Electrochemical Technology for Wastewater Treatment: Dares and Trends

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Abstract
For treating wastewater, electrochemical engineering has been rediscovered during the last four decades through the world for its inherent advantages comparatively with traditional technologies especially the chemical and biological techniques. However, the expansion of this technology founded on electric current applying has been retarded by several technical-economic factors especially the detection of disinfection by-products (DBPs) formation. This work focuses on the challenges and future tendencies for this highly-efficient technology to reach the full-scale implementations particularly in disinfecting water. Lately, new versions of electrochemical techniques have been suggested such as employing sulfate radical anion ($\bullet SO_4^{2-}$) and sunlight to generate $\bullet$OH radicals in TiO2 photocatalysis and photo-Fenton water treatment. These improvements elevated the electrochemical engineering efficiency and acceptance. However, more efforts remain to be accomplished for water reuse vision. Future researches would focus on integrating membranes processes such as nanofiltration and reverse osmosis for a safe removal of DBPs.

Subject Areas
Environmental Sciences

Keywords
Wastewater Treatment, Electrochemical Engineering, Electrodisinfection, Electrocoagulation, Electroflotation, Electrooxidation

1. Introduction
Implementing the electrochemical technique in ecological treatment has been
the subject of numerous investigations during the last four decades [1]. Thousands of researches have focused on presenting novel techniques or enhancing previous methods (Figure 1). Following these extended years, very few techniques are being used at full-scale and most processes assessed are only viewed as “encouraging” methods. Most possess established advantages; however, considerable practical and cost hindrances may be listed, which remain linked to lost pieces in the gain series of the technique [2].

Electrolytic techniques involve the cathodic deposition of metals observed in the largely employed electrowinning and electorefining methods and the oxidation of organic matters [3] [4] [5] [6], either directly on the anode surface or mediated via oxidants formed on the anode or on the cathode surface [7] [8]. This last situation is of huge importance since hydrogen peroxide (H₂O₂) may be efficaciously generated from the reduction of oxygen employing gas diffusion electrodes (GDEs) [2] [9] or more newly utilizing cross-flow electrodes surprisingly with implementing elevated pressures [2], conducting to more performant techniques. Moreover, electrocoagulation (EC) processes are launched through liberating electrolytically coagulants from a sacrificial anode and may be utilized to fragment emulsions in industrial wastes or to eliminate colloid contaminants in such wastes and in the course of treating surface water [10] [11] [12] [13] [14].

Not only electrodialysis [15] and capacitive deionization [16] (which let the concentration of ions in liquids) are comprised in electrochemically assisted separation

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Number of publications per year related to different environmental electrochemical technologies according to Scopus [2].
methods, but as well electrokinetic techniques (which permit the transfer of species in solid-liquid mixtures like soil or sludge) [2] [17] [18].

Not all electrochemically founded techniques are at the identical technology readiness level (TRL) (Figure 2) [2]. Huge gaps are observed among electrowinning or electrodialysis and the electrolysis of wastewater contaminated with organic chemicals. Occasionally, comprehending such gaps is required for companies wanting to expand these techniques, particularly if there is a shortage of choices. If competitive alternatives are completely merchandised, it is hard to dislodge them, except if the benefits of the fresh technique would assist to reach a so quick return. Morals have to be taught concerning the prosperous application of electrodialysis and electrodeposition of metals, to attain total pertinency of different electrochemical techniques and to permit paybacks on spent money to companies and society. Plenty of electrochemical techniques, comprising the electrochemical oxidation of wastewater, electrodisinfection [19] [20] [21] [22] [23] and soil electroremediation are presently in status to elevate TRLs [24]. Occasionally, the dare to be confronted is practical; in other circumstances it is economic.

The following concentrates on a short description of electrodisinfection [25]. Further, this work discusses the needed procedures to attain the full-scale utilizations of the green electrochemical engineering especially in disinfecting wastewater.

**Figure 2.** TRL of the main environmental electrochemical technologies, including the key challenges that have to be overpassed to increase this level: no significant challenges (0); further fundamental work (1); components development (membranes, electrodes, cells, etc.) (2); scale up (3); competition with efficient technologies (4). TRL: technology readiness level [2].

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2. Environmental Electrochemical Technology: One-Step Closer to Let Full-Scale Usages

2.1. Dares in Electrochemically Disinfecting Water

During the time that the employment of mixed metal oxide anodes has been revealed for disinfecting water, especially generating chlorinated disinfectants, a hard work stays to drive the technique from classical disinfection of saline swimming pools or spas, in which numerous small and medium enterprises (SMEs) are concentrating their business [2] [26].

With a view to satisfying this perspective, two key dares should be resolved. The first one is to define how to evade the generation of toxic by-products like chlorates or trihalomethanes [13] [27]. Chlorates are produced via oxidation of hypochlorite or by its disproportionation, which is a natural phenomenon that also takes place through the aging of the disinfected water [28]. This chemical is linked to grave health issues as it is established to touch the nervous system. The second kind of dangerous agents is surprisingly more debatable. Chlorinated chemicals are produced from the integration of organic matter with active species of chlorine; however, such agents are linked to cancer and other so severe illnesses. These chemicals are not distinctive of the electrochemical technology since they are also created through the usage of traditional chlorination techniques [28] [29] [30] [31]. The additional dare remains in implementing changes for mixed metal oxide anodes, like diamond-like coatings, which are able both to oxidize chloride ions and generate more performant disinfectants, comprising hydroxyl radicals (OH) [32] [33] [34]. If utilizing such electrodes, issues related to the formation of dangerous chemicals may be worsened, since the well-known generation of perchlorates throughout oxidation of chlorates [2]. Such fresh electrode materials conquer the hope of encouraging the contribution of diverse oxidizing species, like, ozone and peroxosalts [35] to assist eliminate resistant pathogens. Appropriate residence period among water and the anodes in the electrolyzer, an enough big specific current, and the cathodic production of H₂O₂ to avoid more oxidation of chlorine to chlorates and perchlorates remain between precautions viewed to bypass such issues [36].

Chen et al. [37] followed the conversion of roxarsone (ROX) throughout UV disinfection employing Fe(III). Fe(OH)²⁺, as the main Fe(III) species at pH = 3, forms OH under UV irradiation conducting to the oxidation of ROX. Dissolved oxygen [38] has an extremely significant contribution in the constant transformation of produced Fe³⁺ to Fe³⁺, which guarantees a Fe(III)-Fe(II) cycle in the device. The existence of Cl⁻ / HCO₃⁻ / NO₃⁻ has a small impact on the ROX conversion; however, PO₄³⁻ attains an evident inhibitory influence. The conversion of ROX conducts to the generation of inorganic arsenic comprising a much higher quantity of As(V) than As(III). LC-MS analysis depicts that phenol, o-nitrophenol, and arsenic acid were the major conversion products. Both the radical scavenger test and electron spin resonance data establish that the OH is in charge of ROX
conversion. The poisonous transformation products are observed to possess inherent ecological dangers for nature, organisms, and humans.

2.2. Dares Allowing Electrocoagulation (EC) to Rival with Coagulation

Electrocoagulation (EC) remains another possibility of chemical coagulation [39]. In EC, the coagulant is furnished via solubilizing sacrificial electrodes [40]. The ease of running and the secondary phenomena implying the formation of bubbles are the main benefits. In the first situation, the injection of coagulant may be set easily by adjusting the current intensity applied, and the manipulation of chemicals is averted. In the second circumstance, a suitable mechanical cell scheme may assist to use oxygen and hydrogen microbubbles to enhance turbulence and improve the flocculation of particles (in so-named electroflocculation). Every so often, separation may be elevated through flotation, once microbubbles have fixed to the surface of the flocs, reducing their global density (in so-named electroflocculation [14] [41]). In chemical coagulation, the chemicals are usually salts of iron [42] or aluminum [30]; the principal-agent in EC remains hydroxyl ions with \( \text{Fe}^{2+}/\text{Al}^3+ \) [43] [44] [45], and the counterion does not elevate the salinity of the treated water. In traditional coagulation, salts injected work as Lewis acids and necessitate neutralization [46] through alkali additions, to reach an appropriate pH. This elevates both the salt charge of the treated waste and the volume of sludge, conducting to an effluent with so more important conductivity [2]. Reciprocally, EC by itself adjusts the pH, so there is no need of introducing pH-neutralizing chemicals [47] [48] [49] [51].

Even if conceiving an EC at the lab-scale remains so easy, its scale-up stays difficult [40] [52] [53] [54]. On the other hand, it is not forever doable to employ tank cells with sheets of iron and aluminum; further, there is a requirement to utilize cheap materials as sacrificial electrodes [2] [55]. Employing low-quality iron or aluminum could let bipolar electrode arrangements to be utilized [56] [57] [58]. Integrating EC with free radical-assisted techniques stays an encouraging procedure to promote its application at full scale [59] [60] [61] [62] [63].

2.3. Dares in Dealing with Industrial Wastes

During the last decade, one of the most thrilling research fields has been the expansion of techniques dealing with industrial wastes in situations where using biological processes and else inexpensive methods are inactive [2] [64] [65] [66] [67]. In this context, numerous methods have been suggested, most of them being categorized as advanced oxidation processes (AOPs) [32] [33] [34]. The fundamental oxidant implicated is the \( \bullet \text{OH} \). This radical possesses two magnificent benefits as contrasted with diverse conventional oxidants, as in the instance of chlorine: the \( \bullet \text{OH} \) diminishes the production of dangerous by-products [68] and could be quicker and more efficacious, due to the severe oxidation circumstances. For all the excellent expansions in this domain, illustrated in a huge amount of publications, numerous dares stay [69].
With respect to the link among such AOPs and electrochemical engineering, many characteristics should be mentioned: 1) the affirmation in 2003 of the strong contribution of hydroxyl radicals in the electrochemical oxidation with diamond electrodes [70]; and 2) the application of the integration of Fenton and electrochemical techniques [71] [72] conducted to the admission of a fresh class of AOP methods, i.e., electrochemical AOPs [2] [73] [74] [75].

Concerning the existing situation of this technique, implementing electrochemical AOPs for eliminating numerous kinds of organic contaminants has been largely investigated [2]. Numerous researches have been dedicated to clarifying the contribution of electrochemical cell schemes and sorts of electrode on the electrochemical phenomena. It has been emphasized that a fundamental need in the inherent pertinence of electrochemical engineering resides in the judicious usage of all the pieces of the electrochemical setup [76] [77] [78]. This involves not only the usage of an appropriate anode but also the synergistic usage of the cathode reaction and the advancement of mediated oxidation methods in the bulk throughout the remediation. Moreover, enhancing the mass transfer rate within the device is also crucial. Consequently, the efficacious mechanical conception of the setup and a judicious selection of the running parameters are fundamental to attain excellent efficiency. For all such attempts, the technique stays at an average TRL (Figure 2) and huge expansions are required to attain bigger readiness degrees which admit the appropriate mechanical scheme of the electrochemical device to reach excellent models for flow and current distribution [79], scale-up either via elevating electrode size of through stacking [80], the control of hydrogen formed [81] [82] and direct current electrical power necessities [83].

2.4. Dares in Sanitary Effluents: Perspective for Electrochemical Technology

Hospitals generate sanitary effluents with an elevated charge of a huge diversity of chemical products (like pharmaceuticals, detergents, disinfectants, heavy metals, radionuclides) and highly pathogenic microorganisms [2]. Usually, they are immediately ejected in public sewage for remediation at traditional urban wastewater treatment plants (WWTPs). The inadequacy of biological processes at the WWTPs to deal with sanitary effluents conducts to the dispersal of hazardous chemicals and pathogens in nature, destructively influencing both aquatic organisms and human health [84]. Consequently, many investigations focused on technical solutions to diminish the effect of sanitary effluents in nature [85]. Two major programs have been proposed: 1) supporting efficient treatments at WWTPs via implementing supplementary remediation; and 2) pretreatment prior to introducing them into WWTPs [2]. The last choice is rising as the fundamental substitute since it deals with the issue in more concentrated effluents and the volume of wastewater handled is further much lower than in the first situation. Included in the accessible techniques, a solo electrochemical approach like electrochemical oxidation or electro-Fenton and the integration of free radical-assisted electrochemical technologies have shown total disinfection and partial oxidation of
chemicals towards the reduction of toxicity and augmentation of biodegradability of sanitary effluents [2].

Olvera-Vargas et al. [86] proposed a sequential electrochemical process for integral treatment of anaerobic sludge, merging for the first time electrochemical peroxydation (ECP) and electro-Fenton (EF). In the first stage, ECP (consisting of H$_2$O$_2$-assisted EC with Fe electrodes [87]) was used as a conditioning and stabilizing technique, whose synergistic EC/Fenton oxidation impacts greatly diminished the COD, TOC and total suspended solids (TSS) by 89.3%, 75.4% and 85.6%, respectively, under regulated parameters (initial pH of 5, [H$_2$O$_2$]/[Fe$^{2+}$] dose ratio of 5, 15.38 mA/cm$^2$ and 2 h treatment). In addition, total coliforms were completely killed during the first hour of treatment. In the second stage, EF was successfully utilized to mineralize the remaining organic fraction in the liquid effluent after dewatering, attaining 91.6% and 87.2% of COD and TOC removal, respectively, after 4 h of treatment under regulated circumstances (pH 3 and 25 mA/cm$^2$), while almost total COD and TOC removal was attained in 8 h (Figure 3). The Fe sludge produced at the end of the ECP treatment was readily dewatered by filtration and 20.9 g of nutrient-rich dry sludge were formed. The overall cost of the ECP-EF treatment was $0.05/L sludge. The merged impacts of coagulation [88]-[96] and Fenton oxidation throughout ECP established that the treatment performance is strongly dependent on the rheological properties of the sludge sample (Figure 4).

3. Electrochemical Engineering for Disinfecting Water

3.1. Demobilizing Pathogens Using Sulfate Radical

During the last decade, demobilizing pathogens employing sulfate radical anion ($\text{SO}_4^{2-}$) has obtained more and more interest because of increasing requirements...
to manage toxic disinfection by-products (DBPs) and improve water treatment setups especially for efficacious microbial handling [32] [97]-[102]. Xiao et al. [103] concentrated on the fundamental rules and actual research conditions of SO₄²⁻-founded demobilization technique, and juxtaposed it with *OH-founded demobilization of microbes. They discussed the key pathways of radical reactions with biomolecules and the demobilization kinetics and routes via SO₄²⁻. They established that SO₄²⁻ oxidatively destroys the cell membrane, proteins, and genetic materials (i.e., DNA and RNA), conducting to the demobilization of the microorganisms (Figure 5). They reviewed the present issues, dares, and likely solutions in engineering implementations.

3.2. Demobilizing Pathogens Using Solar Photocatalytic Processes

Malato et al. [104] discussed the usage of sunlight to generate *OH radicals in TiO₂ photocatalysis and photo-Fenton water treatment. They defined the reaction setups required for solar photocatalysis and presented a global view of utilized compound parabolic collector photoreactors. They explained how solar photocatalysis might greatly participate in dealing with water containing persistent toxic compounds. They presented the usage of solar photocatalysis in demobilizing microbes existing in the water. In the same direction, Alvarez-Guerra et al. [105] sized the Photovoltaic Solar Electro-Oxidation process that merges the effectiveness of the electrochemical oxidation founded on boron-doped anodes...
to mineralize organic matter, with the autonomy and environmentally friendly features of photovoltaic solar energy [106].

3.3. Electrochemical Engineering for Water Reuse

For water reuse [107] [108] [109] [110] [111], Lefebvre [112] presented the NE-Water successful case of water reuse in Singapore and demonstrated that electrochemical approaches will constitute the centerpiece of such infallible projects. Other researchers attained the same conclusion [113] [114] [115] thanks to the established efficiency of the techniques founded on the electric current application.

4. Conclusion

For treating wastewater, electrochemical engineering has been rediscovered during the last four decades through the world for its inherent advantages comparatively with traditional technologies especially the chemical and biological techniques. However, the expansion of this technology founded on electric current applying has been retarded by several technico-economic factors especially the detection of DBPs formation. This work focuses on the challenges and future tendencies for this highly-efficient technology to reach the full-scale implementations particularly in disinfecting water. Lately, new versions of electrochemical techniques have been suggested such as employing sulfate radical anion (SO₄²⁻) and sunlight to generate *OH radicals in TiO₂ photocatalysis and photo-Fenton water treatment. These improvements ameliorated the electrochemical engineering. However, more efforts remain to be accomplished for water reuse vision. Future researches would focus on integrating membranes processes [116] [117] [118] [119] [120] such as nanofiltration and reverse osmosis for a safe removal of DBPs.
Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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