I J C R M
International Journal of Contemporary Research In Multidisciplinary

Research Article

Electro-Photo-Fenton Process: A Comprehensive Review of Advanced Wastewater Treatment Technology

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DOI: https://doi.org/10.5281/zenodo.18996639

Abstract

Modern industries generate wastewater laden with organic pollutants—often toxic, mutagenic, or carcinogenic—that resist conventional biological and physico-chemical treatment. Advanced Oxidation Processes (AOPs) address this by generating highly reactive hydroxyl radicals (•OH) capable of degrading even the most recalcitrant organic compounds. Among these, the Electro-Photo-Fenton (EPF) process combines electrochemical reactions, Fenton chemistry, and photochemical activation for exceptional pollutant removal efficiency. This review traces the evolution from classical Fenton chemistry to EPF, analyzes critical operating parameters (pH, temperature, electrode configuration, current density, iron concentration, and H_2O_2 dosing), and demonstrates EPF's superior performance across pharmaceutical, agrochemical, petroleum, and textile industry wastewaters. COD and TOC removal rates of 60–98% confirm EPF as a transformative approach to industrial wastewater management.

Manuscript Information

- **ISSN No:** 2583-7397
- **Received:** 01-07-2025
- **Accepted:** 27-08-2025
- **Published:** 30-08-2025
- **IJCRM:**4(3); 2025: 760-764

- **Plagiarism Checked:** Yes
- **Peer Review Process:** Yes

How to Cite this Article

Hiral Tailor. Electro-Photo-Fenton Process: A Comprehensive Review of Advanced Wastewater Treatment Technology. Int J Contemp Res Multidiscip. 2025;4(3):760-764.

Access this Article Online

www.multiarticlesjournal.com

KEYWORDS: Wastewater treatment, Chemical oxygen demand (COD), Advanced oxidation processes, Fenton process, Electro-Fenton, Electro-photo-Fenton, Environmental remediation, Operating parameters

1. INTRODUCTION

Industrial Pollution and Conventional Treatment Limitations

Heavy industries discharge wastewater containing organic contaminants exhibiting high COD yet low BOD—indicating microorganisms cannot break them down—making conventional biological treatment ineffective. Physico-chemical methods (flocculation, chlorination, ozonation, filtration, adsorption) handle routine wastewater but share a fundamental limitation: no single conventional method achieves acceptable removal of refractory toxic chemicals. Direct oxidation processes can achieve high degradation efficiencies but are constrained by pollution load variability, process-specific selectivity, and demanding operating conditions.

Advanced Oxidation Processes

Advanced Oxidation Processes (AOPs) generate hydroxyl radicals (•OH)—one of the most powerful oxidants in water treatment (second only to fluorine)—that indiscriminately attack and mineralize virtually any organic molecule into CO_2, water, and mineral salts. Key advantages over conventional methods include:

Complete mineralisation: eliminates pollutants rather than transferring them between phases

Non-selective reactivity: degrades diverse, complex pollutant mixtures

Heavy metal co-removal: alkaline precipitation of metal hydroxides $[M(OH)_x]$

Integrated disinfection: •OH inactivates bacteria, viruses, and pathogens simultaneously

Minimal chemical footprint: unreacted •OH combines to form water, introducing no hazardous byproducts

II. The Evolution of Fenton Chemistry

A. Classical Fenton Process

In 1890, Henry John Horstman Fenton discovered that ferrous iron (Fe^{2+}) dramatically accelerates hydrogen peroxide's oxidation of organic compounds, first demonstrated on maleic acid oxidation. The core reaction mechanism is:

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \bullet OH$ (hydroxyl radical generation)

$RH + \bullet OH \rightarrow R\bullet + H_2O$ (pollutant degradation)

$Fe^{2+} + \bullet OH \rightarrow Fe^{3+} + OH^-$ / $R\bullet + Fe^{3+} \rightarrow R^+ + Fe^{2+}$ (iron cycling)

Classical Fenton's practical limitations for industrial application include: (i) high iron requirements increasing chemical costs; (ii) iron sludge formation at neutral/alkaline pH requiring disposal; (iii) narrow optimal pH window of 2.5–3.5; (iv) H_2O_2 storage and transportation safety risks; and (v) requirement for precise dosing of both Fe^{2+} and H_2O_2 with continuous pH control.

B. Electro-Fenton Process

Electrochemical Advanced Oxidation Processes (EAOPs) resolve classical Fenton's limitations. The Electro-Fenton (EF) process replaces external H_2O_2 addition with continuous in-situ electrochemical generation at the cathode:

$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ (cathodic H_2O_2 generation)

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \bullet OH$ (Fenton reaction)

$Fe^{3+} + e^- \rightarrow Fe^{2+}$ (electrochemical iron regeneration)

Specialized carbon-based cathode materials (graphite felt, carbon felt, activated carbon fiber) provide high surface area for oxygen reduction. The electrochemical iron regeneration cycle means a small initial Fe^{2+} dose continuously participates in oxidation, dramatically reducing iron requirements, sludge formation, and chemical costs. Once operating conditions are optimized, the process runs continuously requiring only electrical power and air/oxygen supply.

C. Electro-Photo-Fenton Process

UV irradiation of the Electro-Fenton system creates EPF—a synergistic combination generating •OH through three additional photochemical mechanisms:

$H_2O_2 + h\nu \rightarrow 2\bullet OH$ (direct H_2O_2 photolysis at ~254 nm)

$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + \bullet OH + H^+$ (photo-reduction of Fe^{3+})

$[Fe(C_2O_4)]^+ + h\nu \rightarrow Fe^{2+} + CO_2 + CO_2\bullet^-$ (photo-decarboxylation of iron-oxalate complexes)

Photo-decarboxylation simultaneously regenerates Fe^{2+} and degrades persistent carboxylic acid intermediates (particularly oxalic acid) that would otherwise accumulate. The three mechanisms—electrochemical H_2O_2 generation and Fe^{2+} regeneration, Fenton chemistry, and photochemistry—work synergistically, often achieving degradation rates 2–5 times faster than Electro-Fenton alone. Current EPF research focuses on herbicides (atrazine, glyphosate), phenolic compounds, synthetic dyes, and pharmaceutical residues.

III. Research Highlights: Proven Performance

Table 1 summarises key experimental studies demonstrating EPF and related Fenton-based process effectiveness:

Table 1: Advanced Oxidation Process Research Summary

Application	Electrode Configuration	Operating Conditions	Results	Ref
Alizarin Red Degradation	Anode: Cylindrical grids Cathode: Graphite felt (60 cm^2, 0.5 cm thick)	pH: 3, Current: 300 mA, Temp: 25°C, Fe^{2+}: 0.2 mM, Time: 210 min, Rotation: 700 rpm	TOC removal: 95%	[8]
Real Dyeing Wastewater Colour Removal	Anode: Pt/Ti Cathode: Graphite rod	pH: 3, Current: 68 A/m^2, Time: 150 min, Fe^{2+}: 15 mM, Temp: 25°C, O_2: 0.3 dm^3/min	Color removal: 70.6%	[11]
Aniline Oxidation with H_2O_2 Effects	Anode: Ti/RuO_2-IrO_2 Cathode: Stainless steel	Aniline: 0.01 M, Fe^{2+}: 1.07×10^{-3} M, SiO_2: 74 g/L, Current: 4 A, pH: 3.2, Time: 60 min	Aniline removal: 96% TOC removal: 20–30%	[1]
2,6-Dimethylaniline Degradation Kinetics	Anode: Ti/RuO_2-IrO_2 Cathode: Stainless steel	pH: 2, Fe^{2+}: 1 mM, H_2O_2: 20 mM, Current: 7.6 A/m^2	TOC removal: 60%	[12]
Synthetic Wastewater Treatment	Iron electrodes	pH: 3, Voltage: 30 V, H_2O_2: 50 mL/L, Time: 25 min	Removal: 97%	[10]
Real Industrial Wastewater	Anode: Ti/IrO_2-RuO_2 Cathode: Cylindrical Ti DSA	pH: 2, Current: 20 A, Fe^{2+}: 2000 mg/L, H_2O_2 (50 wt%): 6 mL/min, Time: 2520 min	TOC removal: 98% COD removal: 97%	[9]
Phenol-Containing Wastewater	Anode: RuO_2, SnO_2, PbO_2 Cathode: Stainless steel	pH: 3, Current: 1.0 A, H_2O_2: 1.2 QT	Removal: 78%	[4]
Acetonitrile Aqueous Mixture	Anode: Platinum (16 mm^2) Cathode: Carbon felt (80 cm^2)	pH: 3, Current: 200 mA, Fe^{2+}: 0.2 mM	Removal: 100%	[5]
COD Removal from Landfill Leachate	Anode: Ti/IrO_2-RuO_2-TiO_2 (10×15 cm) Cathode: Titanium (10×15 cm)	pH: 3, PDS: 62.5 mM, Fe^{2+}: 15.6 mM, Current: 13.89 mA/cm^2, Time: 240 min	COD removal: 67.7%	[15]
Tissue Paper Wastewater	Anode: Turbine impeller (8 flat blades) Cathode: Cylindrical iron	pH: 2, Current: 20 mA/cm^2, H_2O_2: 0.2 M	COD removal: 80%	[13]
Azo Dye Wastewater	Anode: Pt Cathode: Carbon felt	pH: 3, Current: 60 mA, Fe^{2+}: 0.1 mM, Time: 6 h	TOC removal: 98%	[3]
Azo Dye-Containing Water	Anode: Pt Cathode: Carbon felt	pH: 2	COD removal: 80%	[2]

Key observations: TOC/COD removal is consistently 60–98% across diverse wastewater types; optimal pH is 2–3 for all applications; effective Fe^{2+} concentrations range from 0.1 to 2000 mg/L; carbon-based cathodes (graphite felt, carbon felt) Prove most effective for H_2O_2 generation; dimensionally stable anodes (DSA) with oxide coatings show excellent durability.

IV. Critical Operating Parameters

Parameter	Optimal Range / Guideline	Key Considerations
pH	2.0–3.0 (optimal ~2.8–3.0)	Most critical parameter. Fe $(OH)_3$ precipitates above pH 4; H_2O_2 is too stable below pH 2. Requires acidification before treatment and neutralisation before discharge.
H_2O_2 Concentration	Self-regulating in EF systems	In classical Fenton, excess H_2O_2 causes •OH scavenging (H_2O_2 + •OH → HO_2• + H_2O). EF systems regulate via O_2/air supply rate.
Ferrous Ion (Fe^{2+})	0.1–5 mM typical	Too low limits •OH generation; too high scavenges •OH and increases sludge. EF reduces requirements through electrochemical regeneration.
Current Density	Application-specific	Higher current increases H_2O_2/Fe^{2+} production but with diminishing returns and higher energy costs. Excessive current causes unwanted side reactions.
Temperature	20–40°C (ambient preferred)	Higher temperature accelerates kinetics but increases H_2O_2 decomposition. Ambient operation preferred to minimize heating/cooling costs.
Electrode Distance	Minimize within hydraulic constraints	Shorter distance reduces electrical resistance and energy consumption; longer distance may improve mixing but requires higher voltage.
Supporting Electrolyte	Sulfate preferred	Chloride may form hypochlorite, complicating chemistry. Phosphate complexes iron, reducing catalyst availability. Higher ionic strength reduces electrical resistance.
Chelating Agents	Avoid unless neutral pH required	EDTA, citrate, or oxalate maintain iron solubility at higher pH but compete with pollutants for •OH and increase treated water COD.
Initial Pollutant Concentration	50–500 mg/L COD optimal	High concentration requires longer treatment or higher reagent doses. EPF works best at moderate concentrations.

V. Practical Applications

Industry / Source	Key Contaminants	EPF Advantage
Pharmaceutical manufacturing	Active pharmaceutical ingredients, synthesis intermediates, solvents	Mineralizes pharmaceutical residues resistant to biological treatment; prevents aquatic ecosystem contamination at trace concentrations
Agrochemical / Agricultural runoff	Herbicides, insecticides, fungicides	Degrades persistent, bioaccumulating pesticides that conventional oxidation cannot fully destroy
Petroleum refinery	Hydrocarbons, phenols, benzene derivatives, sulfur compounds	Handles variable compositions typical of refinery operations; reduces hazardous organics to acceptable discharge levels
Textile / Dye	Synthetic azo dyes, aromatic amines	Excels at decolorization and complete mineralization of dyes that

manufacturing		resist biodegradation
Landfill leachate	Complex degraded organics, heavy metals, and persistent pollutants	Significantly reduces COD and improves treatability prior to biological polishing
Hexavalent chromium (Cr^{6+})	Toxic/carcinogenic Cr^{6+} ions	Reduces Cr^{6+} to less harmful Cr^{3+} for subsequent precipitation and removal

VI. Advantages Over Alternative Methods

Compared To	EPF Advantage
Biological treatment	Hours vs. days/weeks; handles non-biodegradable organics; unaffected by toxic shocks that kill microbes; smaller footprint than activated sludge
Chemical oxidation (Cl_2, O_3)	•OH more reactive than Cl_2 or O_3; minimal harmful byproduct formation; better performance on resistant compounds; fewer handling/safety concerns
Physical separation (adsorption, membrane)	True destruction—eliminates rather than transfers pollutants; no secondary waste (spent adsorbent, concentrate) requiring disposal
Other AOPs (photocatalysis, radiolysis)	More economical than photocatalysis or radiolysis; simpler than combined UV/O_3 systems; superior to H_2O_2/UV alone

VII. Challenges and Future Directions

Current Limitations

1. Iron sludge: Some iron precipitation still occurs despite reduction vs. classical Fenton, requiring periodic removal
2. pH adjustment: Acidification and post-treatment neutralisation add chemical costs and operational complexity
3. Electrode fouling: Cathode surface deposits reduce H_2O_2 generation efficiency over time
4. Energy consumption: Electrical costs add to operational expenses
5. Scale-up uncertainty: Most data is from bench/pilot scale; industrial-scale performance requires validation

Research Priorities

1. **Reaction intermediate identification:** Understanding degradation pathways to predict byproduct formation and optimise treatment
2. **Mechanistic rate expressions:** Developing kinetic models for better reactor design and process control
3. **Scale-up parameters:** Establishing criteria for full-scale reactor design from pilot data
4. **Economic optimisation:** Balancing degradation efficiency against operational costs for different wastewater types
5. **Electrode material development:** Improving cathode materials for higher H_2O_2 generation efficiency and stability
6. **Process integration:** Combining EPF with biological or physical treatment for synergistic performance

VIII. CONCLUSION

The evolution from Henry Fenton's 1890 discovery to modern Electro-Photo-Fenton technology illustrates how fundamental chemical insights transform into powerful environmental solutions through electrochemical and photochemical engineering. EPF addresses the core failure of conventional treatment—inability to degrade recalcitrant organic pollutants—by generating hydroxyl radicals through multiple synergistic pathways. Research consistently demonstrates 60–98% COD/TOC removal across pharmaceutical, agrochemical, petroleum, textile, and landfill leachate applications. EPF offers compelling operational advantages: minimal chemical addition, reduced reagent consumption, and operational simplicity compared to multi-stage conventional treatment. Continued research into reaction mechanisms, intermediate identification, scale-up parameters, and cost optimization will establish EPF as a standard tool for challenging wastewater treatment as regulatory standards tighten and clean water resources become increasingly critical.

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