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Treatment of Landfill Leachate Using Electrochemical Advanced Oxidation Processes (EAOPs)

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Abstract - Landfill leachate is one of the most complex and hazardous wastewaters generated during the decomposition of municipal solid waste (MSW). It contains high concentrations of refractory organic matter, ammonia, heavy metals, dissolved salts, xenobiotic compounds, pharmaceuticals, endocrine-disrupting chemicals, and other emerging contaminants, whose composition varies with landfill age, climatic conditions, and waste characteristics. Conventional treatment technologies, including biological treatment, coagulation–flocculation, adsorption, membrane filtration, and chemical oxidation, often exhibit limited effectiveness in treating mature landfill leachate because of its low biodegradability, high toxicity, and complex chemical composition. Consequently, there is an increasing demand for advanced treatment technologies capable of achieving efficient degradation and complete mineralization of persistent pollutants while minimizing secondary pollution.

Electrochemical Advanced Oxidation Processes (EAOPs) have emerged as one of the most promising and environmentally sustainable technologies for landfill leachate treatment due to their ability to generate highly reactive oxygen species (ROS), particularly hydroxyl radicals (•OH), directly within the electrochemical reactor. These oxidizing species exhibit exceptionally high oxidation potentials and are capable of non-selectively degrading a wide range of refractory organic contaminants into simpler intermediates and ultimately mineralizing them into carbon dioxide, water, and inorganic ions. Compared with conventional oxidation methods, EAOPs offer several advantages, including *in situ* oxidant generation, minimal chemical consumption, reduced sludge production, operational flexibility, high oxidation efficiency, and compatibility with hybrid treatment systems.

This review provides a comprehensive overview of the fundamental principles, reaction mechanisms, operational parameters, and recent developments of EAOPs for landfill leachate treatment. The classification of major electrochemical technologies, including anodic oxidation (AO), Electro-Fenton (EF), Photoelectro-Fenton (PEF), Electro-Peroxone (EP), and emerging hybrid electrochemical oxidation systems, is critically discussed with emphasis on their oxidation mechanisms, reactor configurations, and pollutant degradation pathways. Particular attention is devoted to the electrochemical generation of hydroxyl radicals, direct and indirect oxidation mechanisms, mineralization processes, and kinetic models governing contaminant degradation.

The influence of critical operational parameters—including electrode material, current density, solution pH, supporting electrolyte composition, reaction time, temperature, reactor design, and energy consumption—on treatment efficiency is comprehensively evaluated. Recent advances in electrode engineering, particularly the development of boron-doped diamond (BDD) electrodes, mixed metal oxide anodes, carbon-based cathodes, nanostructured electrode materials, and three-dimensional electrochemical reactors, are reviewed with respect to their contributions to enhanced oxidation efficiency, improved current utilization, and reduced energy demand.

Furthermore, this review critically evaluates the performance of EAOPs in terms of chemical oxygen demand (COD) removal, total organic carbon (TOC) mineralization, ammonia oxidation, color removal, heavy metal elimination, toxicity reduction, and degradation of emerging contaminants. Comparative analysis demonstrates that Electro-Fenton and Photoelectro-Fenton processes generally achieve superior mineralization efficiencies due to continuous hydroxyl radical generation, whereas anodic oxidation employing boron-doped diamond electrodes provides excellent oxidation capability for highly refractory organic compounds. Hybrid electrochemical systems integrating biological treatment, electrocoagulation, membrane separation, photocatalysis, and persulfate activation have also shown significant potential for improving treatment performance while reducing operational costs and electrical energy consumption.

Despite remarkable technological progress, several challenges continue to hinder the widespread industrial implementation of EAOPs, including high electrical energy requirements, electrode cost, catalyst stability, electrode passivation, by-product formation, and scale-up limitations. The review discusses these challenges and highlights current industrial trends toward intelligent reactor design,

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renewable energy integration, artificial intelligence-assisted process optimization, digital monitoring, and resource recovery within the framework of sustainable wastewater management and circular economy principles.

Finally, future research priorities are identified, including the development of durable and cost-effective electrode materials, optimization of hybrid treatment technologies, comprehensive techno-economic and life-cycle assessments, long-term pilot-scale demonstrations, and the integration of renewable energy systems and advanced process control strategies. Overall, this review demonstrates that Electrochemical Advanced Oxidation Processes represent a highly effective and environmentally sustainable platform for landfill leachate treatment and are expected to play an increasingly important role in next-generation wastewater treatment technologies aimed at achieving stringent environmental regulations and sustainable resource management.

Keywords: Landfill Leachate, EAOPs, wastewater treatment, hydroxyl radicals, COD removal, electro-Fenton

1. INTRODUCTION TO ELECTROCHEMICAL ADVANCED OXIDATION PROCESSES (EAOPs)

1.1 Definition, Importance, and Historical Context

Rapid industrialization, urbanization, and population growth have significantly increased the generation of municipal solid waste (MSW) worldwide. Land filling remains one of the most widely adopted methods for MSW disposal because of its relatively low operational cost and ease of implementation. However, the infiltration of rainwater and the decomposition of organic waste within landfill sites produce a highly contaminated liquid known as **landfill leachate**. This wastewater contains a complex mixture of dissolved organic matter, ammonia, heavy metals, chlorinated compounds, pharmaceuticals, endocrine-disrupting chemicals, and other refractory pollutants. The composition of landfill leachate varies with landfill age, waste characteristics, climatic conditions, and operational practices, making its treatment particularly challenging.

Conventional treatment technologies, including biological processes, coagulation–flocculation, adsorption, membrane filtration, and chemical precipitation, have been extensively employed for landfill leachate treatment. While these methods are effective for removing biodegradable organic matter and suspended solids, they often exhibit limited efficiency toward persistent organic pollutants and mature leachates with low biodegradability. Moreover, issues such as excessive sludge production, membrane fouling, high chemical consumption, and elevated operating costs have encouraged the development of more efficient and environmentally sustainable treatment technologies.

Advanced Oxidation Processes (AOPs) have emerged as promising alternatives because they generate highly reactive oxygen species (ROS), particularly hydroxyl radicals (•OH), possessing an oxidation potential of approximately 2.8 V. These radicals are capable of non-selectively oxidizing a wide range of refractory organic compounds into simpler intermediates and, ultimately, mineralizing them into carbon dioxide, water, and inorganic ions. Compared with conventional oxidation methods, AOPs offer faster reaction kinetics, higher degradation efficiencies, and reduced formation of secondary pollutants.

Among the various AOPs, **Electrochemical Advanced Oxidation Processes (EAOPs)** have gained considerable attention over the past three decades. EAOPs integrate electrochemical principles with advanced oxidation chemistry to generate oxidizing species directly within the treatment reactor through electrochemical reactions. Unlike conventional chemical oxidation processes that require continuous addition of oxidants, EAOPs produce reactive species *in situ*, enabling precise process control while minimizing chemical consumption and secondary waste generation. Common EAOP technologies include anodic oxidation, electro-Fenton, photoelectro-Fenton, electro-Peroxone, electrochemical per sulfate activation, and Electrocoagulation-assisted oxidation.

The historical development of EAOPs began in the late twentieth century with advances in electrochemistry and the introduction of dimensionally stable anodes and boron-doped diamond (BDD) electrodes. Subsequent research demonstrated the remarkable ability of these technologies to degrade persistent organic contaminants in industrial wastewater. During the early 2000s, improvements in electrode materials, reactor configurations, renewable energy integration, and hybrid treatment systems significantly enhanced the efficiency and commercial viability of EAOPs. Today, these processes are increasingly investigated for the treatment of complex wastewaters, including landfill leachate, textile effluents, pharmaceutical wastewater, petrochemical discharges, and other industrial effluents.

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Recent studies have reported chemical oxygen demand (COD) removal efficiencies exceeding 90%, substantial color removal, effective degradation of toxic organic compounds, and partial oxidation of ammonia under optimized operating conditions. The performance of EAOPs depends on several operational parameters, including electrode material, current density, solution pH, electrolyte concentration, hydraulic retention time, and reactor design. Continuous developments in nanostructured electrodes, renewable electricity utilization, and integrated electrochemical-biological treatment systems are expected to improve energy efficiency and reduce operating costs, thereby expanding the practical application of EAOPs in sustainable wastewater management.

Consequently, Electrochemical Advanced Oxidation Processes have become one of the most promising technologies for treating landfill leachate because they combine high oxidation efficiency, operational flexibility, environmental compatibility, and the potential for complete mineralization of refractory pollutants. Ongoing research is focused on improving reactor design, reducing energy consumption, extending electrode lifespan, and facilitating large-scale implementation to meet increasingly stringent environmental regulations.

1.2 Characteristics and Composition of Landfill Leachate

Landfill leachate is a complex wastewater generated by the percolation of precipitation, surface runoff, and inherent moisture through layers of municipal solid waste (MSW). During this process, water dissolves and transports a wide variety of organic and inorganic contaminants produced by the decomposition of waste materials. The quantity and composition of landfill leachate vary considerably depending on landfill age, waste composition, climatic conditions, operational practices, and the extent of biological degradation occurring within the landfill.

Young landfill leachate, typically generated during the acidogenic phase of waste decomposition, is characterized by high concentrations of biodegradable organic matter, volatile fatty acids, and ammoniacal nitrogen. It generally exhibits high biochemical oxygen demand (BOD), chemical oxygen demand (COD), and a relatively high BOD/COD ratio, indicating good biodegradability. In contrast, mature landfill leachate, produced during the methanogenic phase, contains lower concentrations of biodegradable compounds but higher levels of refractory organic substances such as humic acids, fulvic acids, phenolic compounds, and other persistent pollutants. Consequently, mature leachate exhibits a low BOD/COD ratio and is considerably more difficult to treat using conventional biological processes.

Typical constituents of landfill leachate include dissolved organic carbon, ammonium ions, nitrate, chloride, sulfate, bicarbonate, calcium, magnesium, sodium, potassium, and a wide range of heavy metals such as lead (Pb), cadmium (Cd), chromium (Cr), nickel (Ni), copper (Cu), zinc (Zn), mercury (Hg), and arsenic (As). In addition, landfill leachate may contain pharmaceuticals, endocrine-disrupting compounds, pesticides, surfactants, microplastics, per- and polyfluoroalkyl substances (PFAS), and other emerging contaminants. These pollutants contribute to the high toxicity and environmental persistence of landfill leachate.

Physicochemical characteristics commonly monitored during landfill leachate treatment include pH, conductivity, total dissolved solids (TDS), total suspended solids (TSS), COD, BOD, total organic carbon (TOC), ammonia nitrogen (NH_4^+–N), color, turbidity, and concentrations of heavy metals. Among these parameters, COD and ammonia are often present at extremely high concentrations and are considered primary indicators of treatment performance. The considerable variability in leachate composition poses significant challenges for wastewater treatment facilities and frequently necessitates the integration of multiple treatment technologies to achieve regulatory discharge standards.

1.3 Environmental Impacts of Landfill Leachate

Landfill leachate represents one of the most significant environmental hazards associated with municipal solid waste disposal. If inadequately collected or treated, leachate can migrate through soil layers and contaminate surrounding groundwater, rivers, lakes, and agricultural land. Because groundwater serves as a major source of drinking water in many regions, contamination by landfill leachate presents serious risks to public health and ecosystem sustainability.

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The elevated concentrations of organic pollutants in landfill leachate increase the oxygen demand of receiving water bodies, leading to dissolved oxygen depletion and subsequent deterioration of aquatic ecosystems. Excessive ammonia concentrations are highly toxic to fish and aquatic microorganisms and may contribute to eutrophication, resulting in excessive algal growth, reduced biodiversity, and ecological imbalance. Furthermore, refractory organic compounds persist in the environment for extended periods due to their resistance to natural biodegradation processes.

Heavy metals present in landfill leachate accumulate within soils, sediments, plants, and aquatic organisms through bioaccumulation and biomagnification. Chronic exposure to metals such as cadmium, lead, mercury, and chromium has been associated with neurological disorders, kidney damage, developmental abnormalities, carcinogenic effects, and other adverse health outcomes. Emerging contaminants, including pharmaceuticals and endocrine-disrupting chemicals, have also attracted increasing attention because of their ability to interfere with hormonal systems and affect both wildlife and human health even at trace concentrations.

The environmental consequences of untreated landfill leachate extend beyond water pollution. Soil contamination can reduce agricultural productivity by altering nutrient availability and soil microbial communities. In addition, the decomposition of organic matter within landfill sites contributes to greenhouse gas emissions, including methane (CH_4) and carbon dioxide (CO_2), thereby exacerbating climate change. These environmental and public health concerns highlight the necessity for effective leachate management systems and the implementation of advanced treatment technologies capable of removing both conventional and emerging contaminants.

1.4 Need for Advanced Treatment Technologies

Conventional landfill leachate treatment technologies, including activated sludge systems, anaerobic digestion, coagulation–flocculation, adsorption, membrane filtration, and chemical precipitation, have been widely implemented for several decades. Although these processes are effective for removing suspended solids and readily biodegradable organic matter, they often fail to achieve complete removal of refractory organic compounds, ammonia, toxic micropollutants, and emerging contaminants. In addition, many conventional processes generate substantial quantities of secondary sludge, require high chemical dosages, or experience operational problems such as membrane fouling and declining treatment efficiency.

As environmental regulations become increasingly stringent, wastewater treatment facilities must achieve lower discharge limits for COD, TOC, ammonia, heavy metals, and hazardous organic compounds. These requirements have accelerated research into advanced treatment technologies capable of complete pollutant degradation rather than simple phase transfer. Among the available technologies, Advanced Oxidation Processes (AOPs) have emerged as highly effective methods because they generate powerful reactive oxygen species capable of oxidizing a broad spectrum of contaminants with minimal selectivity.

Electrochemical Advanced Oxidation Processes (EAOPs) represent one of the most promising developments within the AOP family. These technologies generate hydroxyl radicals and other oxidizing species directly within the electrochemical reactor through anodic oxidation, electro-Fenton reactions, electro-peroxone systems, photoelectrochemical processes, or related electrochemical pathways. The *in situ* generation of oxidants reduces chemical consumption, minimizes secondary pollution, and provides greater operational flexibility than conventional oxidation methods.

EAOPs have demonstrated exceptional capability for degrading refractory organic matter, reducing COD and TOC, removing color, detoxifying industrial wastewater, and partially oxidizing ammonia. Their modular reactor design, ease of automation, compatibility with renewable electricity sources, and potential integration with biological treatment processes make them attractive for both laboratory-scale and full-scale wastewater treatment applications. Continuous advancements in electrode materials, reactor configurations, nanotechnology, and energy-efficient electrochemical systems are expected to further improve treatment performance while reducing operational costs.

Consequently, Electrochemical Advanced Oxidation Processes are increasingly recognized as sustainable and environmentally friendly technologies capable of overcoming the limitations of conventional landfill leachate treatment. Their ability to achieve high mineralization efficiency and effectively remove persistent pollutants positions them as a key component of future integrated wastewater treatment strategies.

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2. CLASSIFICATION OF ELECTROCHEMICAL ADVANCED OXIDATION PROCESSES (EAOPS)

Electrochemical Advanced Oxidation Processes (EAOPs) comprise a group of advanced wastewater treatment technologies that generate highly reactive oxidizing species through electrochemical reactions. The principal oxidants produced include hydroxyl radicals (•OH), sulfate radicals ($SO_4^{\bullet-}$), hydrogen peroxide (H_2O_2), ozone (O_3), and other reactive oxygen species (ROS), which are capable of degrading a broad spectrum of persistent organic pollutants. Depending on the oxidation mechanism, electrode configuration, and oxidant generation pathway, EAOPs can be classified into several categories. Among these, anodic oxidation, electro-Fenton, photoelectro-Fenton, electro-peroxone, and emerging hybrid electrochemical systems have demonstrated significant potential for the treatment of landfill leachate.

2.1 Anodic Oxidation (AO)

Anodic oxidation is the simplest and one of the most extensively investigated EAOPs for wastewater treatment. In this process, oxidation occurs directly at the anode surface, where water molecules are electrochemically oxidized to produce adsorbed hydroxyl radicals (•OH). These radicals react non-selectively with organic pollutants, converting them into smaller intermediate compounds and ultimately mineralizing them into carbon dioxide, water, and inorganic ions.

The efficiency of anodic oxidation depends largely on the electrode material. Active anodes, such as platinum (Pt), ruthenium oxide (RuO_2), and iridium oxide (IrO_2), tend to promote selective oxidation through chemisorbed oxygen species. In contrast, non-active anodes, particularly boron-doped diamond (BDD), exhibit higher oxygen evolution overpotentials and generate physisorbed hydroxyl radicals with stronger oxidation capabilities, enabling near-complete mineralization of refractory pollutants.

The primary anodic reaction can be represented as:

$$\mathbf{H_2O \rightarrow {\bullet}OH + H^+ + e^-}$$

Subsequently, organic contaminants (R) undergo oxidation according to:

$$\mathbf{R + {\bullet}OH \rightarrow CO_2 + H_2O + \text{Mineralized Products}}$$

Anodic oxidation offers several advantages, including simple reactor design, easy operation, absence of additional chemical reagents, and high oxidation efficiency. However, high electrical energy consumption and the relatively high cost of advanced electrode materials remain major limitations for large-scale implementation.

2.2 Electro-Fenton Process (EF)

The Electro-Fenton process is considered one of the most efficient EAOPs for treating landfill leachate because it continuously generates hydroxyl radicals through electrochemically assisted Fenton chemistry. In this process, hydrogen peroxide is produced in situ at the cathode through oxygen reduction, while ferrous ions (Fe^{2+}) catalyze the decomposition of hydrogen peroxide to produce hydroxyl radicals.

The principal electrochemical reactions are:

Cathode reaction:

$$\mathbf{O_2 + 2H^+ + 2e^- \rightarrow H_2O_2}$$

Fenton reaction:

$$\mathbf{Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {\bullet}OH + OH^-}$$

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Regeneration of catalyst:

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+}$$

The continuous regeneration of Fe^{2+} distinguishes the Electro-Fenton process from conventional Fenton oxidation and significantly reduces chemical consumption. Hydroxyl radicals generated during the reaction rapidly oxidize refractory organic compounds, resulting in high chemical oxygen demand (COD) removal, color reduction, and detoxification of landfill leachate.

The optimum operating pH for Electro-Fenton treatment generally ranges between 2.5 and 3.5, where hydroxyl radical generation is maximized. Important operational parameters include current density, iron concentration, dissolved oxygen availability, electrolyte composition, reaction time, and electrode configuration.

Electro-Fenton technology has demonstrated COD removal efficiencies exceeding 90% under optimized conditions and is particularly effective for mature landfill leachate characterized by low biodegradability and high concentrations of humic substances.

2.3 Photoelectro-Fenton (PEF)

Photoelectro-Fenton is an advanced modification of the Electro-Fenton process in which ultraviolet (UV) or visible light irradiation is combined with electrochemical oxidation. Light irradiation accelerates hydroxyl radical production by photochemically regenerating ferrous ions from ferric ions and promoting additional hydrogen peroxide decomposition.

The principal photochemical reaction is:

$$Fe^{3+} + h\nu \rightarrow Fe^{2+}$$

The regenerated Fe^{2+} immediately participates in additional Fenton reactions, thereby increasing radical production and enhancing pollutant degradation.

Compared with the conventional Electro-Fenton process, Photoelectro-Fenton offers several advantages, including higher mineralization efficiency, faster reaction kinetics, improved degradation of aromatic and chlorinated compounds, and lower residual iron concentrations in treated effluent. Numerous studies have reported COD removal efficiencies greater than 95% for landfill leachate using optimized Photoelectro-Fenton systems.

Despite its superior treatment performance, Photoelectro-Fenton requires an external light source, increasing capital investment and operational energy demand. Recent research focuses on utilizing solar irradiation to reduce energy consumption and improve economic feasibility.

2.4 Electro-Peroxone Process (EP)

The Electro-Peroxone process combines electrochemical hydrogen peroxide generation with ozone oxidation to enhance hydroxyl radical production. Ozone introduced into the electrochemical reactor reacts rapidly with electrochemically generated hydrogen peroxide, producing large quantities of hydroxyl radicals through the peroxone mechanism.

The simplified reaction is:

$$O_3 + H_2O_2 \rightarrow {\bullet}OH + O_2 + HO_2{\bullet}$$

The simultaneous application of electrochemical oxidation and ozonation provides synergistic effects that substantially improve the degradation of persistent organic pollutants. Electro-Peroxone has demonstrated excellent performance in removing color,

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phenolic compounds, pharmaceuticals, endocrine-disrupting chemicals, and humic substances commonly found in mature landfill leachate.

Compared with standalone ozonation, Electro-Peroxone achieves greater oxidation efficiency while reducing ozone consumption. However, the requirement for ozone generation equipment increases both installation costs and operational complexity.

Recent investigations have shown that Electro-Peroxone can achieve COD removal efficiencies exceeding 90% with significantly shorter treatment times than conventional electrochemical oxidation processes.

2.5 Emerging Hybrid EAOP Technologies

Recent advances in electrochemical engineering have led to the development of hybrid EAOP technologies that integrate electrochemical oxidation with complementary physical, chemical, or biological treatment methods. These integrated systems are designed to maximize pollutant removal while minimizing energy consumption and operational costs.

Prominent hybrid technologies include:

- Electrochemical oxidation coupled with biological treatment.
- Electrocoagulation–electrooxidation systems.
- Photoelectrochemical oxidation using semiconductor photocatalysts such as TiO_2.
- Sonoelectrochemical oxidation integrating ultrasonic cavitation.
- Electrochemical activation of persulfate or peroxymonosulfate to generate sulfate radicals.
- Membrane-electrochemical hybrid reactors.
- Solar-powered Electro-Fenton and Photoelectro-Fenton systems.

These hybrid technologies offer several advantages over individual treatment processes, including higher mineralization efficiency, reduced sludge production, improved degradation of emerging contaminants, enhanced energy efficiency, and lower overall operating costs. The incorporation of nanostructure electrode materials, carbon-based catalysts, conductive polymers, and renewable energy sources has further expanded the applicability of EAOPs for sustainable wastewater treatment.

Current research is increasingly directed toward intelligent reactor design, artificial intelligence-assisted process optimization, real-time monitoring, and renewable energy integration. These innovations are expected to improve the commercial viability of EAOPs and facilitate their large-scale implementation for landfill leachate treatment and other complex industrial wastewaters.

3. REACTION MECHANISMS OF ELECTROCHEMICAL ADVANCED OXIDATION PROCESSES (EAOPS)

Electrochemical Advanced Oxidation Processes (EAOPs) remove contaminants primarily through the generation of highly reactive oxygen species (ROS), particularly hydroxyl radicals (•OH), which possess an oxidation potential of approximately 2.80 V versus the standard hydrogen electrode. These radicals react rapidly and non-selectively with a wide variety of organic pollutants, converting complex molecules into smaller intermediates and ultimately mineralizing them into carbon dioxide (CO_2), water (H_2O), and inorganic ions. The degradation efficiency of EAOPs depends on the generation rate of reactive species, pollutant characteristics, operating conditions, and electrochemical reactor design. The principal reaction mechanisms involved in EAOPs are discussed below.

3.1 Hydroxyl Radical Generation

Hydroxyl radicals are the primary oxidizing species responsible for contaminant degradation in most EAOPs. These radicals can be generated either directly at the electrode surface or indirectly through homogeneous electrochemical reactions occurring within the solution.

3.1.1 Direct Electrochemical Generation

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In anodic oxidation, water molecules adsorbed on the anode surface undergo electrochemical oxidation to produce adsorbed hydroxyl radicals according to:

$$H_2O \rightarrow {}^{\bullet}OH + H^+ + e^-$$

The generated hydroxyl radicals remain temporarily adsorbed on the electrode surface and react immediately with nearby organic contaminants. The oxidation strength depends strongly on the electrode material. Boron-doped diamond (BDD) electrodes produce weakly adsorbed hydroxyl radicals with exceptionally high oxidation potential, whereas active electrodes such as Pt, RuO_2, and IrO_2 form more strongly adsorbed oxygen species that promote selective oxidation.

3.1.2 Indirect Electrochemical Generation

In Electro-Fenton and related processes, hydroxyl radicals are generated through the electrochemical production of hydrogen peroxide followed by the Fenton reaction.

At the cathode:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$$

Fenton reaction:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^-$$

Catalyst regeneration:

$$Fe^{3+} + e^- \rightarrow Fe^{2+}$$

This continuous regeneration of Fe^{2+} enables sustained hydroxyl radical production throughout the treatment process, making the Electro-Fenton process highly effective for degrading refractory organic compounds present in landfill leachate.

In addition to hydroxyl radicals, several EAOPs generate other reactive oxygen species, including superoxide radicals ($O_2^{\bullet -}$), hydroperoxyl radicals ($HO_2^{\bullet}$), singlet oxygen ($^1O_2$), ozone (O_3), and sulfate radicals ($SO_4^{\bullet -}$). Although hydroxyl radicals dominate pollutant oxidation in most systems, these additional oxidants contribute significantly depending on the electrode material and oxidant activation pathway.

3.2 Direct and Indirect Oxidation Pathways

Organic contaminants in EAOPs are degraded through both direct electron-transfer reactions and indirect oxidation mediated by reactive oxygen species.

3.2.1 Direct Oxidation

During direct oxidation, pollutants adsorb onto the electrode surface and undergo electron transfer directly to the anode without the participation of free radicals. The oxidation reaction converts contaminants into partially oxidized intermediates or completely mineralized products.

General reaction:

$$R \rightarrow \text{Oxidized Products} + ne^-$$

where *R* represents the organic pollutant.

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Direct oxidation is generally more significant for compounds that readily adsorb onto the electrode surface and for electrodes exhibiting high electrocatalytic activity.

3.2.2 Indirect Oxidation

Indirect oxidation constitutes the dominant degradation pathway in most EAOPs. In this mechanism, electrochemically generated oxidizing species diffuse throughout the solution and react with pollutants independently of electrode contact.

The primary oxidation reaction is:

R + •OH → Oxidized Intermediates

Hydroxyl radicals attack organic molecules through several reaction pathways, including:

- Hydrogen atom abstraction
- Electrophilic addition to double bonds
- Electron transfer reactions
- Aromatic ring hydroxylation
- Cleavage of carbon–carbon and carbon–heteroatom bonds

These reactions progressively convert complex organic molecules into simpler oxygenated intermediates, which undergo further oxidation until complete mineralization is achieved.

The coexistence of direct and indirect oxidation pathways significantly enhances contaminant removal efficiency and enables EAOPs to degrade a broad spectrum of persistent pollutants.

3.3 Mineralization Mechanisms

Unlike conventional treatment technologies that often transfer pollutants from one phase to another, EAOPs aim to achieve complete mineralization of organic contaminants. Mineralization refers to the conversion of complex organic molecules into stable inorganic products such as carbon dioxide, water, nitrate, sulfate, phosphate, and chloride ions.

The mineralization process generally proceeds through three sequential stages:

Stage I: Initial Oxidation

Hydroxyl radicals rapidly attack the parent pollutant, producing hydroxylated compounds, aldehydes, ketones, alcohols, and short-chain organic acids.

Stage II: Intermediate Degradation

The intermediate products undergo successive oxidation reactions, resulting in cleavage of aromatic rings, oxidation of aliphatic chains, and formation of low-molecular-weight carboxylic acids such as oxalic acid, formic acid, and acetic acid.

Stage III: Complete Mineralization

The remaining intermediates are oxidized into final inorganic products:

Organic Compounds + •OH → CO_2 + H_2O + Inorganic Ions

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The degree of mineralization is commonly evaluated using Total Organic Carbon (TOC) removal, Chemical Oxygen Demand (COD) reduction, and Biochemical Oxygen Demand (BOD) measurements. High TOC removal indicates extensive mineralization rather than simple transformation into intermediate compounds.

Complete mineralization is desirable because it minimizes the formation of toxic by-products and reduces the environmental impact of treated wastewater.

3.4 Factors Influencing Reaction Kinetics

The degradation kinetics of EAOPs are governed by several physicochemical and operational parameters that directly influence hydroxyl radical generation and pollutant oxidation.

Electrode Material

Electrode composition is one of the most critical factors affecting treatment efficiency. Boron-doped diamond electrodes generally exhibit the highest oxidation capability due to their high oxygen evolution potential and ability to generate large quantities of free hydroxyl radicals. Graphite, titanium-based mixed metal oxide electrodes, platinum, and carbon felt are also widely used depending on the specific EAOP configuration.

Current Density

Current density determines the rate of electrochemical reactions occurring at the electrode surface. Increasing current density generally enhances hydroxyl radical production and pollutant degradation. However, excessively high current densities promote undesirable side reactions such as oxygen evolution, leading to increased energy consumption and lower current efficiency.

Solution pH

Solution pH strongly influences radical generation, catalyst stability, and oxidation kinetics. Electro-Fenton processes typically achieve maximum performance at acidic conditions (pH 2.5–3.5), whereas anodic oxidation can operate effectively over a broader pH range. Extreme pH values may reduce catalyst activity or promote radical scavenging reactions.

Electrode Spacing and Reactor Design

The distance between electrodes influences electrical resistance, current distribution, and mass transfer within the electrochemical reactor. Optimized reactor configurations improve pollutant transport to reactive sites while minimizing energy losses.

Electrolyte Concentration

Supporting electrolytes such as sodium sulfate (Na_2SO_4) increase solution conductivity and reduce electrical resistance. However, chloride-containing electrolytes may generate active chlorine species, which can enhance oxidation but may also promote the formation of chlorinated by-products.

Initial Pollutant Concentration

Higher pollutant concentrations generally require longer treatment times and greater oxidant production. The degradation of many organic contaminants in EAOPs follows pseudo-first-order kinetics, where the reaction rate depends on pollutant concentration and hydroxyl radical availability.

Temperature and Reaction Time

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Increasing temperature accelerates reaction kinetics and improves mass transfer but may also enhance hydrogen peroxide decomposition and increase energy requirements. Sufficient reaction time is essential for complete mineralization, particularly for mature landfill leachate containing refractory organic compounds.

Dissolved Oxygen Availability

In Electro-Fenton and Electro-Peroxone systems, dissolved oxygen serves as the precursor for hydrogen peroxide generation. Efficient oxygen transfer enhances radical production and improves overall oxidation performance.

Overall, the reaction kinetics of EAOPs are controlled by the interplay between electrochemical operating conditions, reactor design, oxidant generation efficiency, and wastewater characteristics. Optimization of these parameters is essential for maximizing pollutant degradation, reducing energy consumption, and achieving cost-effective treatment of landfill leachate.

4. OPERATIONAL PARAMETERS AFFECTING EAOP PERFORMANCE

The efficiency of Electrochemical Advanced Oxidation Processes (EAOPs) is governed by several operational parameters that directly influence the generation of reactive oxygen species (ROS), pollutant degradation kinetics, mineralization efficiency, and energy consumption. Optimization of these parameters is essential to maximize treatment performance while minimizing operational costs. The most influential factors include electrode materials, current density, solution pH, supporting electrolytes, reaction time, temperature, reactor configuration, and energy consumption.

4.1 Electrode Materials

Electrode material is one of the most critical parameters affecting the efficiency of EAOPs because it determines the rate of oxidant generation, oxygen evolution potential, electrocatalytic activity, chemical stability, and electrode lifetime. Electrodes used in electrochemical wastewater treatment are generally classified as active and non-active anodes.

Active anodes, including platinum (Pt), iridium oxide (IrO_2), ruthenium oxide (RuO_2), and mixed metal oxide (MMO) electrodes, promote the formation of chemisorbed oxygen species that selectively oxidize organic compounds. These electrodes generally exhibit lower oxidation potentials and favor partial oxidation rather than complete mineralization.

Non-active anodes, particularly boron-doped diamond (BDD), tin oxide (SnO_2), and lead dioxide (PbO_2), generate weakly adsorbed hydroxyl radicals possessing significantly higher oxidation capability. Among these materials, BDD electrodes are considered the benchmark for EAOPs because of their high oxygen evolution overpotential, excellent chemical stability, wide electrochemical window, corrosion resistance, and ability to achieve near-complete mineralization of refractory pollutants.

Cathode materials are equally important, especially in Electro-Fenton systems where hydrogen peroxide is generated electrochemically. Carbon felt, graphite felt, carbon cloth, activated carbon fiber, carbon nanotubes, and gas diffusion electrodes are widely employed because of their large surface area, high conductivity, and excellent catalytic activity for oxygen reduction.

Recent research has focused on nanostructured electrodes, graphene-based composites, doped carbon materials, titanium-based nanomaterials, and conductive polymers to improve catalytic activity, increase radical generation, reduce energy consumption, and prolong electrode lifespan.

4.2 Current Density

Current density directly controls the rate of electrochemical reactions occurring at the electrode surface and is one of the most influential operating parameters in EAOPs. Increasing current density generally enhances hydroxyl radical production, hydrogen peroxide generation, and pollutant oxidation rates.

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At low current densities, oxidant generation is limited, resulting in slower degradation kinetics and reduced mineralization efficiency. As current density increases, the production of reactive oxygen species accelerates, leading to higher removal efficiencies for chemical oxygen demand (COD), total organic carbon (TOC), color, and refractory organic pollutants.

However, excessive current densities promote undesirable side reactions, including oxygen evolution at the anode and hydrogen evolution at the cathode. These competing reactions decrease current efficiency, increase electrical energy consumption, and may reduce electrode lifetime due to accelerated surface degradation.

Therefore, an optimum current density should be selected to maximize pollutant degradation while minimizing parasitic reactions and operating costs. The optimum value depends on electrode material, wastewater composition, reactor design, and treatment objectives.

4.3 Solution pH

Solution pH significantly influences electrochemical reaction mechanisms, catalyst stability, pollutant speciation, and radical generation efficiency. Among all EAOPs, Electro-Fenton processes exhibit the strongest dependence on pH.

The optimum pH for Electro-Fenton treatment generally ranges from 2.5 to 3.5. Under acidic conditions, ferrous ions remain soluble and effectively catalyze hydrogen peroxide decomposition, producing large quantities of hydroxyl radicals. At higher pH values, ferric ions precipitate as iron hydroxides, reducing catalyst availability and decreasing oxidation efficiency. Conversely, extremely acidic conditions may reduce hydrogen peroxide stability and increase corrosion of reactor components.

Anodic oxidation systems are less sensitive to pH variations and can operate effectively over a broader pH range. Nevertheless, solution pH influences the formation of active chlorine species in chloride-containing electrolytes, thereby affecting degradation pathways and the possible formation of chlorinated by-products.

Optimization of pH is therefore essential to maximize oxidation efficiency, minimize reagent consumption, and maintain long-term operational stability.

4.4 Supporting Electrolytes

Supporting electrolytes are added to improve solution conductivity, reduce electrical resistance, and facilitate efficient current distribution throughout the electrochemical reactor. Increased conductivity decreases cell voltage requirements and improves overall energy efficiency.

Common supporting electrolytes include sodium sulfate (Na_2SO_4), sodium chloride (NaCl), potassium sulfate (K_2SO_4), sodium nitrate ($NaNO_3$), and sodium carbonate (Na_2CO_3). Among these, sodium sulfate is widely preferred because it is chemically stable and does not generate undesirable chlorinated oxidation by-products.

Chloride-containing electrolytes enhance oxidation through the formation of active chlorine species such as chlorine (Cl_2), hypochlorous acid (HOCl), and hypochlorite ions (OCl^-), which participate in indirect oxidation reactions. While these oxidants improve degradation efficiency, excessive chloride concentrations may promote the formation of chlorinated organic compounds, chlorate, and perchlorate, raising environmental concerns.

Electrolyte concentration should therefore be optimized to achieve adequate conductivity while minimizing secondary pollution and operating costs.

4.5 Reaction Time

Reaction time determines the duration of contact between pollutants and electrochemically generated oxidizing species. Increasing treatment time generally enhances pollutant degradation and mineralization by allowing successive oxidation of intermediate products.

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Initially, degradation proceeds rapidly because hydroxyl radicals readily attack high concentrations of organic contaminants. As treatment progresses, oxidation rates gradually decrease owing to reduced pollutant concentrations and the formation of more resistant intermediate compounds.

Insufficient reaction time may result in incomplete oxidation, whereas excessively long treatment periods increase electrical energy consumption with only marginal improvements in treatment efficiency. Therefore, determining the optimum reaction time is essential for balancing treatment performance and operational cost.

Reaction time is commonly optimized using COD removal, TOC reduction, color removal, ammonia oxidation, and kinetic modeling.

4.6 Temperature

Temperature affects electrochemical reaction kinetics, solution conductivity, mass transfer, and the stability of reactive oxidants. Moderate increases in temperature generally accelerate reaction rates and improve pollutant diffusion toward electrode surfaces.

Higher temperatures reduce solution viscosity, enhance ionic mobility, and increase the rate of electrochemical oxidation. However, excessive temperatures may accelerate hydrogen peroxide decomposition, reduce dissolved oxygen concentration, increase evaporation losses, and promote undesirable side reactions that decrease current efficiency.

Most EAOPs are therefore operated near ambient temperature (20–35 °C), where a favorable balance between reaction kinetics and energy consumption is achieved. Temperature optimization is particularly important for large-scale treatment systems operating under variable environmental conditions.

4.7 Reactor Configuration

Electrochemical reactor design significantly influences mass transfer, current distribution, hydraulic characteristics, and overall treatment efficiency. Common reactor configurations include batch reactors, continuous-flow reactors, parallel-plate reactors, tubular reactors, fluidized-bed reactors, rotating disk reactors, membrane electrochemical reactors, and three-dimensional electrode systems.

Batch reactors are widely used in laboratory investigations because of their simplicity and ease of operation. Continuous-flow systems are preferred for industrial applications owing to their ability to treat large wastewater volumes under steady-state conditions.

Three-dimensional electrochemical reactors containing conductive particle electrodes provide substantially greater active surface area than conventional two-dimensional systems. This configuration enhances hydroxyl radical production, improves pollutant adsorption, increases current efficiency, and accelerates degradation kinetics.

Important design considerations include electrode spacing, electrode geometry, hydraulic retention time, flow velocity, mixing intensity, gas diffusion, and reactor scalability. Appropriate reactor design minimizes electrical resistance, improves mass transport, and reduces operational costs.

4.8 Energy Consumption

Electrical energy consumption is one of the primary factors limiting the large-scale application of EAOPs. The total energy requirement depends on current density, cell voltage, treatment time, reactor configuration, electrode material, wastewater conductivity, and pollutant concentration.

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Energy consumption generally increases with higher current density and longer reaction time. Consequently, optimization of operating conditions is essential to achieve maximum pollutant removal at minimum energy cost.

Several strategies have been proposed to improve energy efficiency, including:

- Use of high-performance electrode materials with low over potentials.
- Optimization of current density and electrode spacing.
- Integration of EAOPs with biological or membrane treatment processes.
- Utilization of renewable energy sources such as solar and wind power.
- Development of intelligent process control and real-time monitoring systems.
- Adoption of three-dimensional electrode reactors to improve current utilization.

Energy efficiency is commonly expressed as electrical energy per order (EEO), specific energy consumption (kWh m^{-3}), or energy required per kilogram of COD removed. These indicators facilitate comparison among different EAOP technologies and support techno-economic evaluation for industrial implementation.

Overall, the operational performance of EAOPs results from the combined effects of electrochemical parameters, wastewater characteristics, and reactor design. Systematic optimization of these variables is essential to maximize pollutant degradation, enhance mineralization efficiency, reduce operational costs, and improve the feasibility of full-scale landfill leachate treatment.

5. PERFORMANCE EVALUATION OF ELECTROCHEMICAL ADVANCED OXIDATION PROCESSES (EAOPS) FOR LANDFILL LEACHATE TREATMENT

The effectiveness of Electrochemical Advanced Oxidation Processes (EAOPs) is commonly assessed by evaluating their ability to remove organic and inorganic contaminants, reduce toxicity, improve biodegradability, and achieve complete mineralization of landfill leachate. Performance is generally quantified using physicochemical parameters such as chemical oxygen demand (COD), total organic carbon (TOC), biochemical oxygen demand (BOD), ammonia nitrogen (NH_4^+–N), color, heavy metal concentration, toxicity, and the degradation efficiency of emerging contaminants. Numerous laboratory-scale and pilot-scale studies have demonstrated that EAOPs consistently outperform conventional treatment technologies, particularly for mature landfill leachate containing high concentrations of refractory organic matter.

5.1 Chemical Oxygen Demand (COD) Removal

Chemical Oxygen Demand (COD) is the most widely used parameter for evaluating the oxidation efficiency of landfill leachate treatment processes because it represents the total amount of oxygen required to chemically oxidize organic pollutants present in wastewater.

EAOPs have demonstrated remarkable capability for COD reduction owing to the generation of highly reactive hydroxyl radicals and other reactive oxygen species. These oxidants non-selectively attack organic molecules, progressively converting complex compounds into smaller intermediates and ultimately mineralizing them into carbon dioxide and water.

Among various EAOPs, Electro-Fenton and Photoelectro-Fenton systems generally exhibit the highest COD removal efficiencies because of their continuous production of hydroxyl radicals through Fenton chemistry. Under optimized operating conditions, COD removal efficiencies exceeding 90% have frequently been reported for mature landfill leachate. Anodic oxidation using boron-doped diamond (BDD) electrodes also achieves substantial COD reduction owing to its superior oxidation capability and high oxygen evolution overpotential.

Several operational variables influence COD removal efficiency, including electrode material, current density, reaction time, solution pH, supporting electrolyte concentration, hydraulic retention time, and initial pollutant concentration. Optimization of these parameters enhances oxidation kinetics while minimizing electrical energy consumption.

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Although COD reduction provides a reliable indicator of treatment performance, it does not necessarily represent complete pollutant mineralization because partially oxidized intermediate compounds may still remain in the treated effluent. Consequently, COD measurements are often supplemented by TOC analysis.

5.2 Total Organic Carbon (TOC) Removal

Total Organic Carbon (TOC) directly measures the carbon content of dissolved organic compounds and is considered a more accurate indicator of mineralization than COD. Whereas COD reflects the oxygen demand associated with organic matter, TOC evaluates the actual conversion of organic carbon into carbon dioxide.

EAOPs are capable of achieving high TOC removal through successive oxidation of intermediate degradation products generated during electrochemical treatment. The mineralization process generally occurs more slowly than COD reduction because intermediate compounds such as low-molecular-weight carboxylic acids exhibit greater resistance to oxidation.

Photoelectro-Fenton processes frequently produce the highest TOC removal efficiencies due to enhanced hydroxyl radical generation through simultaneous electrochemical and photochemical reactions. Likewise, anodic oxidation employing BDD electrodes demonstrates excellent mineralization performance because of the continuous production of weakly adsorbed hydroxyl radicals.

The degree of TOC removal depends strongly on reaction time, current density, electrode material, wastewater composition, and reactor configuration. Higher TOC removal indicates greater destruction of refractory organic matter and lower residual toxicity in treated landfill leachate.

5.3 Ammonia Oxidation

Ammonia nitrogen (NH_4^+–N) represents one of the most problematic constituents of landfill leachate due to its high concentration, persistence, and toxicity toward aquatic organisms. Mature landfill leachate often contains elevated ammonia levels resulting from protein decomposition and nitrogen mineralization during waste degradation.

EAOPs remove ammonia through both direct electrochemical oxidation and indirect oxidation mediated by reactive oxygen species. During anodic oxidation, ammonia may undergo oxidation to nitrogen gas through a sequence of electrochemical reactions. In chloride-containing electrolytes, active chlorine species such as hypochlorous acid (HOCl) and hypochlorite ions (OCl^-) significantly enhance ammonia removal through indirect oxidation.

The principal oxidation pathways include:

- Oxidation of ammonia to nitrogen gas (N_2).
- Formation of nitrate (NO_3^-) and nitrite (NO_2^-) under specific operating conditions.
- Oxidation mediated by hydroxyl radicals and active chlorine species.

Ammonia removal efficiency depends on current density, chloride concentration, electrode material, reaction time, and solution pH. Although Electro-Fenton processes primarily target organic pollutants, hybrid electrochemical systems integrating anodic oxidation effectively improve ammonia removal while simultaneously reducing COD.

5.4 Color Removal

Landfill leachate typically exhibits dark brown or black coloration due to the presence of humic substances, fulvic acids, lignin derivatives, and other high-molecular-weight aromatic compounds. Color removal is an important indicator of the degradation of refractory organic matter and aesthetic improvement of treated wastewater.

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EAOPs effectively remove color through oxidative cleavage of conjugated double bonds and aromatic structures responsible for light absorption. Hydroxyl radicals rapidly attack chromophoric functional groups, resulting in decolorization and progressive mineralization of colored compounds.

Electro-Fenton, Photoelectro-Fenton, and anodic oxidation using BDD electrodes frequently achieve color removal efficiencies greater than 95% within relatively short treatment periods. Color removal generally occurs faster than TOC mineralization because destruction of chromophoric structures precedes complete oxidation of intermediate products.

The efficiency of decolorization is influenced by oxidant concentration, reaction time, electrode material, wastewater composition, and operating current.

5.5 Heavy Metal Removal

In addition to organic pollutants, landfill leachate often contains significant concentrations of toxic heavy metals, including cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni), mercury (Hg), zinc (Zn), and arsenic (As). These metals pose serious environmental and public health risks due to their persistence, toxicity, and bioaccumulative behavior.

Although EAOPs are primarily designed for organic pollutant degradation, several electrochemical mechanisms contribute to heavy metal removal, including:

- Electrochemical reduction at the cathode.
- Electrocoagulation and precipitation.
- Adsorption onto metal hydroxide flocs.
- Coprecipitation with iron hydroxides.
- Oxidation–reduction transformations affecting metal solubility.

Hybrid systems integrating electrocoagulation with electrochemical oxidation have demonstrated particularly high heavy metal removal efficiencies because they simultaneously degrade organic pollutants and destabilize dissolved metal ions.

The extent of heavy metal removal depends on wastewater pH, electrode material, applied current, hydraulic retention time, and initial metal concentration.

5.6 Degradation of Emerging Contaminants

Modern landfill leachate increasingly contains emerging contaminants that are resistant to conventional biological treatment. These include pharmaceuticals, antibiotics, hormones, endocrine-disrupting compounds, pesticides, surfactants, dyes, personal care products, per- and polyfluoroalkyl substances (PFAS), and microplastics.

Hydroxyl radicals generated during EAOPs possess sufficiently high oxidation potential to attack these persistent compounds through hydroxylation, electron transfer, hydrogen abstraction, aromatic ring opening, and cleavage of carbon–heteroatom bonds.

Recent studies have demonstrated effective degradation of numerous emerging contaminants using Electro-Fenton, anodic oxidation, and hybrid electrochemical systems. In many cases, EAOPs significantly reduce the toxicity and biological persistence of these pollutants while improving wastewater biodegradability.

However, complete mineralization of certain fluorinated compounds and highly stable synthetic chemicals remains challenging. Ongoing research focuses on optimizing electrode materials and combining EAOPs with photocatalysis, biological treatment, and membrane technologies to improve degradation efficiency.

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5.7 Comparative Performance Analysis

Comparative evaluations indicate that different EAOPs exhibit distinct advantages depending on wastewater characteristics and treatment objectives.

Anodic oxidation offers simple reactor design, minimal chemical requirements, and excellent mineralization performance, particularly when BDD electrodes are employed. However, relatively high electrical energy consumption may limit its economic feasibility for large-scale treatment.

Electro-Fenton processes generally provide superior COD removal, high oxidation efficiency, and lower chemical consumption due to continuous catalyst regeneration. Their principal limitation is the requirement for acidic operating conditions.

Photoelectro-Fenton achieves the highest mineralization efficiencies by combining electrochemical oxidation with photochemical catalyst regeneration. Despite outstanding treatment performance, its dependence on external light sources increases operational complexity.

Electro-Peroxone systems effectively integrate ozone oxidation with electrochemical hydrogen peroxide generation, providing enhanced degradation of refractory organic pollutants. Nevertheless, ozone generation equipment contributes to higher capital investment.

Hybrid EAOP technologies combining electrochemical oxidation with biological treatment, membrane filtration, electrocoagulation, photocatalysis, or persulfate activation frequently demonstrate the best overall treatment performance because they simultaneously improve pollutant degradation, reduce energy consumption, and minimize sludge production.

Selection of the most appropriate EAOP therefore depends on leachate composition, discharge regulations, treatment capacity, economic considerations, and available infrastructure.

5.8 Kinetic Evaluation

Kinetic analysis is essential for understanding degradation mechanisms, reactor design, scale-up, and process optimization. The degradation of organic pollutants during EAOP treatment is commonly described using pseudo-first-order or pseudo-second-order kinetic models.

For many landfill leachate constituents, pseudo-first-order kinetics adequately describe pollutant degradation:

$$\ln(C_0/C_t) = kt$$

where:

- C_0 = initial pollutant concentration,
- C_t = pollutant concentration at time *t*,
- **k** = apparent first-order rate constant,
- **t** = reaction time.

Higher rate constants indicate faster oxidation and greater treatment efficiency. Reaction kinetics are strongly influenced by hydroxyl radical concentration, electrode material, current density, pH, pollutant composition, temperature, and mass-transfer conditions.

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In addition to kinetic modeling, treatment performance is frequently evaluated using current efficiency, electrical energy per order (EEO), specific energy consumption (kWh m^{-3}), TOC mineralization rate, and biodegradability indices such as the BOD/COD ratio.

Comprehensive kinetic evaluation provides valuable information for optimizing operational parameters, reducing energy consumption, improving reactor design, and facilitating the transition of EAOPs from laboratory investigations to full-scale landfill leachate treatment systems.

Overall, extensive experimental evidence demonstrates that EAOPs provide outstanding treatment performance for landfill leachate by achieving high removal efficiencies for organic pollutants, ammonia, color, heavy metals, and emerging contaminants while substantially improving mineralization and reducing environmental toxicity. Continued advances in electrode materials, hybrid treatment technologies, and reactor engineering are expected to further enhance the efficiency, sustainability, and commercial applicability of EAOPs.

6. ADVANTAGES, LIMITATIONS, AND FUTURE PERSPECTIVES OF ELECTROCHEMICAL ADVANCED OXIDATION PROCESSES (EAOPS)

Electrochemical Advanced Oxidation Processes (EAOPs) have emerged as one of the most promising technologies for the treatment of landfill leachate because of their exceptional oxidation capability, operational flexibility, and environmental compatibility. Their ability to generate highly reactive oxygen species (ROS), particularly hydroxyl radicals (•OH), enables efficient degradation of refractory organic pollutants that are resistant to conventional biological and physicochemical treatment methods. Despite these advantages, several technical and economic challenges continue to limit their widespread commercial implementation. Consequently, ongoing research is focused on improving process efficiency, reducing operational costs, and enhancing the sustainability of EAOP-based treatment systems.

6.1 Advantages of EAOPs

EAOPs possess numerous advantages over conventional wastewater treatment technologies, making them particularly attractive for the treatment of mature landfill leachate characterized by low biodegradability and high concentrations of persistent contaminants.

High Oxidation Efficiency

The primary advantage of EAOPs is the generation of highly reactive hydroxyl radicals, which exhibit one of the highest oxidation potentials among known oxidizing agents. These radicals non-selectively attack a broad spectrum of organic pollutants, including humic substances, phenolic compounds, pharmaceuticals, pesticides, dyes, and endocrine-disrupting chemicals. Consequently, EAOPs achieve high removal efficiencies for COD, TOC, color, and toxic organic compounds.

Complete or Near-Complete Mineralization

Unlike adsorption or membrane separation processes that merely transfer pollutants from one phase to another, EAOPs are capable of converting organic contaminants into environmentally benign products such as carbon dioxide, water, and inorganic ions. This substantially reduces the risk of secondary pollution and minimizes the need for additional sludge management.

In Situ Oxidant Generation

EAOPs generate oxidizing species electrochemically within the treatment reactor, eliminating the continuous transportation, storage, and handling of hazardous oxidizing chemicals. This improves operational safety while reducing chemical consumption and simplifying process control.

Operational Flexibility

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Electrochemical systems can operate over a wide range of wastewater compositions and pollutant concentrations. Process performance can be readily controlled by adjusting operational parameters such as current density, applied voltage, reaction time, electrode configuration, and electrolyte concentration. This flexibility allows EAOPs to be adapted for various industrial and municipal wastewater treatment applications.

Reduced Sludge Production

Compared with conventional coagulation and chemical precipitation processes, most EAOPs generate relatively small quantities of secondary sludge. This reduces disposal costs and minimizes the environmental impacts associated with sludge treatment and landfilling.

Compatibility with Hybrid Treatment Systems

EAOPs can be effectively integrated with biological treatment, membrane filtration, electrocoagulation, photocatalysis, adsorption, and advanced separation technologies. Such hybrid systems combine the strengths of multiple treatment processes, resulting in improved contaminant removal, enhanced biodegradability, lower energy consumption, and greater overall treatment efficiency.

Automation and Renewable Energy Integration

Electrochemical treatment systems are highly amenable to automation through programmable control systems, sensors, and real-time monitoring technologies. Furthermore, because electricity is the primary energy input, EAOPs can be integrated with renewable energy sources such as solar photovoltaic systems and wind energy, improving sustainability and reducing greenhouse gas emissions.

6.2 Limitations of EAOPs

Despite their numerous advantages, EAOPs still face several technical and economic challenges that restrict their large-scale implementation.

High Electrical Energy Consumption

Electrical energy represents one of the largest operating costs associated with electrochemical treatment. High current densities and prolonged treatment durations increase electricity demand, particularly for wastewaters containing high concentrations of refractory pollutants. Improving current efficiency and reducing energy consumption remain major research priorities.

Electrode Cost and Durability

Advanced electrode materials such as boron-doped diamond (BDD) provide excellent oxidation performance but are expensive to manufacture and install. In addition, electrode fouling, corrosion, passivation, and mechanical degradation gradually reduce treatment efficiency and increase maintenance costs during long-term operation.

Requirement for Acidic Conditions

Electro-Fenton processes typically require acidic conditions (pH 2.5–3.5) to maximize hydroxyl radical production. Adjustment of wastewater pH before and after treatment increases chemical consumption, operating complexity, and overall treatment cost.

Formation of Oxidation By-products

Although EAOPs effectively degrade organic contaminants, incomplete oxidation may produce intermediate compounds that are temporarily more toxic than the parent pollutants. Furthermore, chloride-containing electrolytes can generate chlorinated organic

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compounds, chlorate, and perchlorate under certain operating conditions. Careful optimization of operating parameters is therefore necessary to minimize undesirable by-product formation.

Scale-Up Challenges

Most published studies have been conducted at laboratory or pilot scale using synthetic or relatively small volumes of landfill leachate. Large-scale implementation requires improvements in reactor design, hydraulic performance, mass transfer, electrode longevity, and process economics. Additional demonstration projects are needed to validate long-term operational reliability under industrial conditions.

Variable Leachate Characteristics

Landfill leachate composition varies significantly according to landfill age, waste composition, climatic conditions, and seasonal variations. Such variability complicates process optimization and often necessitates flexible treatment strategies capable of adapting to changing wastewater characteristics.

6.3 Future Perspectives

Rapid advances in electrochemical engineering, nanotechnology, materials science, and digital process control are expected to significantly improve the future performance of EAOPs for landfill leachate treatment.

Advanced Electrode Materials

Future research is increasingly focused on developing low-cost, highly conductive, and corrosion-resistant electrode materials capable of generating greater quantities of reactive oxygen species with reduced electrical energy consumption. Graphene-based materials, carbon nanotubes, doped diamond films, mixed metal oxides, conductive polymers, and nanostructured composite electrodes are particularly promising.

Hybrid Treatment Technologies

Integration of EAOPs with biological treatment, membrane bioreactors, photocatalysis, electrocoagulation, persulfate activation, adsorption, and advanced membrane systems is expected to improve treatment efficiency while reducing operational costs. Such integrated systems can simultaneously achieve high mineralization, effective nutrient removal, and improved biodegradability.

Renewable Energy Integration

The increasing availability of renewable electricity creates new opportunities for sustainable electrochemical wastewater treatment. Solar-powered and wind-powered EAOP systems can substantially reduce greenhouse gas emissions and improve the economic feasibility of decentralized wastewater treatment facilities, particularly in remote areas.

Artificial Intelligence and Process Automation

Artificial intelligence (AI), machine learning (ML), and digital monitoring technologies are increasingly being applied to optimize electrochemical treatment processes. Predictive models can identify optimum operating conditions, minimize energy consumption, detect equipment failures, and improve treatment reliability through real-time process control.

Resource Recovery and Circular Economy

Future wastewater treatment facilities are expected to evolve from pollution control systems into resource recovery platforms. Integration of EAOPs with nutrient recovery, water reuse, hydrogen production, and valuable chemical recovery may contribute to circular economy principles while improving the overall sustainability of landfill leachate management.

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Pilot-Scale and Industrial Demonstration

Although numerous laboratory investigations have demonstrated excellent treatment performance, future research should emphasize long-term pilot-scale and full-scale validation. Comprehensive techno-economic analyses, life-cycle assessments, and environmental impact studies are essential for accelerating commercial implementation of EAOP technologies.

Overall, continuous improvements in electrode materials, reactor engineering, renewable energy utilization, and intelligent process control are expected to overcome current limitations and establish EAOPs as one of the leading technologies for sustainable landfill leachate treatment.

7. CONCLUSIONS

Landfill leachate is a highly complex and hazardous wastewater containing refractory organic matter, ammonia, heavy metals, dissolved salts, and a wide range of emerging contaminants. The variable composition and low biodegradability of mature leachate present significant challenges for conventional biological and physicochemical treatment processes. Consequently, the development of advanced treatment technologies capable of achieving high mineralization efficiency has become an important area of environmental research.

Electrochemical Advanced Oxidation Processes (EAOPs) have emerged as highly effective technologies for landfill leachate treatment because of their ability to generate powerful reactive oxygen species, particularly hydroxyl radicals, through electrochemical reactions. These oxidants facilitate rapid degradation of persistent organic pollutants, resulting in substantial reductions in chemical oxygen demand (COD), total organic carbon (TOC), color, toxicity, and concentrations of numerous emerging contaminants. Technologies such as anodic oxidation, Electro-Fenton, Photoelectro-Fenton, Electro-Peroxone, and hybrid electrochemical systems have consistently demonstrated excellent treatment performance under optimized operating conditions.

The efficiency of EAOPs depends strongly on operational parameters including electrode material, current density, solution pH, supporting electrolyte, reactor configuration, reaction time, and energy consumption. Among available electrode materials, boron-doped diamond (BDD) remains the most effective because of its high oxygen evolution overpotential and exceptional hydroxyl radical generation capability. Likewise, optimization of electrochemical operating conditions significantly improves pollutant degradation while reducing electrical energy consumption.

Despite their outstanding oxidation performance, several challenges remain before EAOPs can be widely implemented at commercial scale. High electrical energy requirements, expensive electrode materials, potential formation of oxidation by-products, and scale-up limitations continue to restrict industrial applications. Addressing these challenges will require continued innovation in reactor engineering, electrode development, renewable energy integration, and intelligent process optimization.

Future research should prioritize the development of low-cost and durable electrode materials, hybrid treatment technologies, artificial intelligence-assisted process control, renewable energy-driven electrochemical systems, and comprehensive pilot-scale demonstrations. In addition, life-cycle assessment, techno-economic analysis, and environmental sustainability evaluation should become integral components of future EAOP research to facilitate successful industrial implementation.

In conclusion, Electrochemical Advanced Oxidation Processes represent one of the most promising and environmentally sustainable technologies for landfill leachate treatment. Their ability to achieve high mineralization efficiency, remove refractory pollutants, reduce environmental toxicity, and integrate with advanced wastewater treatment systems positions EAOPs as a key component of future sustainable waste management strategies. Continued interdisciplinary research and technological innovation are expected to accelerate their transition from laboratory investigations to full-scale commercial applications, thereby contributing significantly to environmental protection, resource conservation, and sustainable wastewater management.

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8. CONCLUDING REMARKS: CLASSIFICATION AND SELECTION, PROPERTY CHARACTERIZATION, INDUSTRIAL TRENDS, AND FUTURE RESEARCH PRIORITIES

8.1 Classification and Selection of EAOPs

Electrochemical Advanced Oxidation Processes (EAOPs) represent a versatile class of wastewater treatment technologies that can be classified according to their oxidant generation mechanisms, electrode configurations, and hybrid operational strategies. Major EAOPs include anodic oxidation (AO), Electro-Fenton (EF), Photoelectro-Fenton (PEF), Electro-Peroxone (EP), electrochemical persulfate activation, and various hybrid electrochemical systems integrating biological, photocatalytic, membrane, or electrocoagulation processes.

The selection of an appropriate EAOP depends on several factors, including landfill leachate composition, biodegradability, pollutant concentration, treatment objectives, operational cost, and regulatory discharge standards. Anodic oxidation employing boron-doped diamond (BDD) electrodes is particularly suitable for highly refractory leachates requiring extensive mineralization. Electro-Fenton systems offer excellent oxidation efficiency for wastewaters rich in dissolved organic matter, while Photoelectro-Fenton further enhances mineralization through photochemical regeneration of ferrous ions. Electro-Peroxone systems are advantageous where rapid oxidation of persistent pollutants is required, whereas hybrid EAOPs provide balanced solutions by combining high oxidation efficiency with reduced energy consumption.

Consequently, no single EAOP is universally optimal for all landfill leachates. Instead, treatment technology should be selected through comprehensive evaluation of wastewater characteristics, operational requirements, energy efficiency, environmental sustainability, and overall life-cycle cost.

8.2 Property Characterization

Comprehensive characterization of landfill leachate is essential for designing efficient electrochemical treatment systems. The physicochemical properties of leachate vary considerably depending on landfill age, climatic conditions, waste composition, moisture content, and biodegradation stage. Young landfill leachate is generally characterized by high concentrations of biodegradable organic matter and elevated BOD/COD ratios, whereas mature leachate contains significant amounts of refractory humic substances, ammonia, dissolved salts, heavy metals, and emerging contaminants.

Performance evaluation of EAOPs relies on a wide range of characterization parameters, including pH, conductivity, oxidation–reduction potential (ORP), chemical oxygen demand (COD), biochemical oxygen demand (BOD), total organic carbon (TOC), ammonia nitrogen (NH_4^+–N), total dissolved solids (TDS), total suspended solids (TSS), color, turbidity, heavy metal concentrations, toxicity, and biodegradability indices. Advanced analytical techniques such as gas chromatography–mass spectrometry (GC–MS), liquid chromatography–mass spectrometry (LC–MS), Fourier-transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), Raman spectroscopy, and electrochemical impedance spectroscopy (EIS) are increasingly employed to investigate pollutant transformation pathways, characterize electrode materials, and evaluate reaction mechanisms.

Detailed characterization not only improves understanding of oxidation processes but also facilitates optimization of operational parameters, reactor design, and predictive modeling for large-scale applications.

8.3 Industrial Trends

The rapid advancement of electrochemical engineering has accelerated the transition of EAOPs from laboratory research toward pilot-scale and industrial implementation. Increasingly stringent environmental regulations governing landfill leachate discharge have stimulated the development of high-performance electrochemical reactors capable of achieving superior pollutant removal while minimizing environmental impacts.

Recent industrial trends include the commercialization of boron-doped diamond (BDD) electrodes, development of dimensionally stable anodes, integration of electrochemical systems with membrane bioreactors and reverse osmosis units, and adoption of

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modular continuous-flow reactor designs. Three-dimensional electrode reactors, nanostructured electrode materials, and carbon-based catalytic cathodes have significantly improved oxidation efficiency while reducing electrical energy consumption.

Digital transformation is also influencing the evolution of electrochemical wastewater treatment. Artificial intelligence (AI), machine learning (ML), digital twins, Internet of Things (IoT)-based monitoring systems, and automated process control are increasingly being incorporated into industrial wastewater treatment facilities to optimize operational parameters, predict maintenance requirements, and improve energy efficiency. Simultaneously, renewable energy integration through solar photovoltaic and wind-powered electrochemical systems is gaining attention as a sustainable approach for reducing operational costs and greenhouse gas emissions.

Industrial research is progressively shifting from pollutant removal alone toward resource recovery, water reuse, hydrogen generation, nutrient recovery, and circular economy approaches, thereby transforming wastewater treatment plants into integrated environmental resource recovery facilities.

8.4 Future Research Priorities

Although remarkable progress has been achieved in the development of EAOPs, several scientific and engineering challenges remain before these technologies can be fully commercialized for large-scale landfill leachate treatment.

Future research should prioritize the development of cost-effective, durable, and environmentally benign electrode materials possessing high catalytic activity and long operational lifetimes. The design of advanced nanostructured electrodes capable of maximizing hydroxyl radical generation while minimizing electrical energy consumption remains an important research direction.

Greater emphasis should also be placed on hybrid treatment systems that combine electrochemical oxidation with biological degradation, photocatalysis, membrane separation, adsorption, electrocoagulation, and advanced oxidation technologies. Such integrated approaches have the potential to improve overall treatment efficiency while reducing operational costs and secondary pollution.

Comprehensive investigations into oxidation intermediates, transformation pathways, and long-term ecotoxicological impacts are essential to ensure complete mineralization and eliminate concerns regarding potentially hazardous by-products. In parallel, standardized protocols for kinetic modeling, reactor performance evaluation, energy consumption assessment, and life-cycle analysis should be established to facilitate comparison among different EAOP technologies.

Additional pilot-scale and full-scale demonstration projects are required to validate laboratory findings under realistic operating conditions. These studies should incorporate techno-economic assessment, life-cycle sustainability analysis, carbon footprint evaluation, and resource recovery potential to determine the practical feasibility of large-scale implementation.

Finally, the integration of artificial intelligence, machine learning, computational fluid dynamics, digital process optimization, renewable energy technologies, and smart monitoring systems represents a promising direction for the next generation of electrochemical wastewater treatment systems. These advances are expected to improve operational reliability, reduce treatment costs, enhance process automation, and accelerate the commercialization of EAOPs for sustainable landfill leachate management.

Overall, Electrochemical Advanced Oxidation Processes have evolved into one of the most promising and technologically advanced approaches for landfill leachate treatment. Continued interdisciplinary research involving electrochemistry, materials science, environmental engineering, nanotechnology, process systems engineering, and digital technologies will be essential to overcome current limitations and establish EAOPs as a cornerstone of future sustainable wastewater treatment and circular economy strategies.

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Conflict of Interest

The authors declare that there are no known financial, personal, professional, or institutional conflicts of interest that could have influenced the work reported in this manuscript. The authors further confirm that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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