



Review Removal of Organic Micro-Pollutants from Wastewater in Electrochemical Processes—Review

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Abstract: The aim of the paper is to present information from the literature concerning the course of electrochemical wastewater treatment processes in regard to organic micro-pollutant removal. Most often, in order to remove xenobiotics that are difficult to degrade biochemically, advanced oxidation processes and photochemical processes with or without catalysts are used. The efficiency of these processes can be supported by the flow of electric current through the solution being purified in a special system. This paper presents the theoretical foundations of processes such as electrocoagulation, electroflotation, and advanced chemical and photochemical oxidation supported by electric power. Among the processes where the Fenton's reagent is the oxidant, the electro-Fenton and photo-electro-Fenton processes are also described. This information is supplemented with examples of the use of these processes for removal/degradation of selected organic compounds such as pesticides, dyes, pharmaceuticals, cosmetic ingredients, and other organic xenobiotics from wastewater.

Keywords: xenobiotics; electrocoagulation; electroflotation; electro-Fenton process; wastewater



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1. Introduction

The amount of organic micro-pollutants introduced into the aquatic environment from anthropogenic sources is much greater than that resulting from natural processes. This applies mainly to industrial activities in which coal and metal ores are processed, crude oil is refined, and chemicals, pharmaceuticals, textiles, or cosmetics are produced [1,2]. The concentration of organic micro-pollutants in the industrial wastewater depends on the type of industrial activity, type of raw materials, production technology, as well as the applied methods of wastewater treatment. Many processes are used to pre-treat the contaminated outflows before they are put into sewage systems or into an aquatic environment. However, even highly pre-treated wastewater contains organic compounds that are difficult to degrade and is characterised by high chemical oxygen demand (COD) values and relatively low biochemical oxygen demand (BOD) values. The low values of the ratio between these indicators shows a low susceptibility to biodegradation [3]. Persistent organic micropollutants (POPs) include polycyclic aromatic hydrocarbons (PAHs), halogenated organic compounds (AOX), di-2-ethylhexyl phthalates (DEHP), nonylphenols (NPE) and nonylphenol ethoxylates (NPEO), as well as selected surfactants such as linear alkylbenzene sulfonate (LAS), pharmaceuticals (PhACs), cosmetics (PPCPs-pharmaceuticals and personal care products), flame retardants (FRs), and many more [4–6]. POPs accumulate in the tissues of living organisms and display carcinogenic, mutagenic, and other undesirable health effects, such as endocrine disorders [7,8]. The removal rate of organic compounds from wastewater by biological methods used in conventional treatment plants is insufficient; thus, the treatment requires additional processes to ensure effective removal of organic compounds [9–13]. These include those that provide only the separation of pollutants but do not solve the problem of their occurrence, and those that ensure the degradation of compounds that are difficult to decompose [14]. Separation methods include coagulation, adsorption, flotation, and membrane separation. Among the membrane methods, pressure methods such as ultrafiltration, nanofiltration, and reverse osmosis are the most widely used in wastewater technology [15]. Methods ensuring degradation of persistent organic compounds include advanced oxidation processes (AOPs) [16–19]. These include chemical and catalytic processes, supported by an additional source of energy, as well as ones that do not use the latter. In these processes, as a result of subsequent chemical reactions, free radicals are generated, mainly hydroxyl radicals (HO[•]) with a high oxidizing potential, facilitating the destruction of most organic compounds. However, a disadvantage of these processes consists of the formation of intermediate products with different activity toward test organisms. Therefore, new solutions are currently being sought and research is being undertaken to modify known and used processes to ensure complete oxidation of organic compounds and reduce the toxicity of post-reaction solutions. In this respect, the proposed solutions concern, among others, supporting classic processes with solar, ultraviolet, or gamma radiation, as well as electricity. In relation to methods supported by electricity, such processes as electrocoagulation, electroflotation, and chemical and photochemical AOP (electro-Fenton, sono-electro-Fenton, photo-electro-Fenton) can be included [20–26].

The aim of the study was to present the mechanism of organic pollutant degradation during oxidation processes supported by electricity and to assess the possibility of using them to remove selected organic micro-pollutants from aqueous solutions and wastewater.

2. Electrocoagulation

Electrocoagulation (EC) is a wastewater treatment method based on chemical reactions between a coagulant formed under the influence of an electric current released from a given electrode. Electrocoagulation is a technology that properly combines electrochemistry, coagulation, and flotation (or sedimentation) [23,27]. This technology consists of four main stages: electrolytic reaction on the surface of the electrode, formation of metal hydroxides (coagulants), adsorption of soluble (colloidal) particles on coagulants, and removal by sedimentation or flotation [28]. Reactions between the coagulant and pollutants lead to precipitation of sediments which are removed by sedimentation or flotation (Figure 1).



Figure 1. Scheme of the electrocoagulation process.

Flotation is caused by micro bubbles of gas released as a result of the redox reaction that takes place during the flow of electricity through the solution. The precipitates are collected in the form of scum on the surface and create sediments after degassing. The materials most often used for constructing electrodes utilized in the electrocoagulation process are aluminium and iron. As a result of the flow of electric current through the solution (sewage), AI^{3+} aluminium cations and Fe^{2+} iron cations are released—Reactions (1) and (2). Aluminium ions form hydroxide (Reaction (3)), while hydrogen is released on the cathode (Reaction (4)) [23,29].

Anode:

$$Fe^{0}_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^{-}$$
 (1)

$$Al_{(s)} \rightarrow Al_{(aq)}^{3+} + 3e^{-}$$
⁽²⁾

$$Al_{(aq)}^{3+} + 3H_2O \rightarrow Al(OH)_{3(s)} + 3H^+$$
 (3)

Cathode:

$$H_2O_{(1)} + 3e^- \rightarrow 1.5H^+_{(g)} + 3OH^-_{(aq)}$$
 (4)

During electrocoagulation, iron hydroxides are formed as a result of Reactions (1) and (5)–(7).

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$$
 (5)

$$\mathrm{Fe}^{2+} - \mathrm{e}^{-} \to \mathrm{Fe}^{3+} \tag{6}$$

$$Fe^{2+} + OH^{-} - e^{-} \rightarrow Fe(OH)_{3}$$
(7)

During the electrocoagulation process, depending on the reaction of the environment, transitional ionic forms of iron $(Fe(OH)_2^+, Fe(OH)_4^-, Fe_2(OH)_2^{4+}, Fe(H_2O)_4(OH)_2^+)$ may be created, which then form iron (III) hydroxide [30]. The consumption of an aluminium electrode (C) in reference to the unit of treated wastewater (kg Al/m³) is calculated using the Faraday law according to Equation (8):

$$C = \frac{I \cdot t \cdot M \cdot 10^{-3}}{z \cdot F \cdot V}$$
(8)

where

- I the current intensity (A);
- t the retention time (s);
- V the volume of the treated wastewater (m^3) ;
- F the Faraday's constant (96.487 C/mol);
- M the mass of aluminium (26.98 g/mol) and mass of iron (55.847 g/mol);
- z the number of electron transfer (e.g., $z_{A1} = z_{Fe} = 3$).

Specific energy consumption, E, is calculated according to Equation (9) [29]:

$$\mathbf{E} = \frac{\mathbf{U} \cdot \mathbf{I} \cdot \mathbf{t}}{(\mathbf{C} \mathbf{O} \mathbf{D}_0 - \mathbf{C} \mathbf{O} \mathbf{D}_t) \cdot \mathbf{V}} \tag{9}$$

where

- E the specific energy consumption (kWh/kg of COD removed);
- U the applied voltage (V);
- I the current intensity (A);

t the retention time (h);

 COD_0 the chemical oxygen demand before treatment (g/L);

 COD_t the chemical oxygen demand after treatment (g/L);

V the volume of the treated wastewater (L).

The system consists of a reactor equipped with a stirrer (or allowing the solution to be mixed), a set of electrodes, a source of electricity, and a system for dosing and discharging the polluted solution. The possibility of removing the post-coagulation sediment, and in some cases changing the electrode connection to the power source, is also taken into account. The basic parameters that affect the process are electrode material and distance between them, electric current intensity and density, pH value of the solution, and initial concentration of pollutants. The literature data indicate that the electrocoagulation process was used to remove pollutants occurring in wastewater such as: tannery, galvanic, and dyeing wastewater, waste from metal processing plants, waste containing oil emulsions, textile wastewater, wastewater from oil presses, and laundry wastewater [17,27,28,31]. This method has been shown to be useful for removing arsenic, polyvinyl alcohol, 4-nitrophenol, dyes, fluorine, nitrates, petroleum derivative hydrocarbons, chromium, phosphates, as well as phenol and phenolic compounds [22,26,32–39].

Example studies concerning using the EC method to remove dyes from solutions, and the results of these studies demonstrated that the efficiency of removal of these xenobiotics can reach 97%. The decrease in the value of COD was at the level of 92%. Example studies examining the application of the electrocoagulation process concerned removal of pharmaceutical residues from actual sewage [33] also demonstrated that this method can be used for removal of fluorides from contaminated water. The research was carried out in a labyrinth reactor, where properly set partitions ensured flow between them, which extended the reaction time. The reactor included six alloy electrodes and was powered by a 30 V direct current. The initial fluoride concentration was at the level of 20 mg/L. Three process parameters were optimized: current density (1.5, 2.5, and 3.5 mA/cm²), pH (4, 7, and 10), and the distance between electrodes (5, 10, and 15 mm). After 30 min of the process, the fluoride concentration did not exceed the limit value for drinking water determined by the WHO (<1.5 mg/L) at pH 7, current density of 2.5 mA/cm², and the distance between electrodes equal to 5 mm. The purification cost was estimated at 0.346 USD/m^3 with energy consumption at the level of 5.03 kWh/m³. Smoczyński et al. conducted research concerning electrocoagulation of model wastewater using electrodes made of iron [30]. The research was carried out at a constant current intensity (0.3 A) analysing changes in pH, suspensions and turbidity, COD, and total phosphorus in the purified solutions. At fixed time intervals (256 s), the direction of current flow on the electrodes was changed in the system. Changing the role of the contaminated cathode into a soluble anode allowed it to be purified as a result of anodic dissolution. The efficiency of organic compound removal expressed by the COD index was 43%, and the removal of turbidity was equal to 62%. There was a decrease in the concentration of suspensions by 81% and phosphorus by 51–58%. It was determined that the most favourable conditions for phosphorus removal occur when the molar relationship Fe:P is greater than 1:3, which at the same time prevents the formation of post-coagulation sediments: Fe₃(PO₄)₂, FePO₄, (FeOH)₃(PO₄)₂, and (FeOH)₃PO₄.

In the EC process, the amount of sediment is smaller than in the classical coagulation process, the system is not complicated, does not require any large objects to be provided, and can also be mobile. There is no thickener required as there would be in chemical classic coagulation, which reduces the operation cost. Other advantages include: no risk of residual chemicals in the effluent (toxins and odours), metals can be recovered from the solution. In most cases, this process does not require much energy to operate the coagulation equipment. This low level can easily be produced using green energy sources.

3. Electroflotation

Electroflotation (EF) is the separation of suspended particles from water by means of gas bubbles generated at electrodes during electrolysis of water [40]. The electroflotation process involves the following stages: electrode oxidation (coagulant ions are formed), water electrolysis, and generation of bubbles of gas. At a stainless anode and cathode, Reactions (10)–(12) take place:

Anode:

$$Fe \to Fe^{2+} + 2e^{-} \tag{10}$$

$$H_2O \rightarrow 2H^+ + 0.5O_2 + 2e^-$$
 (11)

Cathode:

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2$$
 (12)

When Reactions (11) and (12) are dominant, bubbles of oxygen and hydrogen at electrodes are observed. On the cathode, hydroxide ions are formed (13) and pH value is increased:

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$$
 (13)

Because of the pH value increase in the solution, different ions are formed—Reactions (14)–(16) [40].

$$Fe^{3+} + H_2O \to Fe(OH)^{2+} + H^+$$
 (14)

$$Fe^{3+} + 2H_2O \rightarrow Fe(OH)_2^+ + 2H^+$$
 (15)

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$$
(16)

The electroflotation process is used for treatment of synthetic wastewater. The efficiency of this process in removal of selected metals (Pb, Zn) is, on average, 97% [40]. Other research [41] concerns the results of removal of doxycycline (antibiotic) from an aqueous solution. The effectiveness of the removal of doxycycline is in the range of 90–96% [41].

Electroflotation makes possible effective recovery of dispersed particles beyond the efficiency of conventional treatment processes.

Micro-pollutant efficiency removal by electrocoagulation, electroflotation, and modified methods is compiled in Table 1.

Process	Electrode	Distance of Electrodes (cm)	Current Density (mA/cm ²)	pН	Power Consumption	Pollutant/ Initial Concentration (mg/L)	Removal Efficiency (%)	References
	Aluminium electrode	5–15	1.5–3.5	4–10	5.03 kWh/m ³	Fluoride/20 mg/L	93%	[33]
	Aluminium anode/ iron anode	5–25	20	4–12	0.054–0.221 kWh/kg COD _{removal}	Fruit juice wastewater COD 960–48,500 mg/L	COD 59-84%	[24]
	Aluminium anode/ Fe cathode	2			-	Wastewater from production of corn flour/COD 3164 mg/L, turbidity 1 NTU	COD 84% turbidity 98%	[42]
Electrocoagulation	Aluminium electrodes			6.2–8.3	$2.0-45.0 \text{ kWh/m}^3$	Textile wastewater/turbidity 22–28 NTU	Turbidity 75.4%	[20]
	Fe/Al, Fe/Fe, Al/Al, Al/Fe electrode	2	15.56	7.89	0.48 kWh/kg COD	Pharmaceutical wastewater/COD 5000 mg/L, turbidity 3280 NTU	COD 95% turbidity 98%	[29]
	Spiral rod anode made from aluminium, cylindrical stainless-steel cathode	0.15	4–26	3–10	1.54–48.16 kWh/kg COD	Petroleum wastewater/COD- 955 mg/L	COD 73.36%	[22]
	Iron electrodes	1		7.2–9.1		Synthetic wastewater/ COD 14,000 mg/L, turbidity 100 NTU, phosphorus 124 mg/L	COD 43% turbidity 62% phosphorus 51–58%	[30]
	Fe and Al anodes and Cu cathode	2	10	7.2		Microplastic	93.2% for PE, 91.7% for PMMA, 98.2% for CA, and 98.4% for PP	[43]
Elec- troflo- tation	Stainless-steel wire	1	35	10	14 kWh/m ³	Heavy metal/15 mg/L	Pb, Ba, Zn 89–97%	[40]
Electro- coagula- tion/Elec- troflo- tation	Aluminium electrodes/graphite cathode/stainless anode	1.0-2.5	3.59–14.39	6.03-8.02	1.505–3.675 kWh/m ³	Doxycycline hyclate/60–180 mg/L	90–96%	[41]
Electro- coagula- tion and ultrasound (20 kHz)	Iron electrodes; aluminium electrodes		9.1–36.4 16.7–66.8	7.6–8.8	-	Oil wastewater, heavy metal/COD 288–310 mg/L, Cr 71 mg/L, Ni 86 mg/L, Pb 118 mg/L	COD 27–35% Cr, Ni, Pb 91–99%	[27]

Table 1. Micro-pollutants efficiency removal by electrocoagulation, electroflotation, and modified methods.

4. Electrochemical Advanced Oxidation Processes

The methods of advanced oxidation include chemical, photochemical, sonochemical, and electrochemical processes, which are implemented as homogeneous and heterogeneous processes. In homogeneous (single-phase) processes, the catalyst and the substrate, or only the substrate, form a single phase. In heterogeneous processes, the catalyst and substrate form two or more phases and the catalyst is a solid. Advanced oxidation processes include energy using processes and processes without the participation of an external energy source. An external energy source can consist of solar radiation (including ultraviolet), gamma electromagnetic radiation, ultrasonic waves, and electricity. The division of energy-assisted AOPs is presented in Table 2 [31,44–47].

Sources of External Energy: Ultrasound UD/UV	Electrical Energy
Sono-Fenton: $UD/H_2O_2 + Fe^{2+}$	Electro-Fenton: EF
Photo-Fenton: $UV/H_2O_2 + Fe^{2+}$	Sono-electro-Fenton: UD/EF
Sono-photo-Fenton: $UD/UV/H_2O_2 + Fe^{2+}$	Photo-electro-Fenton: UV/EF
Ozonation/oxidation with hydrogen peroxide with exposure to UV radiation or ultrasound $UD/O_3; UD/H_2O_2$ $UV/O_3; UV/H_2O_2$ $UV/O_3/H_2O_2$	Electrochemical oxidation Anodic oxidation

Table 2. Classification of AOPs supported by external energy [31,44–47].

Free reactive radicals play the most significant role in advanced oxidation processes. The mechanism of forming free radicals varies depending on the chemical reagent, its reactivity, and whether it is multi-stage. Free radicals (hydroxyl, sulphate, peroxide, and singlet oxygen) are characterized by high values of oxidation-reduction potential, which makes it possible to decompose the most persistent and toxic organic compounds such as pharmaceuticals, pesticides, phenols, dyes, petroleum products, and others [48,49].

The Fenton process is mentioned among the AOPs that have the widest range of applications in the degradation of organic xenobiotics. In the classic Fenton process, Fenton's reagent (a mixture of hydrogen peroxide and iron(II) ions) is used to generate reactive HO[•]. The basic technological parameters of this process are molar ratio of Fe^{2+}/H_2O_2 , solution reaction, initial concentration and type of pollutants, and temperature. Fenton's reaction mechanism is multi-stage (products of each stage become a substrate of the following reaction) and Fe^{2+} ions play the role of a catalyst in this process [31,49]. The course of forming free radicals in a cumulative manner can be recorded in the form of a Reaction (17) [50]:

As described above, the course of the reaction is multi-stage and is described using Equations (17)–(24) [25,51].

$$Fe^{2+} + H_2O_2 \to Fe^{3+} + OH^- + HO^{\bullet}$$
 (17)

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2 + H^+$$
 (18)

$$OH^- + H_2O_2 \rightarrow H_2O + HO_2 \tag{19}$$

$$Fe^{2+} + HO^{\bullet} \rightarrow Fe^{3+} + OH^{-}$$
⁽²⁰⁾

$$Fe^{3+} + OH_2 \rightarrow Fe^{2+} + O_2 + H^+$$
 (21)

$$Fe^{2+} + HO_2 + H^+ \to Fe^{3+} + H_2O_2$$
 (22)

$$2HO_2 \rightarrow H_2O_2 + O_2 \tag{23}$$

$$\mathrm{HO}^{\bullet} + \mathrm{HO}^{\bullet} \to \mathrm{H}_2\mathrm{O}_2 \tag{24}$$

The degradation of organic compounds in Fenton's process also occurs in a multistage manner. In the initial phase, the hydrogen atom from the organic compound molecule reacts with the hydroxyl radical. This reaction produces an organic peroxide radical. The following step consists of a reaction of the organic peroxide radical with oxygen contained in the reaction environment, the product of which is an organic peroxide radical (ROO[•]). Furthermore, at the same time, a reaction of reducing Fe³⁺ ions to Fe²⁺ ions (18) occurs. Then, a reaction between the organic peroxide radical (ROO[•]) and an organic molecule occurs, producing another organic radical (R[•]). The course of these reactions can be described with Equations (25)–(30) [51].

$$\mathrm{HO}^{\bullet} + \mathrm{RH} \to \mathrm{H}_{2}\mathrm{O} + \mathrm{R}^{\bullet} \tag{25}$$

$$R^{\bullet} + O_2 \to ROO^{\bullet} \tag{26}$$

$$\mathbf{R}^{\bullet} + \mathbf{F}\mathbf{e}^{3+} \to \mathbf{R}^{\bullet} + \mathbf{F}\mathbf{e}^{2+} \tag{27}$$

$$ROO^{\bullet} + RH \rightarrow ROOH + R^{\bullet}$$
 (28)

$$ROOH + Fe^{2+} \rightarrow RO^{\bullet} + Fe^{3+} + HO^{\bullet}$$
⁽²⁹⁾

$$ROOH + Fe^{3+} \rightarrow RO^{\bullet} + Fe^{2+} + H^+$$
(30)

In simple terms, the degradation of organic compounds can be presented as a Reaction (31) [51,52].

$$HO^{\bullet} + RH \rightarrow intermediate \text{ products}$$
 (31)

If sulphate radicals are used for degradation of organic compounds, the source of radicals may be peroxydisulfate (PDS, $S_2O_8^{2-}$) or permonosulphate (PMS, HSO₅⁻). The mechanism of formation of sulphate radicals is similar to the reaction of formation of hydroxyl radicals. The formation of these radicals with use of sodium persulfate Na₂S₂O₈ proceeds according to the Equations (32) and (33) [47,53,54]:

$$Na_2S_2O_8 \to 2Na + S_2O_8^{2-}$$
 (32)

$$S_2O_8^{2-} + activation agent \rightarrow 2SO_4^{-\bullet}$$
 (33)

Thermolysis, UV radiation, ultrasound, and alkaline and carbon-based materials can be used as activation agents in the production of sulphate radicals. The formation of sulphate radicals is possible through transfer of electrons using metals such as iron, cobalt, silver, and manganese [54]. For effective production of sulphate radicals, electroactivation of persulphates can also be used [55].

Sulphate radicals are transformed rapidly to hydroxyl radicals at alkaline conditions. At neutral environmental pH values, the redox potential of sulphate radicals is similar (2.6 V) to the redox potential of hydroxyl radicals (2.7 V). Sulphate radicals have a longer lifetime in comparison to hydroxyl radicals. The lifetime of sulphate radicals is in the range of 40–50 s, whereas the lifetime of hydroxyl radicals is equal to 10^{-3} s. In acidic

$$SO_4^{-\bullet} + H_2O \rightarrow SO_4^{2-} + HO^{\bullet} + H^+$$
(34)

$$\mathrm{SO}_4^{-\bullet} + \mathrm{OH}^{\bullet} \to \mathrm{HSO}_4^- + 0.5\mathrm{O}_2$$
 (35)

As a result of these reactions, the efficiency of organic compound degradation is decreased [48,53,54]. The electrochemical methods of using pyrosulfates on water contaminated with pesticides and other xenobiotics was tested. In most cases, no dangerous by-products or intermediates were found after the process [53–55]. Data in the current literature indicate that the processing costs of using persulphates are higher than the costs associated with using solar or UV with hydrogen peroxide [56].

The main disadvantage of the process is the formation of intermediate decomposition products that might demonstrate toxicity to organisms higher than that of the basic compounds. These include carboxylic acids, benzoic compounds, aldehydes, ketones, ketoacids, and organic halogenated compounds such as trihalomethane (THM), haloacetic acids (HAA), chloral hydrate (CH), and inorganic ozonation by products (OBP), e.g., nitrates (III), chlorates, or bromates [52]. In order to increase the oxidation efficiency of organic compounds and also to ensure oxidation of intermediate products, the basic form of the Fenton process is modified [50]. Modifications integrating the action of the classic Fenton reagent with UV radiation, ultrasound, ionizing radiation, or electrochemical processes (electro-Fenton), which yield additional HO[•] and enhance the regeneration of the Fe²⁺ catalyst with Fe³⁺, are also widely used.

4.1. Electro-Fenton Process

The electro-Fenton (EF) process is one of the most effective and, at the same time, the least invasive modifications of the basic Fenton process [57]. Similar to the classic Fenton process, the mechanism of hydroxyl radical formation has multiple stages. The efficiency of generating free radicals depends on the intensity of the current and the concentration of dissolved oxygen. Organic compounds are oxidized as in the classical process and on the surface of the anode. Reagents such as hydrogen peroxide and Fe²⁺ iron ions can be added to the reactor or generated as a result of electrochemical processes [58–62]. In the case of the electro-Fenton process, hydroxyl radicals are generated in situ in an electrocatalytic manner, and Fe²⁺ ions act as a catalyst [63]. An additional advantage consists of regenerating Fe²⁺ iron ions on the cathode (Figure 2).



Figure 2. Scheme of the electro-Fenton process.

Studies reported in the literature indicate high efficiency of this process in the degradation of persistent organic micro-pollutants such as pesticides, synthetic dyes, phenols, and pharmaceuticals. In any case, the basis for obtaining high efficiency of removing these compounds is optimization of the technological parameters. Currently, much attention is paid to developing electrode materials, catalysts, and the possibility of combining the process with other physical/chemical processes [64]. The electro-Fenton process can be used to remove not only organic but also inorganic pollutants. Removal efficiency is also often assessed in terms of the overall rate of organic pollutants, i.e., COD, and in terms of individual organic and/or inorganic pollutants. For example, in the case of wastewater from the tanning industry, a decrease in COD value ranged from 60 to 70% depending on the pH of the reaction, whereas 100% of sulphides were removed after 10 min of the process [65]. In other studies, COD, turbidity, and colour decreased, respectively, by 75, 100, and 92% after 60 min of electrochemical oxidation. Furthermore, none of the tested pathogens (Escherichia *coli. Salmonella* sp. *Shigella*) were detected after the conclusion of the process [66]. The EF process was also used to remove azobenzene, a compound used in the production of organic dyes. In this case, the COD value was reduced by 80% [38]. The EF process can also be effectively used in urban wastewater treatment aimed at treating wastewater and removing pathogens and landfill leachates as one of the unit processes [66]. In studies concerning landfill leachate treatment, the decrease in COD value ranged between 65% and 83%, depending on the concentration of iron (III) ions [67].

Due to the need to maintain specific conditions regarding the pH environment (low values) and the formation of sediments during homogeneous electro-Fenton (EF) processes, the conditions of heterogeneous electro-Fenton (HEF) reactions using solid catalysts were developed [18]. The advantage of this solution is the possibility of recovering and reusing these catalysts. Currently, much attention is paid to catalysts on carriers due to their unique physical, chemical, and electronic properties. These materials include large-area porous carriers, such as activated carbon, bio-carbon, and natural materials acting as a catalyst and cathode. Impurities are adsorbed on their surface, facilitating the course of the Fenton reaction and the degradation of pollutants [25,68]. Studies show the suitability of chitosan and alginate-based catalysts for the degradation processes in both periodic and continuous EF reactors. In addition, zeolite catalysts, perlite, silica, as well as graphene and carbon nanotubes are structurally stable and can be used repeatedly. However, an important factor determining the usage is initial preparation. Their preparation often requires a high temperature, and their resulting properties depend on the temperature. In turn, preparation of graphene and carbon nanotubes, so they can act as a cathode and catalyse the two-electron reduction of oxygen to produce hydrogen peroxide, requires expensive chemicals. Research is currently being carried out on the usefulness of, for example, bio-carbon and various iron minerals and bimetallic catalysts based on iron as carriers, catalysts, and electrodes in the heterogeneous electro-Fenton process. A disadvantage of using graphene is leaching of the latter into the process solution, because it may have a toxic impact on aquatic organisms. HEF processes can be used to remove micro-pollutants such as pharmaceuticals, pesticides, and pollutants in much higher concentrations (dyes, phenols). The HEF process has an advantage over classic EF in terms of shortening the process time, a wider pH range (from acidic to almost neutral) and a lower amount of leached iron compared to the classic process. Electro-Fenton process is effective for removal of hazardous organic pollutants. Additionally, activated carbon fibre is a commonly used cathode because of its advantages such as no toxicity, low-cost, good stability, conductivity, and low catalytic activity for H_2O_2 decomposition [51,52].

4.2. Integrated Sono-Electro-Fenton and Photo-Electro-Fenton Processes

Other modifications taking advantage of electricity include integrated processes such as sono-electro Fenton (UD/EF) and UV/EF photo-electro Fenton (Table 3). These constitute a combination of the above-described unit processes. In integrated processes, it is possible to achieve greater efficiency of producing hydroxyl radicals, reducing the dose of chemical reagents (Fenton's reagent-hydrogen peroxide, Fe²⁺ ion carrier), reducing reaction time and thus reducing process costs. Comparative studies concerning the effectiveness of the electro-Fenton process and photo-electro-Fenton in terms of removing pharmaceuticals were conducted by Rezvan Behfar and Reza Davarnejad [69]. EF studies were carried out maintaining the H_2O_2/Fe^{2+} ratio at 3.8, the current density at 43 mA/cm², and pH of 3. While maintaining the process time at 87 min, the efficiency of organic compounds removal expressed by the COD index amounted to 87%. Under the conditions of UV exposure in the photo-electro-Fenton process, the COD value decreased by 93%. Using electrochemical technologies in combination with processes used in industrial wastewater treatment plants (including landfill leachates) allows increasing the efficiency of xenobiotics removal [70]. Electrochemical processes can also be used in the course of urban wastewater final treatment (the third stage of treatment) and disinfection. As already mentioned, the problem with these processes is ensuring that the formation of by-products is minimised [71]. Table 3 presents the general advantages of selected modified Fenton processes [17,37,45,72].

Process	Basic Chemical Reaction		Advantages		
Fenton reaction	$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO^{\bullet}$	(17)	It only requires the participation of Fenton's reagent. The process works at ambient temperature.		
Photo-Fenton (UV radiation or sunlight)	$\begin{array}{c} \mathrm{Fe}^{3+} + \mathrm{H_2O} + \mathrm{hv} \rightarrow \mathrm{Fe}^{2+} + \mathrm{OH^-} + \mathrm{HO}^{\bullet} \\ \mathrm{Fe}^{2+} + \mathrm{H_2O_2} \rightarrow \mathrm{Fe}^{3+} + \mathrm{OH^-} + \mathrm{HO}^{\bullet} \\ \mathrm{H_2O_2} + \mathrm{hv} \rightarrow \mathrm{2HO}^{\bullet} \end{array}$	(36) (17) (37)	Minimises sewage sludge formation. Generates additional hydroxyl radicals.		
Electro-Fenton	$\begin{split} &O_{2(g)} + 2H^+ + e^- \to H_2O_2(cat.) \\ &Fe^{2+} + H_2O_2 \to Fe^{3+} + OH^- + HO^\bullet \\ &Fe^{3+} + e^- \to Fe^{2+}(cat.) \end{split}$	(38) (17) (39)	In situ generation of H_2O_2 and Fe^{2+} without the need to add substrate. The source of iron may be ions, Fe^{3+} , or a cast iron anode.		

Table 3. The general advantages of selected modified Fenton processes [17,37,44,68].

5. Modifications of AOPs

As part of the modification of advanced oxidation processes, research is also being carried out into sources of hydroxyl radicals other than hydrogen peroxide. These may include compounds such as calcium peroxide, sodium percarbonate, magnesium peroxide, or sodium persulfate [53,73,74]. In previous studies by the authors, calcium peroxide was used in the photo-Fenton process to remove large molecule PAHs present in coking wastewater. The process resulted in a decrease in the COD value in the range of 30–35%, while the concentration of individual hydrocarbons decreased by 89 to 98% [14,74,75]. In the case of magnesium peroxide used for pesticide degradation, it was shown that the removal efficiency of selected pesticides exceeded 96% for all doses of magnesium peroxide used [54,76,77]. The photo-Fenton process using sodium percarbonate as an alternative source of hydrogen peroxide, has also been used to remove Acid Green 16 dye (acid dye), which is particularly toxic to aquatic organisms [38,73].

In the Fenton process and its modifications (Fenton-like processes), metals other than iron compounds can also be used as catalysts. Iron is most often used in the form of metal salts (Fe^{2+} or Fe^{3+}), metal oxides (e.g., Fe_2O_3 , Fe_3O_4), and zero-value metal (Fe^0). In order to prevent precipitation of iron, an acidic reaction environment should be provided. That is why a better catalyst consists of a compound that occurs at various degrees of oxidation and can possibly be regenerated from an inactive form in accordance with the redox cycle [47,61,78,79]. If possible, active and inactive states should be stable over a wide pH range. Elements meeting these criteria are chromium, cerium, copper, cobalt, manganese, and ruthenium. They can be used as catalysts and by means of mechanisms similar to the Fenton process, directly facilitate the decomposition of H_2O_2 generating hydroxyl radicals. An example pathway for generating hydroxyl radicals in the presence of cerium and hydrogen peroxide has an analogous course as the basic Fenton process and in accordance with Reactions (40) and (41) [46,80].

$$\operatorname{Ce}^{3+} + \operatorname{H}_2\operatorname{O}_2 \to \operatorname{Ce}^{4+} + \operatorname{OH}^- + \operatorname{HO}^{\bullet}$$

$$\tag{40}$$

$$Ce^{4+} + H_2O_2 \rightarrow Ce^{3+} + HO_2^{\bullet} + H^+$$
 (41)

Table 4 shows the efficiency of micro-pollutants removal by electro-Fenton and modified methods. Various other materials are also used in the Fenton process to perform auxiliary functions. These can be natural or synthetic materials such as zeolites, clay, resins, activated carbon, and ashes, as well as pumice particles [81]. For electrochemical processes, research focuses on the selection of electrode materials, catalysts, and the possibilities of combining them with other physical/chemical processes and biological processes (bioelectro-Fenton process) [50,60,82]. Therefore, integrated biological and electrochemical processes are promising for the removal of organic xenobiotics from water and wastewater. The use of these methods to remove persistent organic compounds is possible, but comprehensive control of various process parameters is required. The results of research can be used to modernise conventional wastewater treatment plants to remove persistent organic compounds.

Process	Electrodes, Fe:H ₂ O ₂ Ratio/Catalyst Doses (mg/L)	Reaction Time (min)	Current Density (mA/cm ²)	рН	Pollutant/Initial Concentration	Removal Efficiency (%)	References	
Electro-Fenton	Iron electrodes/3.78/	10–70	20-80	3.5–5		COD: 83–87		
Photo-electro-Fenton UVA lamps 3–9 W	Iron electrodes/4.29/	10–70	20-80	2–5	 Pharmaceutical wastewater 	COD: 92–93	[68]	
Electro-Fenton	/3.41–11.37	25	20	3.5	Fruit juice wastewater	COD: 84	[24]	
Electro-Fenton anode oxidation	Activated carbon fibre (ACF) cathode; RuO_2/TiO_2 anode	120 360 480 270	6.67	3.0	Antibiotics: levofloxacin and cefalexin	100 COD: 68 TOC: 72 TOC: 47	[81]	
	Graphite electrode modified activated carbon and polytetrafluoroethylene (PTFE)	35	5.0	3.0	Methyl orange/ 50 mg/L	100		
	Anode Ti/RuO ₂ , graphite cathode/ Fe ²⁺ : 0.3 mM	180	200 mA	3.0	Anionic surfactants LAS/50 mg/L	100		
Electro-Fenton	Platinum anode, graphite cathode/ Fe ³⁺ : 0.2 mM	50	50 mA		Ibuprofen	100	[25]	
	Titanium anode Ti/IrO ₂ -RuO ₂ , continuous system, cathode = gas diffusion electrode		200 mA	3.0	Tartrazine	80		
	Iron electrodes/ $H_2O_2 = 37.2 \text{ mM}$ Stainless steel cathode/nickel anode, $Fe^{2+}: 5 \text{ mg/L}$	5 90	0.8 900 mA	5.2	Phenol/250 mg/L Phenol	100 95		
Electro-Fenton-like	1000 mg/L 2000 mg/L	480	300 mA	3.0	Levofloxacin/0.23 mM sulfamethazine/ 0.2 mM	95	[10]	
catalyst	800 mg/L	180	31.84	7.0	Diclofenac/50 mg/L	85	[18]	
	1000 mg/L	480		3.0	Tetracycline/ 0.2 mM	99		

Table 4. Efficiency of micro-pollutant removal by electro-Fenton and modified methods.

|--|

Process	Electrodes, Fe:H2O2 Ratio/Catalyst Doses (mg/L)	Reaction Time (min)	Current Density (mA/cm ²)	рН	Pollutant/Initial Concentration	Removal Efficiency (%)	References
	Iron catalyst: 50 mg/L; activated carbon	250	12 mA	3.0	Phenol/100 mg/L	100	
Electro-Fenton Supported catalyst	Fe ⁰ catalyst: 0.1 mg/L	120	60 mA	3.0	Phenol/50 mg/L	91	
	Fe-C catalyst; 6 g/L	360	100 mA	6.7	2,4-dichlorophenol (2,4-DCP)	70	
	Cu-doped Fe@Fe ₂ O ₃ (50 wt%Cu)	120	40	3.0	Tetracycline/ 20 mg/L	98	
	FeOCl dose: 0.25%	240	2500 mV	6.5	Tetracycline/0.4 mM	>95	
Electo-Fenton	Graphite felt GF cathode. Pt anode	0–7	2.08–20.83	3.0	Sulphamethazine/	100	[20]
Anodic oxidation	$Fe^{2+}: 0.2 \text{ mM}$	0–90	4.16–20.83	3.0	0.2 mM 90–95	[32]	

6. Conclusions

AOP methods, including electrochemical methods, are highly efficient processes for the degradation of toxic organic micropollutants. The advantages of the use electrochemical processes are:

- highly efficient method of POPs degradation (above 90%);
- easy control of the technical parameters of the process: current density, solution pH, catalyst concentration;
- minimization of consumption of chemical reagents;
- possible reduction of process time;
- anode materials with high overpotential allowing the generation of additional hydroxyl radicals;
- cathode materials with high overpotential increasing H₂O₂ production and allowing the regeneration of iron ions.

Both the choice of method and process conditions should be optimized according to the type and concentration of contaminants, as well as the presence of other components in the treated wastewater. The process parameters, the choice of reagent doses, and selection of the energy used are all aimed at mineralizing organic pollutants, as well as minimizing the formation of intermediate products and the toxicity of the post-process solutions. However, sometimes the process of complete degradation can be lengthy and increases the costs of the operation. Modifications of AOPs consist of using various radical precursors, catalysts accelerating the course of radical reactions.

Problems associated with the use of electro-processes are:

- release of inorganic ions during mineralization of POPs containing heteroatoms;
- use of a supporting electrolyte;
- use of an acidic solution for pH correction;
- formation of refractory by-products as intermediates (this is specific to all oxidation processes).

In the case of electrochemical methods, the selection of electrode materials is also important [83–85].

- The challenges and prospects for the use of electro-processes are as follows:
- use of hybrid processes;
- integrated biological and electrochemical processes for the removal of organic xenobiotics from water and wastewater;
- use of renewable energy sources to enhance electrochemical processes;
- development of new electrode materials.

Advanced oxidation processes can be stand-alone or complementary to conventional processes for the treatment of industrial (including landfill leachate) and domestic wastewater.

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