

A critical review of electrocoagulation and other electrochemical methods

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Abstract

There are significant environmental and health risks related to the presence and permanence of toxic wastes such as dyes, medicines, personal grooming products, heavy metals, manure, and insecticides, as well as the items they alter. The problem is made more difficult by the fact that these effluents mix with other water streams that are used for a range of residential tasks, such as irrigation. Water purification and water quality maintenance have been attempted using a variety of methods. Nitrogen species have a remarkable technological capacity to remove a variety of pollutants commonly found in municipal waters, such as refractory organic debris and microbes. Electrochemical techniques have attracted growing interest in recent years. When it comes to treating wastewater, electrochemical procedures provide a variety of benefits over conventional methods. These methods are reliable, easy to use, and flexible enough to react to shifting effluent streams. In addition to providing revised information on the use of electrochemical technology, this review article explains some of the key factors of electrochemical technologies used in wastewater treatment. It was discovered that when electrochemical procedures were combined with ultraviolet light or single treatments were evaluated, the oxidation of the majority of organic pollutants may be greatly accelerated or increased. Low sludge formation and high rates of organic matter decomposition are electro chemical's key benefits. But the costs and need for more space are the biggest downsides.

Keywords: Wastewater, Dyes, Pollutants, Electrocoagulation, Electrooxidation

Full length review article

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1. Introduction

Water sources are becoming more and more contaminated as a result of the increase in population, as well as related manufacturing, urbanization and chemically processed agriculture[1]. The 3 percent of the total of available water in the universe is fresh water. Only a tiny fraction (0.01%) of these freshwater resources can be used by people. According to a statistical report, domestic sewage accounts for 75–80% of all water pollution. Textile, sugar, and other waste products from the electroplating industries are the main sources of contamination [2]. A report by the US Environmental Protection Agency (EPA) estimates that about one-third of the water on Earth is contaminated. In the world, 1.1 billion people lack access to pure water, with 90% of them living in continental Asia and Africa, according to the United Nations' 2015 World Water Development Report. [3]. There are 2.5 billion humans without access to adequate sanitation. By 2025, it is anticipated that three quarters of the earth's population would live in countries with moderate to severe water shortages [4-6]. The presence of heavy metals in industrial and sewage discharge raises serious concerns about

environmental damage. They provide serious threats to the recipient channel's wildlife and plant life as well as the human species. They may be absorbed by the body and accumulate, causing severe health consequences like cancer, damage to organs and the central nervous, and in the most extreme scenarios, death. Additionally, it hinders development and expansion [7]. The photosynthetic ability of plants is significantly hampered by intensely colored textile wastewater. Aquatic life is further impacted by the restricted light penetration as well as oxygen uptake. Some marine species may also perish as a result of the synthetic colors' chlorine and component metal content [8]. Most dyes contain common carcinogens like benzidine, which needs to be processed before being released into the natural environment. In addition to dyes, other pollutants including metals and additives used in dye production may also be present. Diverse methods and procedures for removing colors from industrial effluents and other water sources have been established in order to minimize the harmful effects that dyes have on living things [9].

There are a variety of treatment methods, including biological, physicochemical, and advanced oxidation processes, to eliminate contaminants from wastewater. Physical-chemical methods have high removal efficiency [10]. However, their application is restricted because to the substantial amount of chemicals needed during the procedure and the production of substantial amounts of sludge at the conclusion of the treatment. Researchers have recently demonstrated that electrochemical treatment processes are viable technologies to minimize or lessen pollution issues as a result of restrictive environmental rules and laws [11]. The method of electrocoagulation has been used for a long time to purify water and remove a variety of impurities. However, electrocoagulation has not been regarded as a "mainstream" method of water treatment. Its application has been hampered by the lack of a systematic approach to electrocoagulation reactor design/operation and the problem of electrode dependability (especially the issue of electrode passivation over time). However, electrocoagulation has been given another look in light of recent technological advancements and a growing demand for small-scale, decentralized water treatment plants [12] When compared to conventional procedures, electrocoagulation has many benefits, including high removal efficiency at cheap capital and operating costs, simple and small equipment requirements, and ease of process control, which results in robustness. Comparing this technique to chemical coagulation, less extra chemicals are required and less sludge is produced [13-14].

2. Electrocoagulation (EC)

EC is a sophisticated technique for purifying water of toxic substances, microorganisms, dispersed oils, and suspended solids (TSS). So it combines established methods such as electrochemistry, coagulation, and flotation. However, coupling the three approaches is a topic for which there is not a lot of literature. The reduction of consumption of electricity and effluent processing rates were the initial achievements. Recent technological advancements have made it possible for EC to run at low currents, enabling it to operate solar cells, fuel cells, and wind turbines. An electrochemical reaction with either a cathode or an anode that is linked outside to a source of electricity and submerged in an electrolytic solution makes up the EC unit [15]. Anodes in electrolytic cells oxidize when current is applied, releasing an equal number of electrons when the metal splits into metallic ions that are divalent or trivalent despite the fact that when the electrodes are made of the same substance, hydrolysis only happens at the anode. Equation states that the amount of metallic ions created is determined by Faraday's law (equation 1) and depends on the amount of applied current.

$$m = IM_w T / FZ \quad (1)$$

Where m is the mass of the anode that has been dissolved, F is the Faraday constant (96,485C/mol), T is the operating duration, m is the material's molecular weight, and Z is the number of electrons engaged in the reaction, I is the current [16].

When water is reduced on the cathode, hydrogen gas and hydroxyl ions are generated (equation 2). A metal ion (M^{n+}) is formed when the metal is pushed into the anode (equation 3, 4). When the metallic ions produced on the

cathode interact with the hydroxyl ions group to produce the metal hydroxide, the pH of the solution influences whether monomeric or polymeric, soluble or insoluble metallic hydroxides are produced. Due to their strong propensity to form bindings with contaminants and form flocs due to their huge surface area, metallic hydroxides $M(OH)_n$ are excellent adsorbents of contaminants. Numerous secondary reactions take place in the EC cell, producing gases at the cathode and anode, respectively, such as H_2 and O_2 [14-16]. The process of electrocoagulation is shown in fig. 1.

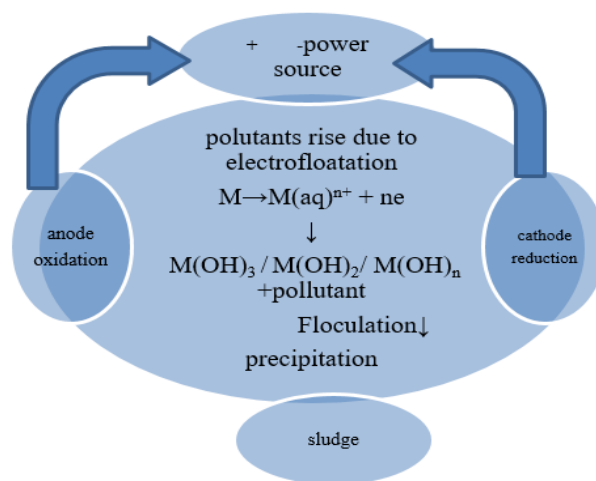
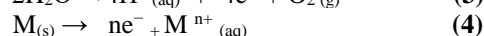
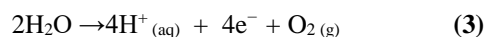


Fig.1. Process of Electrocoagulation

At cathode



At anode

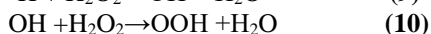
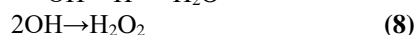
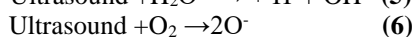
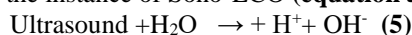


When the dispersed H^+ ion rejoins another H^+ ion that is already present in water, H_2 gas is produced. The removal of flocs that resist gravitational settling requires the gasses H_2 and O_2 (figure 1). In a process known as electrofloatation, the H_2 gas generated brings the agglomerates to the solution's top, where they can be skimmed off. An intermediary that speeds up the degradation of both dangerous and non-dangerous species is hydrogen peroxide, is created when oxygen is generated at the anode. Heavy flocs have a tendency to sink to the bottom where they condense into sludge that may be effectively removed using a number of techniques. [16].

Modern electrochemical (EC) procedures use the concurrent production of in situ hydroxyl (OH) radicals and other chemical oxidants by various means. These highly oxidative species enhance the clearance of contaminants because (i) chemical oxidation's acceleration of the anodes' disintegration and (ii) increase the removal of organic contaminants using radical species' oxidation action (mineralization). The following lists some cutting-edge EC technologies. [17].

2.1. Sono-electrocoagulation

Low frequency ultrasound and a standard electrocoagulation setup are combined to create the Sono-electrocoagulation (Sono-ECO) method. The Sono-ECO technology speeds up the breakdown of contaminants and the pace at which radicals are produced from ultrasound. The development of electrode passivation—deposits on the anode's surface—which leads to higher energy usage for the removal of organics is another significant disadvantage of the ECO method. Therefore, electrode passivation that develops on the electrodes can be reduced by applying ultrasonic waves. The production of hydroxyl species and hydrogen via cathodic reaction occurs after the cathodic reaction in the instance of Sono-ECO (equation 5-11).



Sono-ECO is more effective in removing pollutants than the traditional ECO procedure [17]. In light of this, Ozyonar and associates compared the ability of Sono-effective electrocoagulation to remove reactive and dispersion dye from synthetic solutions to that of regular electrocoagulation using an optimal ultrasonic frequency of 40000Hz, a starting dye amount of 100 mg L⁻¹, an ultrasonic power of 180 W, and current densities are 75 and 50 mA cm⁻² for reactive red and disperse blue, respectively, 99-99.9% decolorization was discovered to be feasible. So, using Sono-ECO, practically all of the color was removed within 4 minutes of electrolysis. However, in 5 minutes of electrolysis time, 92% of the color was removed with traditional ECO. In contrast to conventional ECO, whose electrode passivation happens often, Sono-higher ECO's removal can be linked to a decrease in electrode passivation. Therefore, compared to Sono-ECO, traditional ECO requires a longer operating period to achieve a similar level of contamination clearance. Similar to this, Sono-ECO was employed in another investigation to remove wastewater-borne reactive blue 19 dyes. About 97% of Reactive blue 19 removals were accomplished with an ideal Current Density of 18 mA cm⁻², electrolysis period of 60 minutes, pH of five, and ultrasound of 150 W. Sono electrocoagulation ability to remove disperse blue 19 was 7% more effective than conventional ECO due to the passive film that was removed from the electrode surface as a result of sonication. As a result, the anode's rate of coagulant synthesis increased. Sono-ECO can therefore achieve increased contamination clearance [17].

2.2 Photo assisted electrocoagulation (photo-ECO)

Photo-electrocoagulation is a development of the electrochemical coagulation technology that uses UV (UV light) with a specific wavelength to start oxidation processes and electrochemically produce coagulation factors and active chlorine species. This stimulates the generation of highly reactive oxygen radicals like Hydroxyl, which rapidly degrade the contamination and enhance the ability of conventional ECO to coagulate. In order to generate reactive

species from the cathode and oxidize the ECs as compared to the traditional electrocoagulation setup, the photo assisted electrocoagulation setup comprises of a low-pressure mercury lamp. In a study on the efficiency of photo electrocoagulation with aluminum electrodes for the elimination of phenol from wastewater, it was discovered that there was a 20.1% solidification of phenol with starting amount of fifteen mg L⁻¹ at the current density of 2.7 mA cm⁻² less than two hours of radiation exposure at 254 nm in wavelength. Researchers can now look at the breakdown of Ecs utilizing this sophisticated ECO technique even if photo-ECO has a modest amount of phenol mineralization [17].

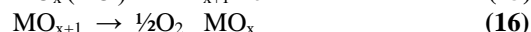
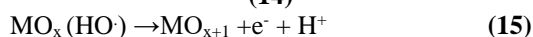
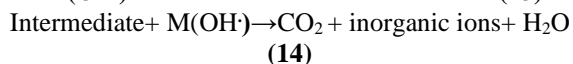
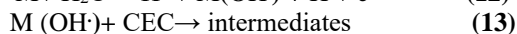
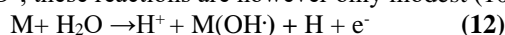
2.3 peroxi-electrocoagulation

Another development in ECO technique is the peroxi-electrocoagulation (peroxi-ECO) procedure, in which iron serves as the sacrificial anode and H₂O₂ is externally dosed in the ECO setup. Additionally, this setup continuously regenerates Fe⁺² in the reaction chamber by iron dissolution, that aids in oxidizing the impurities and increases setup efficiency. Dosing H₂O₂ is primarily designed to generate hydroxyl ions in the electrocoagulation system to degrade the organic effluents given its high oxidation potential of 2.87 V vs. SHE. In general, contaminants with aromatic ring structures, like detergents, phenol, pigments, and medications, can be cleaned up using the peroxi-ECO technique. The aromatic ring of these pollutants can be broken down by the OH radicals, which can then be transformed into a lengthy chain. As a result, the pollutants have a larger surface area, which promotes co-precipitation and adsorption using metal hydroxide flocs. The effectiveness of the peroxi-ECO procedure was evaluated, and it was shown to have removed 81.6% of the sodium dodecyl sulphate detergent from the polluted water. Starting pH was 5.0, first SDS quantity was 60 mg L⁻¹, and beginning current density was 0.5 mAcm⁻². A similar investigation used iron electrodes to assess the removal of phenol using peroxi-ECO, and it found that 92% of the phenol could be removed with start amount of 2.5 mgL⁻¹, at a current density of 10 mA cm⁻², and a 2.0 acidic pH. In the peroxi electrocoagulation procedure, phenol is oxidized by OH radicals while also having the aromatic ring of the phenol broken to enable its adsorption on ferric hydroxide globules. Despite the fact that peoxi-ECO has shown promising results in the removal of pollutants from contaminated water, more study is required to improve the process and mineralize the contaminants [15-18].

3. Electro-oxidation

In the electro oxidation (EO) process, pollutants can be oxidized directly by transferring electrons from the cathode to the anode, or indirectly by reacting chemically with electro generated active species, primarily hydroxyl radicals (HO•). The electrode material is fundamentally connected to oxidation via either direct or indirect pathways in addition to the production of radicals and oxidants. Thus according to study for the oxygen evolution reaction, the electrode material can be split into inactive and active anodes. The most common inactive anodes are made of tin, antimony, lead oxides, and boron doped diamond (BDD). In

inactive anodes, water oxidation results in the production of physically bound HO• on the anode surface (equation 12). After then, the pollutants and HO• interact, causing the breakdown of the contaminants into intermediates or complete mineralization (figure 2a). Inactive anodes have a significant potential for the oxygen evolution reaction because of their limited interaction with the hydroxyl, creating a large working potential window. The created "quasi-free" HO• has the capacity to react in the interfacial layer, speeding up the mineralization of the pollutants equation 13 and 14. Due to the short half-life of the HO•, these reactions are however only modest (10⁻⁶ s).



M (M) stands for the anode substance, and M (HO•) stands for the hydroxyl radical that has been deposited on the anode (M) surface. As a result of the intense interaction seen between electrode surface and HO•, active anodes, encourage the formation of higher state oxides (equation 15). Due to the weak interaction with the HO•, the non-active anodes present a high potential for the OER, allowing, consequently, a wide working potential window oxygen evolution reaction (OER) will occur (equation 16). Additionally, the reaction can only take place on the anode surface since it is believed that the HO• generated is chemisorbed. The most common active anodes are dimensionally stable anodes, mixed metal oxides, and platinum [6-19]. The process of electrochemical oxidation of organic compound and mixed metal oxides are shown in fig 2a-2b, respectively. The fig. 2c shows the generation of oxidants in the process of electrochemical oxidation.

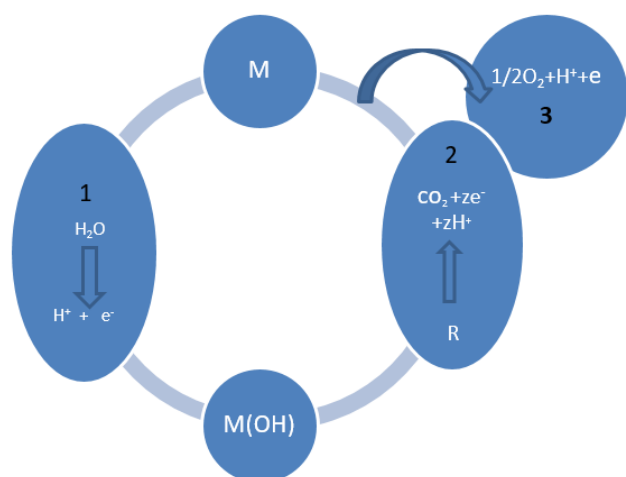


Figure 2a; the process of Electrooxidation of organic compound R (Here, (M) boron doped diamond, where (1) is the water discharge, (2) is the combustion of (R), and (3) is the evolution of oxygen reaction.

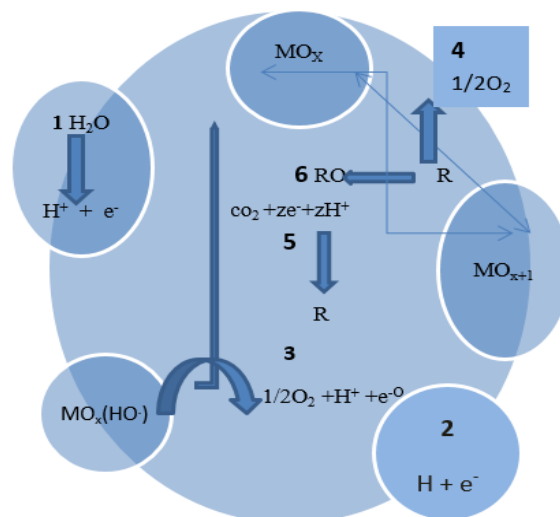
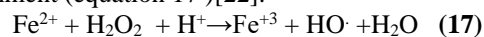


Figure 2b; the process of Electrooxidation of mixed metal oxides (Here, (1) denotes the release of water, (2) denotes the production of a superior oxide, (3) and (4) denote the evolution of oxygen reaction, (5) denotes the burning of R, and (6) denotes the transformation of R to RO (byproducts).

MO_x refers to the metallic oxide surface and MO_{x+1} to newly produced higher state oxides. In addition to these reactions that occur at the electrode surface, indirectly oxidation may also proceed on the fluid layer as a result of a mediator (an oxidizing species) which is reliant on the solution's salts, pH, and the applied power or voltage. For instance, when chloride is available, it is possible to electrolyze active chlorine species (chlorine, hypochlorous, ClO, and ClO_n⁻) on dimensionally stable anode and boron doped diamond surfaces. In contrast, it is conceivable for per sulphate and sulphate radical to develop at BDD and in the existence of sulphate, which can take part in the degradation of CEC in the bulk solution. However, the ratio of diamond sp³/sp²-carbon in BDD electrodes can affect the production of oxidative species [19].

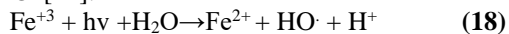
3.1. Electro-Fenton (EF) and photoelectro-fenton

Due to the production of potent oxidizing species, the Fenton method's lower cost when compared to other AOPs, (advanced oxidation processes) and its easy and dependable implementation, the Fenton process has been extensively used in the treatment of pollutants that contained contaminants of emerging concern [14-18-20]. The reaction between H₂O₂ and Fe²⁺ in acidic media generates HO• indirectly catalytically in the Fenton process [21]. Due to the simultaneous addition of both reagents to the reaction fluid, this procedure is homogeneous. The use of Fe²⁺ and H₂O₂, which must be used in safe chemical levels during the operation, provides the Fenton method an advantage over all other advanced oxidation processes in regards to the environment (equation 17) [22].

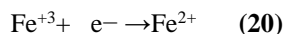
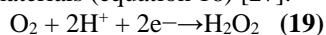


Despite the aforementioned benefits, the Fenton process's mineralization efficiency for complicated chemicals is low since a lot of byproducts are produced [18-

23]. The photo-Fenton approach is utilized to increase the mineralization of CEC (contaminants of emerging concern)-containing effluents, which frequently have complex molecular chains and are difficult to mineralize. In the photo-electro Fenton process, the source of ultraviolet light (UV) converts Fe³⁺ to Fe²⁺, allowing continuous HO• production, in addition to the direct interaction with H₂O₂ and CEC [24].



The H₂O₂ concentration, radiation type, temperature, concentration of Fe²⁺/Fe³⁺, and pH of the aqueous medium all have an impact on the Fenton and PF processes [25]. The electro-Fenton (EF) and photoelectron-Fenton (PEF) procedures were created in order to reduce the accumulation of H₂O₂ during the Fenton or PF process. The electrochemical reduction of dissolved O₂ at the cathode produces the reagent H₂O₂ for the EF and PEF reaction [26]. The Fe²⁺ catalyst, which can also be provided externally, could be refilled by a reduction of the iron cation by one electron on the cathode. Water oxidation at the surface of the electrode might result in the production of HO• based on the electrode materials (equation 18) [27].

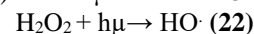
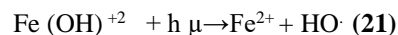


Before it can go through reduction to generate H₂O₂ in EF, molecular oxygen (O₂) needs to be moved from the gaseous phase to the aqueous medium and then deposited on the surface of the cathode. Because O₂ can only be reduced to H₂O₂ after being dissolved in aqueous solution, the dissolved O₂ can actually slow down the EF process by regulating the rate at which H₂O₂ is produced (equation 19) [21]. The cathode needs to have a high over potential for H₂ evolution in order to execute O₂ reduction and carbonaceous materials—PTFE, graphite, Graphene oxide, etc.—typically meet this requirement. Additionally, using BDD with Ni foam as the cathode, it has been shown that it is possible to produce H₂O₂. Given that greater temperatures can prevent O₂ solubility and cause H₂O₂ breakdown, the temperature can also have an impact on the process [28]. Since the pH of the solution is crucial to the reaction's efficiency, this is perhaps among the fundamental shortcomings of the Fenton's reaction. [29]. The production of the peroxonium ion, which occurs at pH 2.5, restricts the reactivity of H₂O₂ with Fe²⁺ (electrophilic attack). However, a pH of less than 4.5 results in the precipitation of Fe³⁺ (elimination of the catalyst) as Fe(OH)₃ (equation 20) [30]. The pH range between 2.8 and 3 is regarded as ideal for the reaction's conduction. As the pH rises, the treatment's effectiveness declines noticeably. Heterogeneous catalysts are shown as a potential substitute for iron precipitation as a result [31]. Solid catalysts, such as iron oxides immobilized on diverse substrates, will be used in the heterogeneous EF process. Ion exchange resins, modified cathodes composed of iron and activated carbon, and an air diffusion electrode made of carbon felt and iron oxide will all be used in this process [32]. The ability to use heterogeneous processes across a larger pH range gives them an edge over homogeneous processes. However, the pH should be neutral or weakly acidic for improved performance (6.5–7).

Iron-based catalysts are really among the most researched because of their low toxicity, low cost, and low

concentration requirements. The ideal Fe²⁺ values range from 1 to 0.1 mM. Higher Fe²⁺ concentrations may result in undesired reactions, such as excessive Fe²⁺ scavenging HO•. With the pH constraints in mind, dissimilar metals can be utilized as accelerators in Fenton-like reactions with the objective of performing the procedure at a pH at about 7 or slightly alkaline. Copper, Mn, chromium, and molybdenum-based catalysts and/or co-catalysts are the main metals used to replace Fe catalysts, and the properties of the metal will affect the catalytic mechanism of degradation and mineralization [30].

Since the EF method may be scaled up in light of the process features, it is employed in the CEC-containing water and wastewater treatment process. However, stable Fe (III) carboxylate complexes might develop in cells of one compartment and then be slowly eliminated by HO• radicals, degrading end products with aromatic chemical groups and delaying the process of total solidification. Concurrently producing the photoelectron-Fenton and UV irradiating the fluid is one way to solve this issue (PEF). Because of this, the solution used in the EF process is exposed to UV radiation at the same time in order to regenerate the catalysts Fe²⁺ and HO• through photo reduction of the Fe(OH)²⁺ under UV A light irradiation (315–400) (equation 21, 22) The HO• will be produced from the photolytic breakdown of the H₂O₂, which was previously electro-generated in the cathode, concluding the cycle, using UV-C irradiation sources (280 nm). In addition, CEC might be directly subjected to photolysis. However, photolytic degradation often has slower kinetics, which results in a smaller contribution to overall mineralization. It can also produce hazardous by products [31].



The pH of the media, which must be between 2.8 and 3, has already been stated as the main disadvantage of Fenton's based procedures. Although further research is needed, certain studies do indicate this reaction under circumneutral pH circumstances. In addition to being successful in treating real and synthetic wastewater containing CEC, including pharmaceutical goods, the PEF procedure is promising and extensively researched.

4. Factors influencing how well electrochemical techniques perform

A number of operating parameters, such as working electrode, CD, solution concentration, time of electrolysis, charge loading, inter-electrode length, amount of contaminants, and others, have an influence on the performance efficacy of ETs in terms of pollutant removal and operating costs [33]. For instance, as there are less metal hydroxide complexes available. An increase in the concentration of pollutants may result in a reduction in the effectiveness of removal of pollutants for the adsorption and co-precipitation of the impurities. So, in this section, a few key factors impacting the efficacy of Electrooxidation and Electrocoagulation have been clarified [17].

4.1. Electrode arrangement

The potential drop across an electrolytic cell is influenced by the thickness and form of the electrodes. The value of the potential drop is calculated using the formula below (equation 23) [34].

$$\eta_{IR} = I d / AK \quad (23)$$

η_{IR} = potential produced by solution resistance IR-drop; d = electrode spacing (m); I = current (Amp); K = specific conductivity (A = active area of anode surface (m^2)).

When surface area is increased while maintaining the same current density, insecticide removal efficiency also rises. Bipolar or monopolar electrode placement in an electrolytic cell, as well as series or parallel electrode arrangement is all possible. Equal anodic or cathodic potential pair of anodes and cathodes is arranged alternately in a monopolar electrode arrangement. When using many electrode pairs, at the same potential, each set of electrodes is similar to a small electrolytic tank. [35]. Electrolytic cells are arranged in parallel in the reactor, and the total current flowing through all of these cells makes up the reactor current. MP- S. In this setup, the interior individual electrode sets are linked, but neither of the two outside electrodes is linked to an internal electrode pair. In this case, the current flowing through each electrode is the same, but the voltages across the unit are computed by summing the voltages of all the tiny electrochemical cells. Sacrificial electrodes are positioned between two outer electrodes while functioning in bipolar mode and the power source is only delivered to the outside electrodes [36].

In this setup, the inner electrodes function as bipolar and the outer electrodes as monopolar. Not attached are the internal electrodes. They are referred to as "bipolar" because each electrode simultaneously functions as a cathode and an anode on both sides. In bipolar setup electrodes are not interconnected to each other [37]. Cathodic reactions take place on the negative of the bipolar electrode, which acts as an anode, whereas dissolution happens on the positive. Bipolar electrodes typically operate at greater voltages and lower currents than monopolar electrodes. Bipolar electrode configuration causes the anode metal to dissolve more quickly, which increases the generation of coagulant. Because bipolar electrodes are simple to use and demand less alimentation, the overall cost of operation determines the optimal electrode design choice. The ratio between the area of electrode and volume of the electrode is a major component that influences removal effectiveness during electrocoagulation along with arrangement of electrodes space between the electrodes and layout of the electrode. The electrode area to volume ratio is critical when converting a lab experiment to a large-scale facility while keeping the same inter-electrode spacing. The ratio of electrode area to electrode volume normally ranges from fifteen to forty-five meters squared as the ratio between the area of electrode to volume of electrode increases current density and treatment time drop. When the area of electrodes is particularly large, concentration of current is used as a key parameter. Current density and electrode Area/Volume ratio are combined in this measure. This parameter determines the quantity of coagulant species released in a batch reactor after specific electrolysis

duration. In a continuous flow reactor, the residence time is governed by the reactor volume and flow rate [38].

According to Faradays law

$$C = M / FZ (I/V).t \quad (24)$$

c = Number of electrons transported per mole of metal during anodic dissolution, Z = Theoretical concentration of metal cations created ($g. m^3$), M is the electrode material's atomic weight, and I is the current (Amperes) V = Working volume of the reactor (m^3), F = Faraday's constant, and t = electrolysis duration [39].

4.2. Design of the reactor

The performance of electrochemical processes is affected by the reactor design in terms of floc generation, path of bubble, and flotation properties. Some important factors, like mode of operation that is either continuous or batch, time of electrolysis, and rate of flow, have been taken into account while designing reactors the majority of published studies on pesticide removal used batch processing. Out of 19 articles, only one continuous-flow study based on EC was discovered [40]. Batch reactors can be employed with decentralized treatment systems in rural areas where just small volumes of treated wastewater are needed. When decentralized treatment systems are used in rural locations where only small amounts of treated water are required, batch reactors can be used a fixed volume of water could be processed per cycle in batch system. Investigating time-dependent effects is easier and more practical in batch mode. As the anode dissolves during electrolysis, coagulants are continuously produced, which removes contaminants and a long-term shift in the solution's pH [41]. A continuous-flow reactor treats water or wastewater while continually feeding it into the reactor. There are a few researches for pesticide removal in continuous-feed method. For the EO of clopyralid, bench-scale continuous-flow equipment was employed. The experiment was conducted with a flow velocity of $8.05 mL min^{-1}$ and a current density of $10 Ah dm^3$. In another investigation, iron and stainless steel were used as the anode and cathode, respectively, to achieve oxyfluorfen elimination efficiency (up to 90%) under ideal operating circumstances. In continuous reactors, the electrolysis period ranged from 2 to 24 hours [42].

4.3. Electrode materials

The electrode material affects how effectively pollutants are removed when utilizing EC or EO technologies. The pollutant, necessary effluent water quality, cost, and oxygen evolution potential are taken into consideration when selecting the electrodes. Iron and aluminum are the most often utilized electrodes in EC experiments for eliminating pesticides. Aluminum, iron, and stainless steel electrodes can perform EC and electroflotation simultaneously because they are dissolved anodically.

Table 1. Removal efficiency of different electrode materials

Electrode material	Maximum removal efficiency %
Iron (Fe)	99
Aluminium (Al)	99
Stainless steel (SS)	94
Iron + aluminium (Fe+ Al)	-
Copper (Cu)	47
Titanium (Ti)	88
Iron +aluminium+ iron plates	-
Iron Fe-aluminium Al- Zinc Zn + Fe	91

Many studies have suggested using aluminum and iron electrodes as pollutant removal methods. Aluminum with an iron electrode combined or stainless steel provides surprising results. The anode materials employed were iron, aluminum, magnesium, and zinc. Iron had the highest 2, 4-D removal (91%), aluminum came in second (82.5%), and zinc had the lowest removal (56.2%). BDD and DSA were the materials utilized the most frequently as anodes for the EO process to remove pesticides. On several substrates, including silicon, molybdenum, titanium, and niobium, a thin diamond film coating is produced when carbon is transformed into diamond crystals at low pressure [43]. Chemical vapor deposition and high pressure-high temperature techniques can be used to create stable BDD electrodes [44]. Due to its great stability in both acidic and alkaline conditions, boron doped diamond has been employed as an anode for electrooxidation on a large scale. Additionally, it generates large amounts of hydroxyl radicals, which can oxidize a variety of organic contaminants [45].

Additionally, it has a low capacity for adsorption and is a great heat conductor. Additionally, it has a low capacity for adsorption and is a great heat conductor. The presence or absence of organic material has no effect on the mineralization process since BDD anodes have high oxidation potential. The oxide electrodes often referred to as Dimensionally Stable Anodes internationally, have improved electrooxidation process efficiency and led to numerous other scientific advancements [46]. Higher mechanical stability and electro catalytic activity with less anodic corrosion are two benefits of using DSA electrodes. By exchanging electrons with the impurities on the electrode surface, these anodes allow for direct oxidation to take place. By contrast, reactive species such as active chlorine, H₂O₂, and O₃ can be produced, which can lead to indirect oxidation [47]. DSAs typically cost more than graphite but less than BDD and produce significant amounts of chlorine and oxygen. Additionally, atrazine degradation efficiency with IrO₂ as an anode material was about 8% higher than with SnO₂ at a significantly lower treatment cost [48].

Electrode materials	Maximum removal efficiency %
Iron Fe	88
Titanium Ti	98
Stainless steel	95
pbO ₂	>99
SnO ₂	>90
IrO ₂	88
RuO ₂	78.6

4.4. Electrode spacing

When using EC and EO technologies, an ideal inter-electrode spacing must be established. The inter-electrode distance has an impact on the cell voltage and resistance. Wider spacing between electrodes reduces mass transfer and enhances Ohmic losses [49]. In batch mode, the impact of interelectrode spacing on the reduction of turbidity from drinking water was investigated. It was shown that when electrode spacing shrunk, electrode consumption rose, increasing the effectiveness of turbidity removal [50]. When the distance between electrodes was reduced from four cm to two cm, turbidity removal effectiveness rose from 80% to 98%. Investigations were done into how electrode spacing affected the clearance of the herbicide Dicofol. The EC experiments were conducted for 120 minutes at pH 5 with a fixed voltage of 15 V and a 500 revolution per minute mixing speed. The removal efficiency was shown to rise as the electrode separation was decreased. However, as current density increases, a short circuit might occur when the inter-electrode spacing is too small. As a result, a 20 mm inter-electrode separation was described as ideal. When the distance between electrodes is smaller, the ions must travel a shorter distance. Therefore, a small inter-electrode distance also results in a lower electrical energy requirement for ion transport. Because it produces good convection properties close to the electrodes, which aid in blending the solution with the produced coagulants, a small inter-electrode distance is advised [51].

4.5. Current density

One of the key factors influencing electrochemical technologies is current density, which is measured as the amount of current flowing through the electrodes per unit of their effective working surface. The electrode dissolution rate to generate ions of metal depends on current density, which has an impact on both the effectiveness of pollution removal and the system's running costs [52]. The efficiency of pollutant removal typically rises with applied current density up to a critical limit. Raising current density above the critical point would not result in the efficient elimination of pollutants because of the emergence of additional side reactions as well as the charge reversal of colloids brought on by the overproduction of coagulants [53]. Therefore, current density must always be adjusted in electrochemical techniques corresponding to other parameters, such as pH of

Table 2. Pesticides removal efficiency of different electrode material

the electrolyte, starting concentration of pollutant, and concentration of electrolyte, in order to effectively remove target pollutants from wastewater. In a test, phenol percentage removal rose from 29percentage points to 90percent when current density is improved from 0.2 to 0.8 mA cm⁻² with a pH level of 2.0 and starting phenol concentration of 2.5 mg L⁻¹. Yet, it was demonstrated that the speed of phenol removal reduced as the current density was elevated from 0.8 to 1 mA cm⁻² while only having a 2% higher removal at the current density of 1 mA cm⁻² relative to 0.8 mA cm⁻² [17].

4.6. Electrolyte concentration

Both the amount of electrolyte present and the elimination of pollutants during ETs are significantly influenced by the electrolyte concentration. The conductivity of the solution can be improved by an increase in electrolyte concentration, which helps to boost transfer of electrons despite the low voltages. As a result, even when low supplied potentials, the electrodes can create significant currents, which can increase the effectiveness of pollution removal [53]. Consequently, the process uses less energy and takes less time to complete. NaCl and sodium sulphate are typically employed as electrolysis since they are inexpensive and widely accessible. A study looked into how much sodium chloride will affect atenolol removal. The findings shown that atenolol elimination rose from 19percentage points to 30percent when Salt content was raised from 0.25 to 2 g L⁻¹ [54]. The elimination of Malathion improved from 80% to 98%, according to another study, when the electrolyte volume was raised from 5 to 35 ml [17].

4.7. Initial pH

It is challenging to draw a link between pH and system efficiency since wastewater pH fluctuates during the electrochemical process as electrolysis time passes. As a result, the electrochemical reaction treats the initial pH set as the pH of the solution. The production of metal hydroxides complexes depends on the pH of the solution, and that the pH affects the solubility of various kinds of metal complexes [55]. For instance, aluminum anode can remove pollutants more effectively when the pH is 7.0 rather than acidic or higher alkaline ranges. This can be attributed to aluminum ions' limited solubility at neutral pH, which allows them to form more hydroxide precipitates and absorb pollutants on their surface [56]. As a result, in order to produce metal hydroxides using a variety of anodes, the dissolution of the flocculants, this relies on the pH value of the solution. According to one study, increasing the pH ranges from three to seven and applying a potential of 60 V increased the elimination efficacy of ten mg per liter of amoxicillin by around 76–98% [57]. A further rise in pH to 9.0 caused a decrease in elimination ability with just 79.4% clearance because of the formation of dissolved metal hydroxides that were not involved in the adsorption of amoxicillin, decreasing the removal effectiveness [17-58].

4.8 Electrolysis time

The duration of electrolysis affects how quickly pollutants react with locally generated coagulants to form flocs. Generally speaking, longer electrolysis times will result in more effective metal removal since more metal complexes will develop up to the ideal moment. The elimination efficiency might stay unchanged and not significantly gradually improve after the ideal time because of the presence of secondary reactions in the system [33-59]. Because extended electrolysis times can also result in higher electricity usage, it is crucial to maximize the electrolysis duration required for the electrochemical reaction. For instance, increasing the electrolysis period from two to eight minutes raised the removal rate of Ten mg/l of methyl green from 30.7percentage points to 80%. [17].

5. Emerging applications

Micro plastics contamination is a significant environmental issue that is gaining international attention because of its negative effects on marine ecology [60]. Micro plastics may remain chemically stable in the aquatic system over several years [61]. Micro pollutants are easily eaten by marine life (such as mussels, seaweeds, prawns, corals, gulls, and sea animals) because of their small size and low density, which can cause intestinal blockage and abrasion [62]. Because the two largest causes of micro plastic pollutants pollution in aquatic environments are washers and treatment plants for wastewater, it is necessary to collect micro plastic from WWTPs to lessen their accumulation and impact on aquatic ecosystems. EC is a useful technology for removing MPs from water sources because it offers excellent particle removal while keeping the benefits of other treatment methods like adsorption and electro flotation. Recent studies have demonstrated removal efficiencies of more than 90% from industrial freshwater, laundry wastewater, actual wastewater samples, and home sewage treatment plant effluent using EC technology. The results of these tests are encouraging, but further research is required to develop and improve the technology before it can be used to remove MPs from wastewater [18-63].

Micro pollutants, often known as emerging contaminants (EmCos), Every year, there are more and more emerging contaminant in the water habitats and because oftentimes more hazardous than the original substances that they convert into they are either scarcely or completely insoluble in water or they are resistant to biodegradation due to their complex aromatic ring structures, traditional wastewater treatment facilities (WWTPs) are unable to effectively remove them. According to a research on the elimination of beta-blockers, emerging contaminants that are usually present in surface water, standard treatment procedures only virtually eliminated less than 20percent of the beta-blockers sotalol and propranolol from wastewater[64]. Chemical coagulation was found to remove just 13% of the carbamazepine that was discovered in household wastewater with an influent concentration of 917 ngL⁻¹ [65-66]. Contrarily, employing EC, 90% and 70% of the drugs carbamazepine and diclofenac were eliminated from a wastewater, respectively (initial concentration 10 mg L⁻¹) [63].

Using iron, aluminum, alloy steels, and copper electrodes, electrocoagulation has been used to remove the

oil and grease from effluent discharge [41]. Three steps are used to use EC to extract oil and grease from wastewater: (i) Compression of the surface-charged oil and grease droplets and diffuse double layer of particles. (ii) The adsorption of metal cations balances the charge on the surface of granules and droplets with opposing charges. (iii) the process of binding colloidal oil and grease into flocs to create sludge [67]. How well an electrocoagulation removes oil depends on a number of factors, pH, power density, reaction speed, electrode area and spacing, electrode materials, and electrode layout are only a few examples. The effectiveness of emerging contaminants oil and grease remediation can be increased by implementing cutting-edge electrode materials, electrode designs, and reactor design optimization. To remove grease and oil, aluminum copper, and iron were employed as anodes; it was found that Cu performed the best. It was believed that removing oil and fat was what was causing the cathode to produce hydroxide ions. The emerging contaminants operating circumstances and extra contaminants found in the effluent also had an impact on performance [63-68].

There has been lot of concern about the advancement of nanotechnology during the past twenty years to be used in environmental cleanup and other applications. Concern over the release of nanoparticles into the environment has grown along with the use of Nano materials. Titanium, Aluminum, iron, and other metals are frequently used to create nanoparticles for environmental purposes [64-69]. Methods must be developed to remove dangerous nps from water and sewage. The use of electrocoagulation for the removal of nanoparticles from water and wastewater has been demonstrated to be a high-performance separation technique [70-71]. The primary methods used by electrocoagulation to remove nps from sewage and water are neutralizing and destabilizing. Nanoparticles can engage with one another after charge neutralization, diminishing them allowing them to be removed by settling [63].

Electrooxidation has been successfully utilized in recent years to remove Emerging contaminants from sewage, including products for personal care (PCPs), endocrine disrupting substances (EDCs), pigments, detergents, medications, and insecticides [72]. In a research, 20 mgL⁻¹ of Capecitabine was anodized and oxidized from sewage using a limited cost Ti/SnO₂-Sb/Ce-PbO₂ anode 93percentage degradation was observed after seven minutes of electrolysis at a current density of 10 mA cm² [14-73]. Similar to this, a novel indium (In) doped PbO₂ electrode was used to destroy aspirin 500 mgL⁻¹ over the duration of two and a half hours at a current Density of 50 mA cm² [74-75]. Additionally, a special 3Dimensional -hexagonal Co₃O₄ anode was created specifically for the anodic breakdown of wastewater containing 10 mg L⁻¹ of 4-np, and within 60 minutes of treatment, about 100% of the 4-np was mineralized [76].

6. Conclusion

Electrocoagulation is a practical process that uses less additional chemical reagents to extract pure metals and organic contaminants. In electrochemical techniques that provide control conditions for the treatment of wastewater containing heavy metals, electrodes are often used for the accumulation of ions in accordance with their charge characteristics. Electrocoagulation is used to gather byproducts and waste materials, and electron Fenton degradation of organic pollutants performed more effectively. Depending on how much energy is used and how much pollution is removed, Sono electro catalysis procedures use compression and refraction mechanisms. Electrochemical methods are always preferred over other technologies due to their increased efficiency, economic viability, ease of operation, and controlled conditions.

7. Future perspectives

The main problems with electrocoagulation include scalability, passivation of electrodes, hydrodynamic behavior, economical electricity generation, lack of full analysis, and reusing of produced sludge. Because vast majority of research studies done on electrocoagulation, in particular, have previously been done in batch operation at a laboratory level, there is little direction for scaling the technology to a commercial or municipal competency. One of the main challenges to classical EC's industrial application is the lack of hydrogen produced while doing it in an open batch reactor. In a number of chemical reactions, this specific type of hydrogen gas can serve as a catalyst or energy source. There is currently less study being done on how to get and use the generated hydrogen gas in the Electrocoagulation process. By doing this, the constraints of the current EC system will be overcome. Future research must therefore focus on the use of a broad-scale continuous mode of operation under varied electrode geometry (such as discs, helical, rods, perforated spiral plates, hollow cylindrical tubes) and arrangement (hybrid bipolar/monopolar series or parallel system) in order to overcome hydrodynamic and passivation problems when scaling up EC technology for industrial and/or municipal use. Incorporating the introduction of industrial cartridge-type EC reactors with bio-electrodes, upcoming EC systems are predicted to be more efficient and financially realistic. In order to achieve low carbon footprint, sewage treatment, and environmentally friendly EC without the need for extensive control, it is anticipated that the integration of affordable fuel cell or green and sustainable energy production system, raw sewage processing, and valuable material recovery modules with the EC in hybrid system will be an inevitable route. This is anticipated to happen at comprehensive treatments for different polluted water streams.

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