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Applications of Combined Electrocoagulation and Electrooxidation Treatment to Industrial Wastewaters

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Additional information is available at the end of the chapter

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Abstract

In recent years, it is aimed to reuse wastewater to form an economical input and to manage it sustainably without threatening human life and ecosystem. High pollutant removal yield from wastewaters was achieved using electrocoagulation method without adding any chemical coagulant or flocculants, thus reducing the amount of sludge. However, electrocoagulation (EC) is an inefficient method for the removal of stable and dissolved organic pollutants. Electrooxidation (EOx), which was evaluated as one of the most promising technologies for the treatment of wastewater containing soluble organic compounds, can directly and indirectly oxidize small organic pollutants. Although electrooxidation provides full mineralization of the organic matter, if suspended solids are present, energy consumption is increased. Since EC is a fast but incomplete process and EOx is a complete but slow process, combining the two processes offers a practical hybrid. In this chapter, mechanisms and applications of EC, EOx, and their combinations will be widely discussed.

Keywords: wastewater treatment, electrocoagulation, electrooxidation, combined, simultaneous, sequential, hybrid, integrated

1. Introduction

Water pollution seriously affects the ecosystems and availability of healthy freshwater [1]. The preservation of water resources is one of the most important issues of the twenty-first century [2]. Nowadays, sources of safe drinking water are limited and under stress [3]. The main problems encountered are population growth, rapid decline of forest areas, urbanization, climate change due to global warming, and industrialization [1]. Large amounts of raw water were consumed by industrial processes for various purposes [4]. Consequently, wastewater is

produced in large quantities [4]. Wastewaters are composed of a complex mixture of different organic and inorganic compounds, which may be toxic and difficult to degrade [4]. The most common inorganic water pollutants are heavy metals, nitrates, sulfates, phosphates, fluorides, and chlorides, which have serious hazardous effects [3]. The organic pollutants found in wastewaters may be generalized as insecticides, herbicides, fungicides, polycyclic aromatic hydrocarbons, phenols, biphenyls, halogenated aromatic hydrocarbons, formaldehyde, detergents, oils, greases, normal hydrocarbons, alcohols, aldehydes, ketones, proteins, lignin, and pharmaceuticals [3]. These pollutants remain either in dissolved, in colloidal, or in suspended form [3]. Mostly, wastewater treatment is carried out by conventional wastewater treatment processes [5]. Conventional wastewater treatment technologies could be categorized as physical processes including screening, flotation, filtration, and sedimentation [6]; chemical processes such as coagulation/flocculation, chlorination, adsorption, and ion exchange [6]; biological processes, i.e., activated sludge, aerated lagoons, and membrane bioreactors [2].

However, it is difficult to degrade the complex refractory organic pollutants in the wastewater by biological methods [7, 8]. In addition, physical–chemical methods are not always effective due to formation of additional pollution caused by the unreacted chemicals and difficulties of treatment of large amount of toxic sludge produced during conventional wastewater treatment [3–5, 9, 10]. With the strict environmental regulations on wastewater discharge, there is a need to develop efficient technologies and approaches at large scale for the treatment and management of industrial wastewater so that clean water quality can be maintained and amount increased while environmental protection and sustainability are achieved [1–5, 8, 11–13]. There has been an increasing interest in the use of electrochemical wastewater treatment technologies, such as electrodeposition [14], electrodisinfection [15], electro-Fenton [16], electrosorption [17], EOx [4] and EC [1] and their sequential [8, 18], and simultaneous [19, 20] combinations for the treatment of industrial wastewaters in recent years.

The foundations of electrochemical water treatment were laid in 1889 [11]. Electrocoagulation for drinking water was first carried out by Fred E. Stuart in 1946 [11, 21]. With the increasing interest in the second half of the twentieth century, many investigations were made on the topic [11]. Among others, EC and EOx methods are the electrochemical technologies that researchers are most interested in regarding water and wastewater treatment [2, 5, 11]. EC is based on the principle that coagulant species including hydroxide precipitates are produced in situ by electrolytic oxidation of the sacrificial anodic material, which is dissolved as ions by electric current applied through metal electrodes such as aluminum and iron [1, 22]. Thus, the EC method is more advantageous than the coagulation/flocculation method in which metal salts and polyelectrolytes are used as coagulants/flocculants in terms of sludge formation [23, 24]. EC aims to remove particles from the wastewater by destabilizing/neutralizing the repulsive forces that keep the particles suspended in the water [2]. When the repulsive forces are neutralized, suspended particles can be separated more easily from water by forming larger particles that can precipitate [2]. EC also provides the removal of pollutants by simultaneous cathodic reactions, either by deposition on the cathode or by flotation based on the formation of hydrogen gas at the cathode [1]. In recent years, EC was reported as an easy-to-operate, efficient, and economical method. Strengths of EC method can be summarized as follows; it requires simple equipment and operating conditions and does not require additional chemicals; treated water is

colorless, odorless, and clear; the amount of the sludge formation is low which can be easily stabilized and dehydrated; compared with chemical coagulation, the effluent contains less total dissolved solids; and the gas bubbles produced in the cathode allow the pollutants to be separated easily by floating them to the surface. However, weaknesses of EC method can be listed as follows: sacrificial electrodes need to be replaced regularly, formation of an impermeable film layer on the cathode may reduce the efficiency of the process and it is inefficient for the removal of persistent dissolved organic pollutants.

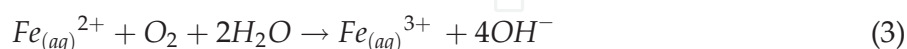
With regard to the treatment of effluents polluted with organic compounds, biological oxidation is the most economical process, but the presence of toxic or biorefractive molecules may prevent this approach [25]. Despite chemical oxidation using chlorine, ozone or hydrogen peroxide is currently used for the oxidation of biorefractive contaminants to harmless or biodegradable products; in some reactions, the intermediate products remain in the solution and may cause similar or higher toxicity than the initial compounds [25]. EOx can completely degrade many harmful organic pollutants before they reach the receiving environment [4]. EOx is based on in situ production of oxidants either directly at the surface of the electrodes or indirectly from the chemical compounds in the treated water during treatment [4]. EOx may occur either through direct oxidation with hydroxyl radicals produced on the anode surface or indirectly through oxidants such as chlorine, hypochlorous acid, and hypochlorite or hydrogen peroxide/ozone formed at electrodes [13]. The hydroxyl radicals can oxidize substantially all of the organic compounds with an oxidation rate 109 times higher than that of ozone [26]. The oxidation power of chlorine and other anode-formed oxidants remains low compared to the hydroxyl radicals and as a result it does not allow many pollutants to be effectively oxidized to carbon dioxide and water [13]. Electrode material selection is very important because it affects process selectivity and efficiency [12]. Electrode material must have the properties such as resistance to erosion, corrosion and formation of passivation layers, high electrical conductivity, selectivity and catalytic activity, low cost, and durability. Noble metal electrodes; metal alloys electrodes; mixed metal oxide electrodes which are also referred as dimensionally stable anodes (DSAs) such as Ti/Ta₂O₅-IrO₂, Ti/SnO₂-IrO₂, Ti/RuO₂-IrO₂, Ti/Sb-SnO₂, Ti/SnO₂-Sb₂O₅-RuO₂, and Ti/TiO₂-IrO₂; carbon and graphite electrodes; and boron-doped diamond (BDD) electrodes are some examples of the electrode materials used in recent wastewater treatment studies [27]. Strengths of EOx method can be summarized as follows: it requires simple equipment and operating conditions, totally mineralizes persistent organic pollutants, has low electrode maintenance cost, and forms disinfecting compounds. However, EOx method has some weaknesses such as: it is inefficient for the removal of suspended solids, and formation of an impermeable film layer on the cathode may reduce the efficiency of the process.

Since EC is a fast but incomplete process and EOx is a complete but slow process, coupling the two processes offers a practical hybrid [26]. EC has the ability to remove pollutants quickly but not completely. EOx is able to remove pollutants slowly but consistently. Sequential and simultaneous operations are combining the best abilities of EC and EOx processes with fast and complete pollutant removal [26]. This chapter focuses on effects of operating parameters on EC and EOx, pollutant removal mechanisms, and recent applications of these methods and their sequential and simultaneous combinations.

2. Electrocoagulation mechanism and operation

2.1. Mechanism

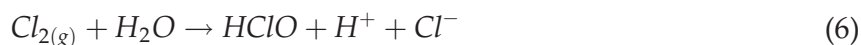
In the EC process, coagulant species are produced in situ using the electrical dissolution of sacrificial anode, usually made of iron or aluminum by electric current applied between metal electrodes [1]. At the anode, metal is oxidized into cations as shown in Eqs. (1)–(3).



In the case of high anode potential, following reactions may occur as shown in Eqs. (4) and (5).



Chlorine formation may lead to the formation of hypochlorous acid, an oxidizing agent which may contribute to the oxidation of dissolved organic compounds as shown in Eq. (6) [1].



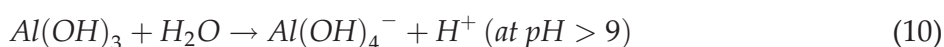
At the cathode, hydrogen gas and hydroxyl anions are formed by the reduction of water as shown in Eq.(7).



The amount of dissolved metal at the anode can be calculated using Faraday's law as shown in Eq. (8).

$$m = \frac{ItM}{zF} \quad (8)$$

where m is the mass of metal in g, t is the electrolysis time in s, I is the electric current in A, M is the atomic weight of the electrode material in g/mole, z is the number of electrons transferred, and F is Faraday's constant (96486 C/mole). The most common phenomenon for metal cations released from the anode is the formation of non-soluble and easily precipitable metal hydroxide sweep flocs which have large surface areas beneficial for a rapid adsorption of soluble organic compounds and trapping of colloidal particles as shown in Eqs. (9)–(13) [1].





Removal mechanisms of various pollutants involve physical removal of dissolved pollutants during precipitation, adsorption, and complexation [1]; electrooxidation [28] or electroreduction [29] of the electro-active ion or molecules on the anode or the cathode; the direct adsorption of pollutants on the electrodes [30]; the compression of the double layer of a colloidal particle [31]; charge neutralization; and colloid entrapment [1].

2.2. Operating parameters

The parameters affecting the effectiveness of the EC process are operating conditions such as the current density, operating time, pH, conductivity, and electrode properties [22]. The bubble density affects system hydrodynamics, which determine the mass transfer between pollutants, coagulant, and gas microbubbles, and determines the collision rate of the coagulated particles resulting in flock formation [1].

The current density determines the coagulant dosage at the anode and the formation of hydrogen gas at the cathode. Unnecessarily high current values may negatively affect the EC efficiency as coagulant overdosage can reverse the charge of the colloids and redistribute them, reducing coagulation efficiency and also reducing electrode lifetime [1].

pH is an important factor affecting EC performance, particularly the coagulation mechanism, since it governs the hydrolyzed metal species formed in electrolyte media [32]. Adsorption and coagulation depend on pH in particular. The superficial charge of Al or Fe precipitates can be explained by the adsorption of charged soluble monomeric species on their own hydroxide precipitates [1]. For Al and Fe electrodes, the amount of insoluble aluminum hydroxide increases sharply with increasing pH from 4.5 to 7 [1]. For a pH above 10, amorphous metal hydroxide is absent. For acidic influent, effluent pH after EC treatment would increase but can decrease for alkaline influent, which is due to the buffering effect of EC [11].

Lower amounts of energy are consumed with decreasing the gap between electrodes. As the distance between electrodes becomes lower, the amount of generated gas bubbles increases, thus leading to a high mass transfer as well as to a high reaction rate between the coagulants and pollutants [1].

Applied potential difference of galvanostatic EC operation depends strongly on conductivity and ionic strength of the wastewater. Applied potential difference decreases with increasing electrolytic conductivity due to the decrease of ohmic resistance of wastewater [1]. Consequently, the energy consumption per unit volume of treated wastewater is reduced as shown in Eq. (14).

$$SEEC (kWh/m^3) = \frac{IVt}{V_E} \quad (14)$$

where SEEC is the specific electrical energy consumption, I is the electric current in A, V is the applied potential difference in V, t is the electrolysis time in h, and V_E is the volume of treated wastewater in L.

2.3. Applications of electrocoagulation

In this section, recent studies on the application of EC method in the treatment of different wastewaters and pollutants such as chemical oxygen demand (COD), total organic carbon (TOC), total phosphate (TP), phenol, oil and grease (O&G), biochemical oxygen demand (BOD₅), and total suspended solids (TSS) are presented. Ranges and optimum values of operating parameters, pollutant removal efficiencies, energy consumption, and operating cost values of previously published work are given in **Table 1**. It has been reported that EC

Ref.	Wastewater	Electrode material	Parameters	Research ranges for parameters	Optimum conditions	Results at optimum conditions
[33]	Olive mill (real)	Al	Electrolysis time (min)	3–20	15	Color removal: 91%
			Current density (A/m ²)	10–4000	250	COD removal: 83%
			NaCl concentration (g/L)	0.5–3	2	Phenol removal: 87%
			Initial pH	2–10	4.2	SEEC: 2.63 kWh/kg COD _r Operating cost: 0.27 €/kg COD _r
[34]	Textile (synthetic)	Al	Current density (A/m ²)	100–400	300	Turbidity removal: 90%
			Inlet flow rate (L/h)	15–60	15	Color removal: 97%
			Initial concentration (mg/L)	50–300	< 300	SEEC: 19.5 kWh/kg dye removed
			Initial pH	2.3–8.8	7.74	
			Residence time (min)	5–55	35	
[35]	Dairy (real)	Al	Electrolysis time (min)	0–60	30	COD removal: 74.56%
			Initial pH	2–12	7	BOD ₅ removal: 96.28%
			Current density (mA/cm ²)	2.5–35	14	Turbidity removal: 98.91%
			NaCl concentration (g/L)	0–2	1	SEEC: 3.36 kWh/m ³
[22]	Pulp and paper (real)	Al or Fe	Electrode material	Al-Fe	Al	COD removal: 65.33%
			Electrical conductivity (mS/cm)	2.3–4.2	2.72	Color removal: 100%
			pH	3–12	5.82	Turbidity removal: 98.61%
			Temperature (°C)	10–50	22.62	TSS removal: 97.06%
			Electrolysis time (min)	5–45	10.83	SEEC: 8.82
			Current intensity (A)	0.5–1.8	1.22	kWh/kg COD

Ref.	Wastewater	Electrode material	Parameters	Research ranges for parameters	Optimum conditions	Results at optimum conditions
[36]	Car wash (real)	Al or Fe	Electrode material pH Current density (mA/cm ²) Operating time (min)	Al-Fe 2–10 0.1–5 5–50	Fe 8 3 30	COD removal: 88% O&G removal: 90% Cl [−] removal: 50% Operating cost: 0.6 \$/m ³ Sludge: 2.1 kg/ m ³
[37]	Industrial estate (real)	Fe	Current density (mA/cm ²) Na ₂ SO ₄ concentration (mM) Initial pH	10–50 1–7 3.12–8.83	30 3 6	COD removal: 62.5% SEEC: 42.44 kWh/m ³ Energy cost: 1.91 €/m ³ Sludge: 1.91 g/g COD

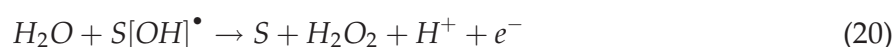
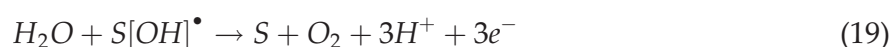
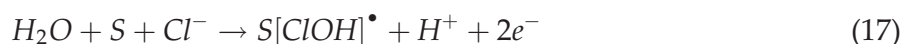
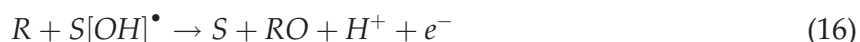
Table 1. EC treatment results of various wastewaters for selected examples in the literature.

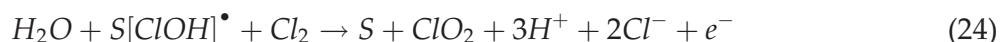
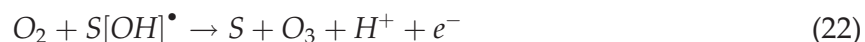
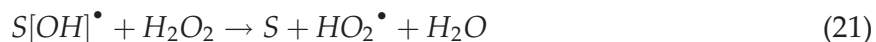
treatment is an effective method in removing organic matter, turbidity, color, phenol, phosphate, heavy metals, pharmaceuticals, O&G from wastewater.

3. Electrooxidation mechanism and operation

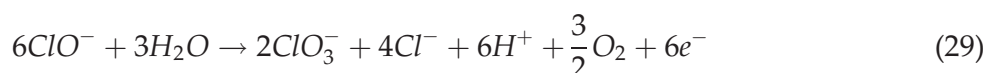
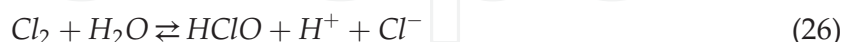
3.1. Mechanism

EOx may occur either by direct oxidation of pollutants using hydroxyl or hydroperoxyl radicals produced on anode surface or by an indirect process where oxidants like chlorine, hypochlorous acid, and hypochlorite or hydrogen peroxide/ozone are formed at electrodes. Direct anodic oxidation of pollutants and formation of indirect oxidizing agents occur according to the reactions given in Eqs. (15)–(24) [26, 38, 39].





Indirect oxidation of pollutants occurs according to the reactions given in Eqs. (25)–(29) [26].



Chlorate is usually an unwanted product in the effluent, and its formation could also prevent the use of EOx in various applications [25]. At the cathode, hydrogen gas and chloride anions are formed as shown in Eqs. (30)–(32).



Here S symbolizes the active sites of the anode surface, and R represents the organic matter. To evaluate the selectivity of an anode material, competition between the oxidation of organic materials and the oxygen formation (the side reaction) at the anode (Eq. (4)) must be taken into account [12]. Oxygen formation is typically considered to be an undesirable side reaction in the electrochemical wastewater treatment because it affects the efficiency of the process and significantly increases the operating costs [25].

Removal mechanisms of various pollutants involve diffusion of pollutants from the bulk solution to the anode surface and direct oxidation at the anode surface either partially or completely [12] and generation of a strong oxidizing agent (i.e., chlorine) at the anode surface and indirect oxidation of pollutants in the bulk solution.

3.2. Operating parameters

Among the variables that are usually studied in EOx treatment, the current density is one of the most frequently referenced terms since it affects the rate of reactions [12]. It should be noted that an increase in current density will not necessarily result in an increase in oxidation efficiency or oxidation rate [12]. The use of higher current densities usually leads to higher operating costs due to the increase in energy consumption.

It should be noted that although there is no agreement on the effect of the conductivity on the overall oxidation efficiency, the cell voltage is reduced for a given current density as the conductivity of the electrolyte increases [12]. For this reason, the electrochemical oxidation process is more cost-effective if the treated wastewater already has a high conductivity [12].

When reactions are carried out in chloride-containing media, the pH value may affect the rate of oxidation because it determines the primary active chloro species present in the effluent [12]. During indirect oxidation, chlorine evolution occurs at the anode (Eq. (25)). At pH values lower than 3.3, the primary active chloro species is Cl_2 , while at higher pH values, it forms HClO at $\text{pH} < 7.5$ (Eq. (26)) and ClO^- at $\text{pH} > 7.5$ (Eq. (27)). Operation at strongly acidic conditions is favorable since chlorine is the strongest oxidant followed by HClO and ClO^- , respectively [12]. Depending on the electrolytic cell design, desorption of chlorine from reaction medium may prevent its action as an oxidizing agent. Thus, neutral or mildly alkali medium may be preferred since HClO and ClO^- species remain almost unaffected by desorption of gases and they can act as oxidizing reagents in the whole volume of wastewater [40].

3.3. Applications of electrooxidation

This section briefly describes the treatment of different wastewater types by EOx method in the last few years. **Table 2** shows a general insight on minimum, maximum, and optimum values of operating parameters, pollutant reduction, energy consumption, and operating cost of EOx

Ref.	Wastewater	Electrode material	Parameters	Research ranges for parameters	Optimum conditions	Results at optimum conditions
[41]	Pulp and paper industry (real)	Anode: Catalytic oxide coated titanium Cathode: Stainless steel	Current density (A/dm^2) NaCl concentration (g/L)	2.5–5 1–5	2.5 3	COD removal: 67.99% SEEC: 37.67 kWh/kg COD
[42]	Textile (real)	Graphite	Initial pH Current density (A/m^2) NaCl concentration (g/L) Electrolysis time (min)	4–10 27.78–138.89 0–2 10–130	4 27.78 2 110	COD removal: 90.78% Color removal: 96.27% SEEC: 23.58 kWh/kg COD
[43]	Olive mill (real)	Anode: Ti/Pt mesh Cathode: Ti mesh	Electrolysis time (h) Mixing rate (rpm) Dilution ratio pH Type of support electrolyte Concentration of support electrolyte (mM) Current density (mA/cm^2) Temperature ($^{\circ}\text{C}$)	1–24 0–600 1/5–5/5 2–8 Na_2SO_4 , KCl, NaCl 0.25–1.25 2.5–15 10–50	5 0 1/5 4.5–4.7 NaCl 0.25 7.69 10	COD removal: 100% TOC removal: 78% Phenol removal: 100% SEEC: 451.25 kWh/m^3 Energy cost: 6.02 $\$/\text{kg}$ COD

Ref.	Wastewater	Electrode material	Parameters	Research ranges for parameters	Optimum conditions	Results at optimum conditions
[44]	Pharmaceutical (synthetic)	Anode: BDD Cathode: Stainless steel	Current density (mA/cm ²)	1.56–6.25	6.25	TOC removal: 80% SEEC: 2.34 kWh/g TOC
[45]	Industrial park sewage (real)	Anode: Mesh-structure plate Cathode: Mesh-structure Ti plate	Anode material Current density (mA/cm ²)	Ti/PbO ₂ , Ti/RuO ₂ , Ti/RuO ₂ -IrO ₂ 2–15	Ti/PbO ₂ 5	COD: 60 mg/L Color: 20 CU SEEC: 4.12 kWh/ton Operating cost: 0.57 \$/ton

Table 2. EOx treatment results of various wastewaters for selected examples in the literature.

treatment. By evaluating the previously published studies, it has been concluded that EOx is a remarkable treatment method in terms of organic matter, turbidity, color, phenol, total Kjeldahl nitrogen (TKN), and O&G removal efficiencies.

4. Combined electrocoagulation and electrooxidation mechanism and applications

4.1. Mechanism

As stated in Section 1, EC is a fast but incomplete process, while EOx is a complete but slow process; coupling the two processes proposes a functional hybrid. COD removal mechanism of a combined EC and EOx process can be summarized as follows: production of metal ions; hydrolysis of metal ions to generate metal hydroxides and/or polyhydroxides in appropriate pH; generation of bubbles of oxygen and hydrogen gases at the anode and the cathode, respectively, which provides the flotation of coagulated pollutants; destabilization of colloidal pollutants and trapping of destabilized colloidal particles to form flocks; removal of pollutants by precipitation [46]; formation of adsorbed hydroxyl radicals on anode surface [39]; degradation of organic pollutants by direct oxidation of adsorbed hydroxyl radicals; generation of indirect oxidizing agents such as chlorine, hypochlorite, and hydrogen peroxide near the anode; and electrochemical combustion of organic pollutants by indirect oxidizing agents [26].

4.2. Applications of combined electrocoagulation and electrooxidation

In the recent years, application of combined treatment has been successfully achieved in the removal of different kinds of pollutants either by sequential EOx treatment of the electrocoagulated

Ref.	Wastewater	Electrode material	Parameters	Research ranges for parameters	Optimum conditions	Results at optimum conditions
[48]	Dairy (synthetic)	Anode: Al Cathode: Ti/Pt	Current density (A/m ²) Electrolysis time (min) Initial pH NaCl concentration (g/L)	0–75 0–5 4–11 0–2	50 2 6.6 1.5	COD removal: 54.16% TP removal: 42.9% Turbidity removal: 37%
[49]	Anaerobic reactor effluent (real)	Anode: MP RuO ₂ /Ti Cathode: MP stainless steel Sacrificial electrode: BP Al	pH Current intensity (A) Detention time (min)	5–10 1–3 10–60	7 3 60	Ammonia removal: 98% TP removal: 98% COD removal: 72%
[50]	Pharmaceutical (synthetic)	Anode: MP stainless steel Cathode: MP stainless steel	pH	4.5–10.9	10.9	Diclofenac sodium removal: 84% COD removal: 80%
[20]	Olive mill (real)	Anode: RuO ₂ /Ti Cathode: Stainless steel Sacrificial electrodes: BP Al	pH Current density (mA/cm ²) NaCl concentration (g/L) H ₂ O ₂ concentration (mg/L) Detention time (min)	3–9 5–40 0.5–3 0–2000 5–30	4 40 1 1000 30	COD removal: 96% BOD ₅ removal: 93.6% Phenol removal: 94.4% Color removal: 91.4% Turbidity removal: 88.7% TSS removal: 97% O&G removal: 97.1% BOD ₅ /COD: 0.46
[19]	Textile (real)	Anode: MP Ti/IrO ₂ Cathode: MP Ti Sacrificial electrode: BP Al or Fe	Sacrificial electrode material Electrolysis time (min) Current intensity (A) pH Interelectrode distance (cm) Stirring speed (rpm)	Al-Fe 20–90 0.2–1 5–10 0.5–1.5 250–750	Al 90 0.6 6 1 500	COD removal: 93.5% TSS removal: 97% Color removal: 97.5% BOD ₅ removal: 90% Turbidity removal: 96% Phenol removal: 99% TP removal: 97% Operating cost: 1.69 US \$/m ³

Ref.	Wastewater	Electrode material	Parameters	Research ranges for parameters	Optimum conditions	Results at optimum conditions
[26]	Pulp and paper mill (real)	Anode: MP graphite Cathode: MP graphite Sacrificial electrode: BP Al or Fe	Electrode material	Al-Fe	Al	COD removal: 87%
			Initial pH	3–9	6	Color removal: 100%
			Electrical conductivity (mS/cm)	3–7	5	Turbidity removal: 100%
			Temperature (°C)	10–30	20	SEEC: 31.6 kWh/kg COD
			Current intensity (A)	0.5–1.5	1	Operating cost: 1.33 \$/m ³

Table 3. Simultaneous EC-EOx treatment results of various wastewaters for selected examples in the literature.

effluent or simultaneous EC and EOx treatment with an appropriate electrode configuration. The aim of sequential EC-EOx is to propose a new approach that combines the synergistic effects of the two methods [47]. Simultaneous EC-EOx offers a hybrid system integrating monopolar (MP) EOx and bipolar (BP) EC in a single reactor that also provides all the advantages of sequential EC-EOx [19]. Recent studies on combined EC-EOx treatment of different kinds of wastewater are presented in **Tables 3** and **4**.

Ref.	Wastewater	Electrode material	Parameters	Optimum conditions	Results at optimum conditions
[18]	Textile (synthetic)	EC: Al	Current density (mA/cm ²)	30	COD removal: ~94%
			Treatment time (min)	5	SEEC: 0.02 kWh/g
		EOx: Graphite	Current density (mA/cm ²)	0.91	
			Treatment time (min)	425	
[8]	Industrial park (real)	EC: Fe	pH	8	Color removal: 100%
			Current density (A/m ²)	800	Turbidity removal: 100%
			Treatment time (min)	30	COD removal: 100%
		EOx: Anode: BDD Cathode: Fe	pH	8	BOD ₅ removal: 100%
			Current density (A/m ²)	800	
			Treatment time (min)	150	
[51]	Car wash (real)	EC: Anode: Fe Cathode: Stainless steel	Electrolysis time (min)	6	COD removal: > 97%
			Current density (mA/cm ²)	2	SEEC: 12 kWh/m ³
		EOx: Anode: BDD Cathode: Stainless steel	Electrolysis time (min)	90	
			Current density (mA/cm ²)	10	
[47]			Current density (A/dm ²)	0.6	

Ref.	Wastewater	Electrode material	Parameters	Optimum conditions	Results at optimum conditions
[52]	Dairy (real)	EC: Al	Operating time (min)	6	Turbidity removal: 100%
					Color removal: 90.4%
	Cardboard (real)	EOx: platinized titanium	Current density (A/dm ²)	1.4	COD removal: 66.4%
			Operating time (min)	15	
		EC: Al	Current density (mA/cm ²)	7.5	Turbidity removal: 98.7%
			Operating time (min)	60	TOC removal: 86.4%
			Initial pH	7	COD removal: 85.3%
		EOx: Anode: BDD Cathode: Stainless steel	Current density (mA/cm ²)	100	
			Operating time (min)	180	
			Initial pH	7.2	
			Na ₂ SO ₄ concentration (g/L)	5	
[53]	Soft drink (real)	EC: Copper	Current density (mA/cm ²)	51	COD removal: 85%
			Initial pH	8	TOC removal: 75%
			Time (min)	20	TP removal: 89%
		EOx: Anode: Niobium substrate BDD Cathode: Copper	Current density (A/m ²)	30	Total nitrogen: 84%
			pH	6	Color removal: 100%
			Time (h)	6	
[54]	Soluble coffee industrial plant (real)	EC: Anode: Al Cathode: Graphite	Current density (A/m ²)	149.2	Color removal: 100%
			Initial pH	7.98	COD removal: 89%
			Treatment time (min)	62	TOC removal: 72%
		EOx: Anode: Graphite Cathode: Al	Current density (A/m ²)	500	SEEC: 45.28 kWh/m ³
			Treatment time (min)	53	BOD ₅ /COD: 0.6

Table 4. Sequential EC-EOx treatment results of various wastewaters for selected examples in the literature.

5. Conclusion

Due to the increasing need for freshwater resources and the large number of pollutants produced by the industries, it becomes more and more important to treat and reuse wastewater. For this purpose, effective, economical, and easy-to-operate wastewater treatment technologies need to be developed. Because of the fact that electrochemical treatment methods have various

advantages, they are still investigated extensively. Besides being simple and effective, they are able to remove almost all kinds of pollutants at the same time. They are also eco-friendly and clean due to in situ generation of metal hydroxides and hydroxyl radicals. Many EC and EOx studies have been published on the treatment of industrial wastewaters such as olive mill, textile, dairy, pulp and paper, tannery, pharmaceutical, bilge, refinery, slaughterhouse, food processing, potato chips manufacturing, and leather. It is reported that EC and EOx methods have been successfully applied for removing COD, BOD, oil, phenol, lignin, phosphate, arsenic, color, turbidity, chromium, sulfate, total coliforms, boron, nickel, copper, and pharmaceuticals from wastewaters. Recent studies were briefly presented in this chapter, and it is observed that a minimum of 54.16% COD, 90.4% color, 90% BOD, 37% turbidity, 94.4% phenol, 42.9% phosphate, 72% TOC, and 97% TSS removal efficiencies and a maximum of 45.28 kWh/m³ SEEC were achieved by applying combined treatment. Since EC is a fast and efficient method for wastewaters containing suspended solids but also an inefficient method for the removal of persistent dissolved organic pollutants and EOx is able to mineralize persistent organic pollutants completely but also a slow and energy-consuming method for the removal of suspended solids, combining these two processes offers a practical hybrid by taking advantage of the synergistic effects. According to the results, it can be concluded that combined EC-EOx process is an efficient alternative for industrial wastewater treatment in terms of pollutant removal and more research on applications to the industrial wastewaters are required.

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