Nature Environment and Pollution Technology
An International Quarterly Scientific Journal

p-ISSN: 0972-6268
(Print copies up to 2016)
e-ISSN: 2395-3454

Vol. 24 | No. 1 | Article ID B4222 | 2025

Review Research Paper | https://doi.org/10.46488/NEPT.2025.v24i01.B4222 | Open Access Journal

A Review on Electrooxidation Treatment of Leachate: Strategies, New Developments, and Prospective Growth

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Abbreviation: Nat. Env. & Poll. Technol.
Website: www.neptjournal.com

Received: 10-05-2024
Revised: 14-07-2024
Accepted: 16-07-2024

Key Words:

Landfill leachate
Leachate treatment
Electrochemical treatment
Polluted wastewater

Citation for the Paper:

Rajesh, R. P. and Saravanakumar, M.P., 2025. A review on electrooxidation treatment of leachate: Strategies, new developments, and prospective growth. *Nature Environment and Pollution Technology*, 24(1), B4222. https://doi.org/10.46488/NEPT.2025.v24i01.B4222

Note: From year 2025, the journal uses Article ID instead of page numbers in citation of the published articles.

ABSTRACT

Improper disposal of landfill leachate, a highly polluted wastewater, can harm living beings and the ecosystem. Of all the treatment technologies available, electrochemical techniques have the most advantages in terms of ease of use, affordability, and the ability to degrade various contaminants found in landfill leachate effectively. Though there are a sufficient number of research articles regarding the electrochemical treatment of leachate, it has many research gaps, such as a study on the mechanism of radicle generation, pollutant degradation, study on different electrodes with various pollutants concentrations, application of green catalysts, byproduct formation assessment, energy recovery, etc. This review article explores the applications of electrooxidation techniques for the treatment of landfill leachate. Key aspects discussed include the (i) fundamental concepts in electrochemical treatment and its mechanism, (ii) factors affecting the electrochemical treatment efficiency, (iii) the applicability of leachate treatment with different electrochemical methods, (iv) recent advances, (v) merits, and demerits and (vi) proposal of future scope and the studies needed. The integration of electrooxidation with other treatment processes and the challenges hindering widespread adoption are also addressed. Overall, electrooxidation demonstrates promise as an effective and sustainable method for managing landfill leachate. Consequently, this article directs chacurrent and future research efforts toward optimizing the leachate treatment through electrooxidation techniques.

INTRODUCTION

Uncontrolled increases in population and industrial production generate masses of solid trash, which is primarily dumped in landfills (Choden et al. 2022, Hadi 2023). In many nations, landfills are the principal technique for disposing of solid trash because it is inexpensive and simple (Gautam et al. 2019, Mohajeri et al. 2010, Mor & Ravindra 2023, Umar et al. 2010). Landfills produce leachate, which has a major impact on living beings and ecological health if improperly handled and disposed of (Baiju et al. 2018, Seibert et al. 2019c). It contains a high range of chemical oxygen demand (COD), ammonia, biochemical oxygen demand (BOD), metal ions, endocrine disruptors, antibiotics, pesticides, microplastics, xenobiotics, and refractory compounds which are carcinogenic and mutagenic even in small concentrations (Deng et al. 2020, Eggen et al. 2010, El-Saadony et al. 2023, Ghosh et al. 2017, Seibert et al. 2019c, Torretta et al. 2017). The contaminants in leachate also include chlorinated aliphatics, aromatic compounds, fatty acids, higher alkanes, phenolic compounds, polyaromatic hydrocarbons, nonylphenol ethoxy carboxylate acids, polychlorinated dibenzofurans, dibenzo-p-dioxins, polychlorinated phthalates, biphenyls, emerging pollutants from personal care product (PCP) & pharmaceutical industries and perfluorinated compounds, pollutants that primarily pertain to the 126 contaminants of priority designated by the US EPA (Eggen et al. 2010, Jin et al. 2022, Oturan et al. 2015). Additionally, it is also expected to

have a few unidentified and unanticipated contaminants (Ding et al. 2021). The leachate composition greatly varies with the type of landfill, precipitation, compaction method, waste composition, age, weather, and its contact with the environment. The strategy of treatment used is mostly influenced by the characteristics and chemical constituents of leachate (Khalil et al. 2018, Pieus Thanikkal & Pooppana Antony 2021, Samadder et al. 2017). For example, biological techniques help treat young leachates with a high BOD_5/COD ratio (Desireddy et al. 2020, Manasa & Mehta 2021). Because biological treatment is more dependable, easy to use, and economical, it is usually used to treat leachate that has high BOD_5 concentrations (del Amo et al. 2023, Ilmasari et al. 2022b, 2022a). However, leachates with a low BOD_5/COD ratio and a high concentration of hazardous components are considered suitable for physicochemical treatment techniques (Clemente et al. 2024, Kanmani & Dileepan 2023, Lei et al. 2023, Umar et al. 2010). So, the leachate pollutant characteristics are mostly signified by its presence of COD, BOD, and ammonia (Renou et al. 2008). The microbial distribution and its toxicity in leachate are rarely encountered (Deng & Englehardt 2006a).

Numerous approaches to leachate treatment have been documented, including leachate reuse, treating alongside household leachate, and utilizing physicochemical procedures like coagulation, adsorption, chemical oxidation, precipitation, air stripping, membrane process, and plasma technology (Deng et al. 2019, Kuang et al. 2023, Mathew & Saravanakumar 2023, Torretta et al. 2017). Various aerobic and anaerobic biological treatments are also reported as standalone, pre-treatment, and post-treatment (Li et al. 2023, Mishra et al. 2023, Seibert et al. 2019a, Yan et al. 2023). AOPs can convert non-biodegradable contaminants into harmless, biodegradable compounds (Mohajeri et al. 2010). Though several treatment methods are available, each method has disadvantages in terms of cost and efficiency. In the past twenty years, researchers have become interested in electrochemical oxidation due to its wide range of applications, low environmental impact, straightforward design and operation, ease of adjusting pressure, applied voltage and temperature, automation capabilities, breakdown of refractory organics, low sludge production, and complete mineralization (Deng et al. 2019, Mandal et al. 2017, Narenkumar et al. 2023). Electrochemical

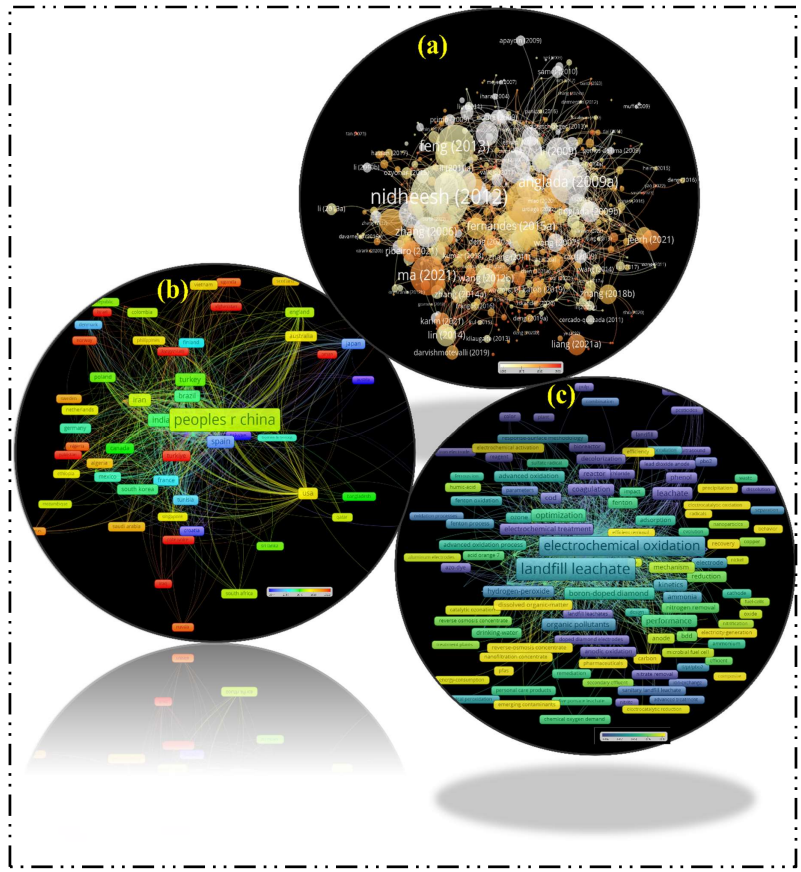


Fig. 1: Web of Science search result for keywords electrochemical oxidation and leachate Vos viewer's overlay visualization of (a) year-wise author citations, (b) country-wise number of publications, and (c) keyword co-occurrence searched on 31st March 2024.

oxidation techniques are well suited to treating wastewater with high salinity and conductivity (Alam et al. 2022). Because of this, the electro-oxidation (EO) process presents an alluring substitute for conventional treatment methods for wastewater with elevated amounts of pollutants (Wang et al. 2012). Electrochemical technologies have discovered a market where they may quickly gain the lead due to their benefits, particularly in the reduction of refractory materials (Liu et al. 2018, Martínez-Huitle et al. 2015). Lower valent compounds, like sulfide and ammonium, can be eliminated by electrochemical oxidation, which can also mineralize refractory organic materials, such as humic and fulvic-like compounds. Certain high-valent compounds, including nitrite and nitrate, can be eliminated by electrochemical reduction (Liu et al. 2023, Wang et al. 2020a, Zhang et al. 2021). Numerous electrochemical techniques, such as electro-Fenton aided with photocatalysis, electro-Fenton, peroxy coagulation with electro-Fenton, and electro-coagulation combined with EO, have shown good effectiveness in eliminating COD, ammonia, and suspended particles from landfill leachate. Fig. 1. represents the web of search results using the VOS viewer software using the keywords 'electrooxidation' and 'leachate'.

BASIC CONCEPTS

In actuality, there are two varieties of EO: indirect and direct oxidation as given by the equation (1) (Ding et al. 2021). EO preferentially transforms organic pollutants into biodegradable compounds using chemisorbed active oxygen and electrolytic combustion. Physisorbed •OH converts the organics completely into H2O, CO_2, and inorganic ions (Priyadarshini Rajesh & Saravanakumar 2023). Electrodes that produce higher oxides, MO_{x+1} (i.e., chemisorbed dynamic oxygen), and electrodes that allow radicals to build up made up of •OH (i.e., physisorbed dynamic oxygen) on their outermost layer are utilized for the selective oxidation of organics by combustion (Martínez-Huitle et al. 2015).

(a) Direct oxidation: During direct oxidation, pollutants are generally adsorbed to the entire surface of the anode, and the anodic electron exchange mechanism degrades the contaminants. This event persists in one or more phases until the ultimate oxidation product, mostly CO_2, is generated (Martínez-Huitle et al. 2015). The other parallel process produces hydroxyl radicals, which is the breakdown of water ions favoring the COD removal, specifically aromatic substrates (Cabeza et al. 2007). Direct EO occurs at a lower current density, before O_2 evolution, at a slower reaction rate, and based on the anode's electrocatalytic activity. The formation of a coating (which consists of polymers) on the surface of the anode causes sluggish reaction kinetics, diffusion limitations, and a reduction in the electrode's catalytic efficiency when solutes are dissolved the disadvantages (Lee et al. 2022, Radjenovic & Sedlak 2015). Fig. 2 shows the overall mechanism of different electrochemical systems.

$$\text{Pollutants (P)} \rightarrow P_{oxi} + ne^- \quad \ldots(1)$$

(b) Indirect oxidation: Through the formation of either chemisorbed active oxygen (oxygen in the matrix of an oxide of metal anode (MO)) or physisorbed active oxygen hydroxyl radical (•OH), indirect or assisted

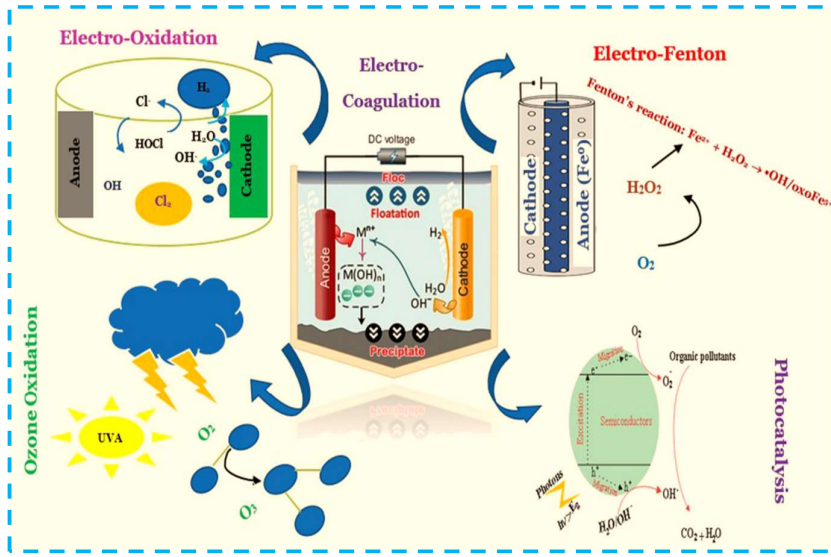


Fig. 2: Overall degrading mechanism of contaminants in various electrochemical systems. (Reprinted with permission from Hajalifard et al. 2023, Copyrights {2023}, Springer Nature)

oxidation takes place at the anode surface (Comninellis & Chen 2010). Removal of ammonium nitrogen is favored if indirect oxidation dominates (Cabeza et al. 2007). To oxidize contaminants through various pathways, powerful oxidants such as radicals of hydroxyls and reactive chlorine ions are first produced near the electrode layer before spreading into an entire solution as given by the equations (2), (3) and (4). Compared to hydroxyl radicals, chlorine ions are more accountable for the breakdown of ammonia (Zhang et al. 2021). The leachate's indirect oxidation of the chloride ions produces active chlorine (hypochlorous acid, gaseous chlorine, or hypochlorite) at the anode surface, which helps remove TOC (Radjenovic & Sedlak 2015).

$$2Cl^- \rightarrow 2e^- + Cl_2 \quad \ldots(2)$$

$$Cl_2 + H_2O \rightarrow H^+ + HOCl + Cl^- \quad \ldots(3)$$

$$R + HOCl \rightarrow H^+ + H_2O + CO_2 + Cl^- \quad \ldots(4)$$

FACTORS AFFECTING ELECTROCHEMICAL OXIDATION

(a) pH: The pH influences the conductivity, solubility of the solution, structure, and morphology of the byproduct formed during the electrochemical process (Yasri et al. 2020). Alkaline pH favors ammonia removal. The quantities of chlorine radicals generation (Cl_2, HClO, and ClO^-) and the NH^{4+}/NH_3 equilibria in leachate are determined by their pH. At pH greater than 10, the una bound NH_3 is mostly present, whereas, at pH less than 8, NH_4 ions are more common. It is demonstrated at pH less than 3, the presence of Cl_2 in leachate, at pH 8-3 for the presence of HClO, and at pH greater than 8 for the decay of protons into ClO^-. Studies confirm that the HClO-mediated chlorination of ammonia occurs at neutral or alkaline conditions ($6 < pH < 9$) was favorable (Zhang et al. 2021).

The solubility of humic substances differs with the pH. The organic matter precipitation decreases the DOC value at pH 3. It is possible to lower the 33% COD by merely acidifying the landfill leachate (Oturan et al. 2015). Organic pollutants' (either unprotonated or protonated) molecular structures can primarily be altered by pH levels, promoting an increase or decrease in the removal rates (Martínez-Huitle et al. 2015). The ubiquitous breakdown of oxidants is largely dependent on pH, as demonstrated by the fact that the reaction between hypochlorous acid and hypochlorite reaches its maximal pace at the neutral pH (Wu et al. 2014).

At very low pH values (pH<2), the highest decay of chlorine gas occurs. The electromigration process, which determines the efficacy of the EO process, is highly impacted by pH (but pH>2 to reduce chlorine loss) (Tomcsaâ Nyi et al. 1999). Increased pH promotes organic oxidation by •OH. Because of reasons like the proton consumption, The pH of the medium doesn't stay exactly constant throughout the EO reaction because of the reaction of hydrogen evolution occurring at the cathode and the reaction called oxygen evolution on the anode. The leachate solution, the diffusion of layers, and the electrodes' porous nature all have different local pH. A lower pH favors chlorine evolution for porous anodes (mostly metal oxide anodes) (Ghernaout et al. 2011). OER causes the solution to become locally acidified and move toward a more anodic potential. Therefore, it is possible to think about OER from a chloride solution as a self-retarding process (Martínez-Huitle et al. 2015).

Ding et al. (2021) found that in acidic circumstances, the electro-Fenton-like mechanism produced more •OH radicals owing to the production of HClO. However, basicity accelerated an undesirable process that converted hypochlorite (ClO^-) ions to chlorate ions, slowing the creation rate of •OH. The improved elimination of COD at acidic pH is mostly due to oxidation by ClO^-/HClO and •OH. However, elevating the pH to 9 increased precipitations in the electro-coagulation process.

Mohajeri et al. (2010) discovered that degradation occurs more slowly at pH 6, which may be due to the generation of fewer hydroxyl radicals than at acidic pH. Moreover, hydrogen peroxide degrades quickly to water and oxygen in basic solutions and is unstable above the pH of 5. Between pH 2 and pH 4, persistent hydroxyl radicals are produced, and this pH range has significant oxidizing potential. Additionally, degradation was reported to be reduced at pH levels below 2. This is because Fe^{2+} cannot degrade H_2O_2 to OH• at pH levels lower than 2. H_2O_2 captures one proton, converting it into $H_3O_2^+$, $H_3O_2^+$ is electrophilic, resulting in a slower rate of reaction between.

According to Wang et al. (2020b), the maximum TOC degradation effectiveness was achieved at the acidic pH. At an elevated pH, additional Fe^{3+} precipitates as $Fe(OH)_3$, possibly reducing the cathode's active areas for the production of H_2O_2. This resulted in a modest drop in TOC removal effectiveness at pH 4 and 5. Equation (6), which describes the reaction between the electro-generated H_2O_2 and the proton to make H_3O^{2+}, was observed when the pH was below three as given by the equation (5). Because H_3O^{2+} is persistent and electrophilic, it slows down the rate at which H_2O_2 and Fe^{2+} interact. Additional studies on the organic molecules' oxidation in leachate have found that Fenton reactions are inhibited at very acidic pH levels (Wang et al. 2012).

$$H_2O_2 + H^+ \rightarrow H_3O_2 \quad \ldots(5)$$

According to Fernades et al. (2017) DOC removal was less impacted by the initial pH in trials conducted at a pH of 5 than the COD removal, suggesting that pH affects the rating process of oxidation more significantly than mineralization. Once more, the generation of the highly unstable hydroxyl radical, which prefers oxidization to mineralization, has been accountable for this (Fernandes et al. 2017). Cossu et al. investigated how pH affected the EO treatment of leachate. From the experimental trials conducted at acidic and basic conditions, it is observed that the rate order constant increased slightly under acidic circumstances. The reason for this trend can be a drop in the amount of CO_3^{2-} and HCO^{3-} ions, which are always present within the leachate. Compared to organic molecules, ions such as these respond to •OH radicles more quickly, making it beneficial to remove carbonates from leachate (Cossu et al. 1998).

(b) Catalyst concentration: The use of catalysts like H_2O_2 and iron in the electrofenton process of leachate improves the degradation efficiency. The •OH radicle concentration changes with the addition of an external catalyst. For instance, in the electrofenton treatment of leachate, a boost in the direct addition of an iron concentration raises the •OH radicle concentration as given in equation (7) (Deng et al. 2021). A higher concentration of •OH radicles results from a rise in H_2O_2 concentration, which also improves the organic compound removal efficiency as given in equation (8) (Priyadarshini Rajesh and Saravanakumar 2023). Similarly, the addition of peroxymonosulfate (PMS) salts in leachate increases the removal of the organics as well as decreases energy consumption by the production of sulfate and •OH radicles as given by equations (6), (7), (8) & (9) (Fernandes et al. 2021). Adding coagulants externally during the electro-coagulation technique increases pollutant removal efficiency. Choosing the optimized dosage of catalyst is highly important because the increase in catalyst dosage leads to adverse reactions like the formation of hydroxides with the salts in leachate with less formation of •OH radicles, thereby reducing the efficiency of pollutants removal (Wang et al. 2012).

$$Fe_3O_4 + 8H^+ \rightarrow Fe^{2+} + 2Fe^{2+} + 4H_2O \quad \ldots(6)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^+ \quad \ldots(7)$$

$$SO_4^{2-} \rightarrow SO_4^{\bullet-} + e^- \quad \ldots(8)$$

$$HSO_4^- + {}^{\bullet}OH \rightarrow SO_4^{\bullet-} + H_2O \quad \ldots(9)$$

The electrode material with/without additional coatings can also be used as a catalyst for the electrooxidation reaction. (Tejera et al. 2021) used iron electrodes as catalysts which dissolution can act to improve COD removal. The results

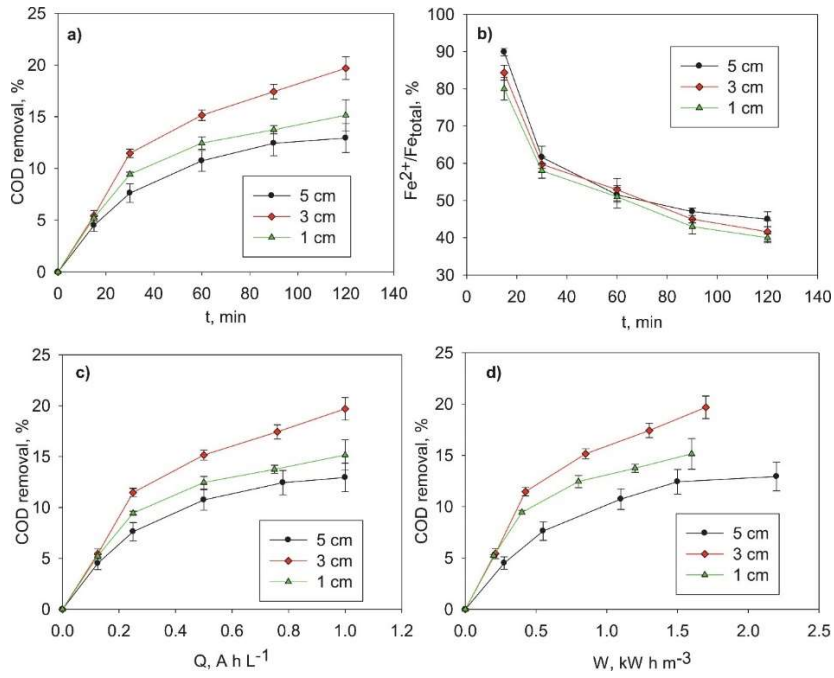


Fig. 3: EC performance applied to leachate considering (a) COD removal different electrode distances (current density, j = 5 mA cm^{-2}, pH =8.3, (b) iron species distribution, (c) COD removal with the applied charge, and (d) COD removal with power consumption. Reprinted with permission from (Tejera et al. 2021), Copyrights {2021}, Elsevier.

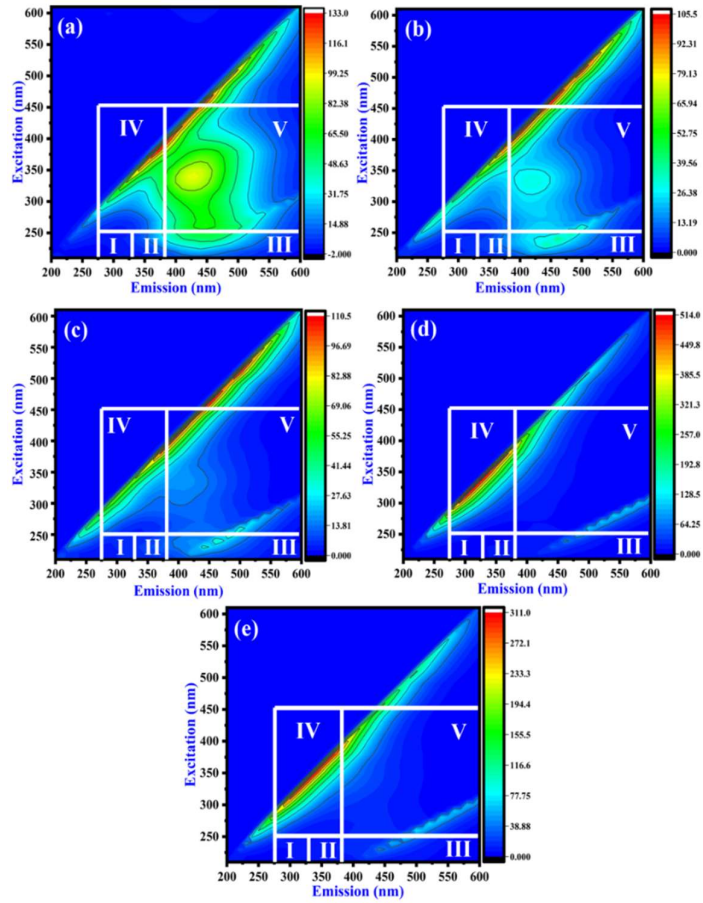


Fig. 4: 3D spectroscopy analysis of (a) raw leachate, and treated leachate under optimal conditions at different time intervals of (b) 10 minutes, (c) 20 minutes, (d) 30 minutes, and (e) 1 hour. Reprinted with permission from Priyadarshini Rajesh and Saravanakumar, 2023, Copyright (2023), Elsevier.

obtained for different conditions of change in the applied charge, distribution of iron species, and power consumption are given in Fig. 3.

(c) Retention time: For continuous performance, one essential aspect is the hydraulic time of retention (Millán et al. 2021). According to Musa & Idrus (2020), a reduced hydraulic retention time is associated with an increased treatment efficacy at a specific unit operating volume. In contrast, the treatment efficacy at the constant state dropped as the hydraulic retention duration decreased (Zhang et al. 2012a). Fig. 4 displays the dissolved organic matter (DOM) elimination process using three-dimensional excitation-emission fluorescence spectroscopy of leachate electro-Fenton treatment at various time intervals (10, 20, 30, and 60 minutes) (Priyadarshini Rajesh & Saravanakumar 2023). The increase in retention time leads to the reaction of degradation of organic compounds from the radicals generated. Hence, sufficient time for the degradation of organics time is important, and more retention time than needed elevates the treatment cost. Hence, optimization of retention time is very crucial in EO treatment (GilPavas et al. 2020, Qiao & Xiong 2021, Wang et al. 2020c).

(d) Electrode surface area: Increased electrode area may result in the generation of more •OH radicals and give more contact area with the leachate (Dong et al. 2022, Salazar-Banda et al. 2021, Sher et al. 2020). Hence, optimizing the electrode surface area is very crucial (Brillas et al. 2009). The research of Wang et al. (2024a) indicates that in the early stages of electro-Fenton treatment, a small drop in the organics elimination rate was seen when the cathode surface was increased from 10 cm^2 to 20 cm^2. This was because when the source of power was switched on, greater amounts of iron would start to accumulate on the bigger cathode, which would reduce the amount of organic material removed during the first step of electro-Fenton treatment by iron flocculation. After the electro-Fenton treatment, the 20 cm^2 cathode removed organics with an efficiency of 82% compared to 73% for the 10 cm^2 cathode.

The carbon–PTFE cathode was the site of both H_2O_2 generation and Fe^{2+} recuperation. Therefore, increasing the cathode area also increases the rates of these processes. Thus, it was possible to develop more potent oxidants for oxidizing the pollutants in leachate by using a larger cathode. Therefore, increasing the cathode area might enhance the organics removal efficiency (Wang et al. 2012). An increase in the treatment's capital expenses is also implied by an increased surface area of electrodes to reactor volume proportion (Radjenovic & Sedlak 2015). Therefore, adjusting the electrode surface area is crucial for evaluating the EO reaction's efficiency (Asfaha et al. 2021, Ghanbarlou et al. 2020, Moradi et al. 2020).

(e) Effect of inter-electrode distance: Ohm's law states that when the inter-electrode distance decreases, current flow rises and cell resistance lowers (Yasri et al. 2020). Reducing the distance between electrodes can help eliminate the constraints on the pollutants' mass transit toward the surface of the electrodes and enhance their electrolytic reaction (Castro et al. 2022, Sanni et al. 2022, Sivaranjani et al. 2020). Yasri et al. tried to shorten the distance between the electrodes while maintaining a steady current to lower interelectrode resistance. However, this increased the issue of gas production and layer development across the electrodes, further decreasing the process efficiency (Yasri et al. 2020). Zhang et al. found that when the gap between the two electrodes was between 1.3 and 2.1 cm, the COD elimination rate was nearly constant. For a 1.3 cm gap, the COD removal effectiveness was 80.4%, and for a 2.1 cm gap, it was 80.8%. The COD elimination efficacy decreased with increasing or decreasing distance above this range. The COD elimination effectiveness was found to be 73.6% at a distance of 0.7 cm and 71.8% at a distance of 2.8 cm. The electro-regenerated ferrous ion at the anode is readily oxidized to ferric ion as given by the equation (10), when the electrodes are positioned too closely together, which lowers the efficiency of continuous Fenton reactions. The increased distance is attributed to the constrained movement of ferric ions toward the cathodes' exterior, in which ferrous ion regeneration occurs, is responsible for the increased distance. As a result, the hydroxyl radicals produced become ineffective in the reactivation of ferrous ions (Zhang et al. 2006). As a result, maximizing the distance between electrodes is crucial to the pollutants' overall rate of degradation.

$$Fe^{2+} \rightarrow Fe^{3+} + e^{-} \quad \ldots(10)$$

(f) Current density: The current density could be expressed as the quantity of electrons that flow across the unit region of operational electrodes. Lower current density increases the treatment time to meet the permitted discharge limit standards, which increases the need for larger facilities and initial investments (Chowdhury et al. 2020, Shahedi et al. 2020). Increased application of current density wastes energy because fractional electrical energy influences the electrolyte and promotes undesirable reactions (He et al. 2022). So, tuning the current density is a crucial aspect of lowering operational expenses. Enhanced current density promotes both indirect and direct electrooxidation. A rise in current density enhances the OER (Fan et al. 2019). The density of current at which no accumulation of oxidizable matter on an anode surface is called limiting current density. If the current density has increased more than this, electrolysis efficiency decreases by the transfer of leachate molecules, such as O_2 at the anode and H_2 at the cathode. Many research works have been undertaken to establish a correlation between limiting current density and COD (Cabeza et al. 2007). Increased current density promotes indirect oxidation by hydroxyl radicals and electrolyte-derived oxidants (Zhuo et al. 2022). COD degradation increases exponentially with high current density (Khaleel et al. 2023). Decreased current density promotes direct oxidation, which removes ammonia more slowly (Meng et al. 2020a). Guan et al. found that ammonia elimination occurred at greater current densities via indirect oxidation via reactive chlorine produced near the anode. A subsequent increase in current density will lower the oxidation performance after the maximum current efficiency is reached due to the inhibition of ammonia circulation, the production of inactive chlorine byproducts, and the transpiration of gaseous chlorine (Zhang et al. 2021). According to Oturan et al. (2015) leachate #1 and leachate #2 are determined to have removed 85.5 and 83.8% of the total organic carbon after 18 hours of electro-Fenton at 500 mA. Leachate #1 and #2 are projected to have a somewhat higher TOC removal degree at 1000 mA, at 89 and 91%, respectively. This outcome shows that at the ideal current density, the removal efficiency was significantly higher (Oturan et al. 2015). Generally, the majority of the investigations are run in the galvanostatic mode. Current density is recorded in several investigations, while anodic potentials are published infrequently. These limited data constraints to study the impact of the current density at the anodes and potential adverse effects (Radjenovic & Sedlak 2015). To indicate the current efficiency, one can use the general current efficiency (GCE), instantaneous current efficiency (ICE), and/or electrochemical

oxidation index (EOI) (Muthuraman & Moon 2012). The ratio of the experimental to the theoretical total organic carbon (TOC) removal is known as the mineralization current efficiency or MCE. As the current increases, various oxidants such as persulfate, hydrogen peroxide, peroxophosphate, chlorine, and so on are formed. Other operational factors, such as temperature, dissolved O_2, inorganic ions, anode type, and pH all have an impact on oxidant generation. A high rate of flow and a small current density minimizes the formation of perchlorate and chlorate ions (Bergmann et al. 2009). Under controlled charge transfer, the majority of organic matter reaches the anodic surface area and consumes the •OH, which is the reason for the hindrance of perchlorate formation (Mousset et al. 2020, Radjenovic et al. 2020, Sharma et al. 2022). When the current density increases, the degrading activity becomes mass transport regulated, rendering the organic pollutants near the electrodes' vicinity insignificant. This makes it possible to produce elevated quantities of perchlorate (Luo et al. 2023, Stiber et al. 2021, Zhang et al. 2020). So, maintaining current at less than limiting current density can minimize the production of ClO_4^- making organic compounds react with the •OH radicle near the anode vicinity. The leachate treatment in conditions of lower pH, high concentrations of NaCl and high organic content, and higher current density with chloride formation will be favorable for efficient abatement (Leow et al. 2020, Luo et al. n.d., C. Wang et al. 2021a, 2021b). Current efficiency can be defined as the equation given below by the equation (11).

$$CE = VF\,(COD_0 - COD_t) / 8It \qquad \ldots(11)$$

Where V *is* the volume of the electrolyte, COD_0 is the chemical oxygen demand at time zero, COD_t *is* the chemical oxygen demand at time t, *F is* the Faraday constant, and I is the current intensity (Zhang et al. 2006). Additionally, as the voltage range increases, the emergence of Fe^{2+}/Fe^{3+} and $HClO/ClO^-$ also increases concurrently (Ding et al. 2021). According to Wang et al. (2024b) (the generation of H_2O_2 increased when the density of current rose from 10 to 40 mA/cm^2. TOC removal effectiveness rose from 10 to 30 mA/cm^2 but then declined slightly when the current increased to 40 mA/cm^2. This suggests that at high current densities, the H_2O_2 generated in situ had not effectively transformed to form •OH radicals (Wang et al. 2012).

(g) Reactor geometry: There is no standard design for the electrochemical reactor. Achieving maximum effectiveness in the removal of organic contaminants is largely dependent on the configuration of electrocoagulation (EC) reactors (Cornejo et al. 2021, Sandoval et al. 2022a). Various EO reactor designs have been used to incinerate organic contaminants, but they all need to meet certain operating requirements based on the properties of wastewater. Designing an EO reactor should consider many factors, such as lowering the ohmic drop, preventing the buildup of gas bubbles, and boosting mass transfer. Optimized by computational fluid dynamics (CFD) modeling. Before the analysis of experiments on the laboratory scale and later when the scaling up of pilot plants, numerical simulation was essential within the development and research of multiple electrochemical procedures because it tests various electrode shapes and materials and characterizes the methods' primary functional variables. Furthermore, CFD models have proven to be an invaluable tool in enhancing several current EO reactor designs that run inefficiently in many conventional procedures (Rivera et al. 2021, Sandoval et al. 2022b). The reactor geometry should ensure the leachate is exposed to uniform electrolysis in all directions and facilitate proper circulation of radicles so that the pollutants get degraded properly in both the batch and continuous systems (Yasri et al. 2020).

(h) Chlorides and bromides concentration: The EO treatment efficiency depends on the concentration of bromides and chlorides in leachate, which forms byproducts such as bromide ions, chlorate, chlorite, chlorine dioxide, hypochlorite, hypochlorous acid, perchlorate, chloramines, brominated and chlorinated organics (Martínez-Huitle et al. 2015, Radjenovic & Sedlak 2015). Numerous factors, including the sort of anode and the number of chloride ions in the electrolyte, affect the effectiveness of chlorine formation, pH, current, voltage, and other coexisting substances. If the chloride concentration decreases, it favors ammonium removal (Zhang et al. 2021).

The bromine and chlorine species generated near the anode vicinity also form poisonous organic bromine and chlorine byproducts during the treatment (Carvalho de Almeida et al. 2023, Leow et al. 2020, C. Wang et al. 2021b). The chloride radical (Cl-), also known as free chloride or active chloride, undertakes rapid addition, abstraction of hydrogen atoms, and immediate transfer of electrons interactions with aromatic compounds at second-order rate constants of 10^8 to 10^9 M^{-1}. If the chloride concentration is higher in leachate, chloride radicals are transformed into dichloride (Cl_2) anion radicals. Cl_2 generated degrades with organic molecules like Cl^- but at a slower magnitude of two to four orders (Radjenovic & Sedlak 2015). This is likely due to their engagement with both chemical and electrochemical reactions (Martínez-Huitle et al. 2015).

$HOCl/OCl^-$ oxidizes the bromides, resulting in hypobromous acid. The HOBr produced is more reactionary than hypochlorous acid when exposed to certain organic molecules, like phenolic compounds. Bromide is a powerful scavenger of ·OH. Chlorate, perchlorate, and bromates are problematic carcinogens and mutagens (WHO 2018, Kurniawan et al. 2022, Xu et al. 2023). Reducing current density minimizes the formation of chloride ions, yet it further decreases the treatment's oxidation efficacy due to decreased formation of ·OH radicals and charge transfer limitations (Radjenovic & Sedlak 2015).

The pH concentration at the anode and in the whole solution affects the transformation of chlorides to chlorine, hypochlorite, and/or hypochlorous acid (Ghernaout et al. 2011, Meng et al. 2020b, Neodo et al. 2012). Thus, the organic material is oxidized by electrogenerated reactive chlorine shlep in conjunction with direct oxidation near the surface of the electrode, and the organic material is oxidized by chloro, hydroxyl, and oxychloride radicals, creating a complex system to predict the role of operating parameters for performance of the process (Kurban et al. 2024, Yang et al. 2013, Zhao et al. 2024). In an atmosphere of NaCl, Boudreau et al. noticed that sulfamethoxazole using BDD (boron-doped diamond) broke down quickly, producing some dangerous chlorine metabolites. Remarkably, the resultant byproducts separated into minerals following prolonged electrolysis, while they accumulated in the mixture following a comparison of chemical hydrochlorination with sodium hypochlorite (Boudreau et al. 2010).

The formation of active chlorine can be affected by both the chemical nature and the pH of the solution available near the anode (Luna-Trujillo et al. 2020). To obtain insight into this process, it is critical to realize that the chloride oxidation is accelerated at low pH and that porous anodes may display significantly lower pH than in the rest of the solution (Ghernaout et al. 2011). A pH difference exists between the anode's surface and the entire solution as a result of OER around the anode acidifying the solution. Chloride oxidation can activate chlorine even in nonacidic solutions because porous anodes maintain a pH value that is extremely low in their porous nature and is mostly devoid of the overall pH (Wu et al. 2021, Yu et al. 2023). It's crucial to keep in mind that metal oxide anodes typically have a porous structure, which promotes chlorine development at nonacidic levels of pH (Scialdone et al. 2009).

It is noteworthy that there has been little research on the impact of the anode's nature on the synthesis of organochlorinated chemicals, and the available data do not permit a comprehensive understanding of this impact. Metal oxide anodes, especially RuO_2 and IrO_2, may effectively oxidize organics and huge amounts of Cl^-. They are typically suitable choices for the oxidation of organics because, for the active production of chlorine, they have elevated current efficiency, minimal production of perchlorate and chlorate, an elevated level of porosity, and long-term mechanical and chemical stability (Kim et al. 2002, Kraft 2008, Radjenovic et al. 2011, Song et al. 2023).

The formation of undesirable organochlorinated compounds, such as active chlorine, should be considered when deciding on an anode (He et al. 2022). Using nonactive anodes, like BDD, is more desirable due to the intermediacy of hydroxyl radicals (Durán et al. 2018, Hu et al. 2021, Medeiros De Araújo et al. 2014). However, among other things, choosing the right operating conditions (such as low current densities) is necessary to avert or at least lessen the generation of perchlorate. For example, because chloroacetic acid is highly resistant to active chlorine, BDD achieved much greater efficiency than metallic oxide anodes, even

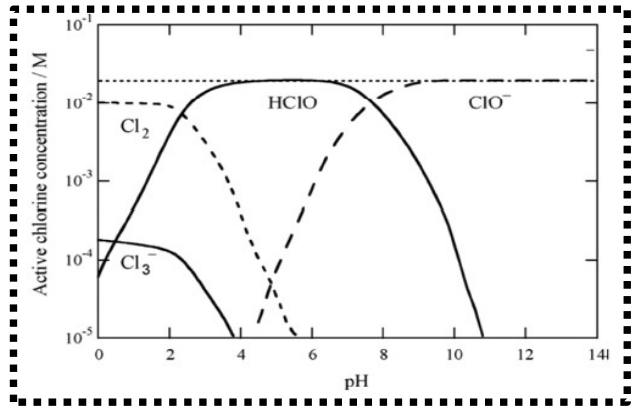


Fig. 5: Radicle production varies with pH and active chloride concentration obtained with permission from Martínez-Huitle et al. 2015, Copyright {2015}, American Chemical Society.

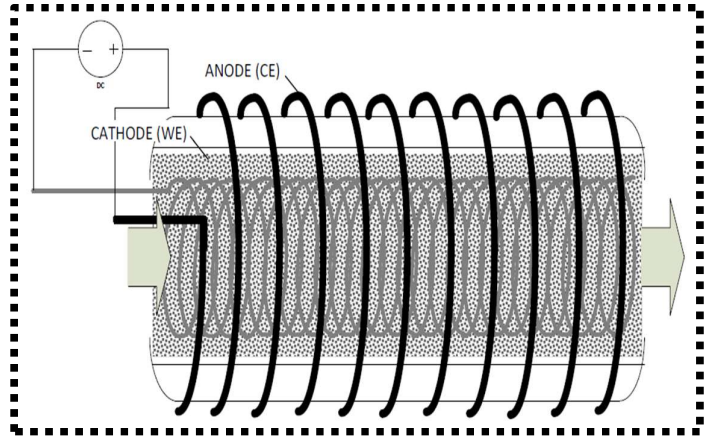


Fig. 6: The working electrode is a three-dimensional reactor made of metal-impregnated activated carbon and designed to treat low-conductivity drinking water. Reprinted with permission from Radjenovic and Sedlak, 2015, Copyright {2015}, American Chemical Society.

in the face of considerable chlorides (Scialdone et al. 2014).

The concentration of chloride drops because additional types of chlorine are formed throughout the tests, and their concentration rises with applied current density. After eight hours of testing, the amount of chloride fell from 11.1 to 8.3 g/L with the greatest rate of decay occurring at a given current density of 1.4 A and monitoring the nitrate quantity that developed during the tests Fig. 5, Since likewise increases the transmitted current intensity, it can be concluded that the best way to remove nitrogen is through the production of nitrogen gas, as the quantity of nitrate produced is far smaller than the proportion of nitrogen eliminated. The finding is supported by literature, which claims that at high chloride concentrations, the primary oxidation product is nitrogen gas production (Pérez et al. 2012). Even with the high chloride level, there was little nitrogen removed. Equation (12), which describes the side reaction between HOCl and ferrous ions, may be the cause of this. Hypochlorous acid will be consumed and unable to convert into ammonium nitrogen as a result (Gómez-Espinosa et al. 2017).

$$2Fe^{2+} + HOCl + H^{+} \rightarrow 2Fe^{3+} + Cl^{-} + H_2O \quad \ldots(12)$$

(i) Pattern and orientation of the electrode: The pattern and orientation of the electrode decide the efficiency of the electrochemical treatment (Durán et al. 2018, Hu et al. 2021, Liu et al. 2022). For instance, tilted electrodes are found to be more effective than vertical electrodes. By enhancing mass transfer, optimizing the electrode's geometrical layout expands the contact area between the electrodes and contaminants. A revolving electrochemical reactor of multielectrode was created by Fan et al. (2019) that broke the bubble curtain formed, increased the mass transfer, decreased the resulting diffusion layer's thickness, encouraged forced convection movement, increased the reaction area on the anode surface, reduced the ohmic resistance at anode due to bubbles formed and increases the reaction rate between the active radicals formed and wastewater. There has been a rise in the phenol decomposition rate from 58.8% to 84.3%. With an increase in the rotational speed of electrodes from 0 to 300 rpm within 100 minutes (Fan et al. 2019).

To get around the mass transfer restrictions in electrochemical systems, plate, and frame filter press reactors can be employed. In a typical flow-by mode, the direction of the current movement is perpendicular to the path of the electrolyte movement. As a result, there are significant limits on mass transmission at the surface of the electrode due to a thin, stationary boundary layer. Due to crossflow filtration, flow-through electrolytic reactors can somewhat mitigate this disadvantage by improving the pollutants' convective transfer to the surface of the electrode (Radjenovic & Sedlak 2015). Fig. 6 represents the three-dimensional reactor. In the case of the flow-through manner, porous three-dimensional electrodes can be used.

Granular and three-dimensional electrodes are used for coupled electrochemical oxidation and adsorption. Granules function as bipolar electrodes and encourage oxidation when they are loaded into a traditional frame reactor and two-dimensional plate with granular or particulate electrode materials like graphite or granular activated carbon (GAC) (Martínez-Huitle et al. 2015). Further research is essential on three-dimensional electrolytic reactors (Fig. 7) with carbon-based fillers since they may be appropriate for treating wastewater with significant potential for the generation of halogenated organic byproducts. Dyes were treated using carbon nanotube (CNT) filters aided with electrooxidation, which oxidized the dyes directly at the CNTs. Poor

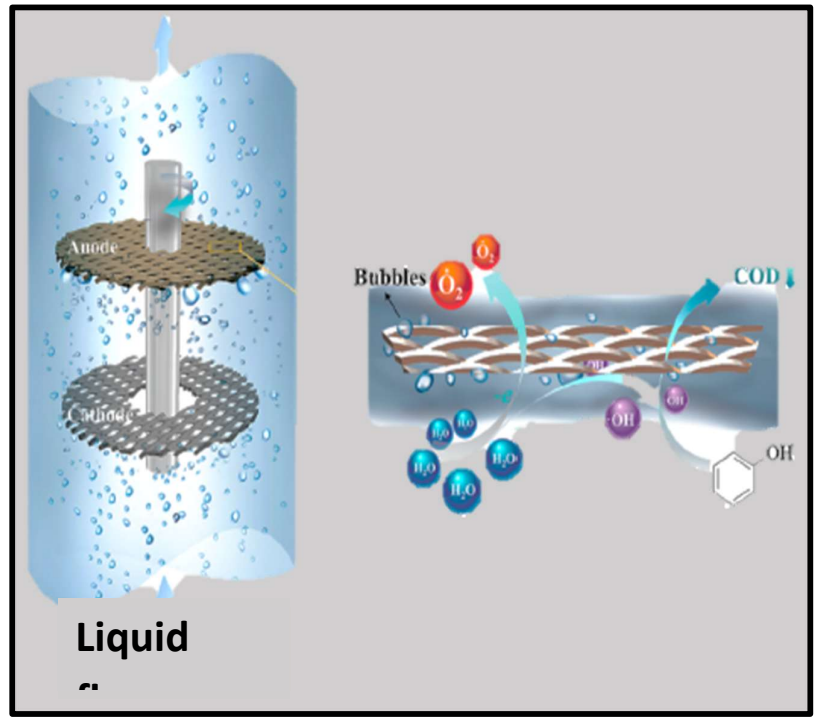


Fig. 7: A 3D rotating electrode schematic representation. Reprinted with permission from (Fan et al. 2019), Copyright {2019}, American Chemical Society.

performance can result from bed blockage, increased pressure in the back caused by the bubble formation, and deterioration of the carbon-based material when using porous electrodes in waste treatment. A crossflow electrochemical filtering device fitted with a porous Ebonex anode produced remarkable phenol removal through electrochemical oxidation and adsorption (Radjenovic & Sedlak 2015). Thus, the pattern and orientation of the electrode play a significant role in the EO's overall efficiency. In-depth studies in the future for variations with different patterns and orientations are necessary for better optimization.

(j) Conductivity: The wastewater with high conductivity of more than or equal to 2000 µmhocm^{-1} favors indirect oxidation predominantly (Martínez-Huitle & Ferro 2006, Yu et al. 2023, Zhou et al. 2011). Because of the existence of different inorganic and metal ions, the leachate conductivity is typically higher than this; hence, indirect oxidation is essential to the electrochemical treatment of leachate (Lin & Chang 2000, Palanivelu 2005, Ramprasad 2012). The voltage reduction in the electrolytic reactors grows with decreasing electrolyte conductivity. Na_2SO_4 or other supportive electrolytes have occasionally been used during wastewater treatment to boost conductivity and accelerate the transfer rate of electrons (Li et al. 2020, Liu et al. 2021, Shih et al. 2018). It prevents the electrolysis process from producing hazardous and cancer-causing chlorinated species. Additionally, more SO_4^{2-}gathering would be adsorbed on the exterior of the electrode as a result of the extra electrolyte, reducing the electrode's active site count. So, it must be added at an optimized level if needed (Fan et al. 2019). It is typically necessary to add sodium sulfate or sodium chloride to achieve the desired conductivity value (Abdel-Fatah et al. 2021, Kerwick et al. 2005). It should be noted that adding chlorides causes Cl^- Chlorine-mediated oxidation, and adding sulfates causes the production of persulfates at inactive anodes. In cases where the conductivity of wastewater is exceedingly inadequate, three main methods may be offered: (1) incorporating salts like $NaSO_4$ or NaCl to increase conductivity, which favors the process by generating Cl^- or SO_4 ions (2) applying special microfluidic reactors, (3) using membrane filtration or another preconcentration procedure before the electrooxidation as a post-treatment. The presence of particulate matter is common in leachate, and its role in EO is rarely focused on in the literature (Martínez-Huitle et al. 2015).

(k) Bubbles formed: The formation of bubbles has multiple effects in the EO process. It occurs mainly in two ways: (i) Gas bubbles cling to nucleation sites and blanket the surface of the electrode, thereby reducing

the active surface area of the electrodes and increasing the electrolyte's resistance. (ii) momentum exchange happens due to micro-convection in the electrode's immediate proximity. The gaseous bubble stratum expands in proportion to the height of the anode. Liu et al. discovered that while the overall size of the gaseous bubble strata remains constant, the void fraction increases when the current density rises. This demonstrates that the velocity of the gas bubble is mostly independent of current density. A high rate of flow reduces the vacancy percentage near the anode surface by boosting the amount of gas production and shortening the time that gas bubbles stay in the area. The gas bubble's tremendous lateral velocity is due to its rapid gas release rate. As a result, the gas bubble layer gets thicker at a high lateral velocity. The hydraulic diameter reduces as the electrode gap rises which also causes the flow velocity to decrease. The rate of gas generation increases as the distance between the electrodes decreases. On the other hand, the void fraction rises, and the overall thickness of the gaseous bubble strata decreases as the space between the electrodes rises. Because of the diverse characteristics of the gas bubbles and the complicated arrangement of the gas bubble strata that form, the coefficient of mass transfer of an electrochemical cell has not been the topic of systematic investigation. This mass transfer distribution could majorly affect the reaction between the gas bubbles and electrochemical oxidation (Liu et al. 2018). The role of bubble formation in the influence of EO rate with leachate treatment has not been studied. Hence, there is a literature gap in the discussion.

(l) Type of electrode: Anodes are classified into two types: non-active and active depending on the strong and faint interaction of hydroxyl radicals (•OH) generated by electrolysis occurring on the electrode surface (Ma et al. 2023).

Active anodes such as IrO_2 and RuO_2 have a lower potential for O_2 generation and a lower ability to degrade recalcitrant organic compounds (Einaga 2022, Radjenovic & Sedlak 2015). The surface at active anodes may combine with •OH to generate a substance known as superoxide (MO) or higher oxide. [$MO + H^+ + e^- \rightarrow M(\bullet OH)$]. This happens when the metal oxide anode can achieve inflated oxidation states greater than the typical potential for O_2 evolution. The MO/M redox pair mediates organic oxidation. ($MO + R \rightarrow M + RO$) and participate in the chemical degradation of the higher oxide species to initiate the side of OER. ($MO \rightarrow M + 1/2O_2$) (Ma et al. 2019, Martínez-Huitle et al. 2015).

Non-active anodes like PbO_2 and SnO_2 exhibit lesser electrochemical reactions for O_2 generation and elevated efficacy in degrading organic compounds (Mandal et al. 2020, Radjenovic & Sedlak 2015). More focus has been placed on non-active electrodes to fully mineralize molecules of organic substances (Liu et al. 2018). Higher oxides cannot form in non-active electrodes, but hydroxyl radicals, also known as physisorbed active oxygen (•OH), enable organics to oxidize nonselectively until they completely decompose into CO_2. The reaction can be given by the equation (13).

$$a\mathrm{M}(\bullet\mathrm{OH}) + \mathrm{R} \rightarrow \mathrm{M} + x\mathrm{H}^+ + n\mathrm{H_2O} + m\mathrm{CO_2} + y\mathrm{e}^- \quad \ldots(13)$$

R is an organic molecule compound requiring a = (n + 2m) oxygen atoms to mineralize to carbon dioxide. R has m atoms of carbon and no heteroatoms. Reduced efficiency can arise from concurrent oxidation or dimerization of the beginning •OH in both types of anodes [$M(\bullet OH) \rightarrow 2M + H2O_2$] or [$M + 1/2O_2 + H^+ + e^-$]. The •OH dimerizes to H_2O_2 on the anode surface due to its reduced adsorption capacity. Accordingly, anodes with lower O_2 evolution overpotential—that is, anodes that are better OER catalysts, cause the organics to partially oxidize; anodes with higher O_2 evolution overpotential, that is, anodes that are worse OER catalysts—cause the organics to completely oxidize to CO_2, which makes it as an ideal suitable electrode for wastewater treatment such as the PbO_2 and BDD. The weaker M–•OH interaction is the reason behind the higher anode reactivity for organic oxidation (Martínez-Huitle et al. 2015).

The materials of anode favor the chlorine evolution reaction (CER), hydroxyl radical formation, and oxygen evolution reaction (Zhang et al. 2021). The ideal electrode material would be inexpensive, show mechanical, physicochemical, and electrolysis medium stability, and have minimal activity against side reactions with significant activity against organic oxidation (Martínez-Huitle et al. 2015). Fig. 8 shows the various radicle generation at variations of pH and different dopings with the electrodes.

The effectiveness of electrochemical treatment methods and the possibility of hazardous byproduct development are contingent on the selection of electrode material (Radjenovic & Sedlak 2015). Because of its high oxidation power and high oxygen overvoltage, the BDD electrode was thought to be the most effective anode among the other anodes utilized for the mineralization of wastewater. Several researchers have used BDD electrodes for the abatement of leachate (Oturan et al. 2015). The BDD property of high O_2 overpotential favoring direct oxidation makes them function well compared to anodes of metal oxide. The adsorption of weakly formed ·OH can explain the elevated contaminant removal efficiency of the anode made of BDD during the electrolysis with the organics as given by equation (14).

$$\mathrm{BDD} + \mathrm{H_2O} \rightarrow \mathrm{H}^+ + \mathrm{BDD}\,(\bullet\mathrm{OH}) + \mathrm{e}^- \quad \ldots(14)$$

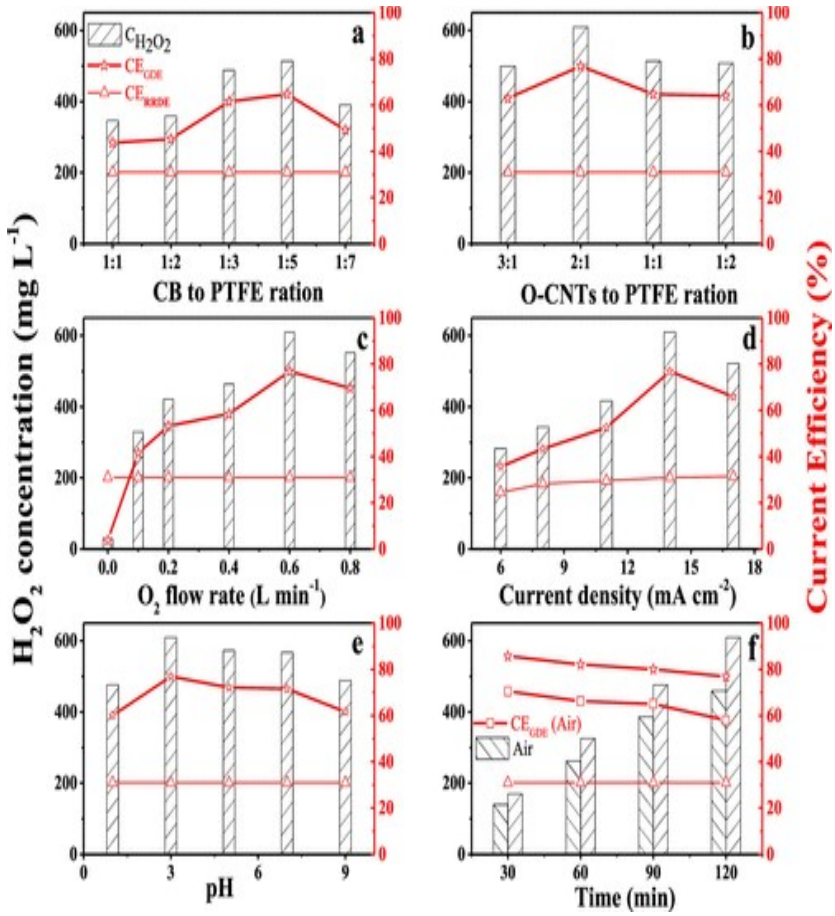


Fig. 8: Effects of (a) carbon black to PTFE ratio, (b) O-CNTs to PTFE ratio, (c) O_2 flow rate, (d) current density, and (e) pH on the yields of H_2O_2 and current efficiency of gas diffusion electrode (GDE). (f) Cumulative H_2O_2 concentration and current efficiency of GDE with different time durations of H_2O_2 generation. Conditions for (f): 0.1 mol L^{-1} Na_2SO_4, carbon black to PTFE ratio: 1:5, O-CNTs to PTFE ratio: 2:1, pH: 3, current density: 14 mA cm^{-2}, and O_2 flow rate: 0.6 L min^{-1}. Electrolysis time for (a–e) is 60 min and other conditions for (a–e) are similar to (f) except the one as variable. Reprinted with permission from (Wang et al. 2020c) Copyright {2020}, American Chemical Society.

The characteristics of the ·OH radicle formed in the BDD electrode are still not fully revealed due to the lack of spectroscopic evidence. A few authors came up with a theory that, due to the higher reactivity of ·OH radicles generated by BDD, the reactions of oxidation are constricted to an adsorbed film near the electrode vicinity (Kapałka et al. 2009). They reported that when BDD anodes were utilized for an electrochemical reaction for acetic acid in a concentrated solution with designated $^{18}O_2$, the involvement of molecules of oxygen in the chain radicle reactions was witnessed by the generation of $C^{18}O_2$ and $C^{16}O^{18}O$. The ·OH electrogenerated may induce the production of organic radicals (R·), which form organic peroxy radicals (ROO·) in the presence of O_2. The resultant peroxy radicals set off further chain reactions that accelerate the rate of organic compound electrooxidation in a non-Faradaic manner (Kapałka et al. 2008).

Along with the oxidizing of organics, the anodes of BDD can also produce H_2O_2, ozone, and ferrate ions. It can also generate peroxy dicarbonate ($C_2O_6^{2-}$), peroxy disulfate ($S_2O_8^{2-}$), and peroxy diphosphate a ($P_2O_8^{4-}$) with carbonate, sulfate, and ions of phosphate. In this, the peroxy disulfate formation occurs in two steps. (1) production of the sulfate radical (SO^{4-}) by either (1) recombining two SO_4^{-} radicals to give peroxy disulfate or (2) reacting of sulphuric acid or HSO_4 with the electrocatalytically generated •OH or through the sulfate ion's direct oxidation at the anode as given by the equations (15), (16), (17) and (18). (Radjenovic & Sedlak 2015).

$$SO_4^{2-} \rightarrow SO_4^{\cdot-} + e^- \quad \ldots(15)$$

$$\cdot OH + HSO_4^- \rightarrow H_2O + SO_4^{\cdot-} \quad \ldots(16)$$

$$\cdot OH + H_2SO^4 \rightarrow H_3O^+ + SO_4^{\cdot-} \quad \ldots(17)$$

$$SO_4^{\cdot-} + SO_4^{\cdot-} \rightarrow S_2O_8^{2-} \quad \ldots(18)$$

A good electrode is expected to have characteristics such as (1) enhanced chemical and physical stability, (2) persistent against corrosion, erosion, and passive layer formation, (2) possessing good conductivity, (3) selectivity, (4) increased catalytic reactions, (5) low cost and (6) high durability (Du et al. 2021). Various electrodes such as granular activated carbon, polypyrrole, activated carbon fiber (ACF), graphite, glassy carbon, massive Pt and platinized Ti, pure and doped-PbO_2 and mixed metal oxides (MMO) of Ir, Ru, Sn, Sb, Ta, and Ti have been experimented till now. Most of the studies have revealed that the greater efficiency was with the "nonactive anodes" like PbO_2 and BDD. Dimensionally stable anodes (DSA), SnO_2, graphite, PbO_2, and BDD reveal higher chemical resistance during electrolysis (Comninellis & Chen 2010).

Carbon electrodes are relatively economical in cost and with increased surface area (L. Xu et al. 2023). Hence are usually used for pollutant oxidation in 3D electrolytic reactors, including fluidized beds, packed beds, porous electrodes, carbon particles, etc., The application of high anodic potentials leads to lower durability due to surface corrosion (Deng et al. 2024). Creating more toxic Pb^{2+} as a secondary pollution is the major drawback in the case of PbO_2 anodes. The Ti/PbO_2 anodes are comparatively stable, and their stability and performance rely on the fabrication method (Shen & Zhang 2023). With identical properties, Ti/SnO_2 has been detected to have limited durability (Meng et al. 2023).

Pt anodes are most utilized in both synthesis and preparative electrolysis owing to their strong corrosion resistance regardless of powerful combative media (Lemeyonouin Aliou Guillaume et al. 2013, Stucki et al. 1991, Tröster et al. 2002). DSA constitutes a Ti stratum veneered with a slim conduction layer of MMO or metal oxide (Ir, Ru, Ta, Sn, Sb, and/or Ti) (Choi et al. 2023, Veerman et al. 2010, Wang et al. 2021a). From the time of this anode production, many researchers made attempts to develop novel coatings for use in electrochemical processes. Many research papers have proved that anodes of BDD make full mineralization of various contaminants such as ammonia, aniline, cyanide, drugs, dyes, hydrocarbons, pesticides, phenols, surfactants, etc. (Brinzila et al. 2012, Fabiańska et al. 2014, Pacheco et al. 2011, Polcaro et al. 2004, Song et al. 2021)

Experiments with different testing electrodes and the relative interaction with radicals of •OH with the organics proved the dual types of behavior (nonactive and active) of BDD in a few experiments (Fabiańska et al. 2014, Pacheco et al. 2011, Song et al. 2021). The frequent reduction of anode performance is due to rust and clogging (Candido & Gomes 2011, Ken & Sinha 2021, Najafinejad et al. 2023, Saha et al. 2020). The electrode passivation, denoting the genesis inhibiting layer formed because of the polymer layer development or adsorption of byproduct in electrolysis occurs in the anodes. It can be reduced by operating in the galvanostatic mode (Martínez-Huitle et al. 2015).

(m) Temperature: Because the temperature rises, there is a larger mass transfer toward the anode because the medium viscosity decreases and increases in mineralization rate (Anglada et al. 2009, Palanivelu 2005, Ramprasad 2012). However, the thermal decomposition of a few oxidants may also occur at higher temperatures. When nonactive anodes are used at higher temperatures and flow rates, the degradation process intensifies and leads to decreased electrocoagulation and higher current efficiency. This was found in EO treatments undertaken at various temperatures in the absence of the formation of any extra oxidants except •OH (Rocha et al. 2012, Särkkä et al. 2015, Un et al. 2008). The EO process is usually preferred to work at ambient temperature as it requires less energy. Hence, an intense study should also be done for the parameter temperature to gain the highest oxidation ability in the electro-oxidation process (Martínez-Huitle et al. 2015, Özyurt et al. 2017, You et al. 2016). Temperature has a minimal effect on organic elimination when compared to other parameters, although having a positive impact on the effectiveness of treatment in Fenton-like procedures. Lower than 8.3 °C temperatures result in weaker early kinetics, which has an impact on the removal performance and reaction rate (Deng & Englehardt 2006b). However, because flocs become unstable at high temperatures, COD removal may be adversely affected by temperatures above 50°C. The most suitable temperature range is between 20°C and 30°C due to the much-improved treatment outcomes in this range. This is because excessively high or low temperatures negatively affect the effectiveness of processes. Hermosilla et al. found that raising the Fenton process's temperature from 25°C to 45°C somewhat enhanced the elimination of COD (Hermosilla et al. 2009). Several further investigations have found similar results for the Fenton process. The scientists discovered that COD removal increased with temperature, even while the proportion of COD removal reduced at temperatures above ambient. Even if the boost in COD elimination resulting from temperature rise is less significant than other factors, higher temperatures are good for organic oxidation (Umar et al. 2010).

(n) Dissolved oxygen: The electrolyte oxidation to O_2 is one of the reactions in the EO of contaminants, and it

intensely decreases the process efficacy and increases the operation costs. Reduction of dissolved oxygen can electrogenerate H_2O_2 as given by the equation (19), according to the cathode material. When Fe^{2+} cations come into contact with dissolved oxygen in acidic media, they oxidize incredibly slowly. However, in alkaline or neutral environments, Fe^{2+} is instantly changed into $Fe(OH)_2$, which is then swiftly oxidized to $Fe(OH)_3$ by dissolved oxygen (Bae et al. 2022, GilPavas et al. 2017, Ouarda et al. 2020).

$$2H^+ + O_2 + 2e^- \rightarrow H_2O_2 \quad \ldots(19)$$

Kapałka et al. have reported that dissolved oxygen (DO) may positively elevate the efficacy of the electro-oxidation process (Kapałka et al. 2009). The external aeration elevates the overall efficacy of the EO process (Priyadarshini Rajesh & Saravanakumar 2023). The role of DO is not deeply investigated, which has to be done in future studies for a better understanding of the prediction of the EO mechanism.

(o) Influence of suspended solids: The increased formation and precipitation of the wastewater's floc had a positive effect on the elimination of COD from the level of suspended matter. The initial concentrate had 500 mg/L of suspended solids. By centrifuging the mixture or introducing 1g/L of kaolin, the suspended solids concentrations ranging from 0 and 1500 mg/L were achieved. The elimination of COD without suspended particles was 41%, however, at 500 mg/L and 1500 mg/L, it was 61% and 71%, respectively, showing the beneficial impact of suspended materials on the EO-like process. Due to the low effectiveness of electro-coagulation, the EO and electro-Fenton-like process predominate contaminants removal in wastewater without suspended solids. Increased suspended solids improved electro-coagulation while slowing down the mass transfer of oxidants and pollutants, which reduced the effectiveness of the EO and electro-Fenton-like reactions for elimination. There were no discernible variations in the amount of ammonia removed between concentrations with either no suspended particles at all or 500 mg/L. This suggests that SS had minimal impact on the in-situ $HClO/ClO^-$ production as well. More suspended solids would, therefore, improve floc generation and precipitation via the electro-coagulation/electro-Fenton-like process but would hinder oxidants' mass transfer in the EF-like process, increasing the breakdown of COD and a negligible effect on ammonia removal (Ding et al. 2021).

BYPRODUCT ASSESSMENT

Thus, the different electrochemical treatments of leachate have been proven not only for removing organics in leachate but also for many emerging micropollutants like Bisphenol-A (Seibert et al. 2019a). This analysis was done

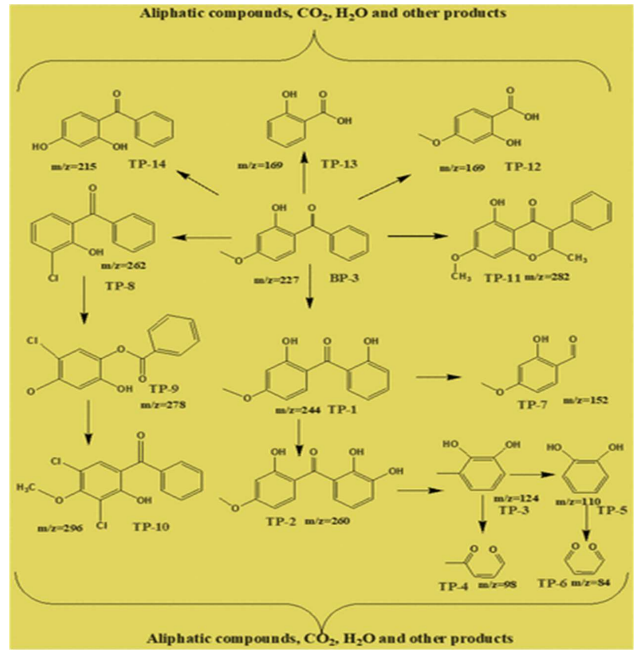


Fig. 9: A suggested pathway for the breaking down of bisphenol-3 utilizing ultrasound and electrocoagulation method. Reprinted with permission from (Patidar and Srivastava, 2023), Copyright {2023}, American Chemical Society.

by using advanced instruments like GC-MS, LC-MS, etc., This analysis is very important not only for assessing the removal of pollutants but also for the byproduct formation. The stabilized leachate was treated using photo-electro-Fenton in which the byproducts formed are less toxic than the parental compounds. Because sometimes the byproducts formed are more hazardous than the parent pollutant during the treatment. However, after some time, the byproducts may convert into another less toxic form during the electrochemical treatment. Hence, the way of byproduct formation, and its degradation pathway are also very important, which influence the determination of optical treatment time. Fig. 9 shows by-product formation in the electrocoagulation of bisphenol-3 degradation with ultrasound assistance. Additionally, the production of byproducts frequently results in a rise in the number of chemicals discovered after treatment, which validates that the degradation of pollutants due to increased molecular weight compounds in raw leachate cannot be detected by these instruments, but the degraded lower molecular weight byproducts can be detected (Seibert et al. 2019a).

The genotoxicity assay is also needed to double-ensure that the leachate has been treated to the desired level. Because only advanced instruments cannot detect all the pollutants accurately in both the raw leachate and raw leachate treated with an EO-EC system, the phytotoxicity of early seed growth was the focus of this investigation. Furthermore, a study was carried out on the unprocessed leachates and produced wastewaters, encompassing an analysis of any possible correlations between the phytotoxicity outcomes and the ICP-OES characterization. Fig. 10 depicts the germination tray used in the phytotoxicity experiments. The results of the phytotoxicity evaluations showed that the suggested treatment strategy reduced the phytotoxicity of the generated effluents. This result can be attributed to changes in the organic matter's molecular configuration. The electrospray ionization techniques for molecular transformation analysis of dissolved organic matter are included in the recent advanced analysis of wastewater treatment. The 3D EEM analysis only shows the rough removal of humic compounds, fulvic-like compounds, soluble microbial byproducts, etc., with its intensity but not the CHNS compounds and byproducts formation in depth. Thus, advanced ionization spray instruments like FTICR-MS and ORBITRAP are essential for the in-depth analysis of the byproducts formed during the electro-oxidation treatment. Such analysis is not done often owing to the unavailability of the instrument or higher analysis costs. The result is often depicted as a van-Krevelen diagram. Fig. 11 shows the van Krevelen diagram of CHON and CHO of dissolved organic matter in leachate concentrate after Anaerobic/oxic biodegradation (a) and coagulation by $Fe_2(SO4)_3$ (b).

RECENT ADVANCES

Using three combinations of EO modes—monopulse (MP), double pulse (DP), and direct current (DC) Jiang et al. attempted to develop a kinetic framework for the breakdown of organic matter in leachate and transform a semicontinuous/batch reactor to a continuously operating tubular unit for catalytic ozonation of leachate using Fe^{2+}. To maintain a constant reaction volume throughout the experiments, the input of ozone, air, catalyst solution, and foam outflow were all controlled. It was successful in converting the semicontinuous/batch unit with a stream of recycle to operate in a continuous flow. This method increased the leachate's biodegradability significantly, demonstrating its efficacy as a pretreatment. The kinetics were studied for the utilization of a continually operating reactor for catalytic ozonation. Using data from experiments, a mathematical model of carbon

Fig. 10: A germination tray was employed in the phytotoxicity trials. Reprinted with permission from (Martínez-Cruz and Rojas-Valencia 2024), Copyright {2024}, MDPI.f

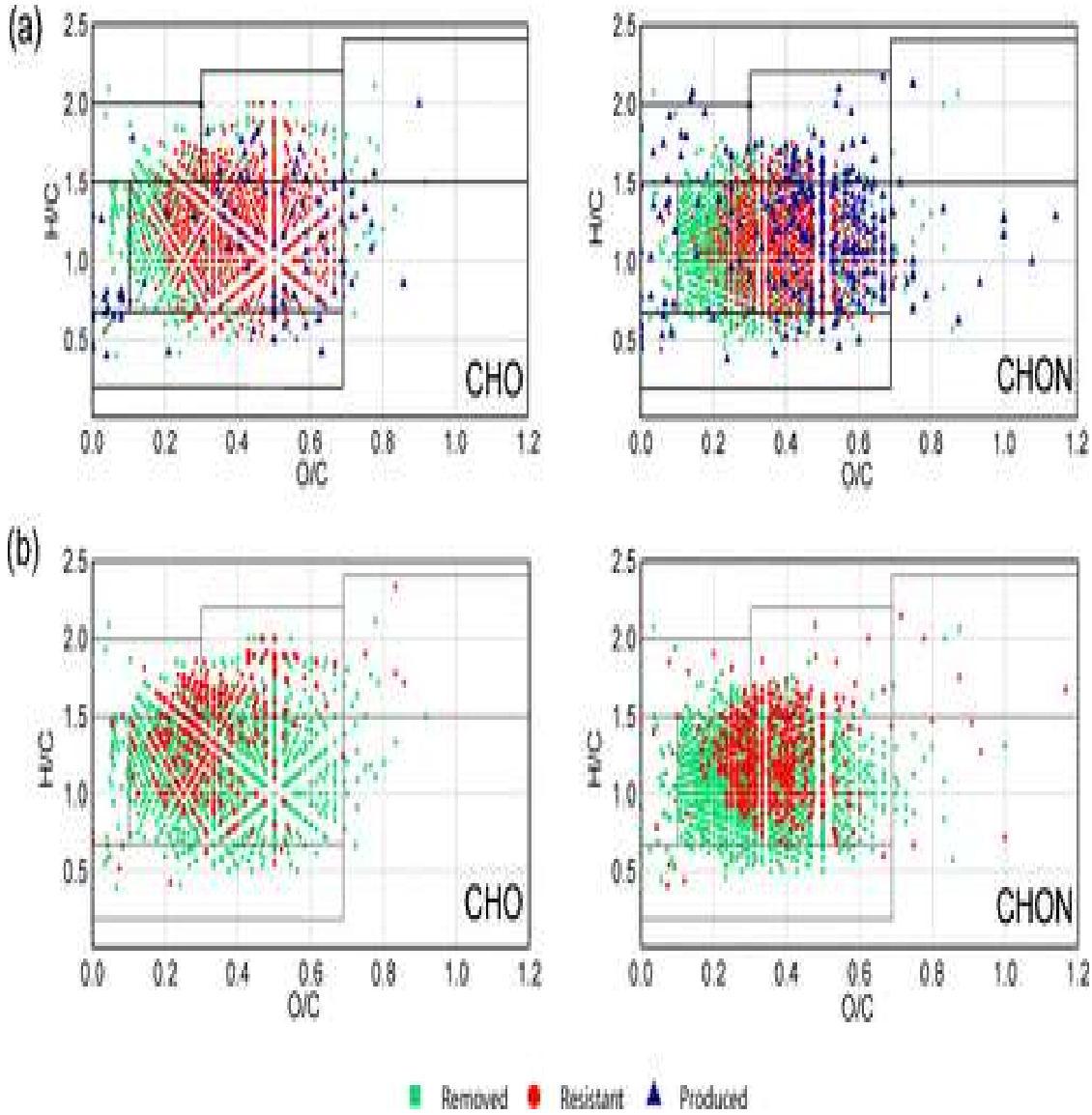


Fig. 11: Van Krevelen diagrams of DOM's CHO and CHON during (a) aerobic and oxic biodegradation in leachate concentration and coagulation by $Fe_2(SO4)_3$ (b) Points in red indicate raw leachate peaks that remained constant (resistant), points in blue indicate new peaks that emerged during biodegradation (generated), and points in green indicate raw leachate peaks that vanished following biodegradation or coagulation (removed). Reprinted with permission from (Yuan et al. 2017), Copyrights {2017}, American Chemical Society.

chain fractionization and decomposition was presented and assessed. The model demonstrated good predictability. The degradation reaction had an average value of 1 × 108 mol L^{-1} s^{-1} as a constant of kinetics under the circumstances of the current investigation. Apart from the breakdown of TOC, the model also forecasts the number of various chemicals in the solution and the progression of the chain length dispersion (humic and fulvic acids, for example), enabling models with varying degrees of confirmation. The radicals HO_3 and O_3^- are primarily responsible for deterioration, according to the model. For operation scaling, the model developed was able to forecast the reagent quantity and the parameters required to achieve a particular degree of degradation of organics. For instance, the proposed model may predict the amount of reagent and operational parameters needed to create a complete system for leachate abatement and attain a certain amount of TOC removal. On the anodes of a typical DC source oxidation process, there is often a formation of the oxide layer. This leads to higher energy consumption in addition to impeding

Table 1: A few recent advanced methods and materials in the electrochemical treatment of leachate.

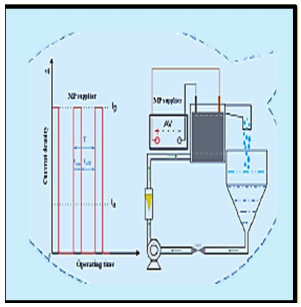
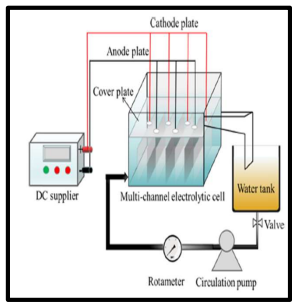
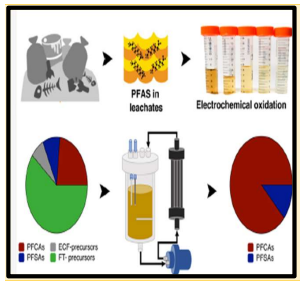
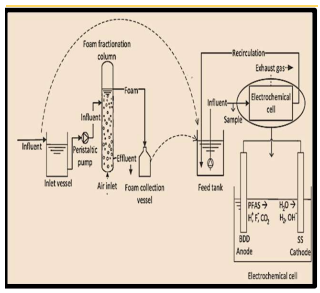
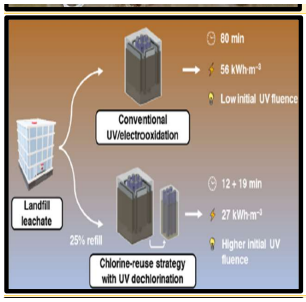
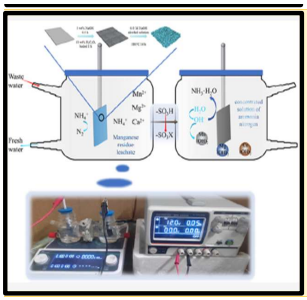
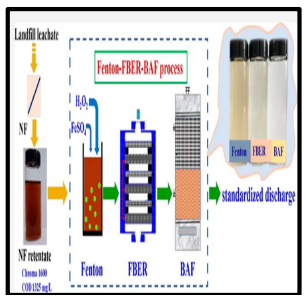
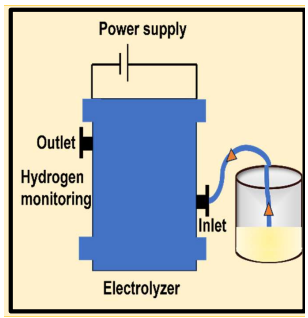
Diagram	Description	Advantages	Ref.
	Pulse Electrochemical Oxidation in a Multi-channel Flow Reactor	Compared to direct current EO, mono-pulse EO gave excellent removal of organics and Nitrogen	(Jiang et al. 2021)
	Multichannel flow reactor for Removal of Simultaneous Desalination and Recalcitrant Organics through electro-oxidation of Reverse Osmosis Leachate	Higher removal of COD (96%), Cl–(96%), and color (99%)	(Yan et al. 2021)
	Electrochemical Transformation Pathways of Perfluoroalkyl Acid (PFAA) in Treatment of Leachate	In-depth study for electrochemical degradation pathways in landfill leachates PFAA	(Maldonado et al. 2022)
	A Pilot-Scale Study on Fractionated Foam aided with Electrochemical Oxidation for leachate PFAS Treatment	Good removal in long-chain PFAS and organofluorine concentration	(Smith et al. 2023)
	A Bipolar Membrane-Integrated Electro chlorination Process	Higher production of HO• & ClO• radicles for higher ammonia removal	(Kuang et al. 2023)

Table Cont....

Diagram	Description	Advantages	Ref.
	Chlorine Reuse in UV/Electrochemical Oxidation of Leachate	Higher reduction of UV_{254} efficiency in less time and energy	(Sato et al. 2023)
	Simultaneous Recovery of NH_3–N and Removal of Heavy Metals from Manganese Residue Leachate Using an Electrodialysis System	87% removal of heavy metals and 95% recovery of NH_3–N	(Yi et al. 2023)
	Hybrid Fenton–Electrocatalytic Membrane Reactor–Biological Aerated Filter for Nanofiltration Retentate Leachate Treatment	The extremely high removal of COD (93%) and color (99%)	(Wang et al. 2024a)
	Electrocatalytic oxidation of landfill leachate coupling with hydrogen production	98% COD removal with 100 ml/min hydrogen production rate	(Wang et al. 2024b)

the anodic oxidation process on the anodes. Comparably, EO treated a biologically processed leachate utilizing power model sources (MP–EO), DC (DC–EO), and DP (DP–EO) in a multi-channel reactor (Jiang et al. 2021). Table 1 shows the publications of some recent studies.

RO concentration from the leachate abatement is extremely tough to cure because of its high concentration of resistant organic compounds, salt content, and color. Utilizing RuO_2/IrO_2-coated titanium material (RuO_2/IrO_2-Ti) serving as the anodes, Yan et al. created a novel multichannel flow reactor created to use electrochemical oxidation to concurrently remove organics and desalinate from RO leachate concentrate. The electrode gaps in the reactor were set at 5 mm. The parameters of the process, like the superficial circulation velocity, current density, etc., affecting the average energy consumption and reducing efficacy of the COD were studied. The findings showed

that the removal efficiency of COD, color, and Cl^-could increase to 96.5, 99.6%, and 96.7 respectively, after three hours of treatment. Thus, a new method for the simultaneous elimination of desalination and COD has been proposed with low energy consumption is very low. To process leachate RO concentrates, this work offers an alternate technology (Yan et al. 2021).

Many contaminants found in leachates are detrimental to the ecosystem and humans, notably per- and poly-fluoroalkyl substances (PFAS) studied by Maldonado et al. Previous literature only focuses on PFAS detection and its biodegradation in leachate, however, the use of oxidative techniques to remove perfluoroalkyl acid (PFAA) precursors from leachates is yet to be investigated. This study assessed the quantities of specific and dubious PFAS in leachate over time while they underwent electrochemical treatment. The leachate contained 19 different classes of 53 PFAS, according to LC-QToF studies. This is the first study to examine the treatment of landfill leachate for various PFAS types. The leachate's molar component included 7% precursors of electrochemical fluorination (ECF), 33% PFAAs, and 60% precursors of fluorotelomer (FT). Other research employing the total oxidizable precursor (TOP) assay identified other precursors that LC-QToF did not detect. Identifying known electrochemical decomposition routes was possible by looking at the transitional and final products generated during the electrochemical process. To summarize, the treatment resulted in the electrochemical conversion of precursors based on fluorotelomer and sulfonamide into perfluoroalkyl carboxylic acids (PFCAs). Furthermore, the findings of the electrochemical treatment revealed that short-chain PFAS, specifically PFBA and PFBS, dominated the concentrations. The degree to which PFBA and PFBS should be degraded influences the amount of and the energy required by the electrochemical method. This critical factor should not be overlooked in feasibility assessments. Furthermore, due to the complexity of leachates and the much higher concentrations of a variety of other substances containing PFAS, pretreatment techniques are required before the electrochemical treatment of PFAS in leachates to boost energy efficacy and shorten the duration of the electrochemical system. Although this study presented an overview of the consequences of electrochemical oxidation of PFAS in leachates, more research is needed to specifically oxidize PFAS and increase the practicality of electrochemical oxidation (Maldonado et al. 2022).

Water around the world contains pervasive manmade pollutants called per- and poly-fluoroalkyl substances (PFAS), which are very challenging to remove using standard water treatment methods. Smith et al. developed a workable treatment method that uses an EO phase to break down the per- and poly-fluoroalkyl substances (PFAS) and foam fractionation to separate them from landfill leachate and groundwater. The research integrated comprehensive characterization methods, such as PFAS total parameters, target, and toxicity assessment, with an upgraded experimental methodology. Furthermore, a recently created associated computational simulation effectively recreated the EO dynamics. Short and long-chain PFAS degraded up to 31 and 86%, respectively, whereas the intended treatment train's mean total PFAS degradation was 50%. By using bacterial bioluminescence bioassays and transthyretin binding, the therapy was able to reduce the water's harmful potency. Furthermore, the water's removable organofluorine content dropped by as much as 44%. When taken as a whole, these results enhance our comprehension of a viable and workable strategy for the on-site treatment of PFAS-contaminated water (Smith et al. 2023).

Although electrochemical oxidation is a useful technique for treating mature leachate, because ammonium is susceptible to oxidation by free chlorine (FC) or HO• at low pH values, it is not a very effective way to remove ammonium. To overcome this issue, Kuang et al. suggest a novel bipolar membrane electrochlorination (BPM-EC) technique. According to the results, the BPM-EC system outperformed divided and undivided reactors in monopolar membranes in terms of reduced byproduct generation, including nitrates and chloramines, improved Faradaic system performance, and lower energy usage. Mechanistic investigations showed that adding BPM helped to create alkaline conditions close to the anode, which in turn helped to produce FC and surface-bound HO•, which in turn encouraged the in situ creation of ClO•, a crucial species that is reactive and primarily responsible for speeding up ammonium oxidation and enabling selective nitrogen shift. The evaluation of batch and continuous flow settings to see how well BPM-EC performed in leachate treatment with different ammonium levels. This supports the enhancement of ClO• in the BPM-EC reactor, which catalyzes the ammonium conversion at acidic conditions. Importantly, the suggested BPM-EC method outperformed the typical undivided EC process in removing COD and ammonium from mature landfill leachate. A kinetic model incorporating the essential factors was created and correctly estimated the number of ideal BPM-EC reactors needed to remove all ammonium. The BPM-EC procedure is promising for treating ammonium-containing wastewater due to its effectiveness and reduced byproduct formation compared to EC methods that utilize divided or undivided cells via monopolar membranes and conventional chlorination procedures with chemical input. The capacity to accomplish total ammonium removal is

particularly desirable, given that little research on utilizing AOPs for leachate treatment has focused on ammonium removal owing to the sluggish reaction between ammonium and HO•. This is in contrast to findings on the combination of monopolar membranes and BPMs for isolation and ammonium recovery in extremely concentrated solutions. The author concepts a method of transformation rather than an exchange process, and it is ideal for processing medium-concentration ammonium containing leachate to eradicate nitrogen pollution. BPM-EC is predicted to be an economical, flexible, and green treatment facility for eliminating ammonium and TN (Kuang et al. 2023)

The leachate from landfills, with simultaneous treatment with city sewage, is still a common procedure in the handling of waste, particularly as it has a high ultraviolet absorption at 254 nm. While oxidation is a promising method for DOM degradation, leachate requires significant chemical dosing. An immediate and required option is electrochemical treatment using ultraviolet radiation (UV/EO), which produces chlorine radicals. However, extended UV/EO raises the problem of residual chlorine formation, resulting in toxic compound formation. Sato et al. modified UV/EO to recycle the residual chlorine, with partial replacement of processed leachate with untreated ones, lessening the UV_{254} of the following batch. The response surface methodology application improved the energy efficiency of the chlorine-reuse process, which involved changing the current and the Reynolds number. Sequentially adding a UV dichlorination unit eliminated formulas resistant to EO/UV, giving rise to an 81% decline in UV_{254}. This strategy enhances leachate abatement, especially in locations with existing cotreatment facilities, by demonstrating the reduced potential for genotoxicity and acute toxicity when discharged with municipal sewage at 3% v/v (Sato et al. 2023).

The issue of elevated NH_3-N and heavy metal concentrations in manganese residue leachate (MRL) requires immediate attention due to the potential impact on nearby ecosystems and potentially the ecological system. Yi et al. propose a unique electrodialysis technique for eliminating heavy metals from MRL and recovering NH_3-N using a titanium dioxide nanowire (TiO_2 NW) electrode. Assessing the ecological concerns associated with reusing recovered NH_3-N involves conducting plant growth tests and ecotoxicity investigations. The electrodialysis device that uses a proton membrane to divide the two chambers can remove heavy metals from MRL by 87%–97% while recovering NH_3–N from MRL by 95%. Plant development can be considerably aided by the recovery solution that is collected from the cathode chamber. The outcomes of the ecotoxicity study additionally show that by encouraging Bacillus reproduction, the retrieved NH_3-N can enhance soil fertility by optimizing the composition of the soil microbial community. This research may offer fresh insight into the safe disposal and resource retrieval of MRLIn order to remove heavy metals from MRL, this work suggests a novel electrodialysis device with TiO_2 NW electrode and the recovery of NH_3-N. The devised technique is capable of eliminating heavy metals (such as lead, cadmium, chromium, etc.) and recovering more than 90% of NH_3-N from the leachate of manganese residue. The produced liquid nitrogen fertilizer appears to be environmentally benign based on the results of the ecotoxicity trial. By encouraging Bacillus reproduction, the recovered NH_3-N can enhance soil fertility by optimizing the composition of the soil microbial community. This research may offer fresh insight into the safe disposal and resource retrieval of MRL, leading to a sustainable green future (Yi et al. 2023).

Wang et al. (2024a) studied a combined biological aerated filter (BAF) and the Fenton processes to create a distinctive hybrid and unified approach relying on the fixed-bed electrocatalytic membrane reactor (FBER) for treating the NF retentate of leachate. The purpose of the FBER procedures and Fenton was to increase the degradation of the NF-concentrated leachate for the BAF process by breaking down the recalcitrant contaminants. With a beginning pH of 3, a molar $[H_2O_2]/[Fe^{2+}]$ ratio of 2/1, and an H_2O_2 dosing of 90 mmol L^{-1}, the Fenton technique removed 64.6% of the chemical oxygen demand (COD). The proportion of BOD_5 to COD rose from 0.05 to 0.38 at a voltage of 2 V and retention 10 min upon treatment with the FBER procedure, exhibiting strong degradation. Finally, during a 48-hour BAF treatment, the removal efficacy of COD and chroma reached 93 and 99% of NF in the retentate, respectively, meeting Chinese wastewater discharge regulations. Thus, the research proposes a highly successful hybrid technique to ease the NF retentate with an extraordinary COD elimination rate (>93%). It is possible to reduce the NF retentate chroma from 1600 to 8, which indicates a 99.5% color elimination performance. A plain carbon membrane-based sequential FBER method demonstrated a high rate of COD removal and outstanding biodegradability increase. This study exhibited the potential benefits of utilizing a comprehensive Fenton-FBER-BAF approach to treating other complicated types of industrial wastewater, such as NF retentate (Wang et al. 2024b).

Wang et al. (2020c) studied leachate treatment with simultaneous hydrogen generation. An integrated electrochemical water system was created involving the anodic electro-oxidation purification of the leachate through a waste incinerator facility in addition to the combined

Table 2: Comparison of different EO of leachate from various countries.

Landfill Site	Nature of leachate	Type of treatment	Percentage removal of pollutants	Type of electrode used	Reference
Wuhan, China	Raw leachate	Electro-Fenton	65% of COD	$Ti/RuO_2–IrO_2$	(Zhang et al. 2006)
Sivas, Turkey	Raw leachate	Electro-Fenton	72% COD, 87% PO_4-P, 90% color, and 26% NH_4-N	Cast iron	(Atmaca 2009)
Penang, Malaysia	Raw leachate	Electro-Fenton	95% color and 94% COD	Aluminum electrode	(Mohajeri et al. 2010)
Beijing, China	Nanofiltration concentrate of leachate	Electro-Fenton	TOC 82%, and total nitrogen 51%	Carbon–PTFE cathode, Pt anode	(Wang et al. 2012)
Wuhan, China	Raw leachate	Electro-Fenton	94% of COD	Ti/RuO2–IrO2–SnO2–TiO2 mesh anodes and Ti mesh cathodes	(Zhang et al. 2012b)
Penang, Malaysia	Raw leachate	Electro-Fenton	100% Coliform removal	Aluminum electrode	(Aziz et al. 2013)
Kochi, India	Raw leachate	Photo-electro-Fenton and membrane bioreactor	89% TSS, 83% COD, 71% BOD, 100% NH_4-N, 58% P, 92% 65% Sulphate, Sulphide and 65% Cl removal	Cast iron	(Nivya and Minimol Pieus 2016)
Portuguese	Reverse osmosis concentrates of leachate	Electro-Fenton	62% COD	Graphite cathode, BDD anode	(Fernandes et al. 2017)
Osona, Spain	Partial nitrification-anammox effluent of leachate	Microbial Electro-Fenton	62% COD	Stainless steel, wire mesh (cathode), rod (anode)	(Hassan et al. 2017)
Shanghai, China	Raw leachate	Electro-ozonation and sequential batch reactor	COD 64.8%, color 90%, and nickel 52%	Ti/RuO2–IrO2	(Mojiri et al. 2017)
Tamilnadu, India	Raw leachate	Electro-Fenton and biological treatment	97% COD	TiO_2/Ti anode and Graphite cathode	(Baiju et al. 2018)
Guangdong, China	Nanofiltration concentrate of leachate	Electro-Fenton	70% COD	Carbon-PTFE cathode and IrO_2-Ta_2O_5 anode	(Hu et al. 2018)
Weifang, China	Raw leachate	Persulfate based EC	72% COD	CuZn cathode and Iron anode	(Deng et al. 2021)
Abadan, Iran	Raw leachate	Combined EC/aeration, PMS/ZVI/UV, and EF	COD, ammonia, and TOC of 98, 94%, and 93% respectively.	Aluminum electrodes	(Khavari Kashani et al. 2023)
Vellore, India	Raw leachate	Electro-Fenton	TOC 79%, UV254 93%, COD 90%, and NH3-N 90%	Stainless steel	(Priyadarshini Rajesh and Saravanakumar 2023)
Not available	Bio-treated leachate	Persulfate EO & electrocoagulation	91, 80, and 39% for biogenic humic-like components C1, C2, and C3, respectively.	Graphite felt cathode and Iron anode	(Guan et al. 2023)
Centre of Iran	Raw leachate	Electro-ozonation with ZnO nano-granules as a catalyst	COD, BOD_5, TOC, P-PO_4^{-3}, NH_4^+-N, color, and turbidity were reduced to 90, 89, 89, 87, 89, 99, and 99%	Iron tubes	(Mehralian et al. 2024)
Suzhou, China	RO concentrate of leachate	EO	84% of humic acid	Cathode as Al and anode as Ti/Ti_4O_7	(Hu et al. 2024)

cathodic electrolysis method for producing hydrogen. Four kinds of electrolyzers were built with varied channels of flow and tested the impact of various factors of the paired reactions' electrolysis. The outcomes show that the pin-type electrolyzer performs better than the energy usage and degrading functioning of the other three electrolyzers. When the current is high At a flow velocity of 100 milliliters per minute and a density of 4000 A/m^2, the pin-type electrolyzer exhibits a minimal potential of 6 V, a COD removal rate of 98% for the leachate and the energy usage of 200 Wh. The creation of hydrogen through the electro-oxidation of leachate presents a viable pathway for the development of

novel hybrid electrocatalytic water treatment systems with energy recovery (Wang et al. 2024b).

MERITS AND DEMERITS

Electrochemical technology is an excellent way to remediate landfill leachate, with the removal of various types of pollutants like dissolved organic carbon, infective microbes, ammonia, etc., as shown in Table 2. It was also found to degrade many emerging pollutants like disinfection byproducts, EDC, pesticides, etc., It has many advantages like less space consumption, rapid treatment, and can be aided with automation for simple operation. Many times, primary or secondary treatment is not essential. Processes like simple electro-coagulation, electro-oxidation, etc., do not need any external addition of chemicals. Because in the electro-Fenton treatment of leachate, iron sludge may be generated with the external addition of iron salt, and H_2O_2 storage in the treatment plant is difficult during the addition as a catalyst. Hence, the persulfate-like non-polluting catalyst is preferred for the EO treatment (Xiao et al. 2020). The EO treatment of leachate has lower energy consumption than many other technologies (Priyadarshini Rajesh & Saravanakumar 2023). The downsides of electrochemical technology include the consumption of power. Green energy, like solar power, can be used as an alternative. The energy recovery in the form

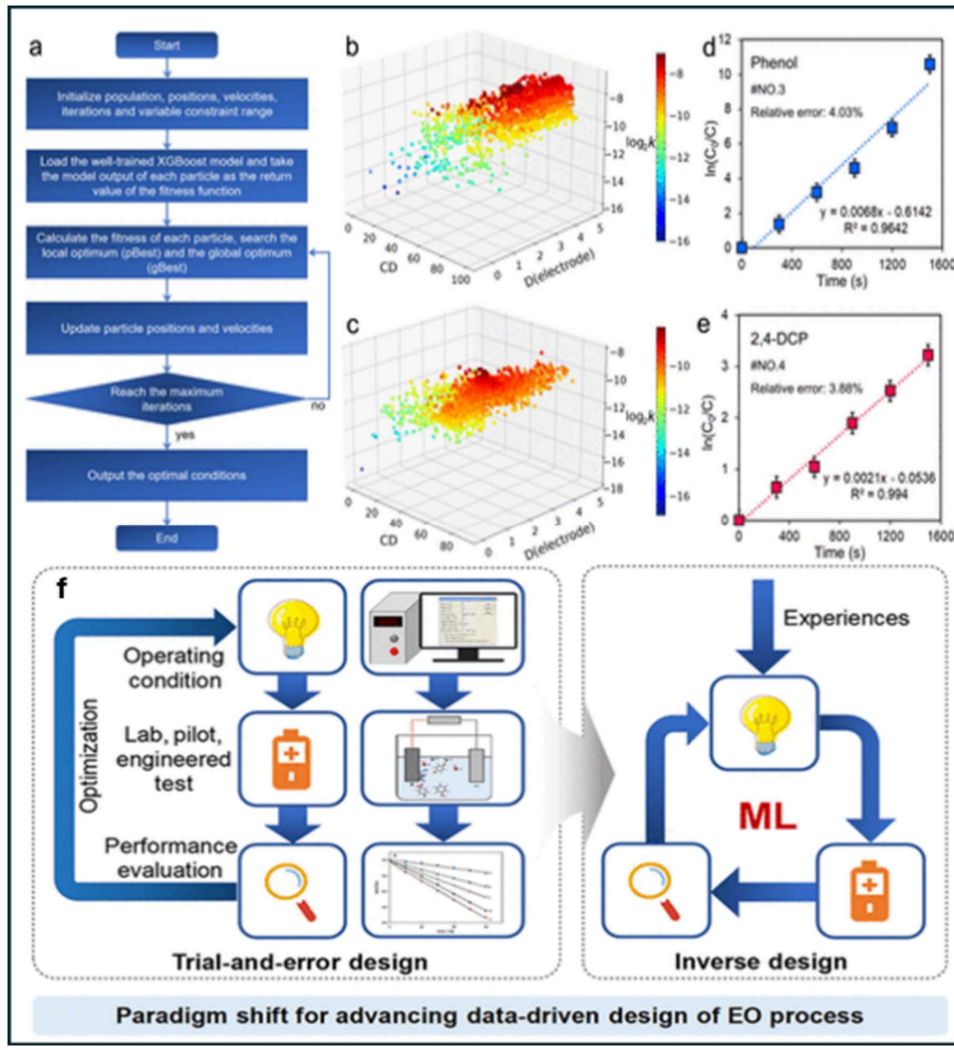


Fig. 12: (a) The PSO algorithm, which maximizes k for the electrochemical oxidation of (b) phenol and (c) 2,4-DCP, the experimental verification (kinetic plots) for the electrochemical oxidation of phenol, (e) 2,4-DCP under the optimized conditions derived from the ML framework for inverse design, and (f) paradigm shift for advancing data-driven design of EO process are the foundations of the schematic flowchart of inverse design. Reprinted with permission from {(Sun et al. 2023)}, Copyright {2023}, American Chemical Society.

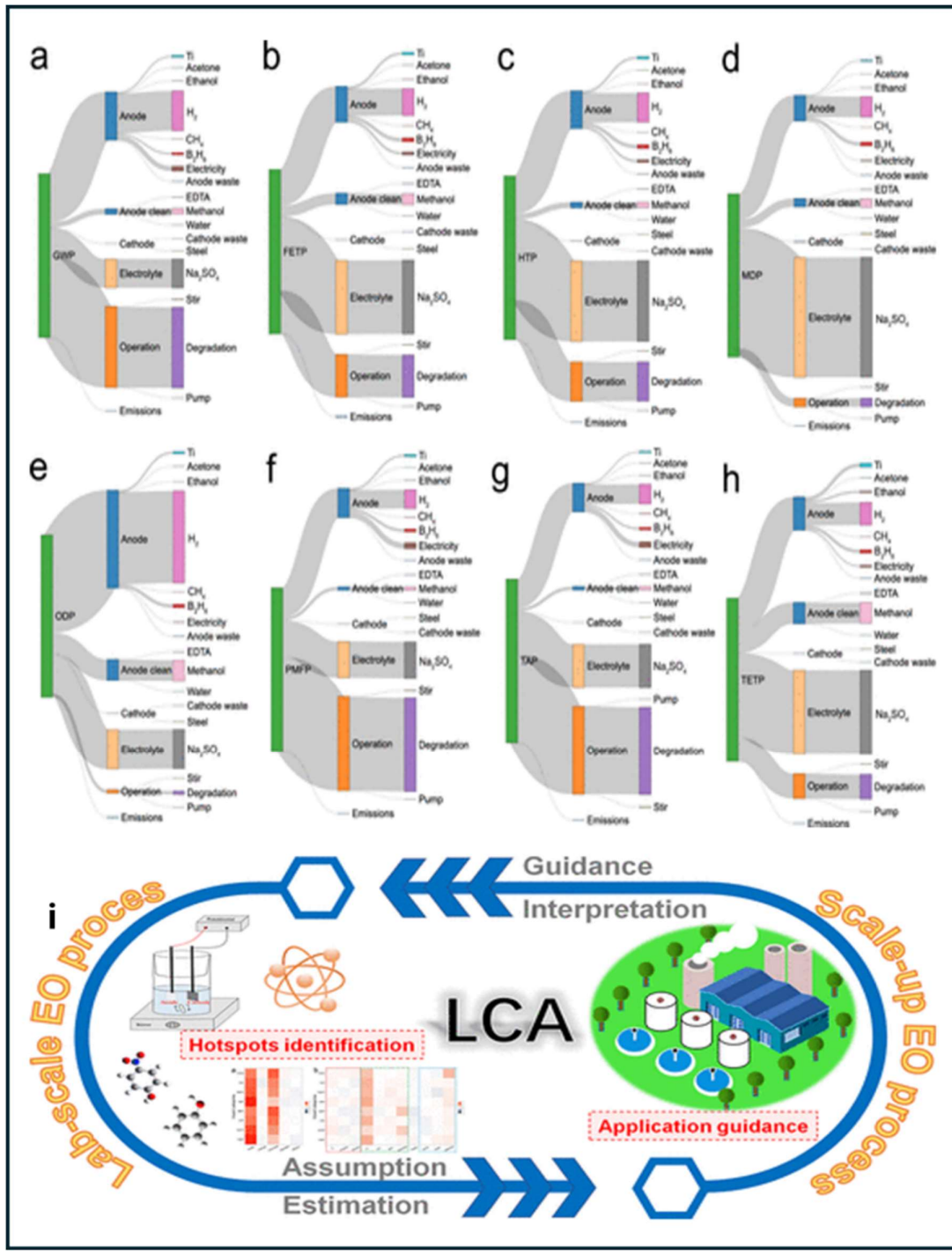


Fig. 13: (a-h) The flow diagram of the Life Cycle Assessment (LCA) and the Sankey diagram of the environmental consequences and primary contributors for the scale-up EO process. Reprinted with permission from {(Sun et al. 2023)}, Copyright {2023}, American Chemical Society.

of hydrogen gas, ammonia gas, chloride gas, etc., from the electrodes will also reduce the overall cost of the process. Using low-cost electrodes like iron or other cheap electrodes will also reduce the overall cost. The byproducts generated should be carefully monitored with proper retention time for degradation, as sometimes they may be higher in risk

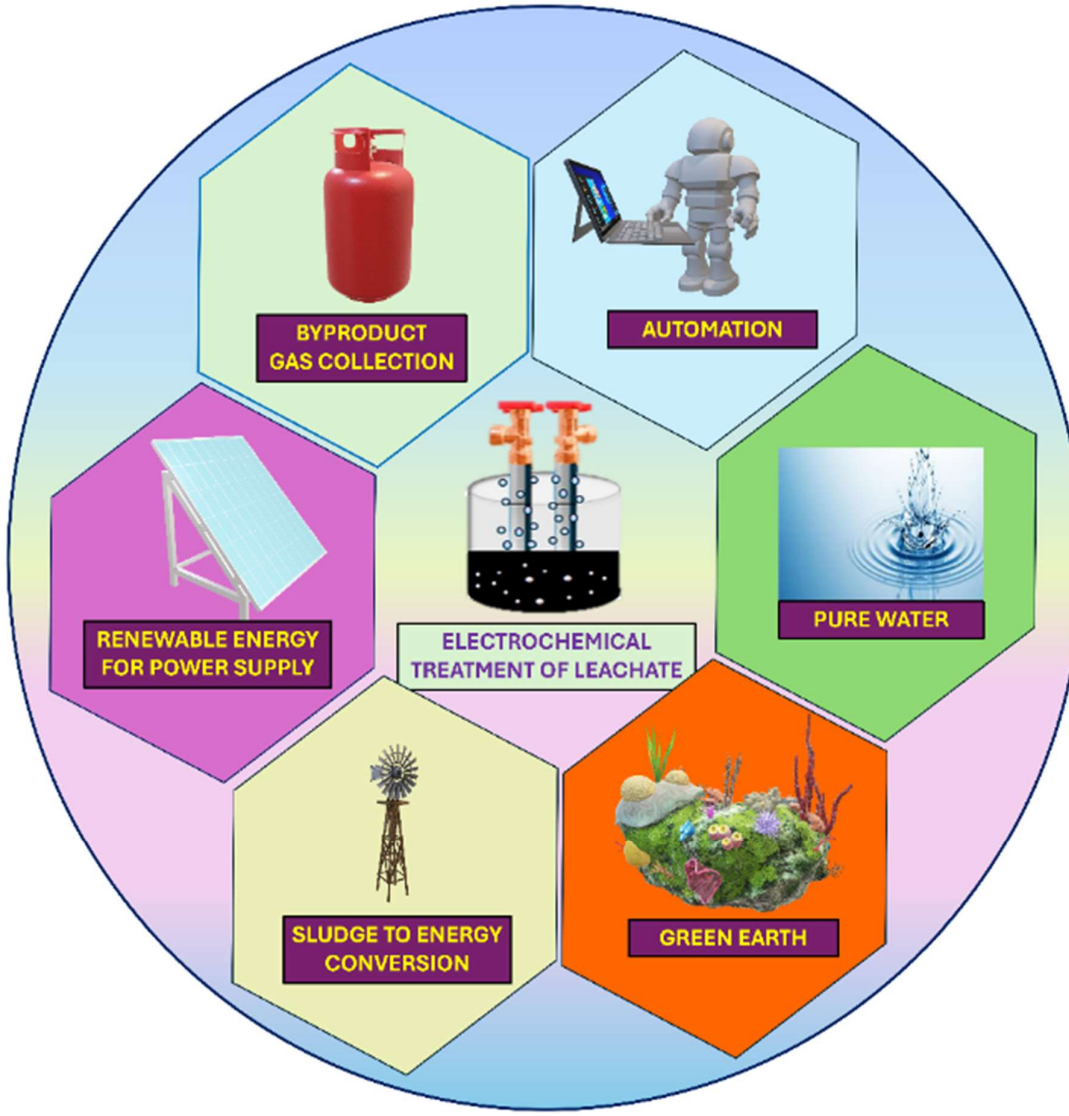


Fig. 14: Multiple benefits of electro-oxidation treatment of leachate for a better future.

than the basic pollutants. Hence, there is a huge research gap in mechanism and byproduct formation in the pollutant treatment of leachate, which in the future has to be filled.

FUTURE STUDIES

(a) Machine learning: The EO treatment of leachate could be studied with machine learning for better prediction, optimization, and automation in the future. Sun et al. present a machine learning (ML) basis for a target-driven inverse model of the electrochemical oxidation (EO) technique for water treatment. Based on retraining the data set associated with pollutant features and response ailments, the XGBoost model performed the best in terms of forecasting reaction rate (k), with Rext 2 of 0.84 and RMSEext of 0.79. Based on 315 data points gathered from the available literature, the contaminant quantity, current density, and gap energy (Egap) were determined to be the most important parameters for the inverse modeling of the EO operation.

Adding conditions for reaction as model input characteristics, for example, made additional details available and increased the sample size of the data set, both of which increased model accuracy. Shapley additive explanations (SHAP) were used to conduct feature significance analysis to identify data patterns and understand features. The ML-based inverse model for the EO technique was extended to a stochastic scenario to adjust to the ideal circumstances,

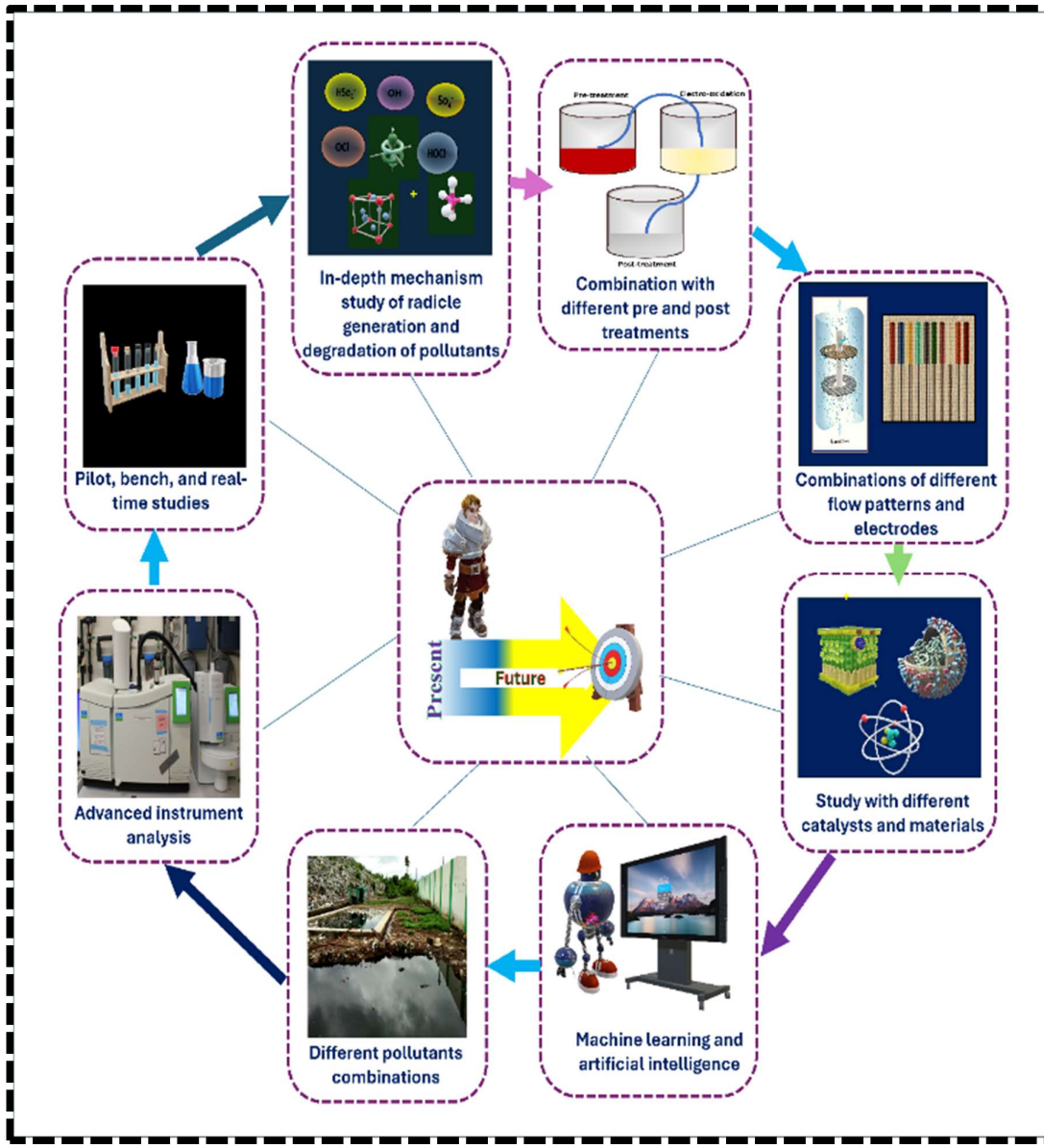


Fig. 15: Literature gap and future perspectives of EO for a sustainable environment.

using 2,4-dichlorophenol (2,4-DCP) and phenol as model pollutants of models. The resulting projected k values were near to the experimental k values after experimental validation, reflecting an absolute error of less than 5%. This investigation proposes a paradigm change from traditional experimentation and error to the data-driven mode for promoting EO procedure advancement through efficient, cost-effective, and environmentally conscious goal-driven tactics, making In the context of zero emissions and global carbon peaking, electrochemical water filtering more economical, efficient, environmentally benign, and time-consuming.

The study included a proof-of-concept demonstration of the machine learning framework for target-oriented inverse design of an EO process for water purification. Firstly, the determination of the important characteristics that influenced EO water treatment procedures (current density, contaminant level, gap energy, Egap) was studied and also supplied readers with open-source data that they could freely obtain. Second, a paradigm shift was demonstrated from the traditional trial-and-error approach to the data-driven inverse design framework for the electrochemical treatment process. Fig. 12, shows the ML overall design of EO.

Thirdly, the required information is obtained, and a suggested inverse design methodology is used to make process and design intensification more sustainable, dependable, and efficient across a range of water treatment processes. In the framework with global peaking of carbon and carbon neutrality, the data-based approach permits the least carbon emission and environmental impact during research and development (R&D) when weighed against experimental methods. Though this much is done, the authors overcome disadvantages, with usage for several considerations like the issue of overestimation arising from the fairly small number of data points used in model development due to the limitations in data availability. An expanded raw data set is necessary to create predictive models that are both sufficiently reliable and useful. Integrating tiny sets of information from different reactions involving oxidation through transferable knowledge may be a useful strategy because the EO process could share certain similarities in fundamentals. However, the ML models were limited to lab-scale situations because the data used in this study came from experimental testing that was already published in the literature. Collecting data at higher scales is necessary for scaling up design using ML models, but sadly, there are not many data points available. Furthermore, the forecasting inaccuracies of the models tied to the initial info collection deviance invariably affected the ML-based inverse design for the EO process. For instance, the original information collection's lacking information was filled in using the kNN technique, which may have introduced bias into the substitution of data and the actual values. More precise approaches, along with greater trustworthy data collection, can help minimize this problem in future efforts. The comprehensibility of the models in this investigation persists to be weak, as the main objective is to create prediction models with exceptional precision for inverse design. Acknowledging the balance that exists between the interpretability and accuracy of the models will remain crucial to comprehending the models' workings. Developing more accurately interpretable models or doing thorough post hoc interpretation of the models are, hence, extremely appealing. In tandem, these findings show that the idea of ML-based inverse design for the electrochemical treatment process is in its early stages, and extra work is required to improve the prospective application, understanding, and correctness of this method (Sun et al. 2023).

(b) Life cycle assessment: Although electrochemical oxidation (EO) is a reliable method for purifying water, the materials and energy used to prepare the electrodes and run the process may have an indirect negative impact on the environment. This study used prospective life cycle assessment (LCA) (Fig. 13) to quantitatively investigate the environmental effects of the new EO technique from laboratories to the workplace. By contrasting two common processes (adsorption and Fenton method) with three indicative anode materials (PbO_2, SnO_2, and boron-doped diamond), the environmental effects of EO technology were evaluated at the laboratory scale. This allowed for the verification of the EO process's rivalry and the identification of the critical elements leading to environmental hotspots. The life cycle inventory was then created when the scaling-up EO LCA was completed to provide direction for use in reality (Sun et al. 2022).

(c) Microplastic degradation studies: Because microplastics are becoming more and more common in the environment, they have become one of the most pervasive contaminants. Microplastics' hydrophobicity and intricate structure may require a lengthy period for them to degrade. The exquisite AOPs can produce hydroxyl (OH) radicals and reactive oxygen. By causing structural alterations that result in the formation of functional groups, including carbonyl, hydroxyl, and modified C-H groups, these radicals start the breakdown of plastic. Modifications in chemical structure provide a substitute to quicken microplastics' breakdown. The degradation of microplastics using the EO method has not been studied yet. Amelia et al. studied that by combining ozonation with hydrogen peroxide (H_2O_2), AOPs were able to modify the molecular nature of PE (polyethylene), microplastics. Using Fourier Transform Infrared (FTIR) analysis, the impact of the AOPs in samples of polyethylene microplastics was assessed. The findings indicate that the O-H and C=O bands are becoming more intense, while the C-H groups are becoming less intense. When applying both the ozonation and hydrogen peroxide methods under a flow rate of 3 $L.min^{-1}$ and pH 12, the maximum carbonyl index (CI) value was 1.33 (Amelia et al. 2021). Tan et al. used graphene oxide/zinc oxide (GO-ZnO) photocatalyst to study the application of photocatalysis in the degradation of LDPE (low-density polyethylene) microplastic with UV light irradiation. At 1000 ppm of GO-ZnO dosage, the amount of microplastic loss in mass from the preliminary investigation was the largest. In comparison to alkaline and acidic conditions, the photodegradation efficiency was largest at the pH 7 solution. Additionally, as the working temperature rose, so did the mass loss of microplastic (Tan et al. 2023). Thus, the combination of different oxidants with EO in the variation of influencing parameters like pH, voltage, etc., has to be studied in the future. Recent studies have also shown that boiling water

reduces microplastic consumption in drinking water (Yu et al. 2024). Hence, the temperature variation in the EO treatment of microplastics in leachate is also to be explored in the future.

An in-depth study with different electrodes, like 3d electrodes, porous electrodes, non-porous electrodes, rotating electrodes, carbonaceous electrodes, etc., with different cathodic and anodic combinations, is needed to bring out the best efficiency of the process. The combination of different additions of green catalysts, and complete byproducts assessment with advanced instruments like LCMS, FTICR-MS, etc., is crucial for ensuring the process's mechanism, efficiency, and safety. The combination with various primary and secondary treatments pre & post-treatment is also to be done. The mechanism for the generation of radicals at each time interval, various should be in detail. The role of aeration is also not studied in detail. Thus, there is a huge gap in determining the overall mechanism of the EO process. The sludge produced can be converted into useful products like biochar for a sustainable environment. Many investigations are done at a lab scale which has to be implemented to bench scale, pilot scale, and real-time. Similarly, there is a literature gap for many emerging pollutants in leachate for its degradation study in EO. The multiple benefits of EO are represented in Fig. 14. Fig. 15 represents the future studies needed for the EO treatment of leachate or any wastewater.

CONCLUSIONS

The EO treatment of leachate has several advantages compared to other methods. Future studies for the optimization of the process for different electrode combinations and integrated electrochemical processes with different green catalysts can reduce the overall cost and improve efficiency. Emerging pollutants like microplastics must be experimented with to know the degradation efficacy. The mechanism needs to be studied in-depth with byproducts assessment using advanced instruments. Green energy like solar energy, can be used for the power supply to reduce the overall cost of the process. The gas generated during the EO may be collected as a useful byproduct. Thus, the EO has several merits in the treatment of heavily polluted wastewater like stabilized leachate. The research gap for the treatment of various emerging pollutants and their combinations needs to be estimated. The life cycle assessment must be done compared with other methods to properly select a method of treatment and a sustainable environment. Thus, optimizing the mentioned suggestions and further study will make the EO technique for wastewater treatment one of the most efficient techniques in the future.

ACKNOWLEDGMENTS

The authors are grateful to VIT, Vellore, for providing all the resources necessary to write this review paper.

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