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Electrochemical-based advanced oxidation for hospital wastewater treatment

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ABSTRACT

Healthcare facility wastewater considerably increases the levels of micropollutants in municipal wastewater. Considering this, the presence of contaminants of emerging concern in the environment has been highlighted as a global environmental problem. Electrochemical advanced oxidation (EAO) generate strong oxidants such as $HO^•$, H_2O_2, and O_3^- which can remove organic pollutants in water including pharmaceutical. This review presents the latest research findings concerning the mechanisms, influencing factors, and innovative approaches for treating wastewater generated by healthcare institutions. Electrochemical oxidation has proven a promising wastewater treatment technology, especially, for pharmaceutical-contaminated wastewater. EAO is widely regarded as a pioneering technique in the field of wastewater treatment because of its strong performance in the mineralization treatment for pharmaceuticals as well as the detoxification treatment of extremely biologically harmful organics. The use of EAO technology is of utmost importance in augmenting the efficiency of electrochemical systems in the decomposition of organic substances. Furthermore, it lays the groundwork for implementing these systems to treat wastewater derived from medical facilities and hospitals. Nevertheless, it is noteworthy that most experimental studies have focused on single-component wastewater that has been artificially prepared in laboratory settings. Wastewater from healthcare institutions often exhibits a complex and diverse composition, influenced by various factors.

Keywords: Electrochemical oxidation; Hospital wastewater; Pharmaceuticals; Electrode material

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1. Introduction

Chemicals are used in healthcare services to ensure proper disinfection, diagnosis, treatment, and patient recovery [1]. These substances are divided into chemicals for preventing nosocomial infections (like disinfectants) and pharmaceutically active compounds necessary for medical procedures (like surgery, investigations, imaging, and drugs) [2].

Pharmaceutical residues in wastewater have grown to be a significant environmental and health hazard during

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the last few decades. They may have an impact on problems with antibiotic resistance, endocrine disruption, carcinogenicity, and general toxicity despite their low concentration in the effluents [3]. Pharmaceutically active chemicals enter aquatic habitats after normal consumption through urine or feces [4]. Then, when their concentration rises over time [5], it is conceivable to find evidence of these compounds in drinking water, groundwater, and even surface waters [6]. Although there are many sources of releases, hospitals produce the most [7]. Hospital effluent is often released into the domestic sewage system and treated at municipal treatment facilities [8]. Pharmaceuticals are highly resilient to water treatment methods using activated sludge or even membrane bioreactors due to their low concentration, complicated structural, and often non-biodegradable properties [9]. Once released into the environment, pharmaceutical contaminants could endanger humans, animals, and even plants [10]. For instance, hormones used for birth control have an impact on fish reproduction [5]. Additionally, the presence of antibiotics and other disinfectants affects the genetic properties of microorganisms and can result in a rise in bacterial resistance to antibiotics [11].

Numerous treatment technologies have been proposed for the treatment of hospital wastewater (HWW). However, it is worth noting that 69% of these studies primarily focused on pilot or laboratory-scale systems, while only 31% addressed full-scale specialized facilities. This distribution highlights the significance of ongoing research in this field, emphasizing the need for further exploration and development in the area of large-scale treatment facilities [12]. Pharmaceutical removal efficiencies vary depending on the water matrix qualities, their nature (physicochemical features), the technology used, and the operating conditions, used during the treatment. For instance, membrane bioreactors (MBR) and even more conventional activated sludge are not effective for the degradation of various polar pharmaceuticals (with typically reported removals of 25%), namely: phenazone, indomethacin, cyclophosphamide, iohexol, sotalol, propranolol, roxithromycin, iodixanol, ioversol, and iomeprol. For gabapentin, ritalinic acid, iopamidol, and carbamazepine, modest removal efficiencies (50%) were reported [13–15]. Hence, it can be deduced that relying solely on biological processes proved insufficient in effectively eliminating all organic residues present in typical HWW. For this reason, physicochemical and oxidative methods or their mixtures have been studied by several investigations. According to Nielsen et al. [13] the classes of cytostatics is very resistant to ozonation removal. Only a few chemicals from these two families were indeed eliminated by 50% to 60% at medium-high ozone levels. This happened with doses of around 1.1 $g/O_3{\cdot}g1$ DOC and 4.1–7.8 $g/O_3{\cdot}g1$ TOC for ifosfamide, cyclophosphamide, iopromide, and iopamidol. Additionally, bromates, an oxidation byproduct that might have ecotoxicological effects, may be formed because of ozonation [12].

Several pharmaceutical pollutants, including metoprolol, paracetamol, omeprazole, sulfachloropyridazine, chloramphenicol, amoxicillin, ranitidine, and fantetra, were successfully degraded by electrochemical advanced oxidation processes (EAOP) [16]. The anode overpotential toward the oxygen evolution reaction and the adsorption enthalpy of the electro-generated hydroxyl radicals are what govern the oxidizing power. Other electrochemical treatment technologies have gained attention for treating wastewater since they are more affordable and effective [17]. One of the quick and efficient electrochemical processes for treating water and wastewater is electrooxidation [18,19]. Through the process of electrolytic oxidation, a suitable anode material undergoes transformation into a coagulant at an optimal pH, facilitating the removal of larger impurities. This method is characterized by its simplicity in equipment requirements and straightforward operational procedures, while also leading to the formation of soluble metal hydroxide [20,21]. These metal hydroxides help suspended particles separate from the aqueous phase by flocculation and coagulation by neutralizing electrostatic charges on them [22,23].

This literature review examines and deliberates on the utilization of electrochemical oxidation techniques for the treatment of wastewater from hospitals and healthcare facilities. Initially, the characteristics of HWW and healthcare service wastewater are highlighted, along with the environmental issues associated with them. Subsequently, the principles and mechanisms underlying the electrochemical oxidation method are elucidated. The third section provides a summary and analysis of recent studies that have explored the application of electrochemical oxidation for the treatment of HWW. Finally, the economic aspects and feasibility of employing the electrochemical oxidation approach are discussed in the concluding part of this review. Overall, the current review offers a specialized and comprehensive analysis of electrochemical oxidation methods for hospitals and healthcare wastewater treatment, incorporating recent research findings and considering economic feasibility. It aims to contribute to the existing body of knowledge on this specific topic.

2. Hospital and clinical wastewater

Hospital wastewater contains a variety of emerging contaminants including, endocrine-disrupting compounds (EDCs), personal care products (PCPs), pharmaceutically active compounds, and hormones [24]. The utilization of chemicals is essential in the healthcare sector to ensure precise diagnosis, effective treatment, proper disinfection, and successful patient recovery [24]. These chemical substances are excreted from patients' bodies through their urine and feces, and often discharge into sewage systems as original forms or as metabolites or conjugates [25]. The emerging contaminants (ECs) found in trace amounts (between μg/L and ng/L) have the potential to bypass wastewater treatment plants and contaminate the environment [26]. The annual use of medicine by healthcare facilities is around 20%–25% of pharmaceutical consumption by humans [27]. Cytostatic, antibiotic, and other medication concentrations in hospital effluents have been estimated to range from tens to several hundreds of micrograms per liter [28].

Hospital effluents make up more than 80% of all PCPs and pharmaceuticals in some low-flow sewage networks' load [29]. HWW is known to be a significant source of ECs [30]. ECs find their way into HWW through various means, including the direct disposal of expired or unused medications, the presence of ECs in landfill leachates, and the application of sewage sludge for enhancing soil fertility [31]. Many studies have consistently revealed the presence of untreated hospital sewage in environmental water bodies, which not only contains medications but also encompasses antibiotics and resistance genes [32,33]. The ecosystem, human health, and biota may all be at risk due to the presence of these pharmaceuticals in several environmental matrices like surface water, groundwater, soil, and sediments [34]. Environmental sustainability and public health are impeded by the presence of micropollutants in the environmental matrices. Thus, For the management of discharged effluents, it is crucial to increase the effectiveness of wastewater treatment plants [34].

3. Electrochemical advanced oxidation

Compared to conventional water treatment techniques, electrochemical water treatment systems (electrocoagulation, electrooxidation, electroflotation) provide several advantages [35]. These advantages include the potential for energy recovery, the capacity to remove many various types of contaminants, *in-situ* chemical synthesis, and modular cell design [36].

4. Fundamentals and mechanisms of electrochemical oxidation

Various EAOs are being investigated for the oxidation of growing concern pollutants [37,38]. In this section, the fundamentals and mechanisms of electrochemical oxidation are presented (Fig. 1).

5. Electrooxidation

The oxidation of pollutants during the electrooxidation process (EO) can take place either directly, by the passage of electrons from the contaminant to the anode, or indirectly, through chemical reactions with electrogenerated active species [39], primarily hydroxyl radicals ($HO^{\bullet}$). According to [38], the electrode material used in the electrochemical process can be classified into non-active and active anodes, particularly for the oxygen evolution reaction (OER). This electrode material plays a crucial role in oxidation through both direct and indirect pathways, as well as in the generation of radicals and oxidants.

Antimony, tin, lead oxides, and boron-doped diamond (BDD) is the most typical non-active anodes [40]. By oxidizing water, non-active anodes produce physiosorbed $HO^{\bullet}$ on their surface [Eq. (1)]. Following this, the $HO^{\bullet}$ reacts with the pollutants, causing their breakdown to intermediate or total mineralization [Eqs. (2) and (3)] [41].

$$M + H_2O \rightarrow M\left(HO^{\bullet}\right) + H^{+} + e^{-} \tag{1}$$

$$CEC + M\left(HO^{\bullet}\right) \rightarrow \text{intermediates} \tag{2}$$

$$\text{intermediates} + M\left(HO^{\bullet}\right) \rightarrow CO_2 + H_2O + \text{inorganic ions} \tag{3}$$

where M is the anode material and M ($HO^{\bullet}$) is the hydroxyl radical adsorbed on the anode (M) surface. The non-active anodes have a high potential for the OER because of the weak interaction with the $HO^{\bullet}$, which allows a broad working potential window [42]. The resulting “quasi-free” $HO^{\bullet}$ can react in the diffusion layer [43], enhancing the mineralization of the pollutants [44]. However, the short lifetime of the $HO^{\bullet}$ (106 s) restricts these reactions [45]. On the other hand, because of the intense interaction between the electrode surface and $HO^{\bullet}$ [Eq. (4)] [46], active anodes encourage the creation of higher-state oxides. With these electrodes, the superoxide is decomposed, resulting in the OER [Eq. (5)] [47], which means the OER will occur at a lower potential, presenting a constrained work potential window. Additionally, because the $HO^{\bullet}$ produced is thought to be chemisorbed, the reaction can only occur on the anode surface. Dimensionally stable anodes (DSA®), mixed metal oxides, and platinum are the most often used active anodes [47].

$$MO_x\left(HO^{\bullet}\right) \rightarrow MO_{x+1} + H^{+} + e^{-} \tag{4}$$

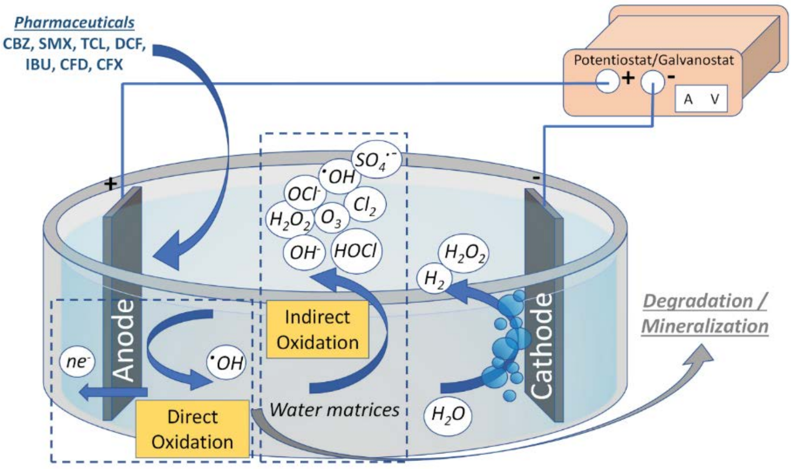

Fig. 1. Basic figuration of electrochemical oxidation process [3]. Reprinted with permission from MDPI. Copyright 2021, Environments, MDPI.

$$\mathrm{MO}_{x+1} \rightarrow \mathrm{MO}_x + \frac{1}{2}\mathrm{O}_2 \tag{5}$$

where MO_x denotes the metal oxide surface and MO_{x+1} the higher state oxides that were created.

In addition to these reactions taking place at the electrode surface, indirect oxidation can also occur in the bulk solution due to the interaction of a mediator (an oxidizing species) that depends on the salts in the solution [48], the applied current or voltage, and pH, [41]. For instance, it is possible to produce active chlorine species (Cl_2, HClO, ClO, and ClO at BDD surface [49] when chloride is present. However, at BDD and in the presence of sulfate, it is feasible to produce persulfate $\mathrm{S}_2\mathrm{O}_8^-$ and the sulfate radical SO_4^{2-}, which can take part in the CEC oxidation at the bulk solution [50]. However, the ratio of diamond sp3/sp2 carbon in BDD electrodes can affect the production of oxidative specialties [51]. Fig. 2 illustrates direct and indirect electrochemical oxidation.

6. Photo-electrooxidation

Photocatalytic technology utilizes both homogeneous and heterogeneous processes. In the homogeneous phase, the catalyst is dissolved, resulting in the absence of a catalyst-liquid interface [52]. However, a challenge with homogeneous methods is that the catalyst used cannot be reused, rendering the procedure unsuitable for continuous processes [53]. The catalyst, which is often a semiconductor and is a solid in heterogeneous processes, can be used as an anode in an electrochemical cell since it can be supported on a variety of substrates. Photo-electrooxidation (PEO), also known as photo electrocatalysis (PEC), is a hybrid process that incorporates EO, heterogeneous photocatalysis (HP), and direct photolysis (DP). To achieve this, it is required to provide a potential or current density along with an ultraviolet (UV) light source that illuminates the electrochemical cell's semiconductor anode [54]. There are more options for $\mathrm{HO}^\bullet$ formation when PEO is used, including one path by HP and another by EO. Titanium dioxide (TiO_2) is the most popular and routine semiconductor type utilized in PEO [55].

Three different forms of TiO_2, namely rutile, anatase, and brookite, are recognized as distinct polymorphs of the compound [56]. These phases have band gaps of 3.2, 3.0, and ~3.2 eV, respectively [57]. One electron from the valence band (VB) is promoted to the conduction band (CB) when light photons (hv) with an energy larger than the band gap illuminate TiO_2, creating a positive hole (h^+_{VB}) in the VB [Eq. (6)]. To create $\mathrm{HO}^\bullet$ radicals, the holes may oxidize the water molecule [Eq. (7)] [55]. In addition, the superoxide radical anion ($\mathrm{O}_2^{\bullet-}$) [Eq. (8)] can be created by the interaction of the electrons in the conduction band (e^-_{CB}) and adsorbed molecular oxygen.

$$\mathrm{TiO}_2 + \mathrm{hv} \leq 387\,\mathrm{nm} \rightarrow e^-_{\mathrm{CB}} + h^+_{\mathrm{VB}} \tag{6}$$

$$\mathrm{H}_2\mathrm{O} + h^+_{\mathrm{VB}} \rightarrow \mathrm{HO}^\bullet + \mathrm{H}^+ \tag{7}$$

$$e^-_{\mathrm{CB}} + \mathrm{O}_2 \rightarrow \mathrm{O}_2^{\bullet-} \tag{8}$$

However, one restriction [58] that can be removed by doping the semiconductor with transition metals is the recombination of photogenerated charges, $e^-_{\mathrm{CB}}$and h^+_{VB}. The development of the DSA® type by [59], who introduced ruthenium oxide (RuO_2) on TiO_2, was crucial for that. The semiconductor can be employed in PEO with DSA® as a photoanode and, in the presence of a counter electrode, it can be polarized to reduce $e^-_{\mathrm{CB}}/h^+_{\mathrm{VB}}$ pair recombination and increase photocatalytic efficiency for oxidizing pollutants. Through the application of an external potential or current, the photocatalysis process can be electrochemically aided in this configuration [60]. Consequently, the combined effect

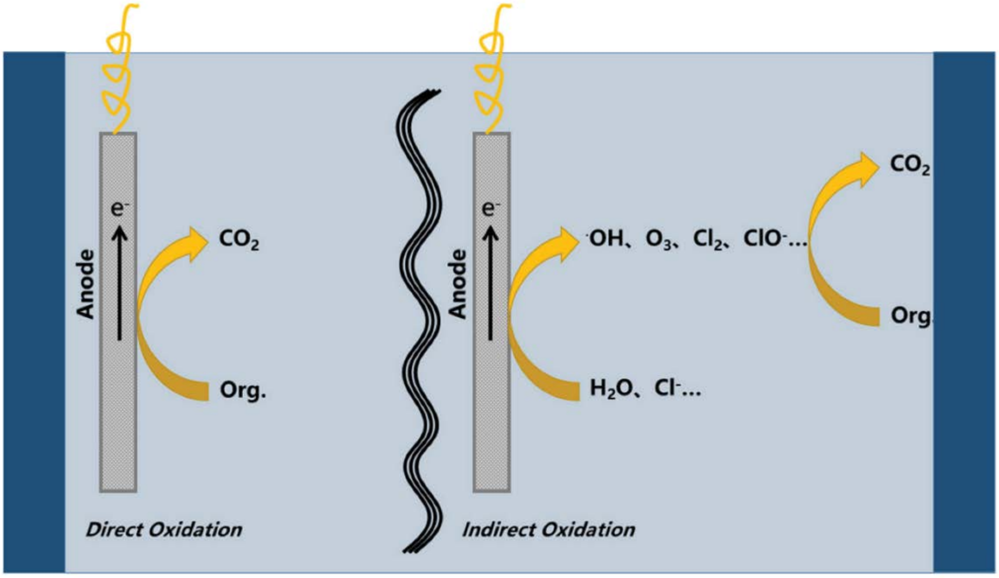

Fig. 2. Direct and indirect electrochemical oxidation [17]. Reprinted with permission from MDPI. Copyright 2022, Water, MDPI.

allows for a greater number of electrons to be transferred through the external circuit compared to what each individual process could achieve independently. This amplification in electron transfer enhances the rates of oxidation [61]. The differential in concentration caused by the polarization's favoring of oxidation reactions on the electrode surface encourages the migration of species in solution to the surface of the photocatalyst and boosts the reaction's effectiveness [62].

A drawback of using TiO_2 doped with semiconductors like RuO_2, CeO_2, or WO_3 is that these materials are considered critical elements due to their high global demand and limited availability, necessitating the development of materials without the use of critical elements. Studies on doping TiO_2 with elements like SnO_2, which are considered no-critical elements, are now being conducted [63]. Moreover, ongoing research is exploring the incorporation of natural chemicals into TiO_2 to enhance its absorption of radiation in the visible spectrum. This is important because TiO_2 typically generates the radicals mentioned earlier only when exposed to UV light with a wavelength of 400 nm [64]. In addition, studies on PEO applications have also been conducted [65], although most scientific works have focused on the synthesis, characterization, and assessment of the catalytic characteristics as well as the usage of TiO_2 electrodes sensitized with natural dyes in HP processes [66].

7. Electro-Fenton and photoelectro-Fenton

Due to the generation of highly oxidizing species, and simple and reliable application, the Fenton process' lower cost than other advanced oxidation process (AOPs), which make it a choice for the treatment of effluents that contain CEC (Fig. 3) [67]. In the Fenton process, the interaction between H_2O_2 and Fe^{2+} [Eq. (9)] in acid media results in the indirect catalytic generation of $HO^\bullet$. This method is homogenous since both reagents are added simultaneously to the reaction media [68]. The Fenton process has an environmental benefit over other AOPs since it uses non-toxic chemicals in the amounts needed for the process [69]. This is due to the usage of Fe^{2+} and H_2O_2.

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + HO^\bullet + H_2O \tag{9}$$

Despite the benefits, the Fenton process's mineralization efficiency for complex chemicals is low since a lot of by-products are produced [70]. The photo-Fenton (PF) technique is employed to achieve higher mineralization of effluents containing CEC, which are often complicated molecular chains and challenging to mineralize. In the PF process, in addition to the direct reaction with H_2O_2 and CEC, the source of ultraviolet light (UV) is responsible for converting Fe^{3+} to Fe^{2+}, allowing continual $HO^\bullet$ formation [Eq. (10)].

$$Fe^{3+} + hv + H_2O \rightarrow Fe^{2+} + HO^\bullet + H^+ \tag{10}$$

Temperature, type of radiation, H_2O_2 concentration, Fe^{2+}/Fe^{3+} concentration, and pH of the aqueous medium are all factors that affect the Fenton and PF processes [71]. The electro-Fenton (EF) and photoelectron-Fenton (PEF) processes, which attempt to produce H_2O_2 in situ, were created to reduce the amount of H_2O_2 added during the Fenton or PF process [72,73]. The electrochemical production of H_2O_2 at the cathode for the EF and PEF processes involves the reduction of dissolved O_2 [Eq. (11)]

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{11}$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \tag{12}$$

A single electron reduction of the ferric cation [Eq. (12)] on the cathode can replenish the Fe^{2+} catalyst, which can also be externally added [74]. $HO^\bullet$ can be created by

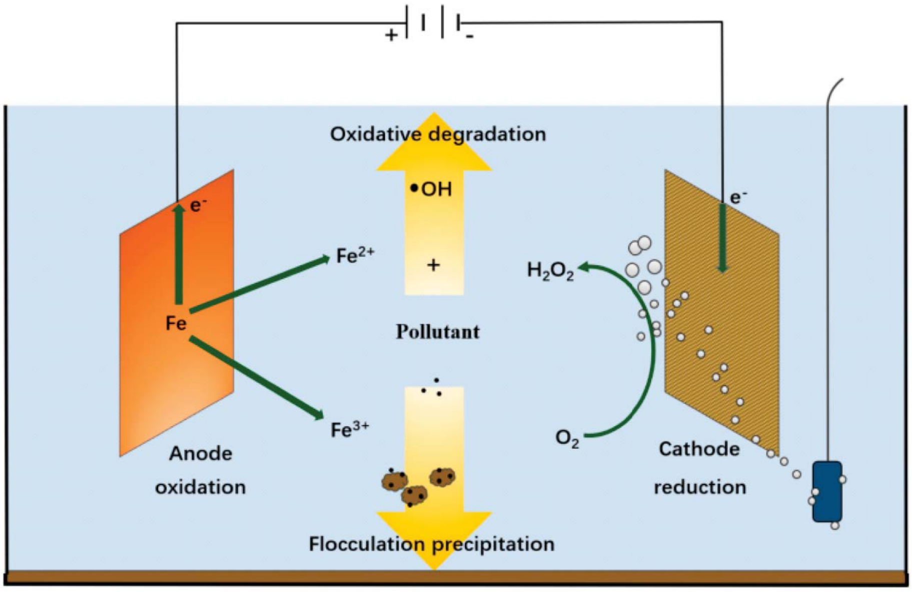

Fig. 3. Electro-Fenton process [68]. Reprinted with permission from MDPI. Copyright 2023, Process, MDPI.

water oxidation at the anode surface, which depends on the anode material [75] [Eq. (1)]. Prior to its reduction process to produce H_2O_2, molecular oxygen (O_2) in electrophoretic fluid (EF) must first be transported from the gas phase to the aqueous phase and adsorbed on the cathode surface [76]. Since O_2 can only be reduced to H_2O_2 when it is dissolved in the aqueous phase, as a result, the amount of dissolved oxygen can control how much H_2O_2 is produced throughout the EF process [77].

The cathode must have a high overpotential for H_2 evolution to conduct the O_2 reduction, a need typically met by carbonaceous materials, particularly graphene oxide, carbon-PTFE, graphite, etc. [78]. In addition, the ability to create H_2O_2 has been demonstrated by BDD with Ni foam employed as a cathode [79]. Given that greater temperatures can prevent O_2 solubility and cause H_2O_2 breakdown, the temperature can also have an impact on the process [80].

The pH of the solution is one of Fenton's reaction's biggest drawbacks because it is crucial to the process efficiency [81]. The production of the peroxonium ion ($H_3O_2^+$) at pH 2.5 restricts H_2O_2 reactivity with Fe^{2+} (electrophilic attack). Contrarily, a pH of 4.5 results in the precipitation of Fe^{3+} (catalyst elimination) in the form of $Fe(OH)_3$ [53]. Between 2.8 and 3 is the pH range that is thought to be ideal for the reaction's conduction [82]. As the pH rises, the treatment's effectiveness declines noticeably. [83].

Heterogeneous catalysts are shown as a potential substitute for iron precipitation [53]. The catalyst for the heterogeneous EF process will be solid, like iron oxides immobilized on various substrates. The catalyst will be applied in this instance to membranes, modified cathodes Fe/activated carbon, ion exchange resins, and carbon felt-iron oxide as an air diffusion electrode [84]. The application of heterogeneous procedures across a larger pH range gives them an edge over homogeneous methods [53]. However, the pH should be neutral or weakly acidic for improved performance (6.5–7). Iron hydroxide layer development on the available iron during higher pH circumstances may reduce catalytic activity. Along with this, H_2O_2 stability at higher pH levels is changed, since there is a higher chance that it will follow a destructive pathway rather than a radical-forming pathway, which also results in poorer efficiency [85].

Iron-based catalysts are among the most investigated because they are inexpensive, low-toxic, and need low concentrations [76], with ideal Fe^{2+} values between 1 and 0.1 mM [86]. Unwanted reactions involving $HO^•$ scavenging by increased Fe^{2+} may result from higher Fe^{2+} concentration. However, because of the pH limitations, other metals can be used as catalysts in Fenton-like processes, to perform the treatment at a pH of around seven or slightly alkaline. The most common metals used to replace Fe catalysts include Mn, Cu, Cr, and Mo-based catalysts and/or co-catalysts [87], with the metal's properties controlling the catalytic mechanism of mineralization and degradation. The EF process is used in the treatment of water and wastewater containing CEC because it is adaptable and can be ramped up, considering the process parameters [88].

However, stable Fe(III)-carboxylate complexes can develop in cells of one compartment and then be slowly eliminated by $HO^•$ radicals, which causes the breakdown of end products with aromatic chemical groups and slower processes to complete total mineralization. By concurrently exposing the solution to UV radiation and producing the photoelectron-Fenton (PEF), it is possible to get around this issue [89]. Thus, to renew both the catalyst Fe^{2+} and $HO^•$ (Eq. 13), the solution used in the EF process is simultaneously exposed to UV radiation via photoreduction of the $Fe(OH)^{2+}$ under UVA light irradiation (=315–400 nm) [90].

$$\mathrm{Fe}\left(\mathrm{OH}\right)^{2+} + h\nu \rightarrow \mathrm{Fe}^{2+} + \mathrm{HO}^{\bullet} \tag{13}$$

$$\mathrm{H_2O_2} + h\nu \rightarrow \mathrm{HO}^{\bullet} \tag{14}$$

The cycle will be completed by producing $HO^•$ from the photolytic breakdown of the H_2O_2 (Eq. 14) [91], which was earlier electrogenerated in the cathode, using UV-C irradiation sources (280 nm). In addition, direct photolysis can be a risk for CEC. But photolytic breakdown often has slower kinetics, which means it contributes less to total mineralization and can produce harmful by-products [92].

8. Application of electrochemical oxidation for hospital wastewater treatment

Recent studies [93,94] have used electrochemical technology to degrade pharmaceuticals in hospital wastewater. These methods encourage the production of significant numbers of highly reactive species from *in-situ* oxidation and reduction reactions produced in the effluents without the need for chemicals for the removal of organics [95]. To produce highly effective electrochemical advanced oxidation processes, it is essential to choose the right electrode materials and construct the reactor [96]. The current density is the operating parameter that has the greatest impact on the creation and expansion of electrochemical advanced oxidation processes.

Diamond-based coatings, SnO_2 or PbO_2 are regarded as non-active anodes, while materials based on Pt, Ir, and Ru are examples of active anodes [97]. Serna-Galvis et al. [98] investigated the use of a Ti/IrO_2 anode in electrooxidation for the treatment of HWW contaminated with cephalexin. After 30 min of using a current density of 5 mA/cm^2 at pH 6.5, the antibiotic (40 M) removal efficiency reached 60%. The electrochemical creation of free chlorine by anodic oxidation was aided by the substantial numbers of chloride ions present in the effluent, which accelerated the antibiotic's breakdown via an indirect oxidation process.

Zirconium spiral cathode and Ti/IrO_2 anode electrode materials were employed in experimental setup by Palma et al. [99]. The author investigated the concurrent breakdown of naproxen (40 M) and diclofenac (40 M) in urine at 5 mA/cm^2 and pH 6.0. In this scenario, for diclofenac and naproxen, the results showed electrolysis-induced elimination rates of 30% and 20%, respectively. Jojoa-Sierra et al. [100] investigated a Ti/IrO_2 anode for the elimination of 125 M norfloxacin in urine by using a 6.53 mA/cm^2 current. Due to competition between norfloxacin's breakdown and urea oxidation during urine electrolysis, an antibiotic removal efficiency of around 65% was reached after 180 min.

To remove cefazolin (100 M) from urine, Sordello et al. [101] assessed the viability of the electrooxidation method using a platinum sheet anode and a glassy carbon cathode. The current density range was between 0.5 and 150.0 mA/cm^2. The authors concluded that cefazolin can be broken down at current densities of 0.5, 5.0, 50.0, and 150.0 mA/cm^2 at around 500, 160, 40, and 10 min of electrolysis, respectively. To remove 0.1 mM of iomeprol (iodinated contrast medium) from urine, Zwiener et al. [102] used a platinum net as an anode and a reticulated nickel foam electrode as a cathode. During electrooxidation, a 1V voltage was applied. After 120 min of electrolysis, the entire amount of iomeprol was removed.

More recently, Herraiz-Carboné et al. [103] examined the effectiveness of using active and non-active anodes to remove 100 mg/dm^3 chloramphenicol from urine. They found that using BDD anodes allowed for 100% antibiotic elimination for all current densities evaluated (1.25–5 mA/cm^2), but using anodes based on mixed metal oxides (MMO) only achieved removal percentages of about 25% under the same operating. The oxidation of chlorides during the treatment of urine produced free and mixed chlorine species, which helped both anodes contribute to the breakdown of antibiotics. However, the use of BDD anodes also encouraged the electrochemical formation of peroxocompounds from the oxidation of other ions present in urine, favoring the elimination of antibiotics.

Electro-Fenton is another eco-friendly EAO used to remove pharmaceuticals from water bodies [104]. By using BDD and 3D-carbon felt as the anode and cathode, respectively, in electro-Fenton at pH 3, Feng et al. [105] examined the elimination of 0.08 mM piroxicam from HWW and urine. The catalyst was used at a concentration of 0.1 mM Fe^{2+}, and a current density of 4.17 mA/cm^2 was used. Complete removal was reached in both effluents after 120 min. This may be due to pharmaceuticals and other organics, such as urea or acetate found in HWW and urine, engaging in oxidative competitive processes. On the other hand, Ahmadzadeh and Dolatabadi [106] reported using electro-Fenton to treat HWW containing 1.35 mg/dm^3 of acetaminophen. They employed two iron plate electrodes, 122.5 mL/dm^3 H_2O_2, and a pH of 2.75 at 8 mA/cm^2. By electrolyzing the anode, the ferrous iron needed for the Fenton reaction was electro-generated on-site. The results reported that after 10 min, acetaminophen could be completely removed. One of the major drawbacks of the electro-Fenton methods is the significant impact caused by the limited ability of oxygen to dissolve in water under atmospheric pressure. This limitation directly affects the cathode's capacity to generate hydrogen peroxide. To get over this restriction, Moratalla et al. [107] described the use of a pressurized electrochemical reactor outfitted with a jet aerator for the removal of meropenem in urine, proving that high pressures can considerably enhance the electrochemical generation of hydrogen peroxide. With a 3D-MMO-$IrO_2Ta_2O_5$ mesh anode and a modified 3D-titanium mesh with CB/PTFE cathode at 5 mA/cm^2, pH 3, and 10.8 g goethite, they specifically examined the effect of pressure (gauge pressure range of 0–3 bar) on the elimination of 50 mg/dm^3 meropenem in urine by the heterogeneous electro-Fenton process (heterogeneous catalyst). Results showed that the gauge pressure increased the rate of meropenem degradation. At gauge pressures of 0, 1, 2, and 3 the antibiotic removal rate reached 80.60%, 89.03%, 91.60%, and 94.64%, respectively, by exposing EAOs to UV light, it is possible to encourage the photoactivation of electrogenerated oxidants, which favors the generation of free radicals and accelerates the destruction of organic pollutants [108]. Particularly, the photoactivation of electrogenerated hypochlorite and persulphate with UVC light can produce free chlorine and sulfate radicals, respectively [109].

Using active anodes (MMO-Ti/RuO_2IrO_2), Gonzaga et al. [110] examined the removal of 50 mg/dm^3 penicillin G in urine matrixes via electrolysis and photo electrolysis. They applied a current density of 30 mA/cm^2 while using a UVC lamp (9 W). Results indicated that pairing UVC light with electrolysis had a noticeable synergistic effect on the breakdown of the antibiotic, achieving complete elimination of the pollutant in 8 h. Gonzaga et al. [111] compared the electro-Fenton and photoelectron-Fenton processes for the breakdown of penicillin G in an acidic environment (pH 3). BDD and MMO-Ti/$Ru_{0.5}Ir_{0.5}O_2$ were used as two separate anodes, while a modified carbon felt was used as the cathode. Fe^{2+} was present at a catalyst concentration of 0.5 mM, and 120 mA of current was flowing. They claimed that although MMO caused penicillin G elimination to occur more quickly than BDD anode, the impact of the anode material is less significant. Since photoactivation of hydrogen peroxide by UVC light irradiation can also occur, boosting the generation of free hydroxyl radicals in the effluent, the degradation of antibiotics was accelerated during the photoelectron-Fenton process [112].

Finally, Santos et al. [113] assessed the removal of captopril (0.23 mM) by Solar photo electro-Fenton from urine in three distinct synthetic urine matrices (Urine 1, Urine 2, and Urine 3). In this instance, the electro-Fenton process is improved by using the photolytic action of sunshine (UVA light). The studies were conducted in a solar pre-pilot flow plant using a carbon-PTFE air diffusion electrode as the cathode and a Pt plate as the anode. Initial Fe^{2+} concentration was 0.5 mM at pH 3 and 50 mA/cm^2. Other organic constituents, such as creatinine, urea, and uric acid, are presented in varying amounts in each synthetic urine matrix, with urine 1 being the most dilute and urine 3 being the most concentrated. Captopril abatement was conducted at 15, 20, and 30 min during the treatment of urines 1, 2, and 3, respectively, even though these organic substances slow down the process. Table 1 summarizes the recent studies applied electrochemical advance oxidation for pharmaceutical removal from hospital wastewater.

9. Recommendations and future perspectives

The concentrations of pharmaceutical substances used in the EAO experiments were higher than what is typically found in hospital wastewater. Therefore, it is advisable to utilize realistic pharmacological concentrations, either projected or measured, in order to bridge the gap for certain operational parameters. Since natural water often contains various anions, cations, organic matter, and even suspended solids, conducting experiments using realistic media instead of buffer solutions can help elucidate the true interferences and challenges faced in EAO processes before scaling them up. There is a pressing need to significantly enhance energy

Table 1
Electrooxidation treatment results of some pharmaceutical-containing wastewaters in the literature

Technology	Electrodes	Target contaminant	Concentration	Operating parameters	Removal efficiency	Main results	References
Electrocoagulation (EC) and adsorption (AD)	A: aluminum C: aluminum	Ceftriaxone	20.0 mg/L	- pH 7.5 - Current density 6.0 mA/cm^2 - Adsorbent dosage 0.75 g/L - Reaction time 12.5 min	100%	After using the EC/AD hybrid process, the ceftriaxone concentration in the hospital wastewater was eliminated to zero.	[114]
Electro-Fenton	A: Pt or BDD C: 3D carbon felt	Naproxen	0.198 mM	- pH 3 - Electrolysis (50 mM) Na_2SO_4 - Current intensity 50 mA - Reaction time 30 min	100%	EAOs can be great in naproxen removal in complex matrices.	[94]
Electrochemical oxidation	A: BDD, IrO_2 C: stainless steel grid	Psychoactive pharmaceutical caffeine	13 ppm	- Electrolysis Na_2SO_4 - Current intensity = 0.7 A	78%–92%	Anode type followed by electrolysis time is the most important variables affecting caffeine degradation.	[115]
Electrochemical oxidation	A: Pt-SnO_2/Ti C: stainless steel	Diclofenac	500 µg/L	- Reaction time 30 min - Electrolysis Na_2SO_4 - pH (natural) - Reaction time 60 min - Current 16 mA/cm^2	77.5%	The presence of organic substances such as humic acid inhibits DCF removal.	[116]
Electrochemical oxidation	A: Pt/Ti C: Pt/Ti	Carbamazepine	100 µg/L	- Reaction time 80 min	56%	To treat carbamazepine and phosphate in wastewater simultaneously, EAO could be efficiently combined with an MBMBR.	[117]
Photoelectro-Fenton	A: gas diffusion electrode C: gas diffusion electrode	Ciprofloxacin	30 mg/L	- Reaction time 360 min - Current densities (10–100 mA/cm^2)	84%	For the treatment of organic pollutants, the implementation of the photoelectro-Fenton method with *in-situ* electro generation of H_2O_2 utilizing gas diffusion electrode has proven to be suitably promising.	[118]

Table 1 (Continued)

Table 1

Technology	Electrodes	Target contaminant	Concentration	Operating parameters	Removal efficiency	Main results	References
Electrochemical oxidation	A: Pt C: glassy carbon rod	Cefazolin	100 μM	- Current density 0.5–150 mA/cm^2) - pH (5–9) - Reaction time 500 min	100%	The ions phosphate and chloride increase CFZ breakdown, which is mostly unaffected by pH.	[101]
Electrochemical oxidation	A: SA-Yb-PbO_2 C: Pb	Naproxen sodium	30 mg/L	- Current density 50 mA/cm^2) - pH 6	95%	The electrochemical measurements show that SA-Yb-PbO_2 electrodes have higher oxygen evolution over potential value, larger active specific surface area, and more active sites than Yb-PbO_2 electrodes.	[119]

A: anode, C: cathode

efficiency, which involves the development of new degradation platforms and operating guidelines that can minimize parasitic side effects that do not contribute to pollution degradation. To make the most of existing effective resources like BDD in EAO, it is crucial to explore novel and cost-effective preparation techniques. Toxicity analysis is another important aspect that should be included in future investigations. Prioritizing the treatment of pharmaceutical compounds can be based on assessing the toxicity of these substances at their actual concentrations. It is essential to evaluate the toxicity of by-products as well, as they may turn out to be more harmful than the original pharmaceuticals.

10. Conclusion

The presence of pharmaceuticals in aquatic environments, primarily originating from hospital effluent, has become increasingly prevalent over time. Protecting the aquatic ecosystem requires understanding the types and concentrations of pharmaceuticals in hospital effluents. Extensive research has focused on electrochemical advanced oxidation (EAO) techniques as a means to remove pharmaceuticals from hospital wastewater and urine. These techniques utilize electrochemical oxidation to generate highly reactive species that can degrade organic contaminants. To enhance removal efficiency, the combination of EAO with UV light irradiation (photo-Fenton) has been tested, along with photocatalytic procedures using TiO_2 as a catalyst. Persulfate-based EAO, which harnesses the generation of sulfate radicals under UV light, has also shown promise. EAOs offer a novel alternative for breaking down pharmaceuticals in hospital wastewater by producing *in-situ* oxidizing species through oxidation and reduction reactions. The use of various irradiation technologies, such as UVA, UVC, and solar radiation, can further improve these processes. Electrochemical oxidation, employing different types of electrodes, has been extensively explored for pharmaceutical removal, including both active and non-active anodes. Additionally, the electro-Fenton process, utilizing various anodic and cathodic materials, has emerged as a promising technology for pharmaceutical removal from hospital effluents. These advancements contribute to the ongoing efforts to protect the aquatic environment from the harmful effects of pharmaceutical contamination.

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