 Belgrade, Serbia; tanja.brdaric@vin.bg.ac.rs (T.P.B.)

* Correspondence: dankavla@vin.bg.ac.rs

Abstract

This review presents a comprehensive overview of electrochemical-based technologies as emerging and sustainable methods for treating pesticide-contaminated wastewater. Core processes, including electro-Fenton, electrocoagulation, and electrochemical oxidation, as well as their hybrid combinations, have demonstrated high degradation efficiency, operational flexibility, and the ability to achieve complete mineralization of persistent pesticides. A bibliometric analysis covering 1997–2025 reveals growing global interest in these technologies, particularly in hybrid systems such as photoelectro-Fenton and solar-assisted electrochemical treatments, which offer improved degradation rates and reduced energy demand. Compared to conventional and biological approaches, electrochemical methods provide superior pollutant removal without generating excessive sludge or secondary contamination. Future advancements should focus not only on optimizing operational parameters but also on overcoming current methodological limitations through the development of durable and selective electrode materials and the integration of renewable energy sources, ultimately enhancing process efficiency and sustainability. Coupling electrochemical treatments with complementary physicochemical or biological methods may further improve mineralization and reduce costs. Overall, electrochemical technologies represent a promising pathway toward efficient, scalable, and environmentally friendly wastewater treatment systems capable of mitigating pesticide pollution and protecting aquatic ecosystems.

Keywords: electrochemical techniques; pesticides; wastewater treatment; bibliometric analysis; electrochemical oxidation; electro-Fenton; electrocoagulation



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1. Introduction

Pesticides are extensively applied worldwide to control a variety of pest populations. They are generally classified according to their function into categories such as herbicides, insecticides, fungicides, rodenticides, nematicides, microbicides, and growth-regulating agents for plants and insects [1–3]. Their intensive use in agriculture and industrial sectors has contributed to the widespread contamination of both surface and groundwater, a phenomenon closely tied to the regional and seasonal patterns in pesticide application. Among these categories, insecticides stand out due to their broad use in agriculture, industry, healthcare, and household settings [4]. These compounds may be synthetically manufactured or derived from natural plant sources. Since the post-World War II era, insecticide usage has grown significantly, enabling enhanced agricultural productivity.

Nevertheless, these substances readily infiltrate the environment—rain and melting snow can carry them from treated areas into soils and water systems. Once introduced, their chemical resilience allows them to remain for extended periods, often resisting removal by standard wastewater treatment processes [5]. This persistence poses a considerable threat to environmental and public health, as insecticides are linked to chronic toxicity, hormonal imbalances, and genetic damage [4–7]. One major group of modern insecticides is organophosphates (OPPs), a class consisting of esters and thioesters of phosphoric acid. These compounds act by inhibiting acetylcholinesterase (AChE), a key enzyme responsible for the degradation of the neurotransmitter acetylcholine in nerve synapses. Initially introduced as a safer alternative to organochlorine pesticides due to their reduced environmental persistence, organophosphates have nonetheless raised concern because of their broad-spectrum toxicity, which affects both insects and humans [5]. Their extensive use has led to significant environmental contamination, and scientific studies confirm that organophosphate residues are frequently found in aquatic ecosystems just weeks after application. Once in the environment, organophosphates undergo natural degradation, primarily through hydrolysis. The rate and extent of this process are influenced by environmental factors such as pH, the presence of dissolved metal ions, soil microorganisms, and reactive mineral surfaces like iron oxides and clay. These compounds also absorb ultraviolet light in the 240–310 nm range, making them susceptible to photodegradation, either directly through ultraviolet (UV) light absorption or indirectly via reactive species such as oxygen radicals and hydroxyl or peroxy radicals generated by other photochemical reactions. A particularly concerning transformation pathway involves the oxidation of thio-organophosphates into oxons under the influence of sunlight and naturally occurring oxidants. Compared to their parent compounds, oxons are more water-soluble, are less likely to bind to soil particles, and exhibit stronger inhibitory activity against AChE—significantly increasing their toxicity. Environmental persistence of these substances is determined by the catalytic properties of soil, intensity of solar radiation, and climatic conditions such as rainfall [5,6]. Due to their hazardous nature, organophosphate insecticides are subject to strict regulatory oversight, especially in the European Union. Directive 2013/39/EU, which focuses on priority substances in water policy, lists several pesticides as dangerous compounds that must be monitored and controlled in surface waters. Furthermore, Regulation (EC) No. 1107/2009 governs the market authorization of pesticides, mandating thorough toxicological and ecotoxicological assessments prior to approval. Many other countries have implemented similar measures, guided by the standards of the World Health Organization and Codex Alimentarius, to regulate pesticide residues in water and food. In response to these environmental and health concerns, it is critical to develop efficient strategies for removing pesticide contaminants from soil and water. Such efforts not only help protect ecosystems and public health but also ensure compliance with evolving international and national environmental standards [6].

Among the pesticides commonly used in agriculture, carbamates, urea-based compounds, phenoxyacetic acids, triazines, and neonicotinoids are particularly important due to their widespread application, distinct modes of action, environmental persistence, and potential risks to non-target organisms. Carbamates, such as methomyl, carbaryl, carbofuran, and aldicarb, are reversible acetylcholinesterase-inhibiting pesticides used as insecticides, fungicides, and nematicides; they are widely applied in agriculture due to high efficacy and moderate biodegradability but can still pose acute and chronic risks to non-target organisms [7–9]. Urea-based pesticides, including phenylureas, sulfonylureas, and derivatives like tebuthiuron, act as herbicides or insecticides by inhibiting photosystem II, acetolactate synthase, or chitin synthesis in larvae; despite short half-lives, residues can enter the food chain and cause long-term toxic effects [10–14]. Phenoxyacetic acids,

such as 2,4-D, are synthetic auxin herbicides that disrupt plant growth; their persistence and mobility can lead to human and environmental exposure, prompting treatments like biodegradation, oxidation, ozonation, and adsorption [15–18]. Triazines, including atrazine, are stable herbicides that inhibit photosystem II and persist in soil and water, raising risks for aquatic ecosystems and non-target organisms [19–23]. Neonicotinoids, such as imidacloprid, clothianidin, nitenpyram, and thiamethoxam, are systemic insecticides acting on nicotinic acetylcholine receptors; highly persistent and water-soluble, they contaminate soils and water, threaten pollinators and aquatic life, and disrupt ecological food webs, with potential mammalian toxic effects [24–30].

The chemical structure and environmental interactions of pesticides determine their persistence, mobility, and bioavailability in soils, the atmosphere, and aquatic systems. Their fate in the environment largely depends on adsorption and desorption mechanisms on soil particles. Pesticides are often indirectly transported into aquatic ecosystems through surface runoff, reaching rivers, lakes, and oceans. Considering their increasing occurrence in wastewater and their adverse effects on ecosystems and living organisms, researchers have been actively developing and optimizing various remediation technologies based on biological and chemical treatments to achieve effective removal. However, conventional treatment methods are often ineffective in eliminating many pesticides and their residues due to their high stability and persistence. Biological treatment processes rely on microbial degradation; nevertheless, many pesticides are recalcitrant or toxic to microorganisms, limiting biodegradation efficiency [31]. Furthermore, photolysis as a standalone technique for pesticide removal is often limited by its low mineralization efficiency, leading to partial degradation of contaminants and/or their transformation into more toxic intermediates during photodegradation [32,33]. Like adsorption, membrane-based processes—including microfiltration, ultrafiltration, nanofiltration, and reverse osmosis—primarily concentrate pesticides rather than achieving their complete removal from the environment [34]. Adsorption methods, although highly efficient at removing contaminants from water, similarly do not lead to final degradation, as the pollutants are transferred to another phase, often requiring regeneration or disposal of the adsorbent [35–37]. Membrane-based techniques also face high operational costs, along with challenges such as membrane fouling and scaling, which reduce long-term efficiency. Additionally, the concentrated reject stream generated by membranes contains elevated levels of pesticides, posing further environmental risks if not managed properly. Consequently, while both adsorption and membrane processes are effective for removing pesticides from water, they often need to be integrated with other treatment methods to achieve complete degradation or safe elimination of these contaminants from the environment.

One promising approach involves advanced oxidation processes (AOPs), such as photolysis, Fenton, photo-Fenton, and ozonation, which have been extensively studied for the degradation of pesticides in water due to their ability to generate highly reactive species, primarily hydroxyl radicals ($\cdot\text{OH}$), capable of mineralizing persistent organic contaminants. However, conventional AOPs have several limitations. Photolysis often results in partial degradation and the formation of more toxic intermediates, while Fenton-based and ozonation processes are constrained by pH sensitivity, high reagent or energy consumption, and secondary waste generation [32,33]. Additionally, many AOPs require prolonged treatment times or high energy inputs to achieve significant pesticide removal, limiting their practical applicability [5].

Electrochemical techniques, particularly electrochemical oxidation (EO) and electro-Fenton (EF) processes, represent a subclass of AOPs that overcome many of these limitations. In EO and EF, reactive species are generated in situ at the anode or in the bulk solution through an applied electric current, eliminating the need for external chemical

oxidants. These methods can achieve complete mineralization of recalcitrant pesticides, are operable across a wider pH range, and produce less secondary waste compared to conventional AOPs [38]. When combined with other processes such as adsorption, photolysis, ultrasound, or ozonization, electrochemical methods—including electrocoagulation, electrooxidation, and electro-Fenton—offer a versatile, efficient, and environmentally sustainable approach for pesticide removal from contaminated water [39]. These techniques enhance the breakdown of persistent pesticide molecules that are resistant to conventional treatment, promoting both degradation and mineralization. The integration of electrochemical and complementary oxidation methods has led to the development of advanced hybrid systems—such as photoelectro-Fenton (PEF), solar photoelectro-Fenton (SPEF), electroperoxone, sonoelectrochemical, and sono-electro-Fenton (SEF) processes—which have demonstrated superior performance in eliminating a wide range of pesticides from aqueous environments. By generating highly reactive species capable of attacking complex organic structures, these hybrid approaches achieve more complete pesticide degradation, reduced toxicity of by-products, and improved overall treatment efficiency compared to single-process methods [40,41].

This paper provides a comprehensive and systematic overview of electrochemical-based technologies as emerging and promising approaches for the treatment of pesticide-contaminated wastewater. These technologies include electro-Fenton, electrocoagulation, electrochemical oxidation, and a range of integrated and hybrid electrochemical processes. Although previous reviews have largely centered on individual pesticide removal strategies—such as AOPs, adsorption, or biodegradation—studies dedicated exclusively to electrochemical technologies remain limited. To the best of our knowledge, no previous review has simultaneously offered a focused assessment of electrochemical techniques (electrochemical oxidation, electro-Fenton, and electrocoagulation) for pesticide wastewater treatment and a bibliometric analysis of research trends across different pesticide classes. Here, a bibliometric analysis spanning 1997–2025 is performed to identify publication trends, research hotspots, and the evolution of electrochemical methods in this field. Considering the substantial progress in wastewater treatment research over recent decades, a critical evaluation is essential to highlight the growing role and potential of electrochemical technologies in mitigating pesticide pollution and safeguarding environmental quality.

2. Search Methodology and Bibliometric Overview

2.1. Research Metric

In order to quantitatively evaluate research trends, influence, and knowledge structure within the selected topic, bibliometric indicators were employed. These metrics provide an objective insight into publication performance, collaboration patterns, and thematic evolution across the literature. The applied workflow, including literature retrieval, screening criteria, and data extraction and analysis steps, is summarized in Figure 1.

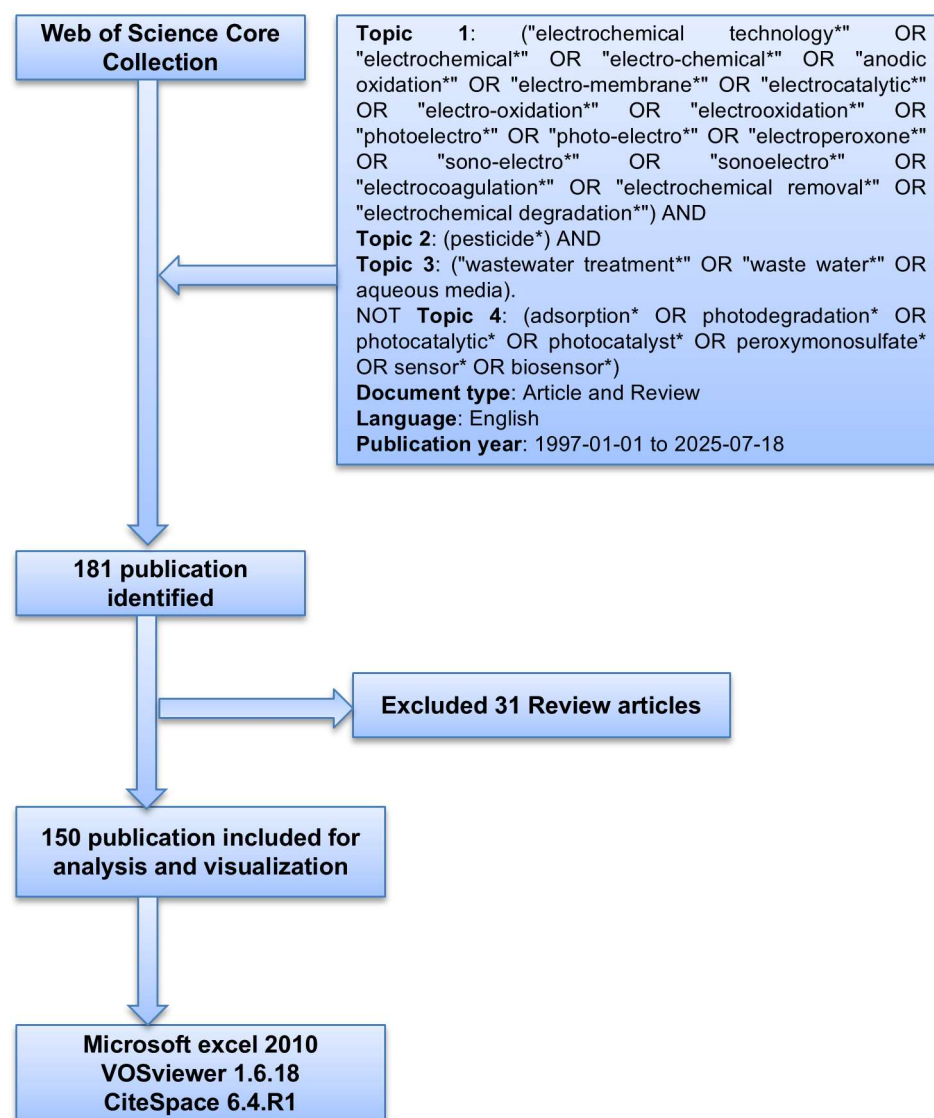


Figure 1. Flowchart of the Bibliometric Workflow: Literature Retrieval, Screening, and Analysis.

2.1.1. Literature Search Strategy

The relevant peer-reviewed publications focusing on the application of electrochemical processes for the degradation of pesticides in aqueous environments were systematically identified through the Web of Science Core Collection database (WoS). The study encompassed papers published over the last period from 1997 to 2025. The data collection was completed on 18 June 2025, ensuring inclusion of all relevant publications within this timeframe.

The literature search strategy involved four structured queries targeting terms within the titles, abstracts, and author-provided keywords (Topic). These queries combined the thematic groups as follows:

- Topic 1—Electrochemical technologies:
("electrochemical technology*" OR "electrochemical*" OR "electro-chemical*" OR "anodic oxidation*" OR "electro-membrane*" OR "electrocatalytic*" OR "electro-oxidation*" OR "electrooxidation*" OR "photoelectro*" OR "photo-electro*" OR "electroperoxone*" OR "sono-electro*" OR "sonoelectro*" OR "electrocoagulation*" OR "electrochemical removal*" OR "electrochemical degradation*").
- Topic 2—Pesticides: (pesticide*).
- Topic 3—Wastewater treatment:
("wastewater treatment*" OR "waste water*" OR aqueous media).

To focus on electrochemical processes, publications related to adsorption, photodegradation, photocatalysis, peroxymonosulfate, sensors, and biosensors were excluded by using the Boolean NOT operator with the following terms:

- Topic 4:
(adsorption* OR photodegradation* OR photocatalytic* OR photocatalyst* OR peroxy-monosulfate* OR sensor* OR biosensor*).

2.1.2. Screening Criteria

Each retrieved publication was screened by evaluating authorship, title, and abstract to determine relevance. Only

- original research articles
- review articles
- articles published in English

were considered.

Books, book chapters, and conference proceedings were excluded.

The full-text review applied the following inclusion criteria:

- (i) Studies focusing on electrochemical methods for the removal of pesticides;
- (ii) Description of degradation and/or mineralization of single or mixed pesticides in aqueous matrices;
- (iii) Detailed information on experimental setup, operational parameters, analytical methods, and criteria for assessing treatment efficiency;
- (iv) Comprehensive discussion of results, including
 - Pesticide removal rates;
 - Kinetic analyses;
 - Reductions in chemical oxygen demand (COD) and biochemical oxygen demand (BOD) and total organic carbon (TOC);
 - Influence of operational variables;
 - Comparison with other treatment approaches;
 - Evaluation of energy consumption and operational costs;
 - Toxicity assessments;
 - Identification of degradation by-products with proposed degradation pathways.

Based on the applied criteria, after searching the Web of Science database and performing manual screening to exclude articles that did not meet the criteria,

- 31 review articles and
- 150 research articles

were identified and extracted for further analysis.

2.1.3. Data Extraction and Analysis

For visualizations and network analysis of research articles, we used

- VOSviewer (version 1.6.18) and
- CiteSpace (version 6.4.R1).

The publication dynamics of research articles focusing on electrochemical technologies for pesticide removal from wastewater are presented in Figure 2.

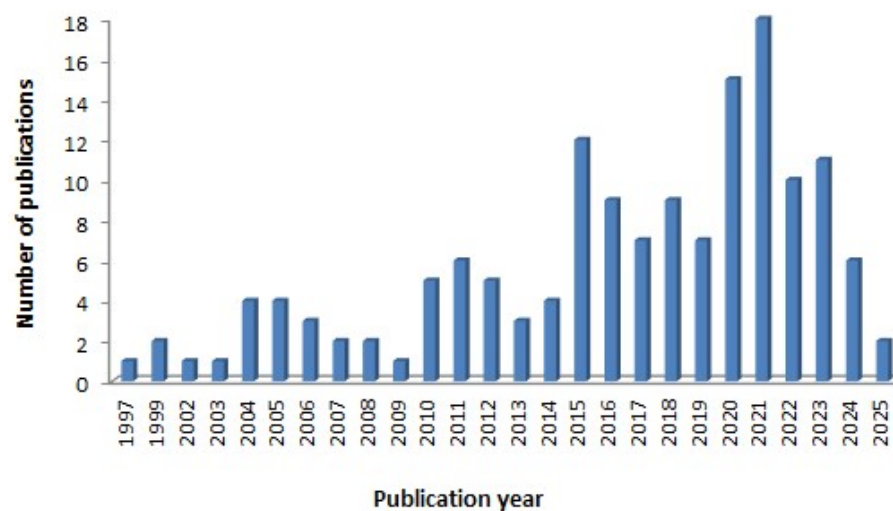


Figure 2. Annual distribution of research articles related to electrochemical technologies for pesticide removal from wastewater.

The data reveal a gradual rise in research interest beginning in the late 1990s, with fewer than five articles published per year until 2010. In the following years, the progressive increase is evident, reaching a publication peak in 2021 with 18 articles. A slight decline in the number of publications has been noted in the following years, which may reflect shifting research priorities or a saturation of the field. However, this trend does not necessarily indicate a real decrease in research activity. The most plausible explanation is the delay in indexing of recently published papers in WoS, since database updates may lag for several months or even more than a year, particularly for the most recent period (2022–2025). Additional contributing factors include thematic saturation, as many foundational studies on widely used EO systems (e.g., BDD, PbO_2) have already been completed, as well as a gradual shift toward emerging technologies such as photocatalytic, photo-assisted, or bio-electrochemical hybrid processes, which may no longer be indexed under classical EO-related keywords. Consequently, the observed decline is primarily linked to indexing delays, while thematic maturity and the redirection of research interest only partially contribute to this pattern.

The analyzed publications were classified into five WoS categories: #0 Environmental Sciences, #1 Chemistry, Applied, #2 Chemistry, Multidisciplinary, #3 Engineering, Chemical, and #4 Electrochemistry (as presented in Figure 3).

This distribution highlights the broad and cross-disciplinary character of research related to pesticide removal and water treatment. A notable overlap between Environmental Sciences and Chemistry, Multidisciplinary suggests that many studies simultaneously address environmental impacts and the chemical or electrochemical mechanisms driving pollutant degradation. The strong representation of Chemistry, Applied and Engineering, Chemical reveals the field's technological orientation, focusing on the development and optimization of treatment processes. Additionally, the inclusion of Electrochemistry reflects the increasing importance of electrochemical-based technologies as innovative and sustainable approaches to pollutant remediation.

2.2. Most Cited Articles

The bibliometric network map of publications cited more than five times was constructed and visualized using VOSviewer and is shown in Figure 4.

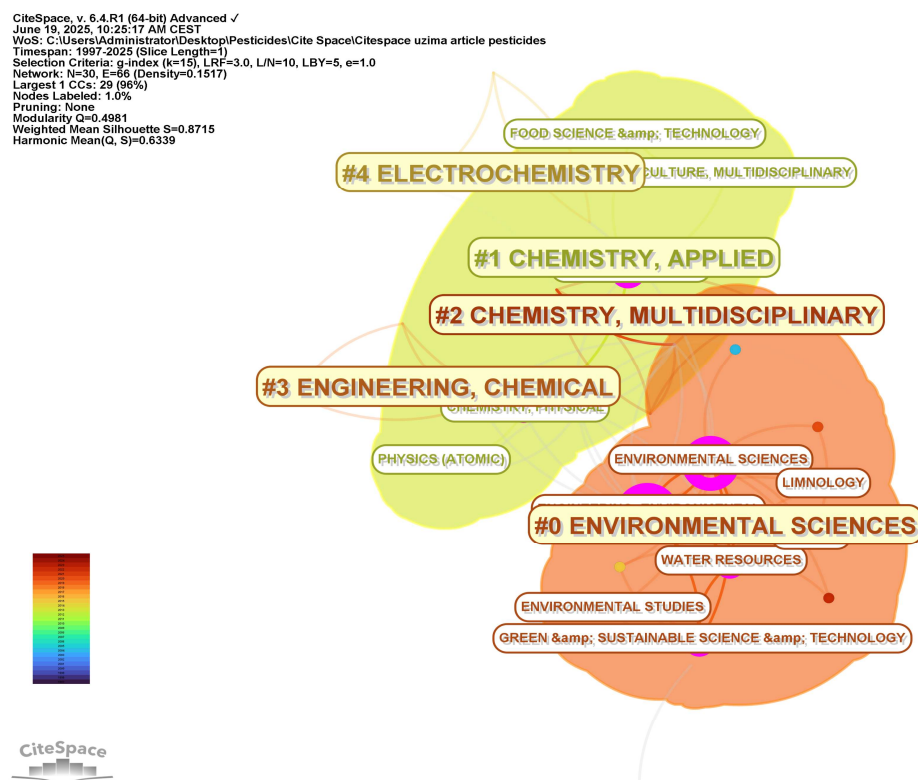


Figure 3. WoS category distribution of the analyzed publications.

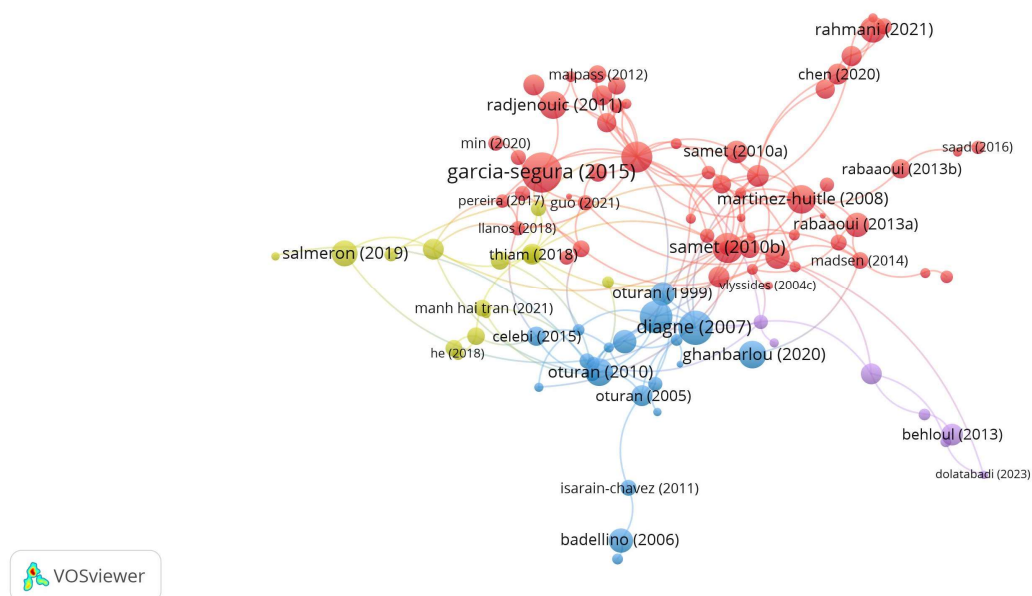


Figure 4. Network visualization of document clusters (≥ 5 citations) based on citation analysis in VOSviewer.

The items are organized into distinct clusters according to their citation relationships, reflecting thematic connections among the studies. Each cluster, represented by a unique color, corresponds to a specific research focus within the field. The red cluster predominantly comprises studies on electrochemical oxidation processes, while the blue cluster includes works centered on electro-Fenton treatment. The purple cluster groups publications addressing electrocoagulation techniques, and the yellow cluster represents studies exploring integrated or hybrid treatment approaches. This clustering structure reveals the main thematic domains of research and illustrates the degree of interconnection between

publications through shared citation networks, thereby mapping the overall structure of research in electrochemical-based pesticide removal studies.

A deeper examination of the cluster network reveals clear differences in scientific influence and thematic maturity. The red cluster is the largest, demonstrating that electrochemical oxidation remains the dominant and most widely cited research line in the field. The blue cluster, associated with electro-Fenton processes, is slightly smaller but still highly prominent, indicating its strong and growing role in advanced electrochemical treatment. The yellow cluster is smaller than the previous two, representing emerging studies on integrated and hybrid electrochemical processes. The purple cluster, focused on electrocoagulation, is the smallest but remains distinct, reflecting its more specialized application scope.

The co-citation links show that the red (EO) and blue (EF) clusters are strongly interconnected, suggesting frequent methodological and mechanistic overlap in the most influential studies. The yellow hybrid cluster exhibits moderate connections with both EO and EF, indicating that hybrid approaches typically build upon these foundational techniques. In contrast, the purple EC cluster is more weakly connected to the others, consistent with the fact that EC is often explored as an independent process with fewer cross-methodological integrations.

Based on the distribution of recent high-citation papers, there is an increasing number of studies focusing on hybrid electrochemical systems, particularly those integrating EO and EF with additional AOP components. This indicates a growing research interest in approaches that aim to enhance degradation performance under complex wastewater systems.

3. Basic Principle of Electrochemical Technologies for Pesticide Removal

Electrooxidation, electro-Fenton, and electrocoagulation are widely applied electrochemical techniques for the removal of organic pollutants from wastewater. Each method exhibits distinct operational characteristics, advantages, and limitations. This section provides a comparative analysis of these processes, emphasizing their treatment efficiency, energy requirements, electrode usage, and sludge formation, based on scientific literature obtained through bibliometric analysis covering the period from 1997 to the present. In addition, a summary table presents relevant publications on pesticide removal from wastewater using these electrochemical technologies.

3.1. Electrochemical Oxidation

Among the most prominent research directions within electrochemical techniques for pesticide removal is EO, owing to its high efficiency, operational simplicity, and potential for complete mineralization of organic pollutants [42,43]. Bibliometric analysis confirms EO as a central topic in current research trends, indicating an increasing interest in this technique within the scientific community. Electrochemical oxidation operates through two main mechanisms: direct oxidation, which involves electron transfer between the pollutant and the anode surface, and indirect oxidation, which relies on the formation of strong oxidizing species—such as hydroxyl radicals, chlorine, (per)bromate, persulfate, ozone, hydrogen peroxide, and percarbonate—to degrade complex pesticide molecules without adding chemicals [44]. While direct oxidation is generally limited by the low likelihood of pollutant adsorption and electron transfer at the electrode, indirect pathways are more effective in achieving complete pesticide mineralization. In particular, processes involving hydroxyl radicals and reactive halogen species exhibit significantly higher potential for breaking down persistent pesticides [45].

With regard to organophosphate and neonicotinoid pesticides, degradation under electrochemical oxidation also predominantly occurs through these two pathways.

For neonicotinoids, such as clothianidin, experimental studies using Ti/Sb-SnO₂-Eu&rGO electrodes indicate that hydroxyl radicals play the main role in degradation. The key chemical steps involve cleavage of the NeN and CeN bonds between the nitroguanidine and thiazole moieties, as well as reduction and removal of nitro groups ($-\text{NO}_2 \rightarrow -\text{NH}_2$) followed by bond cleavage and mineralization of intermediates [44].

For organophosphates, such as methylparathion and methamidophos, degradation follows a combination of radical-mediated and direct electron transfer mechanisms. Hydroxyl radicals generated at the electrode surface promote oxidative cleavage of P–O, P–S, and C–N bonds, leading to formation of nitrophenols, methylmonothiophosphoric acid derivatives, and eventually low-molecular-weight carboxylic acids (oxalic, formic, acetic acids), inorganic phosphates, and other mineralization products [45,46]. The presence of metal-oxide electrodes, such as Ti/SnO₂ or BDD, can stabilize adsorbed $\cdot\text{OH}$ radicals, enhancing indirect oxidation while partially limiting oxygen evolution [46,47].

Indirect oxidation mechanisms are enhanced in electrolytes containing chloride or sulfate ions, where reactive chlorine species (Cl_2 , ClO^- , H_2OCl^+) or peroxodisulfate ($\text{S}_2\text{O}_8^{2-}$) are electrogenerated. These species contribute to oxidation of recalcitrant pesticide molecules, although organochlorinated byproducts may form during chloride-mediated oxidation [48–50]. In three-dimensional electrode systems, adsorptive particle electrodes can further enhance degradation efficiency by creating localized microelectrolytic cells, increasing the effective electrode surface area for both direct and indirect oxidation [51].

One of the key factors influencing the efficiency of the electrochemical oxidation process is the choice of anode material [52,53]. Electrodes with a low oxygen evolution potential (OEP), known as active anodes—such as platinum and Ti/Pt—have a tendency to promote the formation of chemisorbed oxidizing species, which leads to partial degradation of pesticides and the formation of intermediate by-products like organic acids and phosphorus-based compounds [54]. In contrast, non-active anodes, including boron-doped diamond (BDD), possess a high OEP and facilitate the release of highly reactive hydroxyl radicals from the anode surface into the solution via physisorption. This radical directly and completely degrades the pesticide molecules into CO_2 , H_2O , and inorganic ions [47].

Numerous studies have highlighted the superior mineralization efficiency of BDD electrodes for the degradation of pesticides. Pereira et al. documented an 80% reduction in total organic carbon during the electrochemical treatment of tebuthiuron in a flow-through system, with minimal energy consumption, without formation of persistent by-products in the absence of chloride ions [47]. The enhanced mineralization efficiency of BDD electrodes compared to Pb/PbO₂ and SnO₂ was further confirmed by Martinez et al. and Hachami et al. during the degradation of metamidophos and methidathion [46,55].

While BDD remains widely studied, numerous other electrode materials have also been utilized in the electrochemical oxidation of pesticides. Lead-based anodes (Pb/PbO₂), especially when doped with rare earth elements such as gadolinium or antimony, exhibit good electrocatalytic activity and corrosion resistance, although their practical use is limited by the potential leaching of toxic Pb^{2+} ions into the treated water [56]. SnO₂ anodes, particularly antimony-doped (SnO₂-Sb), are cheaper and easier to synthesize, demonstrating high efficiency in neutral and mildly acidic media, although they possess lower stability and shorter service life compared to BDD [46,57]. Ti/Sb-SnO₂ anodes doped with europium and reduced graphene oxide (Ti/Sb-SnO₂-Eu&rGO) have shown improved electrochemical characteristics as well as selectivity towards clothianidin degradation [44].

Ti/RuO₂ and Ti/IrO₂ (dimensionally stable anodes—DSA) are typical examples of active electrodes, which, as previously reported, favor the formation of adsorbed oxidizing species and often result in only partial degradation of pollutants. Malpas utilized Ti/Ru_{0.3}Ti_{0.7}O₂ for atrazine degradation and demonstrated that the choice of support-

ing electrolyte (NaCl, NaNO₃, H₂SO₄, etc.) is crucial to achieve higher mineralization efficiency [48,58]. In contrast, Zaviska et al. highlighted the high atrazine degradation achieved on IrO₂ anodes. However, these materials frequently require the addition of external oxidants or integration with other treatment techniques to achieve complete mineralization [59].

To overcome the limitations of traditional materials, new generations of electrodes have been developed. For instance, gadolinium-doped lead dioxide (Gd-PbO₂), applied in the degradation of neonicotinoids such as nitenpyram, enables high degradation efficiency through controlled radical release. Furthermore, Yang et al. achieved over 95% removal of nitenpyram using gadolinium-doped PbO₂ electrodes, with hydroxyl radicals identified as the dominant oxidative species responsible for the degradation process [56]. Advanced configurations, such as three-dimensional electrodes incorporating conductive ceramic particles and reactors with enlarged surface areas, allow for improved contact between pollutants and the electroactive surface—an especially advantageous feature when treating wastewater with higher pesticide concentrations [51].

The efficiency of electrochemical degradation is closely linked to the nature of the supporting electrolyte. When NaCl is used, active chlorine species (such as Cl₂ and HClO) can be generated in situ, which significantly accelerates the breakdown of pesticides. However, this approach may also result in the formation of halogenated by-products [49]. On the other hand, the application of inert electrolytes such as Na₂SO₄ supports degradation mechanisms primarily governed by hydroxyl radicals, which are generally more favorable for achieving complete mineralization [48]. The influence of operating conditions—such as temperature, initial pollutant concentration, and mass transport—was highlighted in the work by Samet et al., who studied the degradation of chlorpyrifos under galvanostatic conditions. Optimal performance was observed at 70 °C and 20 mA cm^{−2}, leading to complete COD removal within 6 h. The kinetic behavior followed a pseudo-first-order model under mass transport control, confirming similar trends reported by other authors [60].

The pH of the solution also plays a significant role in determining the dominant reaction pathway. Acidic conditions favor the formation of free chlorine, whereas neutral and alkaline environments enhance the contribution of reactive oxygen species. For example, Martinez et al. reported faster degradation rates of methamidophos at pH 3, while also noting that BDD anodes exhibit improved selectivity and operational stability under near-neutral conditions [46].

Moreover, hybrid systems that integrate electrochemical oxidation with other advanced treatment methods—such as photocatalysis, ultrasound, or AOPs—are gaining increasing interest. Combining EO with UV radiation can enhance radical formation, while ultrasonic waves assist in improving mass transport and in desorbing pollutants from electrode surfaces [50]. These combined approaches often result in synergistic effects, leading to superior removal efficiencies, particularly when treating complex wastewater matrices, as presented in Table 1.

Table 1. Publications on pesticide removal from wastewater by electrochemical-EO technology.

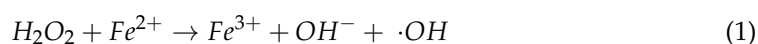
Author	Pesticide	Optimal Conditions	Cell Type/Electrodes	Degradation/Mineralization (TOC/COD/BOD) Efficiency
Garcia-Segura et al. (2015) [49]	Mixture (29 pharmaceuticals and pesticides)	Real municipal effluent (Cl [−] pre-sent)	Batch, BDD anode, SS cathode	Near-complete degradation and mineralization
Muff et al. (2009) [61]	Multiple organophosphorus pesticides	Drainage water pH 4.2, 310–1131 mA/cm ² ,	Flow cell, Ti/Pt ₉₀ –Ir ₁₀ anode, SS cathode	Complete degradation
Li et al. (2015) [51]	DTMHP	Na ₂ SO ₄ , pH 3, 15 V	Undivided cell, Pb alloy, SS cathode	Degradation: 83.4%; COD 35.2%

Table 1. Cont.

Author	Pesticide	Optimal Conditions	Cell Type/Electrodes	Degradation/Mineralization (TOC/COD/BOD) Efficiency
Samet et al. (2010) [62]	Chlorpyrifos	H ₂ SO ₄ , pH 2, 10–50 mA/cm ²	Divided cell, Nb/PbO ₂ anode, graphite carbon bar cathode	Complete degradation, COD: 76%
Martinez-Huitile et al. (2008) [46]	Methamidophos	Na ₂ SO ₄ , pH 2, 5, 6, 9; 50 mA/cm ²	Divided cell, Si/BDD, Pb/PbO ₂ , Ti/SnO ₂ anode, Zr cathode	BDD-complete degradation/mineralization;
Arapoglou et al. (2003) [63]	Methyl-parathion	NaCl, 36 A	Undivided cell, Ti/Pt anode, SS cathode	COD, BOD > 80%
Vlyssides et al. (2005) [64]	Monocrotophos, Phosphamidon	NaCl, 30–36 A	Undivided cell, Ti/Pt anode, SS cathode	Monocrotophos: COD 42.5%; Phosphamidon: COD 42.4%
Vlyssides et al. (2004) [54]	Methidathion phosalone, azinphos-methyl	NaCl, 30 A	Undivided cell, Ti/Pt anode, SS cathode	COD > 70%
Hachami et al. (2015) [55]	Methidathion	NaCl, pH 3, 60 mA/cm ²	Undivided cell, BDD and SnO ₂ anode, Pt cathode	BDD: COD 85% SnO ₂ : COD 73%
Moteshaker et al. (2020) [65]	Diazinon	Na ₂ SO ₄ , pH 5, 25 mA/cm ²	Undivided cell, Pb/β-PbO ₂ anode, SS cathode	Near complete degradation TOC: 79.86%
Hosseini et al. (2015) [66]	Diazinon	KCl, pH 7, 40 mA/cm ²	Undivided cell, Al anode, graphite cathode	Degradation: 87%
Malpas et al. (2005) [48]	Atrazine	NaCl, 60 mA/cm ²	Undivided cell, Ti/Ru _{0.3} Ti _{0.7} O ₂ (DSA®) anode, Pt cathode	Complete degradation TOC: 46%
Zaviska et al. (2011) [59]	Atrazine	NaCl, 2 A	Undivided cell, Ti/IrO ₂ , Ti/SnO ₂ anode, Ti cathode	Near complete degradation: 95%
Santos et al. (2015) [57]	Atrazine	NaHCO ₃ , pH 8.48,	Undivided cell, Ti/SnO ₂ -Sb, Ti/RuIr anode	Near complete degradation
Randjelovic et al. (2011) [67]	Mix of pesticides (Atrazine, Triclopyr, 2,4-D, Metolachlor)	Reverse osmosis, pH 7.5, 25 mA/cm ²	Undivided cell, RuO ₂ /IrO ₂ -coated, SS cathode	Near complete degradation
Yang et al. (2020) [56]	Nitenpyram	Na ₂ SO ₄ , pH 5, 70 mA/cm ²	Undivided cell, Gd-PbO ₂ anode, Ti cathode	Degradation: 95.4%; COD: 79.2%
Guo et al. (2021) [44]	Clothianidin	Na ₂ SO ₄ , pH 5, 25 mA/cm ²	Undivided cell, Ti/Sb-SnO ₂ -Eu&rGO anode, Ti cathode	Near complete degradation
Souza et al. (2017) [50]	Chlorsulfuron	NaCl/Na ₂ SO ₄ , 30 and 100 mA/cm ²	Batch, BDD anode and cathode	Complete degradation and mineralization
Pereira et al. (2017) [47]	Tebuthiuron	Na ₂ SO ₄ ± Cl [−] , 10, 30 and 50 mA/cm ²	Flow cell, BDD anode, SS cathode	Complete degradation, TOC: 80%
Raschitor et al. (2017) [68]	2,4-D	NaCl, 1 V	Electrodialysis/electro-oxidation, DSA® anode	Electrodialysis enhances oxidation
Min et al. (2020) [69]	Pesticide wastewater	Pesticide wastewater	Pilot-scale systems, nano PbO ₂ anode	BOD: 85.7%

3.2. Electro-Fenton

In addition to electrochemical oxidation and electrocoagulation, the electro-Fenton process has emerged as one of the most promising and efficient electrochemical technologies for the degradation of pesticides. Unlike anodic oxidation, where reactions are limited to the electrode surface, this approach enables pesticide degradation throughout the entire solution, mainly due to the in situ formation of hydroxyl radicals. In the electrochemically assisted Fenton process, hydroxyl radicals are generated through the reaction of hydrogen peroxide (H₂O₂) with ferrous iron (Fe²⁺), as shown in the following equation:



Compared to the classical Fenton method, this approach offers two key advantages: the in situ electrogeneration of H₂O₂ and the continuous electrochemical regeneration of Fe²⁺. These features reduce the need for large amounts of external reagents, prevent Fe³⁺ accumulation, and consequently minimize sludge formation.

From the reviewed literature on pesticide degradation using electrochemical technologies, it can be concluded that electrochemical advanced oxidation processes based

on Fenton's reaction chemistry are predominantly represented by the classic EF process. In addition, several combined EF approaches have been widely explored to enhance performance, including photoassisted variants such as photoelectro-Fenton (PEF) and solar photoelectro-Fenton (SPEF), as well as hybrid processes like sonoelectro-Fenton (SEF). These methods have been applied to the degradation of a range of pesticides, including fungicides (*cymoxanil* [70], *mancozeb* [65], *pyrimethanil* [71], *zineb* [65], *difenoconazole* [72]), insecticides (*methomyl* [73], *imidacloprid* [74–76], *methyl parathion* [77], *profenofos* [78], *methiocarb* [79], *carbaryl* [80], *fipronil* [67]), and herbicides (*tebuthiuron* [81], *ametryn* [81], *2,4-Dichlorophenoxyacetic acid* [82–84], *clopyralid* [85], *diuron* [86], *glyphosate* [86], *atrazine* [67]).

Because H_2O_2 is electrogenerated at the cathode and serves as a key component of Fenton's reagent, the choice of cathode material plays a crucial role in the overall efficiency of EF processes, particularly when optimized anode materials are employed. At present, carbon-based cathodes—including carbon black, carbon sponge, carbon felt, activated carbon fiber, carbon nanotubes, and graphene oxide—are the main focus of research and application [87,88]. These materials stand out for their excellent stability, large surface area, and strong catalytic activity for H_2O_2 generation, making them highly suitable for practical and large-scale EF systems. Furthermore, carbon materials offer additional advantages such as tunable surface chemistry, structural versatility, and compatibility with electrode modification strategies that can further enhance their performance. In an electro-Fenton cell, oxygen from the gas phase must dissolve into the liquid and be efficiently delivered to the solid–liquid interface, where it undergoes reduction to form H_2O_2 . Enhancing oxygen transfer is therefore essential to maximize H_2O_2 production and to overcome limitations imposed by oxygen solubility and mass transport. Additionally, optimizing the electrogeneration of H_2O_2 at the cathode can further improve the overall efficiency of the process [89,90]. In a study by Popescu et al., the electro-Fenton process was evaluated using three different carbonaceous cathodes: graphite felt, taffeta carbon fiber, and unidirectional carbon fiber, with pyrimethanil chosen as a model pesticide. The study aimed to investigate the influence of cathode type on H_2O_2 production and to assess the feasibility and efficiency of pyrimethanil degradation via the electro-Fenton process. The findings demonstrated that cathode material plays a significant role in controlling H_2O_2 generation, reaction kinetics, and ultimately the effectiveness of pollutant removal [71]. As shown in Table 2, studies on pesticide degradation by the electro-Fenton process predominantly employ carbon felt and graphite as cathodes, since these materials provide safe and efficient electrodes for the electrogeneration of hydrogen peroxide required to drive the Fenton reaction.

Similarly to the role of anode materials in determining the degradation and mineralization efficiency of pesticides in electrochemical oxidation, their influence is equally critical in the electro-Fenton process. In the study by Nguyen (2020) [75], graphite, platinum, BDD anodes were tested with a $\text{Fe}_3\text{O}_4\text{--Mn}_3\text{O}_4$ catalyst. Graphite exhibited the lowest efficiency and suffered from corrosion, while BDD showed the highest degradation performance due to its strong $\cdot\text{OH}$ generation, high oxidation reactivity, and energy efficiency. Platinum was slightly less effective than BDD, likely because of electrode passivation in Na_2SO_4 and its lower oxygen evolution potential [75]. As indicated in Table 2, studies on pesticide degradation by EF process most frequently employ BDD and Pt as anodes. These materials are preferred because of their excellent electrochemical stability, high overpotential for oxygen evolution, and strong ability to generate hydroxyl radicals, all of which contribute to enhanced degradation efficiency and mineralization of organic pollutants.

The optimization of electro-Fenton process is influenced by multiple operational parameters, including solution pH, the nature of the supporting electrolyte, pollutant concentration, applied current intensity, and temperature. Each of these factors plays a critical role in controlling the generation of reactive species, reaction kinetics, and overall

treatment efficiency, thereby determining the effectiveness and selectivity of the oxidation process. Careful adjustment of these parameters is essential to achieve maximum degradation and mineralization of target contaminants while minimizing energy consumption and the formation of undesired by-products [77].

Table 2. Publications on pesticide removal from wastewater by electrochemical-EF and EF-hybrid technology.

Author	Pesticide	Optimal Conditions	Cell Type/Electrodes	Degradation/Mineralization (TOC/COD/BOD) Efficiency
Diagne et al. (2006) [77]	Methyl parathion	aqueous solution, Fe^{2+} (0.1 mM), pH 3, 13.33 mA cm^{-2}	Undivided cell, Pt anode, carbon felt cathode	Complete degradation /mineralization
Rocha et al. (2016) [78]	Profenofos	K_2SO_4 , Fe^{2+} (0.15 mM), acidic, -0.7 V	Undivided cell, Pt anode, GDE cathode	Complete degradation, 89% mineralization
Sedaghat et al. (2016) [74]	Imidacloprid	Na_2SO_4 , Fe^{2+} (0.36 mM), pH 2.8, -1 V	Undivided three-electrode batch cell, graphite cathode, UV lamp for PEF	Deg. EF: 59.23%; PEF: 80.49%; Min.: EF: 50.73%; PEF: 67.15%
Nguyen et al. (2020) [75]	Imidacloprid	Na_2SO_4 , Fe_3O_4 – Mn_3O_4 nanoparticle catalyst, pH 4, 15 mA cm^{-2}	Undivided cell, graphite, Pt, BDD anode, Graphite cathode	Near complete degradation /mineralization
Iberache et al. (2024) [76]	Imidacloprid	Na_2SO_4 , Fe^{2+} (0.225 mM), pH 3, 17.15 mA cm^{-2}	Undivided cell, BDD anode, carbon felt cathode	Complete degradation
Rosa Barbosa et al. (2018) [86]	Diuron, Glyphosate	Na_2SO_4 , Fe^{2+} (1.0 mM), pH 3, 0.50–1.50 A	Divided reactor, Ti/RuTiO ₂ DSA plate anode, carbon felt cathode	Diuron-66.2%, Glyphosate-complete degradation
Cai et al. (2022) [83]	2,4-D	aqueous solution, Fe^{2+} (0.5 mM), pH 3, 3.52 mA cm^{-2}	Flow-through system	Degradation: 85% Mineralization: 25.3%
Badellino et al. (2006) [82]	2,4-D	K_2SO_4 , Fe^{2+} (1 mM), pH 3.5 and 10, -1.6 V	Undivided cell, Rotating RVC cylinder anode, Pt cathode	Near-complete degradation, 67% TOC in acidic, 0% in alkali
Brillas et al. (2007) [84]	2,4-D	Na_2SO_4 , Fe^{2+} (1.0 mM), pH 3, 100 A	Undivided cell, Pt or BDD anode, graphite bar cathode)	Complete degradation /mineralization
Souiad et al. (2020) [79]	Methiocarb	NaCl , Fe^{2+} (0.18 mM), pH 3, 5 mA cm^{-2}	Undivided cell, Pt anode, carbon felt cathode	Complete degradation, 11.4% mineralization
Çelebi et al. (2015) [80]	Carbaryl	Na_2SO_4 , Fe^{2+} (0.1 mM), pH 3, 300 mA	Undivided cell, Pt or BDD anode, carbon felt cathode)	Complete degradation, TOC > 90%
Oturan et al. (2010) [73]	Metomyl	Na_2SO_4 , Fe^{2+} (0.1 mM), pH 3, 100 mA	Undivided cell, Pt anode, carbon felt cathode	Near complete degradation
Carboneras et al. (2019) [85]	Clopyralid	Soil washing effluent/synthetic groundwater, pH 3, 200 mA	Undivided cell, Pt anode, carbon felt cathode	Degradation: 80% Mineralization: 30%
Popescu et al. (2018) [71]	Pyrimethanil	Na_2SO_4 , Fe^{2+} (0.1 mM), pH 3, 0.05–0.3 A	Batch and continuous treatment, BDD anode, different carbon cathode	Complete degradation, 25–40% mineralization

In the EF process, an acidic medium (pH $\approx$ 2.8–3.0) is typically used because Fe^{2+} remains soluble and stable, allowing efficient generation of hydroxyl radicals via the Fenton reaction. At higher pH, Fe^{2+} tends to precipitate as $\text{Fe}(\text{OH})_3$, which significantly reduces $\cdot\text{OH}$ production, and H_2O_2 becomes less stable. This limitation can be overcome by using heterogeneous Fe catalysts immobilized on solid supports, by complexing Fe ions with ligands (e.g., citrate or EDDS) to maintain solubility at near-neutral pH, or by combining EF with photo or sono processes to regenerate Fe^{2+} and sustain radical production. Although most of the studies summarized in Table 2 investigated pesticide degradation under acidic conditions, Badellino et al. extended their experiments on 2,4-dichlorophenoxyacetic acid to alkaline medium (pH 10) in addition to the commonly applied acidic pH. Their results showed that degradation was successful in both media, but with markedly higher efficiency under acidic conditions. This behavior can be attributed to anodic oxidation processes occurring in the background, which partially sustain pollutant removal even at higher pH. However, mineralization data obtained from TOC analysis clearly confirmed the well-established principle that the EF process is more effective in acidic environments, achieving 67% mineralization compared to only 20% under alkaline conditions [82]. According to the results presented in Table 2, EF process is capable of achieving almost complete degradation

of pesticides in most cases. In contrast, mineralization is often limited, with significant removal of TOC or COD observed only under specific conditions [75,77,84].

Since the traditional EF approach often faces limitations such as relatively slow reaction kinetics and incomplete mineralization, several combined EF approaches have been developed to overcome these drawbacks. By integrating external energy sources (light or ultrasound) with EF chemistry, these advanced methods enhance hydroxyl radical generation, improve mineralization efficiency, and broaden the range of target pollutants that can be effectively degraded.

The photoelectro-Fenton (PEF) process represents an advanced oxidation technology that builds upon conventional EF by coupling it with light irradiation, UV or visible light. A key advantage of PEF over standard EF lies in its ability to continuously regenerate Fe^{2+} via photoreduction of Fe^{3+} , thus preventing Fe^{3+} accumulation, maintaining optimal Fenton activity, and increasing $\cdot\text{OH}$ yields. In addition, the photodegradation of EF intermediates contributes to higher treatment efficiency and reduces the risk of toxic by-product formation [84]. This combined system improves pollutant elimination by facilitating photochemical reactions that regenerate Fe^{2+} , break down resistant intermediates, and speed up the mineralization of organic contaminants such as pesticides [72]. The application of PEF technology demonstrates practical advantages, including shorter degradation and mineralization times, which reduce energy consumption and improve cost-effectiveness. Moreover, compared to conventional Fenton systems, PEF produces less iron sludge, thereby minimizing secondary waste management challenges. Sedaghat's group study investigated the degradation efficiency of imidacloprid, a model pesticide, using EF and PEF processes in an undivided three-electrode cell under batch operation. Experiments were carried out at pH 2.8, with Fe^{2+} (0.36 mM), Na_2SO_4 (0.15 M), and a fixed graphite cathode potential of -1.0 V vs. SCE. After 180 min, the EF and PEF processes achieved degradation efficiencies of 59.23% and 80.49%, respectively, demonstrating a strong synergistic effect of UV irradiation through Fe^{2+} regeneration and enhanced hydroxyl radical production. TOC removal after 300 min reached 50.73% with EF and 67.15% with PEF, indicating higher mineralization efficiency in the UV-assisted system [74]. Inticher et al. used PEF process with a BDD and demonstrated high degradation efficiency for atrazine (95.7%), difenoconazole (97.3%), and fipronil (96.5%) in mixture form, while achieving 47.3% mineralization within 15 min under optimized conditions. Although complete mineralization was not reached, the process effectively reduced pollutant concentrations and their associated risks. These results emphasize the environmental significance of PEF-BDD as a rapid and reliable treatment strategy for pesticide-contaminated waters, offering reduced toxicity and promising applicability to real wastewater treatment [91].

The solar photoelectro-Fenton (SPEF) process is an enhanced variant of the conventional PEF method that employs solar energy as the main light source. This sustainable approach reduces reliance on artificial UV or visible light, lowers energy consumption, and minimizes environmental impact. This eco-friendly method achieves degradation efficiencies comparable to conventional EF or PEF while reducing energy consumption and environmental impact. In the study conducted by Gozzi et al., the SPEF process has been effectively applied to degrade herbicides, including tebuthiuron and ametryn, in single and mixed formulations [81]. Using a boron-doped diamond (BDD)/air-diffusion cell coupled with a solar photoreactor, SPEF demonstrated superior oxidation and partial mineralization compared to anodic oxidation with electrogenerated H_2O_2 and conventional EF. The enhanced performance of SPEF is attributed to sunlight-driven photo-oxidation of intermediates and Fe^{3+} complexes. These results indicate SPEF as a viable, environmentally friendly method for treating herbicide-contaminated waters. Salmeron's group advanced the approach by constructing a pilot-scale SPEF system that efficiently degraded a pesticide

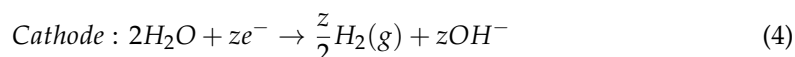
mixture (pyrimethanil and methomyl) in water, combining H_2O_2 electrogeneration at an air-diffusion cathode with a boron-doped diamond anode. Optimized operating conditions facilitated rapid Fe^{2+} regeneration and hydroxyl radical production, achieving over 50% pesticide removal within 5 min, with high current efficiency (89.3%) and low energy consumption (0.4 kWh m^{-3}), demonstrating a fast, energy-efficient, and environmentally friendly method for treating pesticide-contaminated water [92].

Sono electro-Fenton (SEF) combines ultrasonic irradiation with EF process to enhance the generation of hydroxyl radicals and improve pollutant degradation. Ultrasonic waves increase mass transfer between electrodes, continuously clean the electrode surface, accelerate the in situ production of H_2O_2 at the cathode, and facilitate the breakdown of recalcitrant compounds. The process reduces treatment time and energy consumption while improving mineralization efficiency, offering an environmentally compatible approach for wastewater treatment [93]. Dargahi et al. investigated the degradation of the herbicide 2,4-D using a three-dimensional sono-electro-Fenton (3D/SEF) process. The system employed powder-activated carbon/ Fe_3O_4 (PAC/ Fe_3O_4) particle electrodes combined with an SS316/ $\beta\text{-PbO}_2$ anode. The authors optimized key operational parameters—such as pH, initial 2,4-D concentration, Fe^{2+} dose, electrolysis time, H_2O_2 concentration, current density, catalyst dose, and supporting electrolyte—using a Taguchi design. Among these, solution pH had the highest influence on degradation efficiency (39.52% contribution). Under optimal conditions, removal efficiencies of 2,4-D, COD, and TOC reached 96.2%, 92.3%, and 86.5%, respectively, with significant reduction in effluent toxicity [94].

3.3. Electrocoagulation

Electrocoagulation (EC) is a major category of electrochemical treatment technologies. It is considered attractive because of its operational simplicity, low maintenance, and effectiveness in removing fine and colloidal particles. Compared to conventional methods, EC offers key advantages, such as eliminating the need for added chemicals, since electrons act as the primary reagent that breaks down pollutants. Electrocoagulation has evolved as an efficient in situ water treatment technique, providing an alternative to traditional chemical coagulants. Therefore, EC can be applied to treat various types of wastewaters and is particularly promising for the removal of emerging contaminants, including pesticides, as shown in Table 3.

During electrocoagulation, the anode provides metal ions (e.g., Fe^{2+} , Fe^{3+} , Al^{3+}) that hydrolyze to form coagulant hydroxides, while the cathode generates hydroxide ions and hydrogen gas, and together they create conditions for pollutant removal via coagulation, adsorption, and flotation. Within EC, the dominant reactions can be summarized as:



These hydroxide species aggregate into flocs with large surface areas and active sites, which effectively adsorb and destabilize colloidal and dissolved pollutants. The hydrogen bubbles enhance flotation, assisting in the separation of contaminants. By simultaneously generating coagulants and flotation effects without chemical additives, electrocoagulation offers a simple and efficient approach for treating various wastewaters, including those containing emerging pollutants such as pesticides.

Aluminum and iron are the most widely used anodic metals for EC because of their many advantages, such as high availability, low cost, and the non-toxic nature of their hydroxides. Halkijevic et al. demonstrated the significant impact of electrode material, cur-

rent density, ultrasound, and operation time on imidacloprid removal. Among aluminum, copper, and iron electrodes, complete degradation of imidacloprid was achieved in 20 min using aluminum electrodes at 2040 A/m², whereas 96.5% removal was obtained with iron electrodes at 680 A/m² in 3.5 L of a 10 mg/L solution without pH adjustment [95].

Table 3. Publications on pesticide removal from wastewater by electrochemical-EC and EC-hybrid technology.

Author	Pesticide	Optimal Conditions	Cell Type/Electrodes	Degradation/Mineralization (TOC/COD/BOD) Efficiency
Dolatabadi et al. (2022) [96]	Diazinon	FeCl ₃ /NH ₄ Cl, pH 8.5, 11.75 mA/cm ²	Undivided cell with magnetic guar gum, Fe anode, cathode	Near complete degradation
Sankar et al. (2021) [97]	Malathion	NaCl, pH 7.5, 15 V	Undivided cell, Fe or Al electrode	Near complete degradation
Behloul et al. (2013) [98]	Malathion	NaCl, pH 6, 10 mA/cm ²	Undivided cell, Al electrode	90% degradation
Abdel-Gawad et al. (2012) [99]	Malathion	NaCl, pH 6–7, 1 mA/cm ²	Undivided cell, four Fe electrodes connected in bipolar mode	Near complete degradation
Halkijevic et al. (2024) [95]	Imidacloprid	NaCl, pH 7.2, 68–204 mA/cm ²	Undivided cell Fe, Cu, or Al electrode	Fe-96.51% Cu-87.04% Al-complete degradation, COD 56%
Raschitor et al. (2019) [100]	Oxyfluorfen, Lindane	Na ₂ SO ₄ , 17.73–25.47 mA/cm ²	Undivided cell, Fe anode, SS cathode	Lindane-61%, Oxyfluorfen-30% degradation

Electrocoagulation has been successfully applied in various laboratory and pilot-scale studies for the removal of a wide range of pesticides, including diazinon, malathion, imidacloprid, chlorpyrifos, oxyfluorfen, lindane, and others. The removal efficiency depends on several factors, such as solution pH, current density, electrode spacing, treatment time, and the presence of competing ions in the solution. Under optimal conditions, EC has demonstrated the ability to remove more than 90% of pesticides, especially when combined with other processes such as adsorption on carbon-based nanomaterials or prior oxidation [97–99,101].

For example, several studies have demonstrated that electrocoagulation using iron electrodes can significantly reduce pesticide concentrations in industrial wastewater. Composite strategies that combine processes such as adsorption on graphene, electro-Fenton oxidation, or ultrasonic activation further enhance removal efficiency, particularly in complex matrices like wastewater.

This was also demonstrated by Dolatabadi et al., who effectively removed the organophosphorus pesticide diazinon from water using EC process assisted by magnetic guar gum (MGG) as a coagulant aid. The results showed that MGG significantly enhanced pesticide removal efficiency compared to traditional coagulants. Under optimal conditions (pH 8.5, current density 11.75 mA cm^{−2}, 2.38 g L^{−1} MGG, 20 min), a maximum diazinon removal efficiency of 98.8% was achieved. These findings highlight EC with MGG as a rapid, efficient, and environmentally friendly approach for treating pesticide-contaminated water [96]. Unlike previous studies, Raschitor's group used electrocoagulation as a pre-treatment step before electrooxidation or the electro-Fenton process for the removal of oxyfluorfen and lindane from concentrated wastewater [100].

Despite its high efficiency, EC faces several limitations, including the need for periodic replacement of sacrificial electrodes, formation of passive layers on cathodes that reduce process efficiency, and accumulation of sludge requiring further treatment. The primary sludge from electrocoagulation consists of amorphous Al/Fe hydroxides formed by sacrificial electrode dissolution, with surfaces that adsorb organics, solids, and, if present,

heavy metals or anions (e.g., phosphates, fluorides). Additionally, excess metal ions in the treated water may necessitate subsequent removal or neutralization, and the high energy consumption of EC systems can limit their practical applicability. These disadvantages can be mitigated by integrating EC with complementary techniques, such as ultrasound, where the mechanical effects of ultrasonic cavitation help reduce electrode passivation and improve overall process efficiency. In the study by Halkijevic's group, the use of ultrasound during electrocoagulation was shown to increase removal efficiency by an average of 7% for aluminum and copper electrodes and 12% for iron electrodes, highlighting EC as an effective and adaptable method for treating pesticide-contaminated water [95]. The physicochemical characteristics of the sludge are greatly influenced by the wastewater matrix, pH, current density, and electrode material, whereas its toxicity is primarily affected by the type and concentration of contaminants removed. Compared with chemically generated sludge, electrocoagulation sludge typically exhibits reduced volume, improved settling behavior, and superior dewaterability due to the formation of compact, well-aggregated flocs. Dewatered non-hazardous sludge may be safely disposed of in landfills, whereas sludge enriched with pesticides, dyes, or heavy metals often requires stabilization or solidification prior to disposal as hazardous waste.

However, due to its simplicity, potential for automation, and broad applicability, electrocoagulation is increasingly recognized as a sustainable method for pesticide removal from water—particularly in the treatment of persistent, toxic, and poorly biodegradable compounds that pose risks to human health and the environment.

3.4. Comparative Evaluation of Electrochemical Techniques

Based on the bibliometric analysis of the scientific literature, it can be observed that the electrochemical techniques described in the previous sections are effective methods for removing pesticides from wastewater. Each electrochemical technique has distinct operational characteristics, advantages, and limitations, which are summarized in Table 4. While various types of anodes can be used in EO, inert electrodes such as BDD, Ti/Pt, Ti/IrO₂, SnO₂, or PbO₂ are most commonly employed for pesticide degradation. The EF process typically uses similar anodes (BDD, Pt), while carbon-based materials, such as carbon felt, graphite, or GDE, are applied as cathodes. In contrast, EC relies on sacrificial electrodes (Al, Fe, or Cu), which gradually dissolve during operation and require periodic replacement. These sacrificial electrodes generate sludge during EC, which represents one of the main drawbacks of the process. Sludge formation in EO is negligible, while in EF it is low to moderate, depending on the concentration of Fe²⁺ ions that produce iron hydroxide sludge.

EO operates at relatively high current densities of 10–100 mA/cm², or even higher in some cases, such as those reported by Muff et al., which can result in substantial energy consumption, particularly for large-scale applications. Although this process is energy-intensive, it not only achieves complete pesticide degradation but also ensures their full mineralization. EF operates at intermediate current densities (up to 20 mA/cm²), balancing energy input with high oxidative performance. As shown in Table 2, this method can achieve complete mineralization of pesticides, but within a narrow pH range. EC typically functions at lower current densities (1–20 mA/cm²), providing moderate energy efficiency. While EC effectively removes pesticides via coagulation and flocculation, it does not achieve full mineralization, often necessitating a subsequent treatment step—such as EO or EF—to ensure complete detoxification.

Importantly, the differences in operational conditions and degradation pathways among EO, EF, and EC influence not only the efficiency of pesticide removal but also the nature and composition of intermediate by-products formed during treatment.

Table 4. Comparison of Key Electrochemical Treatment Technologies.

Electrochemical Techniques	Electrode	Advantages	Limitation
EO	BDD, Ti/Pt, PbO ₂ , SnO ₂ , carbon, SS, Ti/IrO ₂	• Demonstrates high removal rates of persistent organic pollutants • Capable of near-complete mineralization • Generates minimal secondary sludge	• High energy consumption under certain operational conditions • Requires expensive electrode materials
EF	Pt or BDD anode; graphite, carbon felt, GDE cathode	• Demonstrates high removal rates of persistent organic pollutants • Capable of near-complete mineralization • Moderate energy consumption	• May require additional reagents (Fe²⁺, H₂O₂) and/or gas supply • Moderate sludge formation (iron hydroxides) • Mostly efficient under acidic pH
EC	Al, Fe, Cu (sacrificial)	• Low energy consumption • Simple installation and low-cost equipment	• Produces moderate amounts of sludge requiring disposal • Limited efficacy for highly persistent organic pollutants • Electrodes are consumable and require periodic replacement

EO degrades pesticides through both direct anodic oxidation and indirect oxidation mediated by reactive species such as hydroxyl radicals, active chlorine, and peroxodisulfate. These reactions often generate intermediate compounds, including short-chain carboxylic acids (e.g., formic, acetic, oxalic acids), aldehydes, chlorinated organics, and partially oxidized nitrogen- or phosphorus-containing derivatives. Although many of these by-products are less persistent than the parent pesticides, some chlorinated organics may retain residual toxicity or bioaccumulative potential, highlighting the need for careful monitoring of treated effluents [45–47,102,103]. In EF, hydroxyl radicals generated in situ via the Fenton reaction attack pesticide molecules, producing similar intermediates such as carboxylic acids, aldehydes, and halogenated derivatives [85]. For example, organophosphates can form phosphoric acid derivatives, while neonicotinoids may yield nicotinic acid derivatives [76,86]. EC removes pesticides predominantly through their adsorption onto, and co-precipitation with, metal hydroxide flocs generated in situ (typically Al(OH)₃ or Fe(OH)₃). Although this technique efficiently decreases pesticide concentrations, it does not achieve full mineralization of the organic compounds. Consequently, the produced sludge may retain organic residues and metal–pollutant complexes, which can present disposal challenges and pose potential environmental risks if not adequately treated prior to discharge [96,97,101].

Based on the above, it can be concluded that no single technique is universally optimal. EO is ideal for complete mineralization without sludge formation, but it has high energy consumption; EC is practical for metal–organic removal but produces sludge and does not achieve full mineralization, and EF is highly effective for pesticide removal, although under more limited operational conditions.

4. Conclusions and Future Directions

This review provides an in-depth evaluation of electrochemical-based technologies as emerging approaches to the removal of pesticides from contaminated water. The analysis covered core processes such as electro-Fenton, electrocoagulation, and electrochemical oxidation, as well as hybrid systems that integrate these methods with complementary treatments. Electrochemical techniques have demonstrated notable advantages over conventional and biological treatments, offering high degradation efficiency, flexible operation, and the potential for complete mineralization of persistent pollutants. However, several challenges remain, including high energy demand, electrode degradation, and limited scalability for large-scale applications. Future research should optimize operational parameters

and develop advanced, nanostructured electrodes to boost catalytic activity and reactive oxygen species generation for efficient pesticide mineralization.

Integrating renewable energy, particularly solar power, offers a promising way to reduce costs and carbon footprint in electrochemical treatments. Solar-assisted processes, such as the solar photoelectro-Fenton, show high degradation efficiency under environmentally friendly conditions. Coupling electrochemical methods with physicochemical or biological post-treatments can further enhance mineralization and reduce secondary pollution. Future trends focus on advanced hybrid systems—photoelectro-Fenton, solar photoelectro-Fenton, sono-electro-Fenton, and combinations of EO, EF, and EC—that improve degradation kinetics, selectivity, and cost-effectiveness, supporting potential full-scale applications.

The bibliometric analysis (1997–2025) reveals increasing global attention to electrochemical pesticide remediation, focusing on hybrid processes, advanced electrodes, and model-driven optimization. Transitioning from laboratory studies to practical, sustainable applications will require close collaboration among chemists, materials scientists, and environmental engineers to ensure efficiency and cost-effectiveness.

In conclusion, electrochemical-based technologies offer a highly adaptable and environmentally sustainable platform for pesticide removal from water. Continued advancements in electrode materials, system integration, and renewable energy utilization will be crucial for improving performance and ensuring large-scale applicability. The evolution of these methods positions electrochemical technologies as a central component of next-generation wastewater treatment systems aimed at mitigating pesticide pollution and protecting aquatic ecosystems.

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Abbreviations

The following abbreviations are used in this manuscript:

·OH	Hydroxyl radicals
2,4-D	2,4-Dichlorophenoxyacetic acid
AOPs	Advanced oxidation processes
BDD	Boron-doped diamond
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
DSA	Dimensionally Stable Anodes
EC	Electrocoagulation
EF	Electro-Fenton
EO	Electrochemical oxidation
Fe ²⁺	Ferrous iron
H ₂ O ₂	Hydrogen peroxide

OEP	Oxygen Evolution Potential
PEF	Photoelectro-Fenton
SEF	Sonoelectro-Fenton
SPEF	Solar Photoelectro-Fenton
TOC	Total Organic Carbon
UV	Ultraviolet
WoS	Web of Science Core Collection database

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