

Electrochemical Advanced Oxidation Processes: An Overview of the Current Applications to Actual Industrial Effluents

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Abstract. Many human activities result in the production of wastewater. Usually, physical, chemical and biological processes are successfully combined for the treatment of municipal wastewater, attaining good removal efficiencies. However, some industrial processes introduce anthropogenic recalcitrant pollutants in wastewater that are quite difficult to remove or degrade using conventional means and that should be removed due to their hazardousness. In such cases, the application of an Advanced Oxidation Processes (AOP) uses to be a good and/or promising alternative to attain an appropriate effluent. These processes rely on generating hydroxyl radical, which is a powerful oxidant that mineralizes efficiently pollutants contained in wastewater. In this review, we focus on the use of electrochemical methods to produce hydroxyl radical, using directly or indirectly electrochemical technology, within the so-called Advanced Electrochemical Oxidation Processes (EAOP). These processes include electrochemical, sono-electrochemical and photoelectrochemical technologies and this work describes the fundamentals, main cases studied in the literature related to actual industrial waste treatment and tries to help in the elucidation of the range of applicability of each technology.

Key words: Advanced oxidation processes, industrial wastewaters, surface processes, bulk processes.

Resumen. En la actualidad uno de los principales problemas medioambientales de nuestra sociedad es la generación de grandes cantidades de aguas residuales. Generalmente, estas aguas son tratadas empleando combinaciones de métodos físicos, químicos y biológicos lo que permite alcanzar elevados rendimientos. Sin embargo, algunas aguas residuales industriales presentan contaminantes recalcitrantes, difíciles de eliminar empleando los métodos de tratamiento mencionados anteriormente, por lo que es necesario recurrir a otras técnicas de tratamiento. En estos casos, el empleo de técnicas de oxidación avanzadas (TOA) representa una prometedora alternativa para alcanzar la eliminación del contaminante. Las técnicas TOA se basan en la generación del radical hidroxilo, que es un poderoso agente oxidante, para mineralizar eficazmente los contaminantes del agua. En este artículo de revisión, se presentan las técnicas electroquímicas empleadas para generar el radical hidroxilo, empleando para ello técnicas electroquímicas tanto directas como indirectas, dentro de los denominados procesos de oxidación electroquímica avanzados (POEA). Estos procesos incluyen, tecnologías electroquímica, sonoelectroquímica y fotoelectroquímica. En este trabajo se describen los fundamentos y se presentan los principales casos de estudio publicados, con el objetivo de profundizar en el conocimiento de esta tecnología para ampliar su rango de aplicación.

Palabras Clave: Procesos de oxidación avanzada, aguas residuales industriales, procesos superficiales, procesos en la película líquida.

Introduction

At the earliest 70's Weber wrote a book entitled *Physicochemical Processes* [1]. In this book a special emphasis was made on physical and chemical unit operations that could be used in wastewater treatment. At that time, he introduced a chapter entitled *Chemical Oxidation* in which he compiled the ultimate research studies of some chemical oxidants that could react in aqueous solution. He postulated that from a thermodynamic point of view, oxidations of organic compounds with oxidants such as O₂, O₃, KMnO₄ and ClO₂ are favorable, whereas rates vary drastically. According to this proposal, in conventional biological wastewater treatments the dissolved pollutants are transformed into new cells, which in the clarifier can be separated by gravity. However, the sludge handling and final disposal always has associated costs [2, 3]. On the contrary, when using oxidation the final products are CO₂, H₂O and in some cases mineral acids e.g. HCl. Thus, there is not sludge generation and this represents a tremendous advantage since there is not

a handling and final disposal cost and also the environmental impact is diminished [4, 5].

In 1989, Eckenfelder in his book *Industrial Wastewater Pollution Control* [6] highlighted the stringent environmental regulations had become and the need of redefinition of conventional technologies for wastewater treatment with new technologies. Indeed, as new pollutants were present in wastewater, many wastewater facilities became obsolete.

Almost 20 years later, in 2005, Tchobanoglous et al., in their book *Water treatment Principles and Design* [7], dedicate a vast chapter on chemical oxidation and reduction. For the first time the Advanced Oxidation Processes (AOP) were detailed and described in a 30 pages subchapter. One of the most important postulates was the declaration about AOP are feasible for full-scale use to destroy organic compounds because they generate hydroxyl radicals at ambient temperature and atmospheric pressure. Although a detailed description of the types of AOPs was included, the Electrochemical Advanced Oxidation Processes was not mentioned. These methods were

first described in books focused on electrochemistry and more particularly in environmental electrochemistry [8-12].

The Electrochemical Advanced Oxidation Processes (EAOP) are, consequently, a very new class of oxidation processes that have been under research and although the state of the art results are published in scientific journals, a summary of the recent advances is not available, therefore this review paper aims to compile the information in a single document that indicates the principles and trends in this area.

All the AOP rely on the hydroxyl radical formation. The hydroxyl radical ($\cdot\text{OH}$) is a highly reactive radical which can rapidly degrade recalcitrant organics such as aromatic, chlorinated and phenolic compounds. The hydroxyl radical has a high oxidation potential as shown in Table 1 and can be produced in ozone oxidation, Fenton oxidation and, as it is going to be described in this manuscript, various electrochemical oxidation systems. In addition, this radical can also be produced from water by irradiation of light or ultrasound. This radical readily reacts with pollutants in wastewater; however they could also react with radical's scavenger such as bicarbonate ion, causing a reduction in the efficiency of the process [13].

Electro-Fenton was the first technology which could be considered as an EAOP because of the production and active role of hydroxyl radical on the oxidation of organics [14]. This technology is based on the promotion of one or several of these processes:

- the electrochemical regeneration of iron (II) from iron (III) species on the cathodic surface,
- the cathodic formation of hydrogen peroxide from the reduction of oxygen and

These processes lead to the catalytic decomposition of hydrogen peroxide into hydroxyl radical.

In 2003, Marselli and co-workers [15] demonstrated that the production of hydroxyl radicals during conductive-diamond electrolysis of aqueous wastes was possible. This was a milestone for the electrochemical oxidation, because it demonstrated that anodic oxidation also belongs to the group of the EAOP. From that moment, many other technologies have appeared, including combination of electrochemical production of oxidants and sound or light irradiation decomposition technologies.

Table 1. Oxidizing potential for some oxidizing agents [13].

Oxidizing Agent	Oxidation Potential (V)
Fluorine	3.06
Hydroxyl radical	2.80
Oxygen (atomic)	2.42
Ozone	2.08
Hypochlorite	1.49
Chlorine	1.36
Hydrogen peroxide	1.78
Chlorine dioxide	1.27
Oxygen (molecular)	1.23

In this review, we focus on the use of electrochemical methods to produce hydroxyl radicals using direct or indirect electrochemical oxidation technology, within the so-called Advanced Electrochemical Oxidation Processes (EAOP). These technologies include electrochemical, sonoelectrochemical and photoelectrochemical processes and involve surface and bulk oxidation processes. Their advantages and disadvantages are critically reviewed in this work, reviewing the main works in which the treatment of actual industrial wastewaters have been assessed.

Electrochemical processes in wastewater treatment

Over the last two decades, various applications of electrochemical technology have arisen in the field of environmental remediation. Treatment of liquid wastes coming from different types of industries (by electrocoagulation, electrolysis or electrodialysis) and electrokinetic soil remediation processes become the most significant.

From the scientific point of view, electrolysis and electrocoagulation have been the two most exciting research topics in this period with hundreds of very significant references [16-18]. Electrocoagulation has demonstrated to be a very interesting technology for removal of turbidity, decolorization of dyes and breakup of wastes consisting of emulsions. However, it is not a final treatment but a pretreatment and hence, it is particularly interesting for the coarse removal of pollution [19].

Opposite to electrocoagulation, electrolysis should not be used as a treatment for the coarse removal of pollution in industrial waste because the amount of energy required for the abatement depends directly on the concentration of pollution to be removed. Likewise, it cannot be proposed as an alternative to biological oxidation processes, because these latter processes are much cheaper (typically by one magnitude order) and just in case biological oxidation could not be applied electrolysis can take a chance in the treatment of industrial waste. Hence, its target is the treatment of effluents polluted with anthropogenic organic species, either toxic or refractory to biological treatments, and within a concentration range which should be inside 1,000-20,000 mg Chemical Oxygen Demand (COD) dm^{-3} for direct anodic oxidations [20] and which can be enlarged to smaller values if mediated oxidation processes are promoted (and hence mass transfer limitations are overcome). Use of diamond electrodes has become an outstanding fact in this technology. This type of electrodes favors the production of hydroxyl radicals and their use in the production of other strong oxidants or their use in the harsh oxidation of organic species. This explains the great efficiency obtained and the great relevance of the research results of electrolysis during these two decades. Electrolysis with diamond anodes (often called as conductive-diamond electrochemical oxidation, CDEO) exhibits three outstanding properties as compared with other advanced oxidation technologies and with electrolysis with other anodes [20]:

- robustness, because results found in this latter years demonstrate that it can attain the complete mineralization of almost any type of organic without producing refractory final products
- efficiency, because when it is operated under the no diffusion control, current efficiencies are close to 100%
- integration capability, because it can be easily coupled with other treatment technologies and it can be fed with green energy sources such as wind mills and photovoltaics panels.

However, in spite of the large number of studies carried out, there is still a lot of work to do before its commercial application and many aspects must be enhanced. Two are of particular interest:

- The specificity of diamond electrodes and the elucidation of the influence of the diamond layer characteristics on the efficiency of the oxidation [21, 22]
- The potential improvements that could be obtained by the combination of CDEO with other technologies such as the irradiation of ultrasound or UV-light. This is because in the later years light irradiation and/or ultrasound irradiation have shown to significantly improve the results of many AOPs, in particular avoiding the production of refractory organics during the oxidation of complex pollutants [23-25]. This is not a limitation of the robust CDEO technology, but just a clarification of how sono- and photo- CDEO can improve results of conventional CDEO is worth of investigation.

Anyway, besides electrolysis with diamond anodes many other electrolytic technologies should be reviewed and next sections will deal with this description.

Electrochemical processes on the surface of the electrodes

In the literature, the EAOP are commonly divided into two groups depending on the place where the predominant mechanisms that explain the overall oxidation develop: surface of the electrodes or bulk of the electrochemical cell.

The surface-controlled processes, usually known as Anodic Oxidation processes, are those which take place mainly on the nearness of surface of the electrode. This means that electrode plays a significant role on results and that electrolysis should be considered as heterogeneous processes. Among them, three categories could be distinguished according to the main mechanisms that explain the oxidation carried out:

- Direct electron-transfer processes
- Hydroxyl radical processes
- Heterogeneous photocatalytic processes

Direct electron transfer processes & hydroxyl radicals mediated anodic oxidation: two faces of the same coin

The heterogeneous electrolysis is a well-known technology for the oxidation of organic pollutants contained in wastewaters. In the last years, many studies have been done with both synthetic and real wastewaters, being proved its effectiveness and robustness [20].

In the direct oxidation, pollutants contained in the bulk of the wastewater must reach the electrode surface and the oxidation reaction takes places once they are adsorbed onto this surface. Consequently, the nature of the electrode materials influences the selectivity and efficiency of the oxidation process and mass transfer becomes a very important process, more often than not, the bottleneck of the oxidation rate.

Table 2 shows some anodic materials that have been frequently assessed for the oxidation of organic compounds. They are classified into two groups corresponding to the behavior observed in wastewater electrolysis processes.

At this point, it is worth taking into account that in the 90s of the former century, it was found that electrode materials behave in two different ways when organic pollutants contained in wastewater were oxidized on them. Several anodes (marked into Class 1 in Table 2) produce a soft oxidation of the organics, with the formation of polymers and many refractory species as final products of the electrolytic process. Typically, when the electrolytic process happening on these electrodes was studied with voltammetric techniques it was found a low oxygen evolution overpotential (OEP). On the contrary, the oxidation conditions produced during the bulk electrolysis of organic wastes with other electrodes (Class 2) were very harsh and organics were easily mineralized (transformed into carbon dioxide), with no production of polymers and few or nil concentration of refractory species. As expected, voltammetric studies with these electrodes showed a very high OEP.

Many different explanations were given to this observation but the most convincing was given by the group of Cominelli [26]. They explained the different behavior in terms of the electrolytic oxidation of water to hydroxyl radicals and the interaction of these radicals with the surface of the electrode. It is important to take into account that bulk electrolysis is usually carried out at large cell potentials, clearly over OEP

Table 2. Classification of anodic materials based upon oxygen evolution [125].

Material	Class	Oxygen Evolution Potential
RuO ₂	1	1.47
IrO ₂	1	1.52
Pt	1	1.60
Graphite	1	1.70
SnO ₂	2	1.90
PbO ₂	2	1.90
Boron Doped Diamond (BDD)	2	2.30

and in those conditions oxidation of water, with a first stage of formation of hydroxyl radicals can be expected, although the behavior of the radicals can be completely different. In Class 1 electrodes (also called active electrodes) hydroxyl radical interact with the electrode surface and oxidation of organics was done by a direct transfer of electrons from this electrode surface (chemical oxidation of the pollutant by one of the species contained on the anode surface) and not by the action of hydroxyl radicals. As a consequence, in some cases the oxidation of the electrode results in electrode burning (e.g. graphite) and very low efficiencies are obtained. In other cases, it results in the formation of oxides (e.g. platinum, iridium dioxide electrodes), which attack chemically the organic pollutant with very different results in speciation and efficiency.

Opposite, in Class 2 electrodes (also called non-active), hydroxyl radicals do not interact with the anode surface but directly with organics in a reaction cage (or electrochemical reaction zone) very narrow in the nearness of the electrode surface (because average lifetime of hydroxyl radicals is very short). The very small width of this zone allows researchers to consider this process as an “almost” direct electrochemical process, although it is clearly a mediated electrochemical oxidation and some sort of confusion was made between purely anodic oxidation processes and these new types of processes. Characteristics of these processes are going to be further described in the next section. Opposite, in this section it is important to focus just on the processes happening on the electrode surface. At this point, mass transfer of pollutant from the bulk to the nearness of the electrode surface is the most important

point because in this type of electrodes three stages should be completed: 1) pollutant transfer from the bulk solution to the electrode surface, 2) electrodic reaction (or mediated oxidation by hydroxyl radicals), and 3) oxidized product transfer from the electrode surface to the bulk. These stages are graphically represented in Figure 1.

At this point, if the pollutant does not arrive quickly enough to electrode surface, it is said that the reaction is mass-transfer controlled. The mass-transfer involves the transport of the pollutant by diffusion, convection and migration being convection the most important mechanisms in most electrochemical wastewater treatment technologies. Typically, the mass-transfer rate, can be modeled using Equation (1), where r is the mass transfer rate (g s^{-1}), k_m is the mass transfer coefficient (m s^{-1}), A is the electrode surface (m^2), P_{electr} is the pollutant concentration in the electrode (g m^{-3}) and P_{bulk} is the pollutant concentration in bulk solution (g m^{-3}).

$$r = k_m A (P_{\text{bulk}} - P_{\text{electr}}) \quad (1)$$

Once the pollutant reaches the electrode surface the electrochemical reaction takes place. Two possibilities can be found:

- If there are mass transfer limitations, concentration of the pollutant at the anode surface is nil and rate of the electrolytic process can be simplified to Eq. 2.

$$r = k_m A P_{\text{bulk}} \quad (2)$$

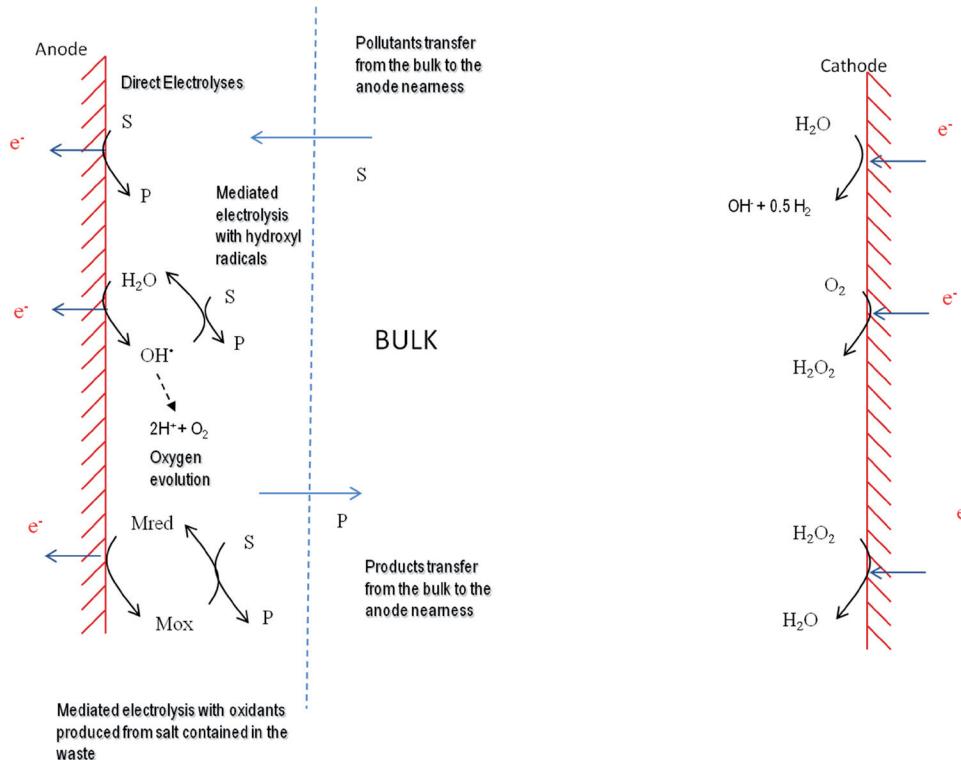


Figure 1. Mass transport controlled processes in anodic oxidation.

- If there are not mass transfer limitations, the rate of the electrochemical oxidation of the compound is modelled in terms of the current density (j), electrode area (A), charge number of the electrode reaction (v) and Faraday constant (F) using Eq. 3.

$$r = \frac{jA}{vF} \quad (3)$$

For a direct electro-oxidation process current density depends primarily on the overpotential (η), through the well-known the Butler-Volmer equation in which dependence on temperature (T) is also included. This equation can be simplified into the Tafel equation (Eq. 4) since the electrochemical oxidation of wastewater usually requires a large overpotential. In this Equation two parameters are considered, the exchange current density (j_0) and the Tafel slope (β).

$$j = j_0 e^{\frac{\beta F \eta}{RT}} \quad (4)$$

For an hydroxyl radical mediated oxidation (with hydroxyl radicals produced on the surface of the electrode surface) and due to the very short average lifetime of hydroxyl radicals and their very high reactivity, no macroscopic differences should be observed with respect to

the kinetics of the direct electrochemical oxidation, because hydroxyl radical production rate is also described by the Tafel equation and the higher the overvoltage, the higher the production of hydroxyl radicals.

Anyway, in both cases mass transfer is controlling the maximum rate and only product distribution and efficiency can help to distinguish between the two limit behaviors: in this context the higher efficiency and effectiveness of the oxidation with hydroxyl radicals is the key to understand the better results with non-active electrodes.

Another interesting point is the formation of oxidants in the reaction media, which will be discussed afterwards in the next sections. In wastewater containing chloride, formation of chlorine and hypochlorite is well known with many types of anodes. However, oxidation of other anions is also possible and this mechanism seems to be promoted in the presence of hydroxyl radical meaning the effective formation of many interesting species such as peroxosulphates, peroxophosphates and peroxocarbonates in the nearness of the electrode surface or if these species are stable (meaning not extremely oxidizing reagents) in the bulk of the solution.

Table 3 shows some of the works in which pollutants treated under proper conditions and with anode materials exhibiting

Table 3. Direct Electrolysis of industrial wastewater using active electrodes.

Type of wastewater	Electrode/ electrochemical cell	Operation conditions	Efficiency / main results obtained in terms of treatability	Ref.
Textile effluent	electrode Ti-Pt/β-PbO ₂ /single flow	Current density: 15 mA cm ⁻² Temperature: 55°C; pH: 7.11	60 % COD removal	[126]
Tannery wastewater in chloride-free aqueous media	electrode Ti/SnO ₂ -Sb-Ir electrode / single flow	Current density: 25 mA cm ⁻² ; Power consumption: 2.547 kWh ⁻¹	2.1 % TOC removal	[127]
Tannery wastewater in chloride-free aqueous media	electrode Ti/SnO ₂ -Sb / single flow	Current density: 25 mA cm ⁻² ; Power consumption: 0.104 kWh g ⁻¹	56.1% TOC removal	[127]
Tannery wastewater	Titanium electrode /single flow	pH: 4; Current density: 100 mA cm ⁻²	41% COD removal after 5 h	[128]
Tannery wastewater	DSA® electrode (Ti/Ir _{0.10} Sn _{0.90} O ₂) /single flow	Current density: 20 mA cm ⁻²	44,6% TOC removal after 5 h, energy consumed 36 kWh m ⁻³	[129]
Tannery wastewater	Ti/TiRuO ₂ anode/single flow	Current density: 600 A m ⁻² ; pH: 10; T: 40 °C	90% COD removal after 6 h	[130]
Tannery wastewater	Ti/Pt anode and Ti cathode / Two electrode stirred batch reactor.	Current 0.09 A; Cell Voltage: 4.16 V	Efficiency 0.802 kg COD h ⁻¹ A ⁻¹ m ⁻²	[131]
Tannery wastewater	Ti/PbO ₂ anode and Ti cathode/ Two electrode stirred batch reactor.	Current 0.2 A; cell voltage: 4.05 V	Efficiency 0.162 kg COD h ⁻¹ A ⁻¹ m ⁻²	[131]
Tannery wastewater	Ti/MnO ₂ anode and Ti cathode / Two electrode stirred batch reactor.	Current 0.2 A; cell voltage: 4.06 V	Efficiency 0.035 kg COD h ⁻¹ A ⁻¹ m ⁻²	[131]
Vinasse from beet molasses	Titanium anode /single flow	Cell voltage: 15 V (DC); current 100 A; T:42°C; pH: 9.5	90% COD removal	[132]

Table 3. Continues.

Type of wastewater	Electrode/ electrochemical cell	Operation conditions	Efficiency / main results obtained in terms of treatability	Ref.
Tannery waste liquors	electrolytic cell using a Ti/Pt anode/single flow	Current density 0.26 A cm ⁻² ; T:45° C; pH: 9	After 30 min and 3 h of electrolysis total COD was reduced by 52 and 83%	[133]
Olive oil wastewater	Ti/Pt anode / Electrolytic cell	Current density: 0.26 A cm ⁻²	After 1 and 10 h of electrolysis total COD was reduced by 41 and 93%, respectively, total TOC was reduced by 20 and 80.4%	[134]
Petrochemical effluent	Ti/IrO ₂ -Ta ₂ O ₅ electrode/single flow	pH: 4; Current density: 5 mA cm ⁻²	80% COD removal after 2 h	[135]
Gelatin production effluent	TiO ₂ electrode/single flow	pH: 5.9; Current density: 12.6 mA cm ⁻²	80% COD removal after 2 h	[136]
Swine wastewater	Pt-Ir electrode/single flow	pH:11, Energy consumption: 3 kWh kg ⁻¹	80% NH ₃ removal	[137]
Digested olive mill wastewater	RuO ₂ electrode/single flow	pH: 8.5	99% COD removal	[138]
Digested olive mill wastewater	IrO ₂ electrode/single flow	pH: 8.5	14% COD removal	[138]
Textile wastewater	RuO ₂ electrode/single flow	pH: 7; Current density: 3 A dm ⁻³	30% COD removal after 2 h	[139]
Dye wastewater	IrO ₂ electrode/single flow	Current density: 0.4 A dm ⁻³	85% color removal after 6 h	[140]
Swine wastewater	RuO ₂ electrode/single flow	pH: 2.8; Current density: 35.7 mA cm ⁻²	99% nitrogen removal after 2 h	[141]
Swine wastewater	Graphite /single flow electrode	pH: 2.8; Current density: 5.5 mA cm ⁻²	90% nitrogen removal after 4 h	[141]
Swine wastewater	RuO ₂ /IrO ₂ /TaO ₂ electrode/ single flow	pH: 2.8; Current density 5.5 mA cm ⁻²	20% nitrogen removal after 2 h	[141]
Olive mill wastewater	Ti/IrO ₂ electrode/single flow	Acidic pH; Current charge applied: 6 Ah L ⁻¹	Color and phenols removal less than 10%	[142]
Textile wash water	TiO ₂ /RuO ₂ electrode/single flow	pH: 2	80% COD and 95% color removal after 6 h	[143]
Petroleum refinery wastewater	Ru-mixed metal oxide (MMO) electrode/ /single flow	Current density 20 mA cm ⁻² ; T:20-25°C	95% phenol removal after 210 min. 70% COD removal after 300 min	[144]

a clear Class 1 behavior (direct electron transfer is expected to be the main oxidation mechanisms) are assessed. As it can be observed efficiencies are low regardless of the operation conditions, in particular in terms of mineralization.

Table 4 shows some of the works reporting about pollutants treated under proper conditions and with different anode materials exhibiting Class 2 behavior (hydroxyl radical is expected to be the main oxidation mechanisms). As it can be observed, and opposite to the results shown in Table 4 efficiencies are very high in particular those related to mineralization.

Heterogeneous photoelectrocatalysis

Photoelectrochemical cells (PECs) were originally designed to undertake the photo-induced cleavage of water, generating oxygen at a titanium dioxide electrode, in an aqueous solution

with the concomitant production of hydrogen gas, most often evolved at a platinum cathode [27].

All PECs rely on light for successful operation. Their use has since been extended for other applications, including the remediation of wastewater [28, 29]. Several works were mainly based on the degradation of dyes, because in addition to their role as pollutants, they consist of large organic molecules in which synergistic effects of electrochemical and photochemical technologies can be more clearly identified. The results obtained indicated that the combination of photo and electrolysis technologies leads to a synergistic effect explained by heterogeneous (external bias contribute to a decrease in the electron-hole pair recombination process and the UV-photons reaching the electrode surface form excited radicals) and homogenous (photoactivation of electrochemically generated reactive species) catalytic processes.

Table 4. Direct Electrolysis of industrial wastewater using non-active electrodes.

Type of wastewater	Electrode/ electrochemical cell	Operation conditions	Efficiency /main results obtained in terms of treatability	Ref.
Tannery wastewater	Ti/PbO ₂ anode, /single flow	Current density: 600 A m ⁻² ; pH: 6.5; T: 20 °C	99% COD removal after 5 h	[130]
Tannery wastewater in chloride-free aqueous media	electrode Si/BDD/single flow	Current density: 25 mA cm ⁻² ; power consumption: 0.084 kWh g ⁻¹	79.1 % TOC removal	[127]
Tannery wastewater in chloride-free aqueous media	electrode Si/BDD/single flow	Current density: 50 mA cm ⁻² ; power consumption: 0.190 kWh g ⁻¹	92.1 % TOC removal	[127]
Tannery wastewater in chloride-free aqueous media	electrode Si/BDD/single flow	Current density: 100 mA cm ⁻² ; power consumption 0.551 kWh g ⁻¹	98.3 % TOC removal	[127]
Landfill leachate	electrode Si/BDD/single flow	pH: 5.5; Current density: 90 mA cm ⁻²	51 % COD and 34 % N-NH ₄ after 8 h of treatment	[145]
Textile effluent	Nb/BDD anode/single flow	pH 7.11	99 % COD removal	[126]
Tannery wastewater in chloride-free aqueous media	Si/BDD anode/single flow	pH: 2.4; Current density: 100 mA cm ⁻²	89 % TOC removal	[127]
Olive-oil mills wastewater	Si/BDD electrode/single flow	pH: 6.0; Current density: 30 mA cm ⁻²	99 % COD removal	[146]
Fine chemicals manufacturing plant	BDD electrode/single flow	pH: 6.0; Current density: 300 A m ⁻²	99 % COD removal BDD	[147]
Petrochemical effluent	BDD electrode/single flow	pH: 7; Current density: 5 mA cm ⁻²	99% COD removal after 2 h	[135]
Mixed industrial wastewater	BDD electrode/single flow	pH: 7.2; Current density: 800 A m ⁻²	99% COD removal after 2 h	[148]
Flame retardant industry effluent	BDD electrode/single flow	pH: 1.5; Current density: 100 A m ⁻²	99% COD removal after 20 h of	[149]
Textile dyehouse effluent	BDD electrode/single flow	pH: 1; Current density: 8 mA cm ⁻²	80% COD removal after 2 h	[150]
Pharmaceutical effluent	BDD electrode/single flow	pH: 8.5; Current density: 50 mA cm ⁻²	85% COD removal after 10 h	[151]
Fine Chemical manufacturing plant	BDD electrode/single flow	pH: 6; Current density: 300 A m ⁻²	99% COD removal	[147]
Oil refinery wastewater	BDD electrode/single flow	pH: 9.5; Current density: 50 mA cm ⁻²	99% COD removal after 8 h	[152]
Textile wastewater	SnO ₂ electrode/single flow	pH: 7; Current density: 3 A dm ⁻³	70% COD removal after 2 h	[139]
Textile wastewater	PbO ₂ electrode/single flow	pH: 7; Current density: 3 A dm ⁻³	65% COD removal after 2 h	[139]
Industrial wastewater	BDD electrode/single flow	Natural pH; Current density: 30 mA cm ⁻²	99% COD removal	[20]
Industrial wastewater	BDD electrode /mixed flow	Oxidation coupled to electrocoagulation	99% COD removal and 100 % color and turbidity removal	[148]
Olive processing wastewater	BDD electrode/single flow	pH: 4.5; current: 30A	73% COD Removal after 14 h, energy consumption efficiency of 16.3 g COD/(m ³ Ah)	[153]
Fenton refractory olive oil mill wastes	BDD electrode/single flow	pH: 7; T: 25°C; Current density: 30 mA cm ⁻²	99% COD removal	[154]
Petroleum refinery wastewater	BDD electrode/single flow	Current density: 5 mA cm ⁻² ; T: 20-25°C	99% phenol removal and 96% COD removal after 40 min	[144]
Textile industrial effluent	BDD electrode/single flow	Current density: 60 mA cm ⁻² ; T: 25°C	21% color removal, 12.6% COD removal after 12 h	[155]
Olive mill wastewater	BDD electrode/single flow	Current: 20 A	20% COD removal, 36% phenol removal after 15 h	[156]

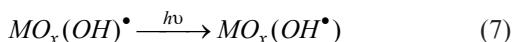
Recent reports have highlighted PEC cells that are capable of spontaneously degrading a wide variety of organic substrates ranging from biomass like polysaccharides, proteins, lignin, and cellulose to simple alcohols and sugars. Various other compounds were also successfully degraded with PECs including nitrogen-containing substances such as ammonia, urea, urine, and synthetic polymers like polyethylene glycol and poly(acrylamide). All these compounds were mineralized while also creating photocurrent [30-33].

Mechanisms of oxidation in heterogeneous photoelectrocatalysis were proposed by Pelegri et al., (2000) in one of the first pioneering [34] and they connect with the two first types of electrochemical surface-controlled processes. Thus,

— in the presence of photons, the external bias can contribute to a decrease in the electron-hole pair recombination process. The reactions that are expected to take place are represented in eqs. 5 and 6. Where h^+_{VB} represents the photogenerated holes and e^-_{CB} the electrons released.



— photons reach the surface of the electrode during the electrochemical step, generating excited radicals according to Eq. 7, which can enhance the treatment efficiency



In literature, pioneering reports were published at the turn of the century and during the last decade. These works were focused on the development of heterogeneous photo-electrocatalysts on the surface of the anodes. These photo-electrocatalysts were based on Mixed Metal Oxides (MMO) anodes. Most of these MMO catalysts were based on the use of titanium dioxide and ruthenium. A 30/70 % composition ratio (Ti/Ru_{0.3}Ti_{0.7}O₂) has been reported in literature to remove complex pollutants such as dyes [35-40] and humic acids [41]. In several works, other metal oxides such as tin dioxide were added to the conventional MMO electrodes with ruthenium and titanium oxides

[34] and in other works the more energetic lead dioxide, instead of ruthenium oxide, was used as additive in the conventional MMO electrodes [42]. Other electrodes reported in literature were based on titanium-supported (Ti/TiO₂ thin film) photo-electrodes [43, 44] and on the conductive diamond electrode [45]. In these works, synergistic effects due to the combination of the photo irradiation and the electrochemical process were observed on results of the treatment, yielding higher removal percentages than expected based on the separate contribution of both oxidation technologies.

Table 5 shows some of the pollutants treated with different anode materials in which heterogeneous photochemical reactions are expected to be responsible for the main oxidation.

Bulk processes in EAOP

The bulk oxidation comprises indirect oxidation processes that require the electrochemical generation of a mediator which can then react in the bulk solution. This mediator can be generated anodically (or cathodically), and it is responsible for the oxidation of pollutants in wastewater. The most common electrochemical indirect agents are chlorine and hydrogen peroxide. However, almost any salt contained in a waste can produce oxidants which act in the bulk and because of this, the role of chlorine [46-49], sulphates [50-52], phosphates [53, 54] and many other types of salt anions on the electrochemical destruction of organics have been extensively studied in the literature.

It is important to bear in mind that production and action of oxidants is a set of processes occurring in all electrolysis and that it could be promoted with the addition of reagents (chloride, oxygen) that promotes the formation of oxidants. There are no pure bulk electrochemical processes but electrochemical processes in which contribution of bulk processes is more important in the oxidation of organics than the contribution of surface processes. This can be clearly observed in Figure 2 in which mechanisms for the oxidation of organic pollutants in wastewater treatment are clearly summarized. Production of oxidant species during electrochemical treatment of wastewater has encouraged many research groups to study the synthesis of particulate oxidants and to isolate them as valuable products.

One very important point to be considered in bulk processes is that oxidants produced in the electrochemical treatments

Table 5. Treatment of industrial wastewater using heterogeneous photo-electrocatalysis technologies.

Type of wastewater	Electrode/ electrochemical cell	Operation conditions	Efficiency /main results obtained in terms of treatability	Ref.
Pharmaceutical wastewater	TiO ₂ electrode/special desing	pH: 7, Current applied: 6 A; irradiated with a 150 W xenon lamp.	55% TOC removal after 2 h	[157]
Dye wastewater	TiO ₂ electrode /special desing	Current density: 1 mA cm ⁻² ; irradiation during 1 h with a UV lamp (21 W cm ⁻²)	25% TOC removal with a operated at	[158]
Tannery wastewater	Ti/TiO ₂ electrode/special desing	pH 2	95 % TOC removal, 100 % color removal, 99 % Cr (VI) reduction	[159]

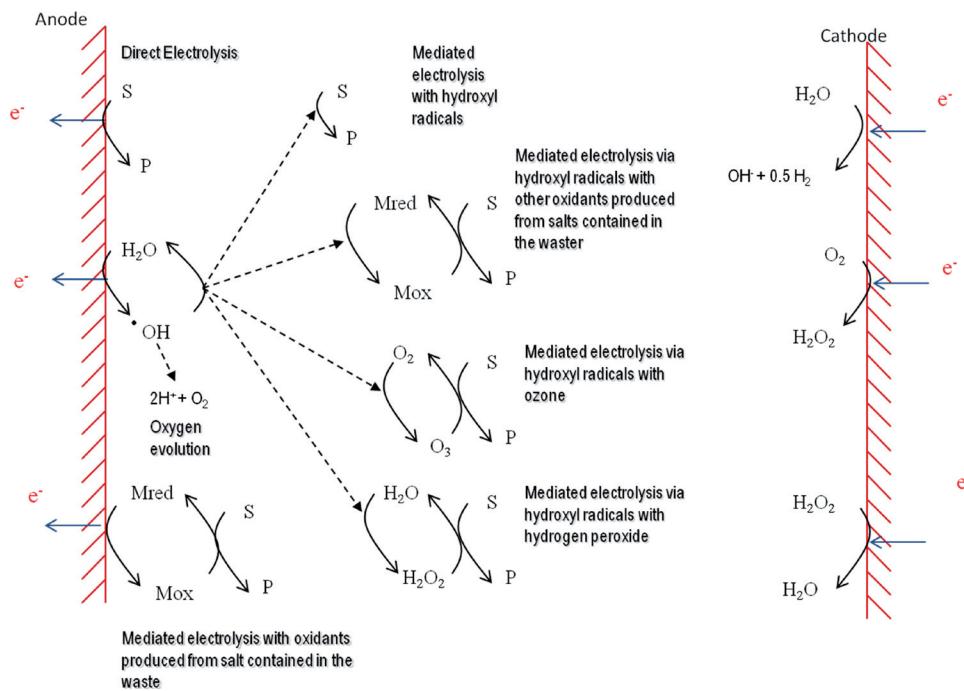


Figure 2. Mechanisms of direct and mediated oxidation of organics.

can be activated by different ways looking for harsher oxidation conditions. For this reason, four points are of particular interest regarding bulk processes

- Production of oxidants
- Chemical activation of oxidants
- Activation of oxidants by light irradiation
- Activation of oxidants by ultrasound irradiation.

Production of oxidants in EAOP

Although many species can play an important role in bulk oxidation, this section is going to be focused only on the most relevant including chlorine, hydrogen peroxide, peroxocompounds and ferrates.

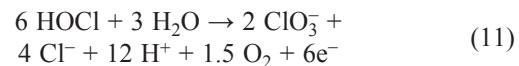
Regarding chlorine, it is easily produced in wastewater containing chloride and because this anion is contained in many industrial wastewater streams, it uses to play a very important role in the electrolysis of many actual wastes. Chlorine is produced on the surface of the anode (Eq. 8) and it suffers many significant speciation reactions in the bulk, which are strongly influenced by pH, including disproportionation (Eq. 9) to hypochlorous acid, and hydrolysis to hypochlorite (Eq. 10).



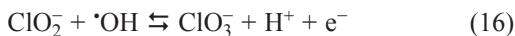
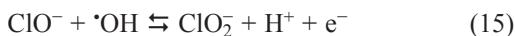
These different species explain the large influence of pH on the results of the electrolysis of industrials wastes. In ad-

dition, although chlorine, hypochloric acid and hypochlorite are powerful oxidants, three drawbacks are associated to their use:

- formation of organochlorinated species by addition reactions of chlorine with different functional groups of organic matter, being these new species typically more hazardous than the parent pollutants. Obviously, their generation advices against the use of the electrochemical technology.
- Production of chlorates which may occur either electrochemically (Eq. 11) or chemically (Eqs. 12 and 13). In the latter case, its production is promoted by the ageing of the hypochlorite and it is a well-known phenomenon typically taking place in the storage of hypochlorite. Chlorate is not a good oxidant for organic matter under the conditions used in electrolysis (very slow kinetically at room temperature).

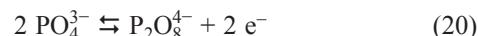
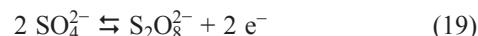
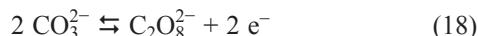


- For some electrodes such as the BDD, perchlorate is also known to be formed during the electrolysis, because of the action of hydroxyl radicals [55, 56] summarized in Eqs. 14-17. The hazardousness of perchlorate prevents the use of this electrode material in the treatment of industrial wastes which contain high loads of chlorides.

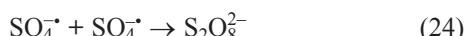
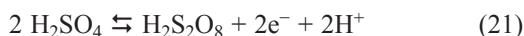


Some papers in which the effect of chlorine has been found to be very relevant for the treatment of actual wastes are summarized in Table 6.

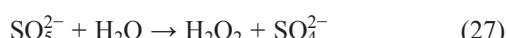
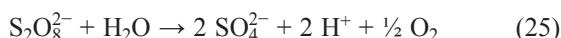
In addition to chlorides, many other salts are present typically in the composition of industrial wastewater. The most significant group of oxidants which can be formed from these salts is the peroxy group, composed of oxidants that are characterized by the presence of oxygen bonds in the molecule (-O-O-). The anodic oxidation production of oxidants such as $\text{C}_2\text{O}_8^{2-}$, $\text{S}_2\text{O}_8^{2-}$, and $\text{P}_2\text{O}_8^{4-}$ has been reported on PbO_2 and BDD anodes. The reactions that take place are [57-59]:



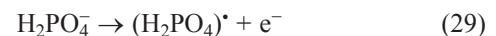
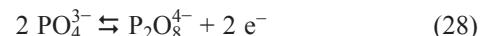
As for chlorine, mediated oxidation with peroxy salts is strongly related to pH, because of the different speciation of these oxidants with the pH. Two subgroups are of particular relevance because of the significant presence of anions in typical industrial wastes: peroxy sulfates and peroxy phosphates. Regarding peroxy sulfates [60, 61], these species are formed from the oxidation of sulfates. There are two different species: peroxy monosulfuric and peroxy disulfuric acids. Both acids have a very high reduction potential (1.81 and 2.08 respectively) and their production can be associated to direct electron transfer processes (Eq. 21) or to hydroxyl radicals mediated oxidation (Eq. 22 to 24)



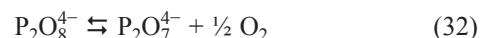
Its effect is known to be smaller at high temperature because it is well known that the peroxy sulfuric acids decompose with temperature to yield sulfuric acid and hydrogen peroxide eq. 25-27.



The other important subgroup is peroxy phosphates. The chemistry of the peroxy phosphates is similar to that of persulfates and two main species can also be found: peroxy monophosphate and peroxy diphosphate. Peroxy monophosphate is stable at acid pH whereas peroxy diphosphate is more stable at alkaline pH. Peroxy diphosphates are also known to be produced by direct electron transfer (Eq. 1) or by the action of hydroxyl radicals as indicated in eqs. 28 to 31.



Temperatures higher than 25°C lead to low conversions and efficiencies in the production of peroxy phosphates. This could be explained by the thermal decomposition of peroxy diphosphate to give pyrophosphate and oxygen (eq. 32).



Production of oxidants from salt cations is much more difficult. One of the few examples that are reported in the literature is the production of ferrates which could become important when iron species are present in wastewater especially because its addition in other treatment processes. Ferrates, FeO_4^{2-} , are characterized by an unusual oxidation state, +6, being a powerful oxidizing agent. Moreover, during the oxidation process, ferrate (VI) ions are reduced to Fe (III) or to ferric hydroxide, making them suitable to be used in a wide range of applications [62-71] and because of that its effect should only be important working at extremely high pHs.

Some papers in which the effect of electrolyte (different of chloride) has been found to be very relevant for the treatment of actual wastes are summarized in Table 7.

The third type of oxidants with relevance in bulk electrolysis is hydrogen peroxide, which is typically produced on the cathode and by decomposition of other oxidants in the bulk. The electrolytic production of H_2O_2 requires the dosing of oxygen gas into the electrochemical cell and a proper electrode surface. Several materials have been tested such as reticulated vitreous carbon, carbon cloth, graphite, oxygen diffusion cathodes and recently boron doped diamond [72-75]. In acidic media the reaction that takes place is shown in Eq. 33.



As indicated by Bard [76], the hydrogen peroxide will form the hydroxyl radical at the cathode (Eq. 34). In aqueous solution a chain reaction then occurs between the hydroxyl radical and an organic compound R [77], summarized in eqs. 35-37. Therefore, the main advantage of hydrogen peroxide is the production of hydroxyl radical, which will react with the organic pollutants present in the wastewater.

Table 6. Treatment of industrial wastewater with high content of chlorides by electrolysis.

Type of wastewater	Electrode/ electrochemical cell	Operation conditions	Efficiency /main results obtained in terms of treatability	Ref.
Synthetic tannery wastewater	Ti/IrSnO ₂ anodes	pH: 3.3; current density 20 mA cm ⁻² ; electrolyte concentration 500 mmol L ⁻¹ NaCl	100 % TOC removal	[129]
Saline industrial wastewaters	BDD anodes	pH Neutral-alkaline; current density:150 A m ⁻² ; minimum concentration of NaCl: 1650 mg L ⁻¹	95 % TOC removal	[160]
Low salinity reverse osmosis concentrates	BDD anodes	pH: 8; current density: 10 mA cm ⁻² ; minimum concentration of NaCl: 600 mg L ⁻¹	99 % TOC removal using with a	[161]
Low salinity reverse osmosis concentrates	RuO ₂ anodes	Current density: 30 mA cm ⁻² ; minimum concentration of NaCl: 600 mg L ⁻¹	30 % TOC removal	[161]
Landfill leachate	BDD anodes	pH: 8.4; current density: 600 A m ⁻² ; minimum concentration of NaCl: 3230 mg L ⁻¹	99 % TOC and NH4 ⁺ removal	[162]
Textile wastewater	Ti/Pt-Ir electrode	pH: 11.5; current density: 260 A m ⁻² ; concentration of NaCl: 2500 mg L ⁻¹	99 % color removal	[163]
Textile wastewaters	Ti/Pt-Ir electrode	current density: 200 A m ⁻² ; concentration of NaCl: 0.1 mol L ⁻¹	90 % dye COD removal	[164]
Tannery wastewaters	Ti/Pt-Ir electrode	current density: 400 A m ⁻² ; concentration of NaCl 0.1 mol L ⁻¹	50 % tannery COD removal	[164]
Simulated dye wastewater	Pt anode and steel cathode	0.2 M NH ₄ Cl	70% COD removal	[165]
Fertilizer production wastewater	Graphite anode and titanium cathode	pH 4; current density 62.5 mA cm ⁻² ; concentration of NaCl: 8 g	82% TOC removal and 492.3 kWh/kg TOC removed	[166]
Pharmaceutical wastewater		pH 6.5; current density: 76 A m ⁻²	35% COD removal after 90 min	[167]
Olive mill wastewater	Ti/IrO ₂ electrode	Acidic pH: Current charge applied: 43 Ah/L, Concentration of NaCl: 5mM; T:80 °C	30% COD removal and complete color and phenols removal	[142]
Olive mill wastewater	Ti/IrO ₂ electrode	Acidic pH; Current charge applied: 6 Ah/L, Concentration of NaCl: 15mM; T: 80°C	30% COD removal and complete color and phenols removal.	[142]
Landfill leachate	BDD anodes	pH: 2.5; current density: 900 A m ⁻² , Concentration of chloride:1350 mg/L	90% COD and NH4 ⁺ removal	[168]
Landfill leachate	Ti _x Ru _y Sn _z O anodes	pH 8.2; T: 25°C, current 2 A; concentration of chlorides: 1800 mg L ⁻¹	35% COD, 65% ammonium and 52% color removal after 8 h	[169]
Landfill leachate	PbO ₂ anodes	pH 8.2; T:25°C, current: 2 A; Concentration of chloride: 1800 mg/L	90% COD, 100% ammonium and 100% color removal after 8 h	[169]
Landfill leachate	Ti _x Ru _y Sn _z O anodes	pH 8.2, T:25°C, current: 2 A; concentration of chloride: 1800 mg L ⁻¹	100% COD, 100% ammonium and 100% color removal after 8 h	[169]
Ink manufacturing wastewater	BDD electrode	Neutral pH; current density: 30 mA cm ⁻² ; Concentration of NaCl: 0.1 M	90 % COD removal	[53]

Table 6. Continues.

Type of wastewater	Electrode/ electrochemical cell	Operation conditions	Efficiency /main results obtained in terms of treatability	Ref.
Molasses wastewater	BDD electrode	pH 7; current density: 30 mA cm ⁻² ; Concentration of NaCl: 35 mM	99 % COD removal	[54]
Aquaculture saline water	BDD electrode	pH 6.9; T: 25°C, Concentration of chloride: 26167 mg/L; Current density: 50A m ⁻²	99 % color and COD removal	[170]
Textile industrial effluent	BDD electrode	Current density: 60 mA cm ⁻² ; T: 25°C; Concentration of NaCl: 5 g L ⁻¹	95% color removal, 100% COD removal after 7 h	[155]
Olive mill wastewater	Ti/Ti _x Ru _y O anodes anode and stainless steel cathode	Applied current: 5 A cm ⁻² ;T: 25°C, Concentration of NaCl: 5 g L ⁻¹	95% COD removal after 20 h	[171]
Olive mill wastewater	Ti anode and stainless steel cathode	Applied voltage: 9 V; T:25°C; Concentration of NaCl:4 %	40% COD removal after 2 h	[172]
Olive mill wastewater	RuO ₂ coated Ti electrodes	Current density: 135 mA cm ⁻² ; T: 40°C; Concentration of NaCl: 2 M	99% COD, turbidity and phenol removal after 7 h	[173]

Table 7. Treatment of industrial wastewater with high content of salts excluding chlorides by electrolysis.

Type of wastewater	Electrode/ electrochemical cell	Operation conditions	Efficiency /main results obtained in terms of treatability	Ref.
Coking wastewater	BDD electrode	pH 7.72; current density: 60 mA cm ⁻² ; 0.2 M Na ₂ SO ₄ generating S ₂ O ₈ ²⁻	99 % COD removal after 4 h	[174]
Ink manufacturing wastewater	BDD electrode	Neutral pH; current density: 30 mA cm ⁻² ; 0.1 M Na ₂ SO ₄ or 0.1 M Na ₃ PO ₄	99 % COD removal	[53]
Molasses wastewater	BDD electrode	pH 7; current density: 30 mA cm ⁻² ; 35 mM Na ₂ SO ₄ or 35 mM KH ₂ PO ₄	99 % COD removal	[54]
Organic wastewater	BDD electrode	pH 12.5; current density: 1250 A m ⁻² ; 1 M K ₃ PO ₄	30 % COD removal of organic pollutants	[161]
Cyanide wastewater	BDD electrode	pH 12.5; current density: 1250 A m ⁻² ; 1 M K ₃ PO ₄	90 % CN- removal	[161]
Industrial waste	Pt anode and stainless steel cathode	pH 10; current density: 0.4 A/ cm ² ; cell potential: 5 V; 0.5 M NaHSO ₄	50% COD removal after 10 hours	[175]
Synthetic wastewater	BDD anode	pH 12.5; current density: 1250 mA m ⁻² ; 1 M K ₃ PO ₄ , oxidant excess over stoichiometry 300%, 20°C		[176]
Landfill leachate	Pt anode, Carbon-PTFE cathode	Ozone addition: 157 mg L ⁻¹ ; current: 350 mA	87% TOC removal after 6 h	[177]
Landfill leachate	Cast iron electrodes	pH 9; 1 g L ⁻¹ Na ₂ SO ₄	70% BOD removal, 68% COD removal, 84% color removal	[178]
Textile industrial effluent	BDD electrode	Current density 60 mA cm ⁻² ; T: 25°C; 10 g L ⁻¹ Na ₂ SO ₄	100 % color removal, 100 % COD removal after 12 h	[155]
Textile effluent	BDD electrode	pH 10.2; current density: 40 mA cm ⁻² ; T 25°C; 5 g L ⁻¹ Na ₂ SO ₄	100 % COD removal after 10 h	[179]



Some recent works focused on the use of hydrogen peroxide to remove pollutants contained in industrial wastes are summarized in Table 8.

Chemical activation of oxidants produced in electrochemical processes

As explained before for the chlorine/ hypochlorite/hypochloric acid, changes in the pH can modify the oxidation capability of the bulk in electrochemical treatments in chloride media, because of the non-electrochemical absorption/hydrolysis processes. This is an example of chemical activation of oxidants, although it is not the most relevant in EAOP because this position is occupied by

- The synergistic interactions of oxidants, some of them (such as the combination of ozone and hydrogen peroxide) leading to the formation of hydroxyl radicals:



- decomposition of hydrogen peroxide into hydroxyl radicals by iron (and copper, as well, although it is less used)



Due to the low solubility of iron species, the second case can be combined with coagulation and two very significant and

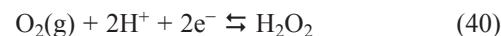
different processes can be distinguished: Electro-Fenton and peroxy-coagulation.

The Fenton's reaction takes place at acidic conditions, the recommended range is an aqueous pH 2 to 4. This can be explained using a thermodynamic study. The existence of Fe(II) and Fe(III) complexes in aqueous solution has been reported [78, 79]. Using this information, the iron distribution diagrams of chemical species can be calculated using the MEDUSA program [80] as Figures 3 and 4 show.

Note in Figure 4 that Fe^{3+} ions and the mononuclear species $\text{Fe}(\text{OH})^{2+}$ and $\text{Fe}(\text{OH})_2^{+}$ predominates in acid solution and while Fe^{3+} decreases, the mononuclear species reach 67% and 18% of relatively fraction as the pH increases. Beyond pH 3, insoluble species appear and the species $\text{Fe}(\text{OH})_{3(s)}$ reach their maximum at pH near 4.

Electro-Fenton is an indirect electrochemical method that is quite powerful in destroying organic pollutants in solution, and it requires the addition of iron salts into solution. This method is also the basis for the next one: peroxy-coagulation [81]. Thus, for a clear understanding in the electrochemical and chemical reactions and the differences between methods the Electro-Fenton is described first.

In the Electro-Fenton process molecular oxygen and ferric ions are simultaneously reduced. Oxygen cathodic reduction in acidic media can be achieved using as electrode graphite causing oxygen reduction and producing H_2O_2 as eq. (40) shows [82].



The ferric ion is also reduced to ferrous ions as shown in Eq. 41.



The Fenton's reaction occurs when ferrous ions react with hydrogen peroxide as shown in Eq. 42.

Table 8. Treatment of industrial wastewater with hydrogen peroxide produced by electrolysis.

Type of wastewater	Electrode/ electrochemical cell	Operation conditions	Efficiency /main results obtained in terms of treatability	Ref.
Dye contaminated aqueous solution	TiO ₂ electrodes and Co and Ni doped TiO ₂ anodes, glassy carbon cathode	Potential difference -0.95 V between carbon and Hg/HgSO ₄ reference electrode	90 % color removal in 10 min	[180]
Textile wastewater	Open and undivided cell using graphite felt (cathode) and Pt (anode) in the presence of copper ions	pH=4, dissolved oxygen 7.8-7.9 mg/L, applied current 250 mA, 7 mM Cu ²⁺ concentration	67.9% decolorization and 56.3% COD removal after 210 minutes	[181]
Landfill leachate	Pt plate as anode and carbon-PTFE as cathode	pH 7, 0.05 M Na ₂ SO ₄ solution	87% of the TOC was removed after 4 h	[177]
Dye wastewater	Carbon/polytetrafluoroethylene (C/PTFE) cathode with a terylene diaphragm	steady concentration of 8.3 mg/L H ₂ O ₂ in the cathodic compartment after 80 min	80% COD removal	[182]
Pulp and paper making wastewater	graphite plate as electrodes assisted by transition metal (Co, Cu) modified kaolin	pH 3, current density 30 mA cm ⁻² , catalyst dose 30 g dm ⁻³	96.8% COD removal in 73 min	[183]

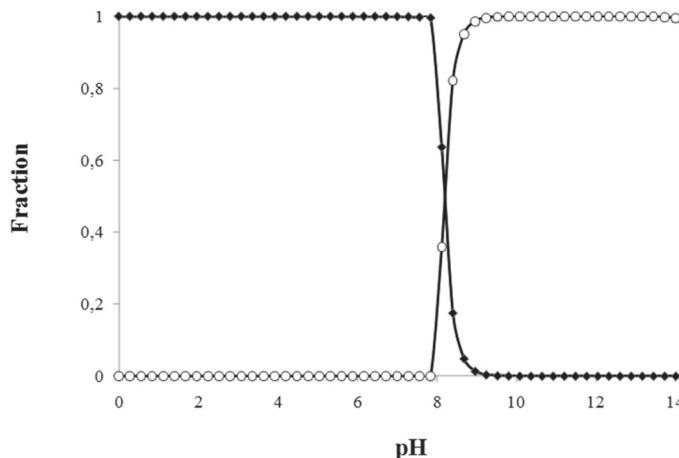


Figure 3. Predominance zone diagram for Fe(II) chemical species in aqueous solution. (◆) Fe^{2+} , (○) $\text{Fe}(\text{OH})_{2(s)}$.

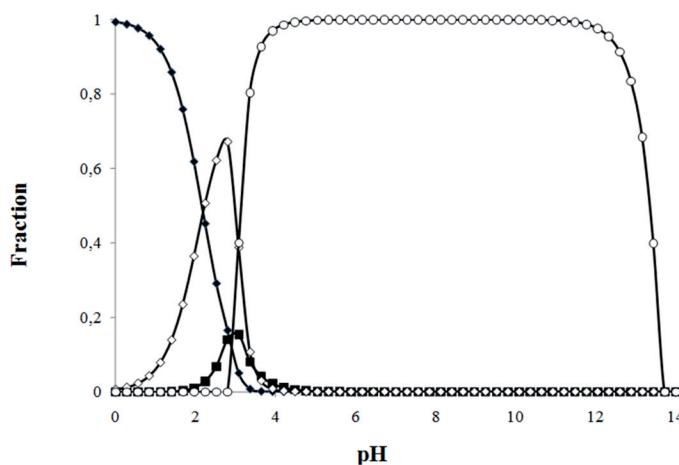


Figure 4. Predominance zone diagram for Fe(III) chemical species in aqueous solution. (◆) Fe^{3+} , (○) $\text{Fe}(\text{OH})_{3(s)}$, (◊) $\text{Fe}(\text{OH})^{2+}$, (■) $\text{Fe}(\text{OH})^{+}_2$.



Organic molecules are destroyed by the action of $\cdot\text{OH}$ radicals produced in the aqueous media. The hydroxyl radical can react with organic matter as reaction (43) indicates.



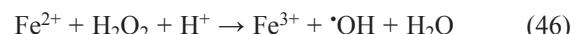
Therefore, the main advantage of adding and electrogenerating H_2O_2 is to produce this hydroxyl radical which will react with the organic pollutants present in the wastewater. The organic radical can react with oxygen or with a hydroxyl radical to produce oxidation products, as shown in reaction (44) and (45).



The Fenton's reagent (H_2O_2 , Fe^{2+}) is generated in situ and electrochemically catalyzed, since the produced Fe^{3+} can be reduced again to Fe^{2+} .

The Electro-Fenton process presents the following advantages: no addition of chemical reagents except a catalytic quantity of ferrous ions, no pollution displacement to another medium and a complete degradation of organic pollutants [83-87].

The peroxy-coagulation process uses a sacrificial iron anode to supply Fe^{2+} ions into aqueous solution and graphite is used as cathode, an oxidizing agent is produced in situ. These two species react in aqueous solution as eq. 46 shows:



The main advantage in this process is the use of sacrificial Fe anode which is electrodissolved supplying stoichiometric amount of Fe^{2+} , which reacts with electrogenerated H_2O_2 so the contaminants are removed by their degradation with $\cdot\text{OH}$ in aqueous solution and their coagulation with the formation of $\text{Fe}(\text{OH})_3(s)$. The H_2O_2 produced in peroxy-coagulation is completely consumed due to its fast reaction with the high Fe^{2+} concentration present in the medium giving a high concentration of oxidizing $\cdot\text{OH}$. It has been reported that efficient degradation of azo compounds can be achieved by this method compared with electrocoagulation [88-93].

Synergistic combination of oxidants is carried out typically in many electrochemical cells. Hydrogen peroxide and ozone are typically formed during electrolysis, directly on the surface of by the action of hydroxyl radicals.

Table 9 presents some of the applications of Electro-Fenton and peroxycoagulation processes that have been recently investigated.

Activation of oxidants produced in electrochemical processes by irradiation of light

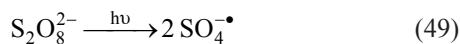
Light irradiation could enhance the effectiveness of many oxidants produced on the nearness of the electrode surface either by direct electron transfer on the electrode surface or by the action of hydroxyl radicals. Photo-activation of electrochemically generated reactive species, such as H_2O_2 or O_3 , by reactions such as those proposed in eq. 47 and 48 could increase the efficiency of the process through homogeneous catalysis.



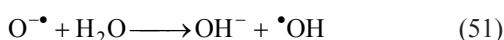
Thus, sulfate radicals and many other strongly-energetic species, in addition to hydroxyl radicals generated by ozone and hydrogen peroxide light assisted decomposition are expected to be produced. The production of sulfate radical from persulfate by light irradiation is shown in eq (49) [94, 95]. It is worth to take into account that the sulfate radical reacts typically 10^3 - 10^5 times faster than the persulfate [96].

Table 9. Treatment of industrial wastewater with Electro-Fenton and peroxicoagulation.

Type of wastewater	Electrode/ electrochemical cell	Operation conditions	Efficiency /main results obtained in terms of treatability	Ref.
Electro-Fenton				
Landfill leachate	Sacrificial iron anode	pH 3.0	72 % COD removal in 20 minutes	[184]
Olive oil mill wastewater	Sacrificial iron anode	pH 3.0	Mineralization in 9 h at 200 mA	[185]
Flame retardant industry wastewater	Sacrificial iron anode	pH 1.5	99.9 removal of P-compunds	[149]
Petrochemical industry wastewater	Sacrificial iron anode		94% COD removal in 5 h	[86]
Slaughterhouse wastewater	Sacrificial iron anode	pH 7.8, 6% H_2O_2 , current density 20 mA cm^{-2}	81% COD removal, 91% turbidity removal	[186]
Dairy industry wastewater	Iron anode and aluminum cathode	pH 6.5-7.0, current density 15 mA cm^{-2} , external H_2O_2 addition 3x 1000 mg L^{-1}	75% COD removal, 91% turbidity removal	[187]
Landfill leachate	Anode (Ti/RuO ₂ -IrO ₂)	pH 3, 0.34 mol/L H_2O_2 , 0.028 mol/L Fe^{2+} , current 2 A	80% COD removal	[188]
Alcohol distillery wastewater	iron electrodes	pH 4, current density 60 mA cm^{-2} , 0.3 M Na_2SO_4 and 60.000 mg L^{-1} H_2O_2	COD removal efficiency of 92.6% TOC removal efficiency of 88.7%	[189]
Photographic processing wastewater	BDD anode, carbon felt cathode. Single compartment cylindrical cell	pH 3, current 300 mA	90% TOC removal	[190]
Photographic processing wastewater	Pt anode, carbon felt cathode. Single compartment cylindrical cell	pH 3, current 300 mA	30% TOC removal	[190]
Wastewater	Platinized titanium electrode	Current density 340 mA cm^{-2} , ratio Fenton reagent to H_2O_2 1:20	100% COD and NH_4^+ removal after 4 h	[191]
Olive mill wastewater		pH 6.5, H_2O_2 g L^{-1} , current 20 A	52% COD removal	[192]
Tannery wastewater	Iron cathode and anode	pH 5, 1670 mg L^{-1} H_2O_2 , energy consumption 15 W	70% COD removal in 10 min	[193]
Landfill leachate	Aluminium electrodes	pH 3, $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ molar ratio 1, current density 49 mA cm^{-2}	94% COD removal and 95% color removal in 43 min	[194]
Landfill leachate	Aluminun electrodes	pH3, $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio 1, 28°C	75% coliform bacteria removal, 85% COD removal	[195]
Landfill leachate	Cast iron anode and cathode Electrodes	pH 4, 750 mg L^{-1} H_2O_2	85% COD removal	[196]
Rayon industry wastewater	Graphite cathode and iron anode	H_2O_2 dose of 1530 mg L^{-1} , current density of 0.90 A dm^{-2}	88% COD was reduced in 50 min	[197]
Fertilizer manufacturing wastewater	Iron anode and aluminum cathode	pH 3, H_2O_2 25mM, current density of 50 A m^{-2}	83% COD removal and 79% TOC removal after 45 min	[198]
Petrochemical wastewater	Stainless steel anode and cathode	pH 3.5, addition H_2O_2 800 mg L^{-1}	87% COD removal	[199]
Dyeing wastewater	Activated carbon fiber cloth anode	pH 3, current density 3.2 mA cm^{-2}	70% COD removal after 240 min	[200]
Peroxicoagulation				
Textile dye solution	Sacrificial iron anode, Carbon nanotube-PTFE electrode	pH 3, current 200 mA	95% color removal in 16 min	[201]
Pharmaceutical wastewater	Sacrificial iron anode, Iron cathode	pH 7, current density 1.9 mA cm^{-2}	55% COD removal after 1 h	[202]
Dye solution	Iron anode and gas-diffusion cathode	pH 3, 0.05 M Na_2SO_4 , current 100 mA	62% color removal in 10 min	[203]



Production of radicals from chlorine has been also described in literature [97, 98], being demonstrated that under non extreme pH, hydroxyl and chlorine radicals are the main end products resulting of the light assisted degradation of hypochlorite.



In literature, it has been also described the enhancement of electrolysis of organics with conductive-diamond electrodes, by irradiation of direct light to the surface of the diamond anode, due to the decomposition of the oxidants generated. To do that, a novel cell design was developed and the effects of chloride and sulfate media on results were described taking into account that hypochlorite and persulfates were formed during the oxidation [99].

Table 10 indicates the use of PEC in the removal of some pollutants with different electrodes.

Activation of oxidants produced in electrochemical processes by irradiation of ultrasound

During the last century, ultrasound irradiation has been used as an effective method for many applications including cleaning, sterilization, drying, degassing, homogenization, extraction, enhancement for chemical reactions, etc. Ultrasound irradiation consists of oscillating sound pressure waves with a frequency greater than the upper limit of human hearing (20,000 Hertz). Its action on chemicals is due to the ultrasonic cavitation, a phenomena caused by the formation, growth, and implosive collapse of bubbles generated when the liquid bulk is irradiated with ultrasound. The collapse of bubbles takes place in very short period of time [100] and, therefore, it can be considered as adiabatic. Because of that, high temperatures and pressures are reached within the bubble due to the gas compression. This causes a huge concentration of energy in a very small place, generating a hot spot, which results in a drastic local increment of the temperature reaching several thousands of Kelvin [101]. This energy is later on dispersed to the environment, which quickly reduces the temperature and the hot spot returns

to the ambient value. However, during a fraction of time, the very high temperature reached can produce significant changes in the chemical composition and to generate new radical species and components. This generation can be controlled by the dose of chemical species, in particular gases, although it must be taken into account that this addition may decrease the temperature of the hot spot. These results indicates that the gas molecules react, generating molecules that easily form radicals, such as oxygen, and therefore increasing the reactivity of the system [102].

In literature, one of the novel applications of ultrasound irradiation is the degradation of pollutants contained in wastewaters. It has been reported a work studying the destruction of six phthalates at low concentrations ($240 \mu\text{g dm}^{-3}$) [103]. This study revealed that ultrasound irradiation was able to remove the four higher molecular mass phthalates studied (di-n-butyl phthalate, butylbenzyl phthalate, di-(2-ethylhexyl) phthalate and di-n-octyl phthalate) within 30-60 min of irradiation. However, the lowest molecular weight phthalates studied (dimethyl phthalate and diethyl phthalate) required much longer irradiation times to be removed, indicating that they were more recalcitrant. This different behavior could be explained because of the different hydrophobicity of the phthalates studied.

Additionally to the applications combining ultrasound irradiation and chemistry (sonochemistry), there are many other applications combining ultrasound irradiation and electrochemistry (sonoelectrochemistry). Therefore, in the recent years, many works have been focused on sonoelectrosynthesis [104, 105], sonovoltammetry [106, 107], electrodeposition [108] electrode coating [109, 110] and electroanalysis [111, 112], etc.

Combination of ultrasound irradiation with electrolysis seems to be an interesting topic. Because of that, sono-electrolysis processes have also been widely studied in the recent years, being proposed as an adequate alternative for the treatment of different kind of wastewaters, leading to good removal efficiencies [106, 113-116]. Results obtained in these works indicate that ultrasound irradiation could be used to enhance mass transfer and to produce changes in the chemical composition of the electrolyte because of the cavitation phenomenon. This process can produce new radical species and components based on the very high pressure and temperature reached, during the implosive collapse of bubbles, when the system is irradiated with ultrasound [101, 102]. Both changes are complementary and even synergistic with the typical ones taking place during electrolysis, which results in a more effective process.

Table 10. Treatment of industrial wastewater with photo irradiation assisted electrolysis.

Type of wastewater	Electrode/ electrochemical cell	Operation conditions	Efficiency /main results obtained in terms of treatability	Ref.
Landfill leachate	DSA anode	UV light irradiation, current density 67.1 mA cm^{-2}	74 % COD removal	[204]
Dye contaminated aqueous solution	Co and Ni doped TiO_2 electrodes and TiO_2 electrodes	UV lamp 365 nm, $750 \mu\text{W cm}^{-2}$	90 % color removal in 10 min	[180]
Landfill leachate	Cast iron anode and cathode electrodes	pH 3, UV lamp 4 W, 2000 mg $\text{l}^{-1} \text{H}_2\text{O}_2$	70% COD removal	[205]

During the last years, electrolytic technologies have been deeply studied and applied for the treatment of many kinds of wastewaters. This has been promoted by the development of the conductive-diamond anode on p-Si support, a novel electrode material with very good properties [16, 18, 20, 117]. The robustness of this technology able to remove all organic pollutants known and its efficiency (100% current efficiency in the treatment of wastewaters when working down to 1000-2000 mg dm⁻³, the typical discharge limit of municipal sewers) are the two major advantages of this technology. The very good performance of this technology can be explained by the production and efficient participation of hydroxyl radicals in the destruction of pollutants [15, 118]. Moreover, it also promotes the generation of many other oxidants, enhancing the current efficiencies significantly with respect to the electrolysis with other anode materials. Its main drawback is low current efficiencies attained in the oxidation of low concentration of pollutants. This can be explained by the appearance of a limiting stage in the reaction caused by the mass transfer of pollutant from the liquid bulk to the anode surface. In this sense, the association of ultrasound with electrolysis seems to be a promising alternative to avoid the inefficiencies, because sono-electrolysis has shown to be able to improve the mass transfer rate and to promote the decomposition of water producing hydroxyl radicals and many oxidants from the interaction of these radicals with other species containing in the wastewater [25, 71, 119, 120].

In literature it has been described the degradation of dimethyl phthalate by electrolysis and sono-electrolysis with conductive-diamond electrodes. Dimethyl phthalate is a well-known plasticizer, widely found in wastewaters, hard to oxidize by ultrasound irradiation [103] and with an oxidation widely studied by many advanced oxidation processes [121, 122], including electrolysis with diamond [123]. Recently, it has been

described the oxidation by sono-electrolysis with great efficiencies [124].

Table 11 summarizes the use of sonoelectrolysis in the removal of some pollutants contained in actual industrial wastes.

Conclusions

The Electrochemical Advanced Oxidation Processes deals with the use of hydroxyl radical to attack the pollutants present in wastewater. This radical can be produced at the electrode surface such as in the direct electro-oxidation processes or in bulk solution such as in the indirect electrolytic processes. The aim in either case is to try to mineralize the pollutants. This technology should be used for the following reasons:

- Good quality of the treated wastewater for recycling into the original production process.
- Eliminate a further polishing water steps. Avoid the sludge generation and the need for sludge final disposal methods and the involved environmental impact.
- In the real applications, the AOP has been used to mineralize pollutants difficult to be oxidize by means of other processes such as those contained in textile, tannery, petrochemical and pharmaceutical wastewaters amongst others.

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Table 11. Treatment of industrial wastewater with ultrasound irradiation assisted electrolysis.

Type of wastewater	Electrode/ electrochemical cell	Operation conditions	Efficiency /main results obtained in terms of treatability	Ref.
Dye effluent	Pt electrodes	40°C, current 60 mA, 0.01 mol L ⁻¹ NaCl, ultrasound 20 kHz	95% COD removal	[106]
Cyan ink effluent	mild steel electrodes	18 V and 1 A.	20% COD removal after 3 h	[115]
Saline wastewater	-	-	Significant level of pollution attenuation was attained during first 15 minutes of electro-sonication. Power higher than 100 W did not render a significant increase in efficiency	[206]
Azo dyes effluent	Pt anode	pH 6, Na ₂ SO ₄ as electrolyte, 25°C, 22 kHz	90% removal after 6 minutes	[207]
Winery wastewater			77% COD removal when combining with electrocoagulation and ozonation-UV processes	[208]
Synthetic textile wastewater	Cast iron plate electrodes	pH 3, 35 kHz, DC current 250 mA, 800 mg L ⁻¹ H ₂ O ₂	95% COD removal	[209]

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