"ELECTROCHEMICAL ADVANCED OXIDATION PROCESSES: TODAY AND TOMORROW. A REVIEW"

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Abstract

In recent years, new Advanced Oxidation Processes based on the electrochemical technology, the so-called Electrochemical Advanced Oxidation Processes (EAOPs), have been developed for the

prevention and remediation of environmental pollution, especially focusing on water streams. These methods are based on the electrochemical generation of a very powerful oxidizing agent such as the hydroxyl radical (•OH) in solution, being then able to destroy organics up to their mineralization. EAOPs include heterogeneous processes like anodic oxidation (AO) and photoelectrocatalysis (PEC) methods, in which •OH are generated at the anode surface either electrochemically or photochemically, and homogeneous ones like electro-Fenton (EF), photoelectro-Fenton (PEF) and sonoelectrolysis (SE), in which •OH are produced in the solution bulk. This paper presents a general overview on the application of EAOPs to the removal of aqueous organic pollutants, firstly reviewing the most recent works and then looking to the future. A global perspective on the fundamentals and experimental set-ups is offered, and lab- and pilot-scale experiments are examined and discussed.

Keywords: EAOPs, anodic oxidation, electro-Fenton, photoelectrocatalysis, photoelectro-Fenton, sonoelectrochemistry, water treatment.

List of symbols and abbreviations

ADE	Air-Diffusion Electrode
AO	Anodic Oxidation
AOP	Advanced Oxidation Process
BDD	Boron-Doped Diamond
CF	Carbon Felt
CNT	Carbon Nanotube
COD	Chemical Oxygen Demand (mg of oxygen L^{-1})
DSA	Dimensionally Stable Anode
e^-	Electron
e^-_{CB}	Electron in the conduction band
E_{anod}	Anodic potential (V)
EAOP	Electrochemical Advanced Oxidation Process
E_{cat}	Cathodic potential (V)
EF	Electro-Fenton
GC-MS	Gas Chromatography coupled to Mass Spectrometry
h	Planck constant (6.626×10^{-34} m^2 kg/s)
HPLC	High Performance Liquid Chromatography

h^+_{VB}	Positively charged vacancy or hole in the valence band
PEC	Photoelectrocatalysis
PEF	Photoelectro-Fenton
R	Organic compound
ROS	Reactive Oxygen Species
RVC	Reticulated Vitreous Carbon
SE	Sonoelectrochemistry
SPEF	Solar Photoelectro-Fenton
TOC	Total Organic Carbon (mg of carbon L^{-1})
US	Ultrasounds
)))	Ultrasounds

Greek symbols

λ	Wavelength (nm)
ν	Frequency (Hz)

1 Introduction

In recent decades the rapid growth of public awareness about environmental problems has induced many governments to introduce legislation that prescribes and limits the emission of pollutants. This has been reflected in a notable increase in both research and the number of businesses concerned with the treatment of industrial effluents. Because of the extremely diverse features of industrial waste that usually contains a mixture of organic and inorganic compounds, no universal strategy of reclamation is feasible and it mainly depends on the nature and concentration of pollutants (Figure 1). As to the treatment of effluents polluted with organic compounds, biological oxidation is certainly the cheapest process, but the presence of toxic or biorefractory molecules may hinder this approach. The traditional incineration method poses problems of emission if the treatment conditions are not perfectly controlled, and above all it can be conveniently applied only for concentrated solutions (Figure 1). Chemical oxidation using chlorine, ozone or hydrogen peroxide is currently used for the treatment of biorefractory contaminants or at least to decompose them into harmless or biodegradable products. However, in some reactions, the intermediate products remain in the solution and they may entail a similar or even higher toxicity than the initial compounds. In these cases the

pollutants can be removed using a special class of oxidation technique known as Advanced Oxidation Processes (AOPs).

Within the framework of liquid polluted streams, AOPs can be broadly defined as aqueous phase oxidation methods based on the intermediacy of highly reactive species (primarily but not exclusively) in the mechanisms leading to the destruction of the target pollutant. Hydroxyl radical is a powerful oxidant (Table 1) which is able to non-selectively destroy most organic and organometallic contaminants until their complete mineralization into CO_2, water and inorganic ions. These radicals react rapidly with organics (R) mainly by the abstraction of a hydrogen atom (aliphatics) or addition on an unsaturated bond (aromatics) to initiate a radical oxidation chain:

$$RH + {}^{\bullet}OH \rightarrow H_2O + {}^{\bullet}R \quad (1)$$

$${}^{\bullet}R + O_2 \rightarrow ROO^{\bullet} \quad (2)$$

$$ROO^{\bullet} + RH \rightarrow ROOH + {}^{\bullet}R \quad (3)$$

$$ArH + {}^{\bullet}OH \rightarrow ArH(OH)^{\bullet} \quad (4)$$

$$ArH(OH)^{\bullet} + {}^{\bullet}O_2 \rightarrow [ArH(OH)OO]^{\bullet} \quad (5)$$

$$[ArH(OH)OO]^{\bullet} \rightarrow ArH(OH) + HO_2^{\bullet} \quad (6)$$

As summarized in Table 2, a large number of AOPs has been developed including non-photochemical and photochemical methods. The AOPs are successfully applied mainly for the treatment of wastewaters, but they are also used in many fields including groundwater treatment, soil remediation, municipal wastewater sludge conditioning, as well as odor and taste removal from drinking water.

In recent years, new AOPs based on the electrochemical technology, i.e., the so-called Electrochemical Advanced Oxidation Processes (EAOPs), have been developed [1-4]. The EAOPs provide several advantages for the prevention and remediation of pollution problems because electron is a clean reagent. Other advantages include high energy efficiency, amenability to automation, easy handling because of the simple equipment required and safety because they operate under mild conditions (room temperature and pressure) and versatility, since they can be applied to effluents with COD in the range from 0.1 g L^{-1} to 100 g L^{-1} (Figure 1). The main drawbacks of some of these technologies include the costs related to the electrical supply, the low conductance of many wastewaters that require the addition of electrolytes, and the loss of activity and shortening of the electrode lifetime by fouling due to the deposition of organic material on their surface. More specific advantages and disadvantages of the technologies will be discussed later.

Key EAOPs include anodic oxidation (AO), in which heterogeneous ${}^{\bullet}OH$ are generated at the anode surface, as well as electro-Fenton (EF), photoelectro-Fenton (PEF) and sonoelectrochemistry (SE) in which homogeneous ${}^{\bullet}OH$ are produced in the solution bulk. It is also possible to couple

various EAOPs such as the AO with EF, PEF or SE in order to produce both heterogeneous and homogeneous •OH.

The growing interest of academic and industrial communities in EAOPs is reflected in the high number of publications in peer-reviewed journals, patents and international conferences. Figure 2a illustrates that more than 50% of the papers published in the last 3 years are devoted to the AO, in particular using the innovative boron-doped diamond (BDD) anode, many papers study the EF and PEF processes, while only few researches are focused in the less conventional but evolving SE processes.

The efficiency and flexibility of the EAOPs have been proven by the wide diversity of effluents treated, as shown in Figure 2b, including either synthetic solutions containing phenols [5-8], dyes [9-12], pesticides [13-17] and drugs [18-20], or real/industrial effluents [21-25]. Despite the large number of publications on the EAOPs and the very good results obtained in laboratory scale tests, their practical application for the treatment of organic pollutants is still insufficient. But nowadays, thanks to intensive investigations that have improved the electrocatalytic activity and stability of electrode materials, optimized reactor geometry and deepened knowledge about reactor hydrodynamics, the EAOPs have reached an advanced stage of development and recently some pilot or full-scale plants have been effectively commercialized for disinfection and purification of wastewater polluted with organic compounds.

Up to date, one of the most developed large-scale applications of EAOPs is the automated disinfection of swimming pool water using BDD anodes. In this field dedicated products such as Oxineo® and Sysneo® have been developed for private and public pools. Compared to the other disinfection methods, these systems have the advantages that there is no chlorine smell, no accumulation of chemicals in the pool, no need of anti-algae and there is a residual action to avoid non-regular or jagged disinfections. Many of these systems have been already installed in private pools all over the world and several public pools and spas in Europe.

CONDIAS and Advanced Diamond Technologies Inc. develop and supply equipment for EAOPs, sold with the trademark of CONDIACELL® and Diamonox®, respectively, which are based on AO with BDD anode. Typical applications of these cells are: (a) water disinfection and (b) industrial wastewater treatment. Some details of the Diamonox® system are reported in Figure 3. For water disinfection, these cells produce a mixture of oxygen-based agents, such as •OH and ozone, directly by water electrolysis, providing high disinfection rate with low energy consumption, without addition of chemicals and they can either be used as a firewall or for volume disinfection.

The treatment of industrial wastewater is based on the production of hydroxyl radicals and other oxidants, such as chlorine, (per)bromate, persulfate, ozone, hydrogen peroxide, percarbonate,

and others, directly on site using only water, salt, and energy. The advantage of industrial wastewater treatment using these EAOPs is the possibility to degrade COD/TOC from a value of several hundred g O_2 L^{-1} to a minimum of a few mg O_2 L^{-1} or even µg O_2 L^{-1}, with the reduction of all organic water components by approx. 99%. Some other advantages related to these processes are the possibility of combination of EAOPs with common methods for wastewater treatment to achieve an optimal cost-effective operation and their easy modular adaptation and scale-up.

Another full-scale application of EAOPs is the EctoSys®, which is an extremely efficient system that provides a reliable and sustainable disinfection of the ballast water in an economical and ecological way. By applying electricity to the special electrodes, disinfectants are produced from the water directly in the piping to eliminate bacteria and organisms. In water with low salinity, the EctoSys® unit produces only hydroxyl radicals as active substances, while in brackish water or seawater, it produces short-living hydroxyl radicals and chlorine/bromine.

In 2007, a BDD electro-oxidation pilot plant (Figure 4) was installed in Marelo (Cantabria, Spain) for the treatment of landfill leachates using traditional and advanced oxidation technologies [26-29]. The plant was constituted by an aerobic treatment followed by chemical Fenton oxidation and a final AO treatment. The latter consists of an electrochemical reactor with BDD anodes of 1.05 m^2. The raw leachate contained about 2.8 g L^{-1} of TOC and 1.2 g L^{-1} of ammonia and the overall efficiency in the combined system was 99% of organic matter mineralization: 50% of the initial TOC was degraded in the aerobic treatment, 35% in the Fenton process and the remaining 15% in the final electro-oxidation step. The ammonia removal efficiency was greater than 90%, the 50% being due to the electrochemical treatment, since the Fenton process was unable to reduce the ammonia concentration.

This paper presents a general overview on the application of EAOPs to the removal of organic compounds, starting each section with a revision of the very last years and then giving a look to the future. A global perspective on the fundamentals and experimental set-ups is offered, and lab and pilot plant experiments are examined and discussed.

2 Production of oxidants by electrolysis, role of oxidants in mediated anodic oxidation

One of the key points to explain the high efficiencies reached by EAOPs in the removal of organic pollutants is the understanding of the role played by mediated oxidation processes in the

overall oxidation carried out during the treatment. Mediated oxidation in EAOPs can be understood as the oxidation of pollutants contained in wastewater by the chemical reaction between these compounds and oxidants produced previously on the electrode surfaces. Thus, AO does not only lead to the direct oxidation of organic pollutants on the anode surface, but it also promotes the formation of huge amounts of oxidants which can act not only on the surface of the electrodes but extend the oxidation process to the solution bulk of the treated waste [3]. The type and extension of the production of oxidants depend on many inputs, being the most relevant the electrode material and the occurrence of suitable raw matter for the production of oxidants in the wastewater. Their influence on the efficiency of EAOPs is very important because the oxidation of pollutants is extended from the vicinity of the electrode surface to the bulk of the electrolyte. However, it should be taken into account that these oxidants largely affect the mechanisms of the oxidation of pollutants and, occasionally, they can lead to the formation of unwanted intermediates or final stable products. Sometimes, the species that promote the formation of oxidants are not contained in the wastewater but added as reagents, which results in well-known and very effective processes. One of the most interesting examples is the treatment of wastes with Ag(II), whose formation was demonstrated to be very effective with conductive-diamond electrodes [30].

However, the most referenced example of mediated electrochemical oxidation arises from the effect of chlorides on the oxidation of organics. Chlorides are commonly contained in most wastewater flowstreams and they are known to be easily oxidized to chlorine by many types of anode materials (Eq. 7). This gaseous oxidant diffuses into the wastewater and forms hypochlorite and chloride in the reaction medium by disproportionation (Eq. 8 and 9). Deprotonation of hypochlorous acid produces hypochlorite (Eq. 10). Since hypochlorite is the primary final product, in literature is common to find the direct transformation of chloride into hypochlorite instead of the complete set of reactions (Eq. 11). However, the oxidation in that media is carried out by a mixture of reagents and the particular concentration of each species depends on the concentration and pH.

$$2\ Cl^- \rightarrow Cl_2 + 2\ e^- \quad (7)$$

$$Cl_2 + H_2O \rightarrow HClO + H^+ + Cl^- \quad \text{(acidic medium)} \quad (8)$$

$$Cl_2 + 2\ OH^- \leftrightarrows ClO^- + Cl^- + H_2O \quad \text{(alkaline medium)} \quad (9)$$

$$HClO + OH^- \leftrightarrows ClO^- + H_2O \quad (10)$$

$$Cl^- + H_2O \rightarrow ClO^- + 2\ H^+ + 2\ e^- \quad (11)$$

The resulting mixture (chlorine, hypochlorite and hypochloric acid) is highly reactive with many organics, being efficient for their mineralization [31,32]. However, it is also known to form many organochlorinated species as intermediates and final products that can be even more harmful than the

raw pollutant. Total depletion of these species is frequently very difficult and even the formation of low molecular weight products such as chloroform becomes a very significant problem, because it could lead to additional treatments increasing significantly the total cost of the remediation [5].

This is a negative and common example of the action of oxidants that does not exclude the promotion of the mediated oxidation processes in EAOPs, but alerts about some drawbacks and limitations of use. Thus, even with chlorides, when no organochlorinated by-products can be formed or when the oxidation of pollutants such as cyanide is aimed, formation of chlorinated oxidants is a great advantage and allows increasing the effectiveness of EAOPs. This is clearly observed in Figure 5 (obtained from data of [33]), where the electrochemical oxidation of cyanide synthetic wastes using sulfate and chlorine supporting electrolytes and three different anode materials is compared in terms of COD removal. As it can be clearly observed, degradation of cyanide is much faster when chloride is contained in the synthetic waste. Likewise, it can be observed that anode material does not behave as a simple sink of electrons but it has a clear role in the reactivity of the system.

Nevertheless, and despite the fact that chlorine mediated oxidation is very well known, it is not the only case of mediated oxidation processes and, of course, it is not the most significant one. Thus, when the objective is focused on the promotion of mediated oxidation, three important aspects should be taken into account:

- Direct electrochemical production of oxidants on the anode surface from non-oxidant species contained in the waste, and transport of these species towards the bulk (wastewater). The raw matter for the production of oxidants should be contained in the wastewater or dosed and, typically, it can be an ion (i.e., chloride, sulfate, etc.), an organic pollutant (acetic acid), dissolved gases (oxygen) or even water.
- Effect of the raw oxidants produced electrodically on the organic pollutants.
- Activation of oxidants in the bulk, that is, formation of highly reactive species from poorly reactive oxidants.

These three points are going to be studied in the following sections. Figure 6 shows a comprehensive summary of the main processes occurring during the oxidation of a pollutant contained in wastewater. It includes the mass transport of species from the bulk of the waste to the electrode surface and viceversa, and the main oxidation mechanisms that are going to be explained in this Section, including direct oxidation and different types of mediated oxidation that typically occur during EAOPs.

2.1 Direct electrochemical production of oxidants

For the formation of oxidants in electrochemical wastewater treatment processes, three main points should be considered:

- Direct oxidation of species on the anode surface, involving the formation of radical species that combine to produce stable oxidants.
- Oxidation of water to hydroxyl radical and further attack of this powerful oxidant to species promoting the formation of radicals. Then, the combination of radicals leads to the production of stable oxidants.
- Reduction of oxygen to produce hydrogen peroxide on the cathode surface.

In the following subsections, a detailed description of these three mechanisms is going to be carried out.

2.1.1 Production of oxidants from direct oxidation processes

The first process pointed out in this subsection is the direct oxidation of species on the anode surface with the subsequent formation of radical species that combine to produce stable oxidants. This is known to occur for many species present in wastewater, in particular for chlorine and peroxo-species, and also for ferrates. With some anode materials like diamond or PbO_2 coatings, formation of radicals from anions such as sulfate (Eq. 12), phosphate (Eq. 13), carbonate (Eq. 14) and even acetic acid is promoted. It can also be explained the formation of chloride radicals (Eq. 15) by this mechanism [34]. These processes are also known to occur with other electrode materials such as platinum, but the efficiency observed is much worse and concentrations produced are quite insignificant to produce an effect on the results of the treatment process [35].

$$SO_4^{2-} \rightarrow (SO_4^{-})^{\bullet} + e^{-} \quad (12)$$

$$PO_4^{3-} \rightarrow (PO_4^{2-})^{\bullet} + e^{-} \quad (13)$$

$$CO_3^{2-} \rightarrow (CO_3^{-})^{\bullet} + e^{-} \quad (14)$$

$$Cl^{-} \rightarrow Cl^{\bullet} + e^{-} \quad (15)$$

These radicals can combine according to reactions shown in Eqs. 16-19, which explains the occurrence of the stable oxidants in the reaction media, including peroxosulfates [36], peroxophosphates [37], peroxocarbonates [38] and chlorine [34].

$$(SO_4^{-})^{\bullet} + (SO_4^{-})^{\bullet} \rightarrow S_2O_8^{2-} \quad (16)$$

$$(PO_4^{2-})^{\bullet} + (PO_4^{2-})^{\bullet} \rightarrow P_2O_8^{4-} \quad (17)$$

$(CO_3^{-})^{\bullet} + (CO_3^{-})^{\bullet} \rightarrow C_2O_6^{2-}$ (18)

$Cl^{\bullet} + Cl^{\bullet} \rightarrow Cl_2$ (19)

Regarding chlorine, it is important to keep in mind that the efficiency is particularly high in electrolysis with some Mixed Metal Oxide (MMO) anodes in which this process is known to be promoted with respect to the water oxidation (DSA type electrodes). As mentioned before, this process produces a very active oxidation mixture, although it is not always a good way to remove organic pollutants because it promotes the formation of organochlorinated intermediates and final products. In addition, this reaction mixture can promote the formation of chlorates. This process is not always electrochemically based, but it is also chemically activated by a well-known disproportionation reaction (Eq. 20) and it is stimulated with the ageing of the reaction mixture [39]. Chlorate is usually an unwanted product in the effluent from an EAOP and its formation could also prevent the use of the EAOP technology in various applications.

$3\ ClO^{-} \rightarrow ClO_3^{-} + 2\ Cl^{-}$ (20)

Regarding direct oxidation, an unresolved case is the formation of ferrates, which have been used to explain the better efficiencies of some EAOPs when iron is present in the treated wastewater, even in electrocoagulation processes [40]. However, conditions used in EAOPs are far away from those required to produce them efficiently from Eq. 17 and it is very difficult to explain this observation in the light of the present knowledge [41].

$Fe^{3+} + 4\ H_2O \rightarrow FeO_4^{2-} + 8\ H^{+} + 3\ e^{-}$ (21)

2.1.2 Production of oxidants from hydroxyl radical mediated processes

For the second process under discussion in this subsection, the mediated production of oxidants by the action of hydroxyl radicals formed electrodically, it is important to know more about the production of such radicals in the reaction media. $^{\bullet}OH$ is an intermediate in the anodic oxidation of water to oxygen (Eq. 22) that is rarely detected in the reaction media, because it combines chemically to components of the anode surface before forming oxygen. In addition, it may be rapidly transformed into hydrogen peroxide (Eq. 23) and into hydroperoxyl radical (Eq. 24) [42].

$H_2O \rightarrow {}^{\bullet}OH + H^{+} + e^{-}$ (22)

$2\ {}^{\bullet}OH \rightarrow H_2O_2$ (23)

${}^{\bullet}OH + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O$ (24)

Oxidation of water to oxygen is an undesired side reaction in the electrochemical treatment of pollutants, because it seriously affects the efficiency of the process increasing significantly the

operation costs (it leads to a non valuable product). The electrodes in which hydroxyl radicals are not effective because they are not free on the surface of the electrode, were defined as active electrodes in a pioneering work of the group of Comninellis [43]. However, for some electrodes classified as non-active, it has been proposed that hydroxyl radicals cannot combine with the components of the electrode surface and then during a very short time, they are available to oxidize organics or other species such as anions contained in the waste [44]. This explains the formation of radical species and the increased efficiency in the production of oxidants when these anode materials are used, which even push some research not only for the treatment of wastewater [45,46], but also for the industrial production of these oxidants. Some of the reactions promoted by $^{\bullet}OH$ are summarized in Eq. 25 to 27 and some of the products formed after combination of radicals can be explained by formerly stated Eqs. 16-19 [35].

$$O_2 + 2\ {}^{\bullet}OH \rightarrow O_3 + H_2O \quad (25)$$

$$HSO_4^- + {}^{\bullet}OH \rightarrow (SO_4^-)^{\bullet} + H_2O \quad (26)$$

$$HPO_4^{2-} + {}^{\bullet}OH \rightarrow (PO_4^{2-})^{\bullet} + H_2O \quad (27)$$

In addition, some new oxidants can be formed by combination of hydroxyl radicals and the new radicals formed by their action [47]. Eqs. 28-30 show some examples.

$$(SO_4^-)^{\bullet} + {}^{\bullet}OH \rightarrow HSO_5^- \quad (28)$$

$$(H_2PO_4)^{\bullet} + {}^{\bullet}OH \rightarrow H_3PO_5 \quad (29)$$

$$CO_3^{-\bullet} + {}^{\bullet}OH \rightarrow HCO_4^- \quad (30)$$

This explains the formation of many new types of oxidants with this non-active materials and this also justifies the higher concentration measured. It also allows explaining the formation of some undesirable species such as chlorates and perchlorates in electrolysis of wastes containing chlorides with non-active electrodes, as it is shown in Eqs. 31-34 [48] and it may also shed light on the formation of rare species such as perbromate, as it is shown in Eq. 35 [49].

$$Cl^- + {}^{\bullet}OH \rightarrow ClO^- + H^+ + e^- \quad (31)$$

$$ClO^- + {}^{\bullet}OH \rightarrow ClO_2^- + H^+ + e^- \quad (32)$$

$$ClO_2^- + {}^{\bullet}OH \rightarrow ClO_3^- + H^+ + e^- \quad (33)$$

$$ClO_3^- + {}^{\bullet}OH \rightarrow ClO_4^- + H^+ + e^- \quad (34)$$

$$BrO_3^- + {}^{\bullet}OH \rightarrow BrO_4^- + H^+ + e^{-} \quad (35)$$

2.1.3 Production of hydrogen peroxide on the cathode

The third way to produce oxidants in the reaction media is very interesting because it complements very efficiently the two approaches described before. It consists in the production of hydrogen peroxide by reduction of oxygen on the cathode surface [50]. From the thermodynamic point of view, hydrogen peroxide is less powerful than oxygen but, kinetically, at room temperature, it is much more efficient. This means that a way to enhance the efficiency of an EAOP is promoting the formation of hydrogen peroxide by the otherwise unproductive reaction at the cathode. Production of hydrogen peroxide by reduction of oxygen develops in most cathode materials, but to increase efficiency some three boundaries points are required, that is, points in which cathode, water and oxygen are in contact. For this reason, a special type of porous cathode, known as gas-diffusion cathode, is employed for this application. Additional information about this process is going to be given in other Sections of this manuscript where Fenton processes are described.

2.2 Effect of the raw oxidants produced electrochemically on the reaction performance

There are many works in the literature in which the effects of the reaction media or small changes in the reaction media on the treatment results are assessed. These works demonstrate that reaction media have a large influence on results and that unexpected results were sometimes obtained [4,11,51,52]. Some illustrative examples are going to be highlighted:

- There are no significant differences in the oxidation of organics in sulfate and phosphate supporting electrolytes using BDD anodes, as it can be clearly observed in Figure 7, in which the influence of COD and supporting electrolyte composition on the instantaneous current efficiency is shown [53]. For many years, phosphate media was used as an inert media, because peroxophosphate production was not expected. The absence of significant differences between electrolyses carried out with organic solutions containing sulfates and phosphates allow realizing that peroxophosphates were produced efficiently, leading to the proposal of a method for their manufacture remove [54].
- The effect of current density is much smaller than expected according to predictions of electrochemical mass transport models [55,56]. This is also observed in Figure 7 in which no significant differences are observed between results obtained for the removal of 4-chlorophenol by AO with BDD anode at current densities within the range 150-600 A m^{-2}.
- The comparative AO of the same organic pollutant in chloride supporting media with DSA and BDD anodes reveals a better performance of DSA electrodes in spite of the expected best characteristics of BDD. With BDD anode, chlorides are not only oxidized to chlorine but also to

chlorate and perchlorate. At room temperature, these latter oxidants are not very effective and this explains the best performance of DSA, in which only chlorine and hypochlorite formation is promoted.

– With non-active electrodes, such as conductive diamond coatings, it is very difficult to find an inert supporting electrolyte and merely perchlorate seems to be the only supporting electrolyte in which no reactivity is obtained.

One important point regarding the oxidants produced during the electrochemical treatment of a particular wastewater is that they are not always detected in the reaction media although their effect is clearly observed by comparison of efficiencies when the composition of the raw wastewater is modified. In this context, the detection and quantification of oxidants during an electrolytic treatment can be understood as an indication of low reactivity of the oxidant with the pollutants contained in the wastewater and not as an improvement of the process performance. The best way to obtain a highly efficient process is to promote the activation of the oxidants produced electrochemically, either by chemical, sonochemical or photochemical methods.

2.3 Activation of oxidants produced electrochemically

As it has been described in the previous section, the reactivity of many of the raw oxidants produced in EAOPs with organics is not very high and some sort of activation is often required to obtain a clear improvement of the process. As an example of the improvement that such an activation can yield, an illustrative example can be considered: the transformation of peroxosulfate into sulfate radicals that may increase the process performance very significantly because sulfate radical typically reacts 10^3–10^5 times faster than the persulfate ions [57]. At this point, activation means formation of highly reactive species from the oxidants contained in the wastewater and, as it has been pointed out in Figure 5, there are three different modes:

– Chemical activation
– Activation by light irradiation
– Activation by ultrasound irradiation

2.3.1 Chemical activation of oxidants

Chemical activation is one of the more important ways to enhance the effectiveness of an oxidant. It involves the combination of the oxidant produced electrochemically with another species (not necessary an oxidant) which leads to the production of a third, very reactive species. This is the case of the well known Fenton processes [2] that are going to be described afterwards in this manuscript. In that processes, a metal ion (most likely iron(II) but also other transition metal cations) catalyzes the formation of hydroxyl radicals in the bulk from the decomposition of hydrogen peroxide. As it is known, hydrogen peroxide is a weak oxidant while hydroxyl radical is one of the more active oxidants known.

Another example of chemical activation is the synergistic combination of oxidants such as the resulting when ozone and hydrogen peroxide are combined (Table 2). This mixture also results in the production of important concentrations of hydroxyl radicals that explains the better efficiency of the processes in which formation of both oxidants is promoted.

Activation of hydrogen peroxide is very important in EAOPs because this species is produced on the cathode of the electrochemical cell and then, it can make double the efficiency of the oxidation processes if properly activated (raw hydrogen peroxide is not very active).

2.3.2 Activation by light irradiation

Light irradiation activation means the promotion in the formation of highly active species by UV light irradiation. This irradiation can be applied naturally (solar driven) or artificially (using UV lamps). Excluding heterogeneous photoelectrocatalytic processes on the surface of the anodes (typically based on the use of Mixed Metal Oxides (MMO) anodes with titanium dioxide as one of the components) because they are going to be reviewed afterwards, in this subsection light irradiation stands only for the decomposition of oxidants in the bulk upon the action of light. Thus, it is well known the photoactivation (or light assisted decomposition) of electrochemically generated reactive species, such as H_2O_2 or O_3, by reactions proposed in Eq. 36 and 37 [58].

$$H_2O_2 + h\nu \rightarrow 2\ {}^{\bullet}OH \quad (36)$$

$$H_2O + O_3 + h\nu \rightarrow 2\ {}^{\bullet}OH + O_2 \quad (37)$$

However, there are more processes with relevance in EAOPs [59]. Radical species are expected to be produced by light decomposition of peroxocompounds such as peroxophosphates, peroxosulfates and peroxocarbonates. As an example, production of sulfate radical from persulfate is shown in Eq. 38 [60,61].

$$S_2O_8^{2-} + h\nu \rightarrow 2\ (SO_4^{-})^{\bullet} \quad (38)$$

Production of radicals from chlorine has also been assessed in the literature [62,63], and it has been demonstrated that under non extreme pH, hydroxyl and chlorine radicals are the main products resulting from the light assisted degradation of hypochlorite (Eq. 39 and 40).

$$ClO^- + + h\nu \rightarrow O^{-\bullet} + Cl^{\bullet} \quad (39)$$

$$O^{-\bullet} + H_2O \rightarrow OH^- + 2\ {}^{\bullet}OH \quad (40)$$

2.3.3 Activation by ultrasound irradiation

Ultrasound (US) irradiation as a treatment technology consists in the production of a cyclic sound pressure with a frequency greater than the upper limit of human hearing (20,000 hertz) in the wastewater. Unlike expected, the main effect of US irradiation on chemicals is not based on the direct interaction of the mechanical acoustic field with chemical bonds of molecules but it is supported on the formation, growth, and implosive collapse of bubbles irradiated with the ultrasound (ultrasonic cavitation). This phenomenon takes place in very short moment and space and it can be considered as adiabatic [64]. As a consequence, high temperatures and pressures are reached inside the bubble due to gas compression. This increase in temperature and pressure generates a huge concentration of energy in a very small place known as hot spot [65]. This energy is dispersed to the surroundings so that the gas temperature in the hot spot quickly returns to the ambient value. However, during a very short time it can produce significant changes in chemical composition of the hot spot and can form new radical species and components and so, it can increase the reactivity of the system [66]. Hence, it is known the formation of hydroxyl radicals and, according to what it has been described before, this will account for the formation of many other oxidation species.

In addition, a further advantage in electrochemical system comes from the increase in the mass transport produced by the mechanical acoustic field which improves the efficiency of processes in which diffusion of pollutants is limiting the rate of direct anodic oxidation. The most representative and studied process that demonstrates such assertion is sonoelectro-Fenton, which will be discussed in Section 5.2.

2.4 Prospects

Perspectives of enhancing mediated oxidation for future EAOP developments seem favorable. As it has been pointed out along this section, mediated oxidation processes become the key point to attain an enhancement in the efficiency of EAOPs. Actually, it is not the production of oxidants, but

their activation in the reaction media the more interesting topic of research. Costs of US technology are very high and improvements in efficiency are not always as good as to propose their coupling with EAOPs. This is a direct consequence of the huge amounts of energy dispersed as heat or mechanical energy with this technology. Any novelty in this topic has to come from a more efficient use of energy in order to promote the formation of many hot spots in which radical reactions could be started up. In contrast, light irradiation already seems to be a very promising alternative with good perspectives to be used in the near future. The synergistic effect of the activation of oxidants has been clearly demonstrated and the energy irradiated is much lower than that applied in US irradiation.

3 Chemical and electrochemical generation of hydroxyl radicals based on Fenton's chemistry

The Fenton's reagent, a mixture of H_2O_2 and Fe(II), constitutes the basis of the chemical generation of the strong oxidant $^{\bullet}OH$. A pioneering work was reported by Fenton in 1894 on the oxidation of tartaric acid [67]. Fenton observed the enhancement of the oxidation power of H_2O_2 in the presence of iron(II) ions. Later, in the 1930s, Haber and Weis undertook a detailed work to clarify the mechanism of the reaction between H_2O_2 and Fe^{2+} (Eq. 41) and showed that Fenton's reagent led to the formation of $^{\bullet}OH$ [68]. They concluded that the catalytic decomposition of H_2O_2 by ferrous ion through a radical and chain mechanism constitutes the origin of the oxidizing power of the Fenton's system. The Eq. 41 was then named "Fenton's reaction".

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \quad (41)$$

More recent studies have demonstrated that the Fenton's reaction could be applied to the degradation/destruction of different type of organic pollutants [69-71] and, because of its significant development during the 20th century in the treatment of wastewater, several review papers have been focused on this process [72,73].

3.1 Fenton's reaction as a source of hydroxyl radicals

Sun and Pignatello showed that the Fenton's reaction can be applied in acidic pH of 2.8-3.0 to efficiently produce hydroxyl radicals [74]. At this pH, the Fenton's reaction (Eq. 41) can be propagated by the catalytic behavior of the Fe^{3+}/Fe^{2+} couple. Indeed, under excess of H_2O_2, ferrous ions can be generated according to the following reactions (Eqs. 42 and 43) in order to catalyse the Fenton's reaction [68]:

$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+$ (42)

$HO_2^{\bullet} + Fe^{3+} \rightarrow Fe^{2+} + O_2 + H^+$ (43)

However, $HO_2^{\bullet}$ radical has a lower oxidation power compared to $^{\bullet}OH$ and, consequently, it is less reactive towards organic pollutants. Besides, these reactions are much slower than Fenton's reaction and lead to the accumulation of Fe^{3+} in the medium, causing the formation of sludge in the form of $Fe(OH)_3$. In addition to pH value, the concentrations of H_2O_2 and Fe^{2+} and their ratio ($[H_2O_2]/[Fe^{2+}]$) play a significant role regarding the practical efficiency of the Fenton process, and have to be optimized for each specific case [75], since for high concentrations, the reagents H_2O_2 and Fe^{2+} react with $^{\bullet}OH$ through the following wasting reactions, Eqs. 40 and 41, that harm significantly the process efficiency.

$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + HO_2^{\bullet}$ (44)

$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^-$ (45)

The Fenton process was applied to the oxidation of organics and treatment of wastewaters starting from the 1960s [76], and many applications were developed in the 1990s [71,77]. However, several studies have shown the limitations of this process in several cases, and the following drawbacks have been highlighted: (i) high cost and risks due to the providing, storage and transport of H_2O_2, (ii) accumulation of iron sludge that must be removed at the end of the treatment, and (iii) lower mineralization efficiency due to the presence of wasting reactions and, as a consequence, the potential formation of intermediates that are more toxic than raw pollutants. Therefore, to improve the practical application for the treatment of wastewaters, the Fenton process has been coupled to other physicochemical processes like coagulation-flocculation, membrane filtration and biological oxidation, in order to eliminate organic pollutants more effectively [78].

3.2 Electro-Fenton process: principles and running

The EF process is among the most known and popular EAOPs and constitutes an indirect electrochemical way to generate $^{\bullet}OH$ in aqueous solutions. It was developed and extensively applied over the last decade, particularly by Brillas' and Oturan's groups since the 2000s [2,79,80]. This process has been developed in order to achieve the implementation of a new and powerful advanced oxidation method by avoiding the drawbacks of the chemical Fenton process. Indeed, it can be defined as an electrochemically assisted Fenton process. $^{\bullet}OH$ is produced via the Fenton's reaction (Eq. 41),

in which Fenton's reagent is electrochemically generated in situ avoiding the use of high quantities of H_2O_2 and iron(II) salt.

The H_2O_2 production rate is one of the crucial parameters of the process efficiency, since the rate of Fenton's reaction is predominantly controlled by this parameter. It can be continuously supplied to the wastewater solution to be treated in an electrochemical reactor from the two-electron cathodic reduction of oxygen gas, directly injected as compressed air, by Eq. 46:

$$O_{2(g)} + 2\ H^+ + 2\ e^- \rightarrow H_2O_2 \quad (46)$$

The current efficiency of H_2O_2 production is generally not very high and depends on some factors such as operating conditions (O_2 solubility, temperature, pH) and cathode properties. It can be destroyed by parasitic chemical decomposition (Eq. 47), cathodic reduction (divided cell) (Eq. 48) or anodic oxidation (undivided cell) (Eq. 49 and 50) resulting in a slower accumulation in the bulk. Therefore, the use of optimal operating conditions (acidic pH, ambient temperature, etc.) and an appropriate cathode material are important to obtain better production rates.

$$2\ H_2O_2 \rightarrow O_{2(g)} + 2\ H_2O \quad (47)$$

$$H_2O_2 + 2\ H^+ + 2\ e^- \rightarrow 2\ H_2O \quad (48)$$

$$H_2O_2 \rightarrow HO_2^{\bullet} + H^+ + e^- \quad (49)$$

$$HO_2^{\bullet} \rightarrow O_{2(g)} + H^+ + e^- \quad (50)$$

Several cathode materials such as mercury, graphite, carbon-PTFE O_2-diffusion, and three-dimensional electrodes like carbon felt (CF), activated carbon fibre, reticulated vitreous carbon, carbon sponge, and carbon nanotubes [81-84] were tested for H_2O_2 production. Based on the results published nowadays, 3D CF and carbon-PTFE O_2-fed cathodes seem to constitute better cathode material for efficient H_2O_2 generation; the use of Hg has been disregarded owing to its potential toxicity.

The second component of the Fenton's reagent, i.e., the Fe^{2+} ion, is initially introduced in a catalytic amount (typically 0.1 mM) in the form of ferrous (or ferric) salts, and is regenerated electrocatalytically (Eq. 51) from reduction of Fe^{3+} formed by Fenton's reaction.

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (51)$$

Thus, the Fenton's reagent is continuously produced in the solution to be treated in a catalytic way, producing $^{\bullet}OH$ via Fenton's reaction to ensure the destruction of organic pollutants in aqueous medium. Formed $^{\bullet}OH$ quickly reacts in the bulk with organics leading to their oxidation/mineralization following Eq. 48 and 49.

$$\text{Organic pollutants} + {}^{\bullet}OH \rightarrow \text{oxidation intermediates} \quad (52)$$

$$\text{Intermediates} + {}^{\bullet}OH \rightarrow \rightarrow \rightarrow CO_2 + H_2O + \text{inorganic ions} \quad (53)$$

Compared to the classical Fenton process, the main advantages of the EF process are: (i) in situ and controlled generation of Fenton's reagent (cost effectiveness), avoiding thus the risks related to transport, storage and handling of H_2O_2, (ii) elimination of parasitic reactions that wasting $^{\bullet}OH$ (very low Fenton's reagent concentration), (iii) total mastership of the processing by current or potential control, (iv) possibility of controlling the degradation kinetics and performing mechanistic studies, and (v) almost total mineralization of organics including the intermediates.

3.3 Influence of applied current on the oxidation/mineralization efficiency

A number of operating parameters has influence on the process efficiency: solution pH, applied current, catalyst (Fe^{2+}) concentration, supporting electrolyte, organic load, etc. Although the optimal value of pH is well known to be 2.8 [74], the process can effectively occur within the range $2.5 < pH < 3.5$.

The nature and concentration of the used catalyst play a significant role in the EF process. To be used in EF, the catalyst should be one of the forms of the redox couple, both forms being soluble in water to allow the electrogeneration of the reduced form in homogeneous medium. To clarify the effect of the nature of the catalyst, a number of $M^{z+}/M^{(z-1)+}$ couples were investigated [85-89]. Cu^{2+} showed good catalytic characteristics in combination with Fe^{2+} or Fe^{3+} [85,89], but when used alone, high concentrations are needed for obtaining the same efficiency than Fe^{2+} [88]. Mn^{2+} was found to be a good candidate in replacement of iron ions when their use is compromised [87]. Co^{3+} and Ag^{+} exhibited catalytic behavior similar to that of Fe^{2+} [86], but their use should be disregarded due to their ecotoxicity. Usually, Fe^{2+} (or Fe^{3+}) behaves as the best catalyst in EF process, particularly because it acts efficiently at lower concentrations, typically about 0.1 mM. In this case, the oxidation/mineralization of organic pollutants occurs efficiently at low concentrations, but the effectiveness of the process decreases with increasing Fe^{2+} concentration, in particular at long treatment times [90], due to the enhancement of the rate of the parasitic reaction (45).

The applied current (or current density) is the most important operating parameter of the EF process, since this parameter governs the rate of generation of H_2O_2 (Eq. 46), as well as the regeneration rate of Fe^{2+} (Eq. 51) and, consequently, the rate of generation of $^{\bullet}OH$ from Fenton's reaction (Eq. 41). In general, the rate of the process increases with applied current since more $^{\bullet}OH$ is formed at a given time. On the other hand, the applied current cannot be increased indefinitely, since high current values promote parasitic reactions leading to the decrease in current and process efficiencies. In particular, the applied current should not reach the reduction potential of H_2O_2 (Eq.

49 and 50) in order to preserve it in the solution. Another wasting reaction that becomes enhanced when increasing the applied current is the evolution of H_2 at the cathode. Figure 8 clearly shows the effect of the applied current in the case of the oxidation of 0.125 mM of the herbicide picloram in aqueous medium at pH 3.0 by EF process [91]. As can be seen, the oxidation kinetics was enhanced with applied current from 50 to 300 mA, although the increase in decay kinetics was not proportional to current due to the gradual enhancement of the parasitic reactions. Further increase in applied current did not yield a positive effect on the oxidation kinetics as shown for the case of 500 mA. Worth noting, the oxidation process was very fast, and the total disappearance of picloram was reached within less than 5 min for applied current values of 200, 300 and 500 mA. Therefore, the value of 200 mA can be considered as the optimal value in order to minimize the energy consumption at practically the same reaction time.

Classical EF process has been initiated by using Pt as the anode. In this case, the process occurs mainly in the bulk solution by $^{\bullet}OH$ generated homogeneously through the Fenton's reaction. Recently, a significant enhancement has been attained by replacing the Pt anode with the more effective BDD anode. The use of BDD anode makes the EF process more potent, since this anode allows generating supplementary heterogeneous hydroxyl radicals (BDD($^{\bullet}OH$)) at its surface (Eq. 54), in addition to those produced in bulk solution from Fenton's reaction. The use of BDD anode in EF process provides also three other advantages: i) the oxidizing power of BDD($^{\bullet}OH$) is higher than other anodes due to a larger O_2 overvoltage, ii) BDD($^{\bullet}OH$) is physisorbed at the surface and thereby more easily available (compared to Pt anode), and iii) high oxidation window of BDD anode (about 2.5 V) allows the direct oxidation of organic pollutants [92].

$$BDD + H_2O \rightarrow BDD(^{\bullet}OH) + H^+ + e^- \quad (54)$$

A recent and interesting study clearly showing the improvement of the EF process by using BDD anode reports the mineralization of the refractory herbicide atrazine [42]. Indeed, a large variety of AOPs have been already applied to oxidative degradation and/or mineralization of atrazine. However, in all cases they yielded the persistent end-product cyanuric acid as predominant by-product, with 40-60% mineralization yields, corresponding to the mineralization of the side-chains of the molecule. In contrast, the use of a BDD anode in the EF process permitted to obtain an almost total mineralization (97% TOC removal) of atrazine aqueous solutions (Figure 9). The great mineralization power of EF with BDD anode relative to the classical process with Pt anode can be clearly appreciated. In addition, the authors showed in the same study that cyanuric acid, which was already reported as recalcitrant to $^{\bullet}OH$, can also be almost completely mineralized thanks to the action of BDD($^{\bullet}OH$) that is more potent than $^{\bullet}OH$ in the mineralization of some recalcitrant organics like carboxylic acids.

3.4 Some recent applications

Since the publication of the first reports on the treatment of wastewaters by EF process [79,80], it has been significantly developed and applied to the treatment of a large variety of wastewaters polluted by toxic and/or persistent organic pollutants such as pesticides [93,94], synthetic dyes [11,95-97], industrial pollutants [98,99], pharmaceuticals and personal care products [100,101], landfill leachates [102], reverse osmosis concentrates [50], and many others. Among all these applications, three applications are especially detailed in the following paragraphs.

The first application deals with the effect of chlorine atom substituent on the oxidation efficiency of the process [103]. This study reports the comparative kinetics of the degradation of several chlorophenols such as monochlorophenols (2-chlorophenol (2-CP) and 4-chlorophenol (4-CP)), dichlorophenols (2,4-dichlorophenol (2,4-DCP) and 2,6-dichlorophenol (2,6-DCP)), trichlorophenols (2,3,5-trichlorophenol (2,3,5-TCP) and 2,4,5-trichlorophenol (2,4,5-TCP)), 2,3,5,6 tetrachlorophenol (2,3,5,6-TeCP) and pentachlorophenol (PCP), using a CF cathode and a Pt anode. It was demonstrated that the number and the position of the chlorine atoms in the aromatic ring influences significantly the oxidation and mineralization kinetics of chlorophenols. This effect was evaluated in terms of apparent and absolute rate constants of the reaction between $^{\bullet}OH$ and chlorophenols. Apparent rate constants were measured following the pseudo-first order kinetics and have been found that decreased with increasing the number of chlorine atoms, in the sequence: 4-CP > 2-CP > 2,4-DCP > 2,6-DCP > 2,3,5-TCP > 2,4,5-TCP > 2,3,5,6-TeCP > PCP. Then the absolute rate constants of second order reaction between chlorophenols and $^{\bullet}OH$ were determined by the competition kinetics method. The values of the absolute rate constants (k_{abs}) were in the 3.56-7.75 $\times$ 10^9 M^{-1} s^{-1} range, following the same sequence of the apparent rate constants (Table 3). The mineralization of several chlorophenols and of their mixture was also carried out by monitoring with TOC removal percentage. Results showed that more highly chlorinated phenols were more difficult to mineralize, the mineralization rate decreasing when increasing the number of chlorine atoms.

The second application focuses on the assessment of solution toxicity when treated by EF process. Indeed, important efforts have been devoted to studies on the removal of a new class of emerging pollutants, the pharmaceuticals and personal care products, because of their occurrence in natural waters and their potentially toxic effects on aquatic species [101]. The removal of many of these substances was studied, including treatment efficiency, determination of apparent and absolute rate constants, mechanistic assessments and mineralization pathways [100,103,104]. A recent study

devoted to removal of the antibiotic sulfamethoxazole from water by EF process focused on a special issue like the changes in the solution toxicity during the treatment [104]. The evolution of global toxicity of the treated solution was monitored by Microtox® bioluminescence method, in which the toxicity is expressed as inhibition percentage of the luminescence of the *Vibrio fischeri* bacteria. Figure 10 highlights an interesting behavior during the EF treatment of sulfamethoxazole. Inhibition percentages were measured after exposition of bacteria to the solution for 15 min. Inhibition curves obtained during application of different applied currents exhibited different peaks appearing as a function of the treatment time. These inhibition peaks can be related to the formation of primary, then secondary or tertiary aromatic (and/or cyclic) intermediates formed during the treatment. The strong increase of the global toxicity at the beginning of the treatment revealed the formation of some oxidation intermediates that were more toxic than the parent compound. This is a behavior often observed during the application of AOPs. Figure 10a shows a strong increase of the luminescence inhibition between ca. 10 min (for I = 300 mA) and 60 min (for I = 30 mA) of treatment. Then, a rapid decrease occurs with appearance/disappearance of minor inhibition peaks at electrolysis times of 30-180 min. As indicated by different curves, the solution toxicity was more quickly eliminated with higher current values. The time-related shifts of luminescence inhibition peaks with the current value can be explained by different formation rate of $^{\bullet}OH$ depending on applied current. As explained above in section 3.3, the formation rate of $^{\bullet}OH$ is governed mainly by applied current, and increases from 50 to 300 mA (Figure 8). As a consequence, the sulfametoxazole and its by-products were mineralized more quickly leading to a rapid decrease in solution toxicity. The HPLC analyses indicated that 3-amino-5-methylisoxazole (AMI) and *p*-benzoquinone (BZQ) were the primary oxidation by-products of sulfametoxazole. To clarify the relative toxicity of these intermediates, their diluted solutions were treated under the same operating conditions. Figure 10b was obtained from diluted solutions of AMI and BZQ effectively attained during the EF oxidation of sulfamethoxazole, and allowed demonstrating that both aromatic (and/or cyclic) intermediates were, at least partly, responsible for the rise of toxicity of sulfamethoxazole solutions, because, at least, one of the major intermediates like BZQ is significantly more toxic than sulphametoxazole towards the *Vibrio fischeri* bacteria.

The third application concerns the removal of the antibiotic drug sulfachloropyridazine from water and its mineralization pathway during the treatment of its aqueous solution by EF process [105]. The suggested mineralization pathway includes fifteen cyclic intermediates (identified by HPLC and GC-MS analyses), five aliphatic carboxylic acids (oxalic, maleic, pyruvic, glyoxylic, and malic acids), and a mixture of released inorganic ions (Cl^-, SO_4^{2-}, NH_4^+, and NO_3^-). Based on the action of

•OH onto four different sites of sulfachloropyridazine, a detailed scheme for the complete mineralization of sulfachloropyridazine was proposed. The reaction of •OH with this pharmaceutical yielded different primary cyclic by-products according to pathways A-D shown in Figure 11. Pathways A and B involve the formation of five benzenesulfonamides promoted by consecutive hydroxylation steps with or without Cl^- release. Pathways C and D occur simultaneously and include the oxidative cleavage of the structure, leading to the formation of a dozen pyridazine and benzenic derivatives. Among these intermediates, 3-amino-6-chloropyridazine (ACP) and BZQ were detected as major intermediates. Successive hydroxylation of the primary intermediates weakens the structure and promotes their ring breaking to yield carboxylic acids, accompanied by the release of inorganic ions like chloride, sulfate, ammonium and nitrate. In addition, the time course of some available reaction intermediates such as ACP and BZQ was satisfactorily correlated with the toxicity profiles determined from Microtox® method in terms of inhibition of *Vibrio fischeri* luminescence. ACP and BZQ, which are the predominant intermediates, were found responsible of the strong increase of toxicity during the first stages of treatment.

3.5 Prospects

The EF process emerged as an environmentally-friendly AOPs about ten years ago, mainly in its two basic versions based on the nature of the cathode material: CF and carbon-PTFE gas diffusion electrode. Nowadays, there are several dozen groups studying and publishing works related to this process. It is very largely investigated at lab-scale, mainly in its two initial versions. The use of the emergent BDD anode significantly enhanced the oxidation power and mineralization efficiency due to the production of supplementary hydroxyl radicals at the anode surface. Therefore, this technology becomes now mature enough for passing to pilot-scale reactor design and application to treatment of large volumes of wastewaters.

The first step will be the conception and design of a pilot-scale reactor. This conception can include combined processes to increase the effectiveness of the treatment. Both batch reactor and continuous (flow) reactor should be considered. The modelling of the process can be useful to optimize the operating parameters and predict the behavior of pollutants and can help for economical and practical application to the real wastewater treatment.

The design of a tubular reactor can constitute an interesting way to reach continuous treatment. A joint project focused on the coupling of EF with nanofiltration in which a carbonaceous material is suggested as both filter and cathode, was recently applied for funding to French ANR (National Research Agency) by three French universities (including LGE laboratory of Université Paris-Est) and a company of the field. The second step will consist of checking if the parameters optimized at lab-scale could be considered for the work in the pilot-scale reactor, before the stage of industrial-scale reactor. Otherwise, the key parameters should be optimized at pilot-scale.

The coupling with a biological process as pre- or post-treatment unit is another promising way for a cost-effective treatment. Some recent studies have shown the feasibility of such a coupling. Indeed, the EF process is able to transform toxic and/or biorefractory molecules to biodegradable species during a short treatment time. The complete mineralization of solutions thus obtained can then be achieved by biological treatment.

To develop cost-effective treatments, the use of green and cheap energy source based on sunlight-driven electrical power systems such as an EF reactor directly powered by photovoltaic panels can also be considered.

4 Photoelectrochemical processes

There is an increasing interest in the use of photoelectrochemical processes for water and wastewater remediation. These photoassisted treatments are based on the irradiation of a contaminated solution or a photoactive electrode with UV or solar light [2,4,106,107]. UVA (λ = 315-400 nm), UVB (λ = 285-315 nm) and UVC (λ < 285 nm) lights supplied by UV lamps as energy sources are commonly employed. The intensity and wavelength of such radiations have significant effect on the destruction rate of organic pollutants. However, the excessive economical cost of artificial light sources for the application of UV-assisted processes is worthy of consideration. This is solved in solar-assisted processes where sunlight (λ > 300 nm) is used as a free, inexpensive and renewable energy source, although frequently the influence of this radiation has been assessed using a solar simulator device. Hereafter, the characteristics and main applications of the most interesting photoelectrochemical processes including photoelectro-Fenton (PEF), solar photoelectro-Fenton (SPEF) and photoelectrocatalysis (PEC), as well as hybrid systems, are described.

4.1 Photoelectro-Fenton (PEF) and solar photoelectro-Fenton (SPEF)

PEF with artificial UVA light and SPEF, its derived sunlight-assisted method, have been envisaged and widely developed by the Brillas' group. These processes involve the treatment of the contaminated solution under EF conditions along with the simultaneous irradiation with UVA or solar light to accelerate the mineralization rate of organics. Oxidizing hydroxyl radicals are produced from Fenton's reaction (Eq. 37), while the undesired accumulation of refractory Fe(III) ions that decelerate the treatment is avoided by the reductive photolysis of $[Fe(OH)]^{2+}$, the predominant Fe(III) species in solution at pH 2.8–3.5, according to photo-Fenton reaction (Eq. 51), thereby regenerating Fe^{2+} (i.e., the catalyst in Fenton's reaction) and producing more radicals [2,4]:

$$[Fe(OH)]^{2+} + h\nu \rightarrow Fe^{2+} + {}^{\bullet}OH \quad (55)$$

The radiation can also promote the photolysis of some oxidation intermediates or their Fe(III) complexes, allowing the regeneration of Fe^{2+} as occur in photodecarboxylation reactions:

$$Fe(OOCR)^{2+} + h\nu \rightarrow Fe^{2+} + CO_2 + R^{\bullet} \quad (56)$$

$$2\ Fe(C_2O_4)_n^{(3-2n)} + h\nu \rightarrow 2\ Fe^{2+} + (2n-1)\ C_2O_4^{2-} + 2\ CO_2 \quad (57)$$

The Brillas' group studied the degradation of drug residues like paracetamol [18], clofibric acid [108], ibuprofen [109], atenolol [20] and flumequine [110], as well as the herbicide cyanazine [17], using a small stirred and thermostated tank reactor containing solutions of 100 mL. A Pt or BDD anode and a carbon-PTFE gas-diffusion cathode, all with 3 cm^2 area, were used. The cathode was fed with O_2 or air for continuous H_2O_2 production. In EF, PEF and SPEF, 0.5 mM Fe^{2+} was usually added as catalyst. A 6 W UVA lamp of λ_{max} = 360 nm was applied in PEF, whereas the SPEF process was made under direct solar irradiation with an average UV intensity of ca. 31 W m^{-2}.

As an example, Figure 12a shows the TOC decay vs. electrolysis time for the comparative EF, PEF and SPEF treatment of 100 mL of 41 mg L^{-1} ibuprofen in 0.05 M Na_2SO_4 with 0.5 mM Fe^{2+} at pH 3.0, 33.3 mA cm^{-2} and 25.0 ºC [109]. The performance of each process increased using a BDD anode instead of a Pt one, as expected by the higher oxidizing power of BDD($^{\bullet}OH$) compared to Pt($^{\bullet}OH$) generated at the corresponding anode surface from water oxidation [3]. The UVA light in PEF enhanced the EF degradation, reaching even more quickly the almost total mineralization in SPEF. For all treatments, the optimal pH value was 3.0, close to the optimum pH of 2.8 for Fenton's reaction [2], and no more than 0.5-1.0 mM Fe^{2+} had to be added. The mineralization current efficiency of SPEF trials was greater than that of EF and PEF assays, and it rose when current density decreased. Figure 12b shows that ibuprofen concentration was removed at a similar rate in EF and PEF, in agreement with a pseudo-first-order reaction, yielding an apparent rate constant (k_1) of about 2.1 ×

10^{-3} s^{-1}. The ibuprofen decay was strongly accelerated in SPEF, as expected if more •OH is produced from the photolytic reaction (Eq. 55) due to the higher UV intensity of sunlight. GC-MS and reversed-phase HPLC analysis of treated solutions revealed the formation of aromatic products like 4-ethylbenzaldehyde, 4-isobutyl-acetophenone, 4-isobutylphenol and 1-(1-hydroxyethyl)-4-isobutylbenzene. Ion-exclusion HPLC allowed the identification and quantification of oxalic acid as the ultimate short-chain carboxylic acid accumulated to a larger extent. Indeed, it could not be removed by EF, but it disappeared quickly by PEF and much faster by SPEF owe to the fast photolysis of its Fe(III) complexes by Eq. 57. This behavior explains the higher mineralization degree attained in PEF and SPEF (see Figure 12a).

The use of Cu^{2+} as co-catalyst in EF and PEF was explored for the degradation of 157 mg L^{-1} paracetamol at pH 3.0 using a Pt/O_2-diffusion cell [18]. The combination of 1 mM Fe^{2+}, 1 mM Cu^{2+} and UVA light was unique, since it led to almost TOC removal after 4 h of electrolysis at 100 mA cm^{-2}. The synergistic effect of all catalysts promoting the quickest decontamination was explained considering that •OH in the bulk destroys the Cu(II)-oxalate and Cu(II)-oxamate complexes, whereas the competitively formed Fe(III)-oxalate and Fe(III)-oxamate complexes are photolyzed by UVA light.

The studies performed with other pollutants [17,20,108,110] confirmed the superiority of PEF over analogous EF treatments and BDD over Pt. For example, for the mineralization of 100 mL of 179 mg L^{-1} clofibric acid with 1.0 mM Fe^{2+} of pH 3.0 using a Pt/O_2-diffusion cell at 100 mA cm^{-2}, 92% TOC removal for PEF vs. only 73% for EF was obtained. The use of BDD in PEF led to a quicker degradation, with more than 96% TOC decay for the same current density at 4 h. A similar k_1 value of $(1.35\pm0.10)\times10^{-2}$ s^{-1} was obtained for all the EF and PEF treatments, a value much greater than that obtained for the anodic oxidation AO process, thus confirming the higher reactivity of •OH formed in the bulk to remove aromatics compared with that of Pt(•OH) or BDD(•OH). Besides, single Pt/air-diffusion electrode (ADE) and BDD/ADE cells and their combinations with a Pt/CF one were checked for the treatment of 100 mL of 158 mg L^{-1} atenolol with 0.5 mM Fe^{2+} at pH 3.0 [20]. While in EF the combined cells led to a greater mineralization than the single ones because of the enhanced generation of the main oxidant •OH, in PEF atenolol was mineralized at a similar rate using both kinds of cells because of the quick photolysis of the iron complexes under UVA irradiation. The GC-MS and HPLC analyses of solutions with aromatic pollutants treated by PEF corroborated that hydroxylation followed by the generation of short-chain carboxylic acids was the main degradation route. The photolysis of final Fe(III)-carboxylate complexes then explains the quickest mineralization by PEF.

Other authors have also shown the higher oxidation ability of PEF using electrolytic cells with different carbonaceous cathodes to generate H_2O_2 [111-117]. Thus, Irmak et al. [111] treated 300 mL of an O_2-saturated 0.6 mM 4-chloro-2-methylphenol solution of pH 2.7 in the cathodic compartment of a divided cell equipped with a Pt gauze anode, a 3 cm × 5 cm CF cathode and a Nafion 117 membrane as separator. At a constant cathodic potential (E_{cat}) of -0.55 V/SCE and 1.8 mM Fe^{2+}, they found a fast and complete degradation of the aromatic ring in the PEF system under UVC irradiation, with 41.7% TOC decay and complete dechlorination after consumption of 141.4 C for 300 min. In EF, 280.7 C was consumed during 450 min of electrolysis to attain a similar removal of initial pollutant, but only yielding 14.9% TOC removal and 89.3% dechlorination. Similar results were obtained in the comparative EF and PEF degradations of 100 mL of 20 mg L^{-1} of the herbicide paraquat in an O_2-saturated solution with 0.05 M Na_2SO_4 and 0.2 mM Fe^{2+} at pH 3.0 and 100 mA using a Pt/CF cell illuminated with a 6 W UVA lamp [114]. HPLC analysis of electrolyzed paraquat solutions allowed the identification of three main aromatic intermediates that led to short-chain carboxylic acids, whereas the initial nitrogen was transformed into NO_3^- ion.

On the other hand, Wang et al. utilized a cell equipped with a Ti/RuO_2 anode and an activated carbon fiber cathode to treat 450 mL of 200 mg L^{-1} of the azo dye Acid Red 14 [113] and 125 mL of 200 mg L^{-1} of the antibiotic sulfamethoxazole [116], using an O_2-saturated solution with 0.05 M Na_2SO_4 and 1 mM Fe^{2+} at pH 3.0 and 360 mA in both cases. After 6 h in EF conditions, TOC was reduced by 59% and 63%, respectively, whereas the comparative PEF treatment with an 11 W UVA lamp led to 95% and 80% mineralization. HPLC–MS analysis allowed the detection of six aromatic products during sulfamethoxazole degradation by PEF process, mainly formed from the hydroxylation of the aromatic and/or isoxazole ring, accompanied by the substitution of the amine group (on aromatic cycle) or methyl group (on isoxazole ring) by •OH. Oxalic, maleic, oxamic, formic and acetic acids were detected, and the initial organic nitrogen was converted into NH_4^+.

In view of the superiority of SPEF over PEF found in the stirred tank reactor, the Brillas' group extended the study to pre-pilot plants aiming at further application at industrial scale. The SPEF treatment of organics was firstly scaled-up to a recirculation flow plant of 2.5 L with a BDD/O_2-diffusion cell coupled to a flat solar photoreactor [14,118-121]. Figure 13a and b show a scheme of the flow plant and the cell used for these trials [14]. The electrodes had an area of 20 cm^2, with a gap of about 1.2 cm. The solar photoreactor was a polycarbonate box of 600 mL of irradiated volume, built-up with a mirror at the bottom and tilted 30° from the horizontal. Solutions with 50-350 mg L^{-1} of TOC in 0.05-0.10 M Na_2SO_4 with 0.5 mM Fe^{2+} at pH 3.0, 50 mA cm^{-2} and flow rate of 180-200 L h^{-1} were usually tested. As found in the stirred tank reactor, SPEF was much more potent to mineralize

organics than AO and EF. For example, TOC was reduced by 95% after 540 min of SPEF treatment of 100-637 mg L^{-1} of the herbicide mecoprop at 50 mA cm^{-2} [14]. Similarly, almost total mineralization was achieved for the dyes Acid Yellow 36 [118], Acid Red 88 [119], Acid Yellow 9 [119], Disperse Red 1 [120] and Disperse Red 3 [120] by SPEF. For all compounds, the SPEF efficiency rose at lower current density and higher pollutant content. The same trend was obtained for the energy consumption per unit TOC mass. This parameter was as high as 259 kWh $(kg\ TOC)^{-1}$ after 240 min of EF treatment of 100 mg L^{-1} TOC of Disperse Red 1 at 50 mA cm^{-2}, whereas it was reduced to 151 kWh $(kg\ TOC)^{-1}$ for the comparative SPEF treatment with > 90% mineralization [120]. This confirms that SPEF is much more economic than EF.

As found with the stirred tank, the performance of SPEF was enhanced from the combined use of Fe^{2+} and Cu^{2+} for the treatment of Disperse Blue 3 dye in 0.10 M Na_2SO_4 with a BDD/ADE cell in the flow plant [89]. Optimum conditions were found for 0.5 mM Fe^{2+} + 0.1 mM Cu^{2+}. Figures 14a and b reveal that the presence of the co-catalyst led to > 95% TOC abatement in the presence and absence of 200 mg L^{-1} dye with energy consumption < 80 kWh $(kg\ TOC)^{-1}$, more rapidly and less expensive than using 0.5 mM Fe^{2+} alone. This corroborates the aforementioned attack of $^{\bullet}OH$ on Cu(II)-carboxylate complexes, competitively formed with Fe(III)-carboxylate ones.

In trials performed using the 2.5 L pre-pilot plant, it was found that the decay of all initial aromatics in EF and SPEF always followed a pseudo-first-order kinetics and the apparent rate constant k_1 increased at higher current density and lower pollutant content. The reaction pathways tend to be rather complex, like in the case of Disperse Blue 3, where up to 15 anthraquinonic and phthalic acid derivatives were identified [89]. Analysis of final carboxylic acids confirmed the quick removal of oxalic acid by photolysis of its Fe(III) complexes, but other recalcitrant acids like acetic and oxamic may slow down the mineralization processes [14,89,118-121]. The heteroatoms contained in the pollutants are usually released in the form of Cl^-, NH_4^+ and NO_3^- ions [89,118-121].

The study of the SPEF process has been lately extended to a 10 L pre-pilot plant, schematized in Figure 15a [122]. This plant has the same components as those shown in Figure 14a, but with a reactor of 90.3 cm^2 electrode area coupled to a 1.57 L solar compound parabolic collector (CPCs) as the photoreactor. The research was focused on the optimization of the SPEF treatment of the drug paracetamol using a Pt/ADE cell by response surface methodology [123]. The optimal variables were found to be 5 A, 0.4 mM Fe^{2+} and pH 3.0 for 157 mg L^{-1} paracetamol with 0.05 M Na_2SO_4, yielding 75% TOC reduction, 93 kWh $(kg\ TOC)^{-1}$ energy consumption and 71% current efficiency at 120 min. HPLC analysis of electrolyzed solutions allowed detecting hydroquinone and various benzoquinones as aromatic intermediates, which were removed by $^{\bullet}OH$, whereas maleic, fumaric, succinic, lactic,

oxalic, formic and oxamic acids were identified as carboxylic acids. Recently, the SPEF treatment of 297 mg L^{-1} of the azo dye Sunset Yellow FCF in 0.05 M Na_2SO_4 and 0.5 mM Fe^{2+} of pH 3.0 using the same system at 7 A demonstrated that total decolorization was feasible at 120 min and that about 94% mineralization with 197 kWh (kg TOC)$^{-1}$ energy consumption was attained at 150 min [12].

The SPEF degradation of 100 mg L^{-1} TOC of solutions with the beta-blockers atenolol, metoprolol tartrate and propranolol hydrochloride in 0.10 M Na_2SO_4 with 0.5 mM Fe^{2+} at pH 3.0 was tested using single Pt/ADE and BDD/ADE cells and also their combination with a Pt/CF cell to enhance Fe^{2+} regeneration from Fe^{3+} reduction [122]. Figure 15b shows a sketch of the combined BDD/ADE-Pt/CF cell. As an example, Figure 16a highlights for a 0.246 mM metoprolol tartrate solution the superiority of combined cells over single ones, BDD over Pt and SPEF over EF regarding the TOC abatement. This can be explained by the greater production of $^{\bullet}OH$ from Fenton's reaction in the combined cells, the higher oxidizing power of BDD($^{\bullet}OH$) and the photolytic action of sunlight in SPEF, as easily deduced from the pseudo-first-order decay kinetics shown in Figure 16b. Nevertheless, the Pt/ADE-Pt/CF cell gave the lowest energy consumption of 80 kWh (kg TOC)$^{-1}$ for 88-93% mineralization, being the most viable system for industrial application.

4.2 Photoelectrocatalysis (PEC)

The PEC method relies on the synergy between electrochemistry and photocatalysis to provide much greater efficiency for wastewater remediation. Traditional photocatalysis has been extensively developed using the nanocrystalline anatase form of TiO_2 for light-induced oxidation of organic pollutants in waters [2,106,107]. This semiconductor material possesses very attractive properties such as low cost, low toxicity and a wide band gap of 3.2 eV, which results in a good stability and prevents photocorrosion. The irradiation of anatase TiO_2 nanoparticles, either in colloidal suspension or deposited as a thin film on Ti, by UV photons of sufficient energy ($\lambda < 380$ nm) promotes an electron from the valence band to the conduction band (e^-_{CB}) generating a positively charged vacancy or hole (h^+_{VB}) as follows:

$$TiO_2 + h\nu \rightarrow e^-_{CB} + h^+_{VB} \quad (58)$$

Organics can then be directly oxidized by the hole or by heterogeneous hydroxyl radical formed from the reaction between the photogenerated vacancy and adsorbed water:

$$h^+_{VB} + H_2O \rightarrow {}^{\bullet}OH + H^+ \quad (59)$$

Besides, other weaker reactive oxygen species (ROS, superoxide radical ion $O_2^{-\bullet}$, $HO_2^{\bullet}$ and H_2O_2) and more $^{\bullet}OH$ can be produced from the photoinduced electron according to the following reactions:

$e^-_{CB} + O_2 \rightarrow O_2^{-\bullet}$ (60)

$O_2^{-\bullet} + H^+ \rightarrow HO_2^\bullet$ (61)

$2\ HO_2^\bullet \rightarrow H_2O_2 + O_2$ (62)

$H_2O_2 + O_2^{-\bullet} \rightarrow {}^\bullet OH + OH^- + O_2$ (63)

The major drop in efficiency results from the recombination of photoinduced electrons with either unreacted holes or adsorbed $^\bullet$OH:

$e^-_{CB} + h^+_{VB} \rightarrow TiO_2 + heat$ (64)

$e^-_{CB} + {}^\bullet OH \rightarrow OH^-$ (65)

On the other hand, the PEC method consists in the application of either a constant current or a constant bias anodic potential (E_{anod}) to a semiconductor-based thin film anode subjected to UV illumination for the continuous extraction of photoinduced electrons by an external electrical circuit. This minimizes the extent of Eq. (60) to (65) and favors the generation of a higher quantity of holes from Eq. (58) and heterogeneous $^\bullet$OH from Eq. (59), thereby largely enhancing organics oxidation and the process efficiency in comparison to photocatalysis [106,107].

The electrolytic cells used in PEC are stirred tanks or flow reactors that permit the passage of UV light directly to the solution or through a quartz window to reach the exposed surface of the photoanode with the minimum loss of incident irradiation. Figure 17 shows a scheme of a stirred tank reactor directly illuminated with a solar simulator for the solar PEC (i.e., SPEC) treatment of bisphenol-A [124]. The most typical photoanodes are based on TiO_2 coatings [124-130], although other materials including ZnO [131,132], Bi_2MoO_6-BDD [133], WO_3 [134,135] and BiO_x–TiO_2 [136] have also been utilized.

The efficient degradation of several dyes by PEC with a TiO_2 photoanode has been well proven. Osugi et al. [125] used Ti/TiO_2 nanotubular array electrodes and nanoporous Ti/TiO_2 electrodes prepared by the sol-gel method to treat 0.05 mM of Disperse Red 1, Disperse Orange 1 and Disperse Red 13 and/or 80 mg L^{-1} of Emulsogen anionic surfactant in 0.10 M Na_2SO_4 under UV light and E_{anod} = +1.0 V/Ag/AgCl. After 60 min, all dye solutions were completely decolorized using the former electrode, with an apparent rate constant almost 2-3 times higher than using the other one. TOC was removed ca. 70% after 3 h with total disappearance of peaks related to aromatics detected in HPLC chromatograms. Zhang et al. [127] prepared a Ti/TiO_2 nanotubular disk electrode of 38 cm^2 area to completely decolorize 36 mL of 50 mg L^{-1} of Methyl Orange dye in 0.01 M Na_2SO_4 after 3 h of illumination with a 15 W UVC lamp at E_{anod} = +0.75 V. Recently, a highly-stable 3 cm^2 TiO_2 coating composed of 29% rutile, 9% anatase and 62% of Ti_7O_{13} on stainless steel support was prepared by atmospheric plasma spray [130]. This novel photoanode was coupled with a 3 cm^2 ADE

in a stirred tank reactor to decolorize 100 mL of Acid Orange 7 azo dye solutions in 0.05 M Na_2SO_4 under direct sunlight. This SPEC process was based on the contribution of both, solar photocatalysis and AO, owing to the larger production of $^{\bullet}OH$ from the higher amounts of holes that can be separated from photoinduced electrons. The best operation variables for SPEC were 15 mg L^{-1} dye, pH 7.0 and anodic current density of 1.0 mA cm^{-2}, for which the dye disappeared in 100 min and the solution was totally decolorized in 120 min, although only 40% mineralization was attained in 240 min. Phthalic, tartaric, succinic, acetic and oxamic acids were detected as intermediates, with release of NH_4^+ ion in larger proportion than NO_3^- ion.

Less is known about the PEC treatment of dyes using other kinds of photoanodes. ZnO nanorods embedded in highly ordered TiO_2 nanotube arrays of 1 cm^2 area, coupled with a Pt anode in a stirred tank reactor and illuminated with a 11 W UVC lamp were able to completely decolorize a 0.05 mM Methyl Orange solution in 0.5 M Na_2SO_4 of pH 6.2 after 90 min of PEC at E_{anod} = +0.60 V/SCE [131]. On the other hand, 93% decolorization with 69% COD reduction has been reported after 3 h of PEC degradation of a textile industrial effluent under recirculation in a single tank reactor equipped with an UV-illuminated transparent ZnO thin film deposited onto a substrate of fluorine doped tin oxide glass by the spray pyrolysis technique [132].

The viability of PEC for the destruction of pharmaceuticals has been checked by several authors [126,129,133,137,138]. Thus, Liu et al. [126] treated synthetic tetracycline wastewaters with a TiO_2 nanotube arrays photoanode at E_{anod} = +0.50 V/SCE illuminated with a 4 W UVC lamp in a stirred undivided three-electrode rectangular quartz reactor. The tetracycline content was reduced by 81% in PEC, whereas it only decayed a 2% for AO, 16% for direct photolysis and 38% for photocatalysis. More recently, this group developed a novel double thin-layer PEC reactor that increased the ratio of electrode area to solution volume enhancing the mass transport and the photonic efficiency, so that, the degradation of tetracycline became much quicker [137]. The same group also examined the SPEC degradation of ibuprofen and naproxen with an innovative porous Bi_2MoO_6 film deposited onto BDD, with 11 cm^2 area exposed to a 150 W Xe lamp to simulate sunlight and immersed into 60 mL of solution with 0.12 mg L^{-1} Na_2SO_4 filling a cylindrical quartz cell [133]. At E_{anod} = +2 V/SCE, 86% decay for 10 mg L^{-1} ibuprofen with 72% TOC removal was found for SPEC, values much higher than 64% and 42% obtained for AO and 21% and 8% for photocatalysis, respectively. The partial effectiveness of AO indicated the ability of Bi_2MoO_6 to generate ROS at the high applied E_{anod}. Recently, Daghrir et al. [129] reported the efficient PEC degradation of 1 L of 25 μg L^{-1} chlortetracycline hydrochloride in 0.05 M Na_2SO_4 solution of pH near 6 using a 110 cm^2 Ti/TiO_2 nanocrystalline anode in a two-electrode cell under UVC illumination. After 120 min of electrolysis at anodic current density of 390 mA, the initial drug concentration diminished up to 98%

while TOC and total nitrogen were reduced by 67% and 69%, respectively. Based on biotesting, these authors demonstrated that the treated effluent was not toxic compared to the untreated one. It has also been described that the COD and color of 500 mL of a real pharmaceutical wastewater with addition of NaCl were reduced by 93% and 78%, respectively, by PEC in a quartz cell equipped with a 10 cm^2 Ni/TiO_2 photoanode exposed to a 250 W high-pressure mercury lamp and a 10 cm^2 multi-walled carbon nanotubes air cathode [138].

Other compounds like bisphenol-A [124] and the herbicide alachlor [128] have also been degraded by SPEC with a Ti/TiO_2 photoanode. Using the photoelectrochemical cell of Figure 17, Frontistis et al. [124] degraded 60 mL of 120-820 μg L^{-1} bisphenol-A at pH between 1.0 and 7.5 and anodic current density from 0.02 to 0.32 mA cm^{-2}. The reaction was favored up to 0.04 mA cm^{-2} and at low substrate concentrations, but it was hindered by the presence of residual organic matter and radical scavengers like bicarbonates. As expected, SPEC was much more efficient than pure TiO_2 photocatalysis or AO. The same behavior was reported by Xin et al. [128] for alachlor treatment, showing a higher performance using a nanotube-shaped Ti/TiO_2 photoelectrode compared to a wormhole-shaped Ti/TiO_2 one.

Finally, the PEC performance of innovative photoanodes such as WO_3 and Ti/BiO_x-TiO_2 on other contaminants has been assessed. The WO_3 photoelectrode was exposed to a visible light either in a reactor configuration that resembled a fuel cell with a Nafion 115 membrane and a Pt/carbon printed onto Teflon/carbon as cathode [134] or in an H-cell where the photoanode and the Pt gauze cathode were separated by an agar-salt bridge [135]. In both systems, very slow removal of 0.25 mM of 2,4-dichlorophenol, along with large formation of chloroderivatives, was obtained after 24 h of PEC as a result of the very little current which was able to circulate by the external circuit causing a large recombination of photogenerated holes and electrons and favoring the oxidation with generated ClO^- ion. In contrast, the BiO_x–TiO_2 acted as an actual photoelectrode and showed a much higher oxidation ability of organics [136]. When this anode was submitted to a 450 W Hg-Xe lamp and coupled with a stainless steel cathode, both of 50 cm^2 area, in a stirred tank reactor with 1.5 L of 1 mM phenol and 0.05 mM NaCl at constant voltage > 1 V, the anodic phenol oxidation rate and the cathodic H_2 production rate were enhanced by factors of four and three, respectively, as compared to the sum of light irradiation and direct electrolysis.

4.3 Hybrid combinations of PEF and PEC

The decolorization of several dyes has been enhanced by combining PEF and TiO_2 photocatalysis (TiO_2/UV), as reported by Khataee et al. [139,140], who optimized the experimental conditions using response surface methodology. These authors utilized open, undivided and cylindrical stirred tank reactors of 1 or 3 L capacity equipped with a Pt anode, a cathode composed of carbon nanotubes immobilized onto a graphite surface (CNT/graphite) fed with air, a 6 W UVC lamp introduced in a quartz tube and TiO_2 nanoparticles immobilized on paper or glass plates covering the inner surface of the cell. For the azo dye Acid Yellow 36 [140], for example, the decolorization rate decreased in the sequence PEF-TiO_2/UV > PEF > EF > TiO_2/UV > UV photolysis. The optimum variables for the former combined process were 25 mg L^{-1} of dye, 0.15 mM Fe^{3+}, 127 min of treatment and 115.6 mA, yielding a maximum color removal of 83%. Worth noting, the operation costs related to the use of the UV lamp were as high as 16.5 kWh m^{-3}, whereas the electrical energy consumption was only 0.88 kWh m^{-3}.

On the other hand, several attempts have also been made to enhance the oxidation ability of PEC by its coupling with EF, although more studies are needed to confirm the use of such combined processes. Xie and Li [141] used the quartz reactor of Figure 18a to study the removal of azo dye Orange G for 5 h by different methods. The cell was filled with 30 mL of a 0.1 mM solution of the dye containing 0.01 M Na_2SO_4 at pH 6.2 and an 8 W UVA lamp was used as light source. Figure 18b highlights that Orange G was not directly photolyzed under UVA irradiation, being slightly destroyed (ca. 3%) by AO with a TiO_2/Pt cell at E_{anod} = +0.71 V/SCE and reaching 8% by TiO_2 photocatalysis, as expected if small quantities of oxidizing species ($^{\bullet}OH$ and/or holes) are formed at the TiO_2 surface. The PEC process using the Pt/TiO_2 cell enhanced the dye removal to 25% due to the photogeneration of more amounts of oxidizing holes. The oxidation ability of this technique increased up to yield 50% dye destruction when the Pt cathode was replaced by a reticulated vitreous carbon (RVC) electrode at E_{cat} = -0.54 V/SCE, making possible the dye oxidation with H_2O_2 produced from O_2 reduction. Interestingly, Orange G disappeared completely when applying PEF with a Fe/RVC cell using ca. 17 mg L^{-1} Fe^{2+}, pH 3.0 and E_{cat} = -0.71 V/SCE. Furthermore, the decolorization rate slightly increased if EF under the same conditions was coupled to PEC using a TiO_2/RVC cell, as a result of the additional formation of large amounts of homogeneous $^{\bullet}OH$ from Fenton's and/or photo-Fenton reaction. As a result, PEC coupled with EF provided the highest mineralization of 74% in 5 h. Peralta-Hernández et al. [142] also described a strong improvement of the decolorization efficiency and TOC removal by PEC coupled to EF in comparison to EF alone using a concentric annular undivided TiO_2/graphite cloth flow cell with a central 75 mW cm^{-2} UVA lamp in batch operation mode.

4.4 Prospects

It is evident that intensification in most novel research pathways in the environmental electrochemistry field will eventually yield positive results regarding the enhancement of photoelectrochemical processes as well. In this sense, attention to advanced electrodes and reactors, along with process modelling, can lead to a comprehensive expansion of such processes into all areas of environmental preservation, including remediation of contaminated waters, gaseous streams and soils. There exists an undoubtedly optimistic background because significant progress has been evidenced from the development of novel electrodes and membranes and the optimisation of the reactor setup, including, for example, the development of more efficient multiple-phase oxidation and three-dimensional electrode reactors. However, a critical analysis of the immediate challenges of the photoelectrochemical processes for the treatment of organic pollutants in waters has to focus on the particularities of PEC and SPEF, given their preponderance.

The use of new advanced anode materials in PEC, such as oxide semiconductors in the form of nanotubes/nanorods/nanowires including those based on TiO_2, has shown an increasing generated photocurrent. Also, the preparation of electrodeposited coatings of pure, doped and composite photoelectrocatalytic materials is a way to be further explored, given the very interesting resulting physicochemical properties and the excellent surface finishing upon use of this manufacturing methodology. Unfortunately, to be realistic, poor results concerning mineralization have been reported so far by means of PEC. TOC and COD removals are usually lower than 100%, as discussed above, and the abatements are always slow as a result of the mass transport limitations that are inherent to an electrode process such as this one. Indeed, this is common major drawback, also found in electro-oxidation, but in that case the alternative mediated oxidation by generation of other oxidants such as active chlorine or peroxo salts (e.g., persulfates, percarbonates, perphosphates) at very powerful anodes like BDD has allowed the enthusiastic rebirth and promising development of new applications of that technology, as for example in water disinfection systems. Of course, new advances on PEC are closely related to the progress in the field of photocatalysis, particularly concerning the ability of materials engineering to propose more efficient photocatalysts that show a higher absorption in the visible range of the solar spectrum. As an immediate consequence of such expected developments, and considering the previously exposed results on PEC, we suggest the alternative combination of SPEC with SPEF, a hybrid system that has not been tested yet, since it would definitely be much more economical than the PEC combinations assessed in recent years.

On the other hand, SPEF is sufficiently promising by itself, and future modifications point out to the economical aspects. Some of us are involved in conceiving sunlight-driven systems based on

solar panels and photovoltaic energy as a cheap source of electrical power. As commented, work conducted at pre-pilot plants under laboratory conditions has confirmed the much superior economic viability of SPEF over other electrochemical treatments such as AO, EF and PEF, especially for the treatment of specific effluents with a notable acidity that allow the straightforward application of Fenton's reaction. A joint project between the Universitat de Barcelona and the Plataforma Solar de Almería (PSA, Spain), which is the largest European facility for research on solar technologies, is seeking the scale-up of the SPEF technology. Hopefully, coupling with other sunlight-assisted processes carried out within that facility will lead to an integral, robust technology which can catch the attention of private entrepreneurs and the public sector.

5 Sonoelectrochemical processes

As deduced from comments in Section 2.3.3, ultrasound (US) is able to produce highly reactive radicals from water as well as the pyrolysis of organic pollutants contained in such matrices. However, its oxidation ability is rather low and, consequently, it is usually combined with other oxidants like H_2O_2, O_2, UV and Fenton's reagent for water remediation [16,143-145]. The study of the combination of US and electrode processes and the application of sonoelectrochemical technology to the combustion of organic compounds are current active research fields [143,145]. This section describes the characteristics of sonoelectrolysis and sonoelectro-Fenton, which are the most important sonoelectrochemical processes used to decontaminate wastewaters.

5.1 Sonoelectrolysis

The combination of an US field with electrochemical oxidation can result in a powerful method for pollutant degradation. US can improve the electrochemical degradation of pollutants by chemical and physical mechanisms [145]. The chemical mechanism is found at high frequency and involves the homolytic fragmentation of H_2O and dissolved O_2 to yield different ROS ($^\bullet OH$, $HO_2^\bullet$ and $^\bullet O$). The physical mechanism is so-called sonication and consists in the production of cavitation microbubbles which grow and collapse, originating great breaking forces with extremely high temperatures (up to 6000 K) and pressures (of the order of 10^4 kPa). Under these conditions, organics can be directly pyrolyzed and the sonolysis of water can take place from Eq. 62, where))) denotes the US, while $^\bullet OH$ thus generated accelerates the organics oxidation.

$$H_2O +))) \rightarrow {}^\bullet OH + {}^\bullet H \quad (66)$$

Besides, the strong cavitational collapse near the electrode surface enhances the mass transport of the electroactive species as well as the cleaning of the electrodes' surfaces by dissolving or pitting the inhibiting layers [143,145]. All these phenomena largely improve the destruction rate of organics, eventually favoring the mineralization process in sonoelectrolysis.

Several experimental setups have been conceived for sonoelectrochemical experiments: (i) immersion of the electrochemical cell inside an US bath, (ii) coupling of the electrolytic cell with the ultrasonic tip through a glass wall or filled liquid chambers, (iii) use of a sonoelectrochemical cell where the electrodes and the ultrasound tip are directly dipped into the working solution, which turns out to be the most used arrangement, and (iv) the simultaneous use of the ultrasound tip as ultrasound emitter and as electrode [144]. Figure 19 shows an image of an ultrasound tip near a BDD electrode in a sonoelectrolytic cell [145]. The vast majority of research in sonoelectrolysis has been carried out at lab scale with individually designed systems based on powerful US horns dipped into traditional glass electrochemical vessels. This procedure is very expensive and has evidenced some drawbacks related to reproducibility, scale-up and design aspects which have slowed down its further development.

The benefits derived from using sonoelectrolysis for the removal of dyes has been explored by several authors. Lorimer et al. [146] treated solutions of 500 mL of about 20 mg L^{-1} of basic dyes like Yoracyl Brilliant Red, Astrazon Golden Yellow GL, Maxilon Blue 5G and Astrazon Red GTLN by low-power (1.1 W cm^{-2}) high-frequency US (510 kHz), and the acidic dye Sandolan Yellow by high-power, low-frequency US (20–100 W cm^{-2}; 20 kHz). US alone decolorized the basic dyes due to the attack of H_2O_2 formed from the dimerization of generated $^{\bullet}OH$, but it was unable to destroy the acidic dye. Subsequently, in sonoelectrolysis tests, a tank reactor containing either a 13.5 cm^2 carbon or a 2 cm^2 Pt anode was placed inside the US bath. All dyes were efficiently removed by electrolysis and sonoelectrolysis in an aqueous chloride electrolyte owing to their reaction with ClO^- ion formed from Cl^- anodic oxidation. Comparative trials showed that the oxidation ability of processes decreased in the sequence sonoelectrolysis > electrolysis > sonolysis. The decolorization rate increased with increasing current from 50 to 300 mA, chloride concentration (up to 0.5 M) and/or US power. The best performances were attained using the low frequency of 20 kHz, being related to the cavitation effects of US that promotes degassing at the electrode surface, improves the mass transport of species across the diffusion layer and favors the continuous cleaning and activation of the electrode surfaces. More recently, it has been described that in a similar sonoelectrolytic system composed of a PbO_2/stainless steel cell submitted to an US source of 300 W and 8 kHz, a solution of 1 L of 50 mg L^{-1} of unhydrolyzed Reactive Blue 19 dye at pH 8.0 attained 90% color removal and 56% TOC

removal after 120 min of sonolysis alone, whereas the use of sonoelectrolysis accelerated the treatment and total decolorization was achieved at 30 min under a cell voltage of 10 V [147]. Lately, a novel Ti/SnO_2–Sb_2O_3/PTFE-La-Ce-β-PbO_2 anode of high density and preferred crystalline structure has been proposed to improve the mass transport and mineralization of the cationic dye Gold Yellow X-GL under sonoelectrolysis [148].

Sonoelectrolysis has also been applied to the treatment of waters contaminated with very refractory compounds like trichloroacetic acid and perchloroethylene. The degradation of trichloroacetic acid was examined by Esclapez et al. [149], who scaled-up to a pre-pilot flow plant equipped with a divided Ti/Pt reactor and an US transducer of 3.8 W cm^{-2} under the recirculation of an anolyte of 1 L of 3 mM substrate with 0.010 M Na_2SO_4 at 100 L h^{-1}. Although 97% of fractional conversion of trichloroacetic acid could be obtained in this system, the degradation efficiency was only of 26% and the current efficiency was as low as 8%. Better results were reported by the same Spanish group for perchloroethylene [150,151]. Preliminary trials were made in a PbO_2/Pb undivided tank reactor of 12 cm^2 electrode area equipped with an US transducer supplying up to 7.52 W cm^{-2} and 20 kHz. The treatment of 200 mL of 0.452 mM perchloroethylene in 0.05 M Na_2SO_4 of pH 6.0 at 3.5 mA cm^{-2} gave 100% degradation efficiency and about 55% of current efficiency, regardless of the power used. It was also found a complete removal of this substrate in the absence of background electrolyte, surprisingly with even greater current efficiency than in the presence of 0.05 M Na_2SO_4. However, the energy cost increased considerably due to the much higher cell voltage applied, which is a drawback for sonoelectrolytic treatment of wastewaters with low salt concentrations.

The effect of US on the electrochemical combustion of organics with a BDD anode has been recently explored. The cleaning of the electrode surface and enhancement of mass transport were evaluated by performing potentiostatic electrolyses of 90 mL of 0.05 mM pentachlorophenol as anolyte in an H-cell using a 0.42 cm^2 BDD anode and an US tip placed at 7 cm in front of it (Figure 18) and supplying a radiation of 14 W and 20 kHz [152]. After 270 min at E_{anod} = +3.0 V/Ag/AgCl, the substrate was removed by 20% for sonolysis, 71% for direct electrolysis and 83% for sonoelectrolysis. The higher removal achieved in the latter system was explained by the increase of mass transport, minimization of the electrode fouling and the combined generation of $^{\bullet}OH$ by both, US and the polarized BDD surface. Similar trends for these processes have been described for the mineralization of the herbicide diuron in aqueous medium [153] and the antibiotic triclosan in methanol/water or methanol solutions [154]. In the latter case, sonoelectrolysis was more efficient in sulfate than in chloride medium and the main intermediates detected by HPLC were catechol,

chlorohydroquinone, 4-chlorocatechol, acetic acid and dichloroacetic acid, due to the oxidative action of generated •OH mainly at the BDD anode.

An interesting work dealing with the electrosynthesis of H_2O_2 from cathodic O_2 reduction in the absence and presence of US was reported by González-García et al. [155]. These authors used a vertical two-compartment three-electrode cell equipped with an RVC cathode of 30 mm × 40 mm x 10 mm in dimension, a SCE reference electrode and a Ni gauze anode with a cationic exchanger membrane as separator. The reactor was subjected to US provided by a horn of 1000 W and 20 kHz. The catholyte was 1.25 L of an O_2-saturated NaOH solution of pH 13 or borate buffer of pH 10.0 under recirculation at flow rate of 70 or 300 L h^{-1}. The application of US at E_{cat} = -1.0V/SCE enhanced both the H_2O_2 concentration and the current efficiency of the process, preferentially at the smaller flow rate. For example, current efficiencies of ca. 60% were reached under the application of US at pH 10 and 70 L h^{-1}, conditions at which the silent electrosynthesis had current efficiency ≤ 20%. This improvement was related to an enhanced mass transport of dissolved O_2 under US.

5.2 Sonoelectro-Fenton (SEF)

The SEF process consists in the application of an US radiation to an acidic solution under EF conditions. It was proposed by Oturan et al. [16], who demonstrated the benefits of this novel procedure for the degradation of herbicides 2,4-D and 4,6-dinitro-*o*-cresol using an undivided Pt/CF tank reactor with a ceramic piezoelectric transducer placed on its base to supply energies of 20, 60 and 80 W at a low frequency of 28 kHz. Figure 20 exemplifies the decay found for 2,4-D concentration in the absence and presence of US. The SEF process enhanced the destruction of this compound compared with EF for the lower energies of 20 and 60 W. This was ascribed to the mass transfer enhancement of O_2 to the electrode by sonication, which produced more H_2O_2 and accelerated the •OH generation from Fenton's reaction, then reacting more rapidly with the herbicide. In contrast, the application of the higher US energy of 80 W strongly inhibited the SEF process, probably because it caused the depletion of dissolved O_2 with the consequent decrease of H_2O_2 accumulation and •OH generation required for the EF process.

More recently, the superiority of SEF over EF and chemical Fenton was demonstrated for the treatment of the cationic dyes Red X-GRL [156] and azure B [157]. An air-saturated solution of 1 L of 37.5 mg L^{-1} of the former dye with 0.05 M Na_2SO_4 and 5 mM Fe^{2+} of pH 3.0 in an undivided tank reactor with a Ti/RuO_2 anode and an activate carbon fiber cathode, each of 100 mm × 90 mm area, was degraded by EF at 8.9 mA cm^{-2}. Comparative SEF trials were made using an US system of 20

kHz and energies of 80, 120 and 160 W with the horn dipped into the solution at 20 mm of its surface and placed between the electrodes. The dye was always completely decolorized in 180 min, although color removal was enhanced by SEF, where it increased as US energy rose. A similar trend was found for TOC decay, which rose from 75% in EF to 83% in SEF at 160 W. For 0.5 mM azure B, it was found that the rate constant for its decay in SEF by applying E_{cat} = -0.7 V/SCE to an RVC cathode under US of 91 W and 24 kHz was 10-fold that of direct sonolysis and 2-fold the one obtained by chemical Fenton under silent conditions. Accordingly, COD was abated 68% in 60 min by Fenton, whereas a much large value of up to 85% was obtained by SEF.

5.3 Prospects

Sonochemistry is an emerging green technology in a large variety of research fields. Particularly, the application of sonoelectrochemical processes to the activation of radicals in electrolytic devices seems to gain a progressive acceptance among the scientific community, but for the moment a great percentage of works have been performed at a laboratory scale. It certainly accelerates the degradation of contaminants found in the liquid phase due to various simultaneous phenomena that take place, although a major detrimental factor is the high cost due to a non efficient use of energy. At present, most of the energy applied is not useful for oxidation but it is dispersed as mechanical energy and heat, which could be ameliorated with an optimized design of the sonoelectrolytic reactors. This should be a hot topic in future years indeed to implement all the beneficial characteristics of acoustic cavitation in water treatment, and papers on modelling can be found lately. It has also been demonstrated that a very high US power is not required, which can then motivate the use of low power pulse waves entailing a much affordable treatment.

Coupling with other processes may give rise to a more efficient decontamination such as in electro-oxidation with BDD or in sonophotoelectrocatalysis recently proposed. Nevertheless, the combination with bulk oxidation processes such as those based on Fenton's reaction is the most adequate target, considering the mechanisms that become activated in the presence of ultrasonic waves. On the other hand, sonoelectrochemistry can allow the recovery of some priced pollutants, as in the case of metals. It is also known that ultrasonic cleaning technology is generally used as ultrasonic baths and thus, cavitation may also prevent electrode fouling. An immediate advantage of those systems is related to avoiding biofouling typically encountered in wastewater treatment facilities. Finally, related to this, US technology is currently under investigation for the inactivation

of microorganisms such as bacteria and virus, therefore being interesting the hybrid technology for carrying out water disinfection.

6 Conclusion

All the work performed in the fields of research, development and manufacturing have shown that EAOPs technology has a huge potential for water purification and treatment in general. A comparison between all the technologies reviewed in this paper regarding their advantages and drawbacks is shown in Table 4. From our point of view, two main challenges are priority: (i) the cut in electrode prices, particularly BDD, and (ii) the use of renewable energy sources to power the processes, thus enhancing the sustainability of all these EAOPs.

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Table 1. Standard potential of some oxidizing species

Oxidizing agent	Standard potential (V)
Oxygen (molecular)	1.23
Chlorine dioxide	1.27
Chlorine	1.36
Ozone	2.08
Oxygen (atomic)	2.42
Hydroxyl-radical	2.80
Fluorine	3.06
Positively charged hole on TiO_2	3.2

Table 2. Main AOPs and related reactions involving the production of $^{\bullet}OH$

Dark AOPs	**Reactions**
Ozone at elevated pH	$3\ O_3 + OH^- + H^+ \rightarrow 2\ ^{\bullet}OH + 4\ O_2$
Ozone + hydrogen peroxide	$2\ O_3 + H_2O_2 \rightarrow 2\ ^{\bullet}OH + 3\ O_2$
Ozone + catalyst	$O_3 + Fe^{2+} + H_2O \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH + O_2$
Fenton	$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH$
Photoassisted AOPs	
Ozone / UV	$O_3 + H_2O + h\nu \rightarrow O_2 + H_2O_2$
Hydrogen peroxide / UV	$H_2O_2 + h\nu \rightarrow 2\ ^{\bullet}OH$
Ozone / H_2O_2 / UV	The addition of H_2O_2 to the O_3/UV process accelerates the decomposition of ozone, which results in an increased rate of $^{\bullet}OH$ generation
Photo-Fenton	$Fe^{2+} + H_2O_2 + h\nu \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH$ $Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + {}^{\bullet}OH$ $Fe(OOCR)^{2+} + h\nu \rightarrow Fe^{2+} + CO_2 + R^{\bullet}$
Heterogeneous photocatalysis (TiO_2/UV)	$TiO_2 + h\nu \rightarrow TiO_2(e^- + h^+)$ $h^+ + H_2O \rightarrow {}^{\bullet}OH + H^+$ $e^- + O_2 \rightarrow O_2^{-\bullet}$

Table 3. Absolute rate constants (k_{abs}) for the oxidation of chlorophenols by •OH generated during electro-Fenton process. Reprinted with permission from [103].

Chlorophenol	k_{abs} (10^9) M^{-1} s^{-1}
4-CP	7.75±0.07
2,6-DCP	6.13±0.05
2,4,5-TCP	5.72±0.05
2,3,5,6-TeCP	4.95±0.07
PCP	3.56±0.06

Table 4. Main advantages and drawbacks of the EAOPs reviewed.

Technology	Advantages	Drawbacks
Anodic oxidation	Treatment of large volumes (need of large anodes or cell stacks)	Electrode fouling
	Very large percentages of organic matter degradation	Expensive, high O_2-overpotential anodes
	No pH restrictions	Attention to halogenated by-products
		Usually work in batch mode
Fenton-based processes	Treatment of large volumes (need of large electrodes or cell stacks)	Need of pH regulation (pH near 3.0) and neutralization
	degradation (more remarkable under sunlight irradiation)	Quick and very large percentages of organic matter removal
	Cathodic generation of H_2O_2	Sludge formation
		Attention to halogenated by-products
		Usually work in batch mode
Photoelectrocatalysis	Small bias potential required	High cost of UV lamps usage
	Slow but large percentages of organic matter degradation	Particular reactor configuration with photoactive anodes and quartz glass Attention to halogenated by-products
	Immobilized photocatalyst (no need of separation filtration after treatment)	Usually work in batch mode
Sonoelectrochemistry	Large enhancement of the mass transport of reactants towards/from the electrodes	High cost of US horns and usage
	Promotion of degassing at the electrode surfaces	Difficult system scale-up
	Prevention of electrode fouling	Usually work in batch mode

Figure captions:

Figure 1. Applicability of water treatment technologies according to the amount of organic load (chemical oxygen demand, COD).

Figure 2. Percentage of publications devoted to the EAOPs in the last 3 years. Distribution by: (a) electrochemical techniques: anodic oxidation (AO), electro-Fenton (EF), photoelectrocatalysis (PEC), sonoelectrochemistry (SE), and (b) type of residue.

Figure 3. Some details of the Diamonox® system. Reprinted with permission of Advanced Diamond Technologies Inc.

Figure 4. EAOP pilot plant for the treatment of landfill leachate in Marelo (Cantabria, Spain) [26-29].

Figure 5. Changes in the COD concentration during the electrochemical oxidation of synthetic wastes polluted with cyanide (375 mg NaCN L^{-1}). Supporting electrolyte: 0.05 M Na_2SO_4 ((▲) DSA; (◆) Pb/PbO_2; (■) *p*-Si-BDD) and 0.05 M NaCl ((△) DSA; (◇) Pb/PbO_2; (□) *p*-Si-BDD). Adapted from [33].

Figure 6. A conceptual approach to mediated oxidation in Electrochemical Advanced Oxidation Processes.

Figure 7. Changes in the instantaneous current efficiency (ICE) with COD in the electrochemical oxidation of wastes containing 4-chlorophenol (C^0: 15 mM). (●) pH 2, 5000 mg Na_2SO_4 L^{-1}, 25 ºC, 30 mA cm^{-2}; (○) pH 2, 5000 mg Na_2SO_4 L^{-1}, 25 ºC, 15 mA cm^{-2}; (▲) pH 2, 5000 mg Na_2SO_4 L^{-1}, 25 ºC, 60 mA cm^{-2}; (◇) pH 12, 5000 mg Na_2SO_4 L^{-1}, 25 ºC, 30 mA cm^{-2}; (△) pH 2, 5000 mg Na_2SO_4 L^{-1}, 60 ºC, 30 mA cm^{-2} and (□) pH 2, 3333 mg Na_3PO_4 L^{-1}, 25 ºC, 30 mA cm^{-2}. Adapted from [53].

Figure 8. Effect of applied current on degradation kinetics of 0.125 mM picloram in aqueous medium at pH 3 and room temperature by electro-Fenton process: (x): 30 mA, (□): 60 mA, (ж): 100 mA, (◇): 200 mA, (△): 300 mA and (+) 500 mA. [Fe^{3+}]: 0.1 mM, [Na_2SO_4]: 50 mM. Reprinted with permission from [91]. Copyright 2008 Elsevier.

Figure 9. TOC removal during the mineralization of 0.1 mM atrazine aqueous solution by electro-Fenton process using Pt and BDD anodes and CF cathode. EF-Pt: electro-Fenton process with Pt anode, AO-BDD: anodic oxidation using BDD anode, and EF-BDD: electro-Fenton process with BDD anode. Reprinted with permission from [42]. Copyright 2012 Springer.

Figure 10. Evolution of the inhibition of the *Vibrio fischeri* bacteria luminescence during the electro-Fenton treatment, with Pt anode and CF cathode, of (a) Sulfamethoxazole (SMX) aqueous solutions, and (b) its cyclic derivatives AMI (3-amino-5-methylisoxazole) and BZQ (*p*-benzoquinone) diluted aqueous solutions, after an exposure time of 15 min. V = 250 mL, $[SMX]_0$ = 0.208 mM, $[AMI]_0$ = 0.016 mM, $[BZQ]_0$ = 0.018 mM, $[Fe^{2+}]$ = 0.2 mM, $[Na_2SO_4]$ = 50 mM, pH = 3, I = 30, 60, 120, 300 mA in (a), and I = 60 mA in (b). Reprinted with permission from [104]. Copyright 2011 Springer.

Figure 11. Reaction pathways for the total mineralization of the drug sulfachloropyridazine by hydroxyl radicals generated during electro-Fenton process. Reprinted with permission from [105]. Copyright 2012 American Chemical Society.

Figure 12. (a) TOC decay and (b) concentration decay vs. time for the degradation of 100 mL of 41 mg L^{-1} ibuprofen (near saturation) in 0.05 M Na_2SO_4 with 0.5 mM Fe^{2+} at pH 3.0 using an O_2-diffusion cathode at 33.3 mA cm^{-2} and 25.0 ºC. The inset panel of plot (b) presents the corresponding kinetic analysis considering that the drug follows a pseudo-first-order reaction. (○) electro-Fenton (EF) with a Pt anode; (●) EF with a BDD anode; (□) photoelectro-Fenton (PEF) with Pt and a 6 W UVA lamp; (■) PEF with BDD under 6 W UVA radiation; (△) solar photoelectro-Fenton (SPEF) with Pt and (▲) SPEF with BDD. Adapted from [109].

Figure 13. Sketches of (a) the 2.5 L pre-pilot plant and (b) the single one-compartment filter-press electrochemical cell with a BDD anode and an O_2-diffusion cathode, both of 20-cm^2 exposed area, used for the solar photoelectro-Fenton degradation of organic pollutants in acid medium. In (a), (1) flow cell, (2) power supply, (3) solar photoreactor, (4) reservoir, (5) peristaltic pump, (6) flowmeter and (7) heat exchangers. Adapted from [14].

Figure 14. Variation of (a) TOC and (b) energy consumption per unit TOC mass with electrolysis time for the SPEF treatment of 2.5 L of a simulated textile dyeing wastewater (330 mg L^{-1} TOC from additives) with 0.10 M Na_2SO_4 of pH 3.0 at 1.0 A, 35 ºC and liquid flow rate of 200 L h^{-1}. The

solutions contained: (□) 0.5 mM Fe^{2+} + 0.1 mM Cu^{2+}; (▲) 0.5 mM Fe^{2+} and 200 mg L^{-1} Disperse Blue 3 (DB3) and (△) 0.5 mM Fe^{2+} + 0.1 mM Cu^{2+} and 200 mg L^{-1} DB3. Adapted from [89].

Figure 15. (a) Experimental setup of a 10 L recirculation pre-pilot plant for the SPEF treatment of organic pollutants. (1) Flow electrochemical cell, (2) reservoir, (3) sampling, (4) peristaltic pump, (5) flowmeter, (6) heat exchanger, (7) solar CPC (photoreactor), (8) power supply and (9) air pump. (b) Scheme of a combined filter-press electrochemical cell. (1) End plate, (2) gasket, (3) air inlet, (4) air outlet, (5) air chamber, (6) 90 cm^2 BDD anode, (7) 90 cm^2 air-diffusion (ADE) cathode, (8) 90 cm^2 CF cathode, (9) 90 cm^2 Pt anode, (10) liquid compartment, (11) liquid inlet in the cell, (12) liquid outlet of the Pt/CF pair connected to 13, (13) liquid inlet in the BDD/ADE pair and (14) liquid outlet of the cell. Adapted from [122].

Figure 16. (a) TOC removal with electrolysis time for the EF and SPEF treatments of 10 L of 0.246 mM metoprolol tartrate in 0.10 M Na_2SO_4 with 0.5 mM Fe^{2+} at pH 3.0 and 35 ºC in the pre-pilot plant of

Figure 15a with single and combined cells. (b) Decay of 0.492 mM metoprolol under the same conditions. The inset panel shows the kinetic analysis assuming a pseudo-first-order reaction for the pharmaceutical. (□) EF in Pt/ADE cell at 3.0 A, (■) EF in Pt/ADE–Pt/CF cell at 3.0–0.4 A, (○) EF in BDD/ADE cell at 3.0 A, (●) EF in BDD/ADE–Pt/CF cell at 3.0–0.4 A, (△) SPEF in Pt/ADE–Pt/CF cell at 3.0–0.4 A and (▲) SPEF in BDD/ADE–Pt/CF cell at 3.0–0.4 A. Adapted from [122].

Figure 17. Experimental setup for the solar photoelectrocatalysis (SPEC) treatment of 60 mL of a bisphenol-A solution. A solar simulator with a 150 W Xe lamp and current density in the range 0.02-0.32 mA cm^{-2} were employed. Adapted from [124].

Figure 18. (a) Experimental setup of the aerated three-electrode undivided quartz cell with 5 cm^2 electrodes used for the photoassisted electrochemical oxidation of 30 mL of a 0.1 mM Orange G solution with an 8 W UVA lamp. In PEC the bias potential applied to the Ti/TiO_2 anode was +0.71 V/SCE, whereas an E_{cat} of -0.54 or -0.71 V/SCE was applied to the reticulated vitreous carbon (RVC) for H_2O_2 electrogeneration. (b) Dye concentration decay from: (●) direct photolysis, (□) AO with a TiO_2/Pt cell, (▲) TiO_2 photocatalysis, (▼) PEC with a TiO_2/Pt cell, (○) PEC with a TiO_2/RVC cell,

(■) PEF with 17.6 mg L^{-1} Fe^{2+} at pH 3.0 with Fe/RVC cell and (△) PEC coupled to EF with 17.2 mg L^{-1} Fe^{2+} at pH 3.0 using a TiO_2/RVC cell. Adapted from [141].

Figure 19. Ultrasound tip in front of a BDD anode (distance = 5 mm) in a sonoelectrochemical reactor for organic pollutant degradation. Adapted from [145].

Figure 20. Decay of 2,4-D concentration with time during the treatment of 250 mL of 1 mM herbicide in the presence of 0.1 mM Fe^{3+} as catalyst, at 200 mA, pH 3.0 and room temperature in a Pt/CF cell. Sonoelectro-Fenton (SEF) process with low frequency ultrasounds of 28 kHz and at output power of: (○) 20, (□) 60 and (△) 80 W; (◆) EF process alone. Adapted from [16].

FIGURES

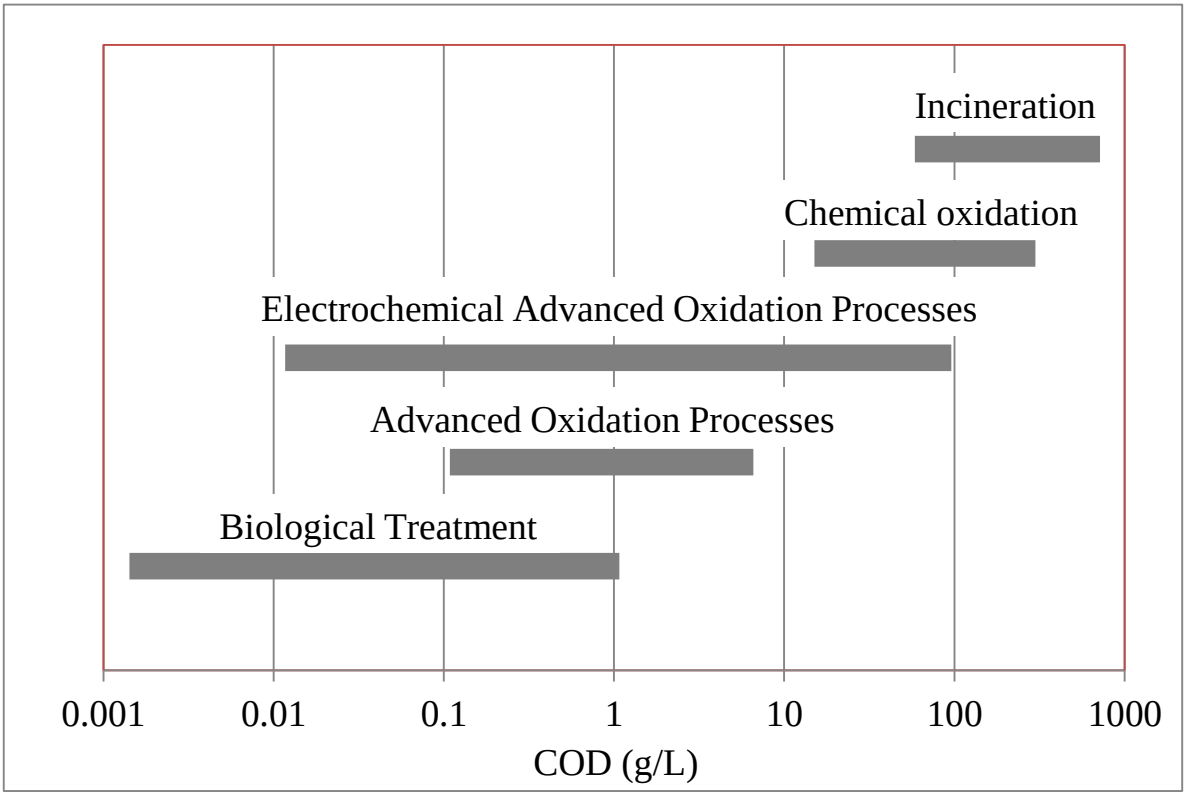
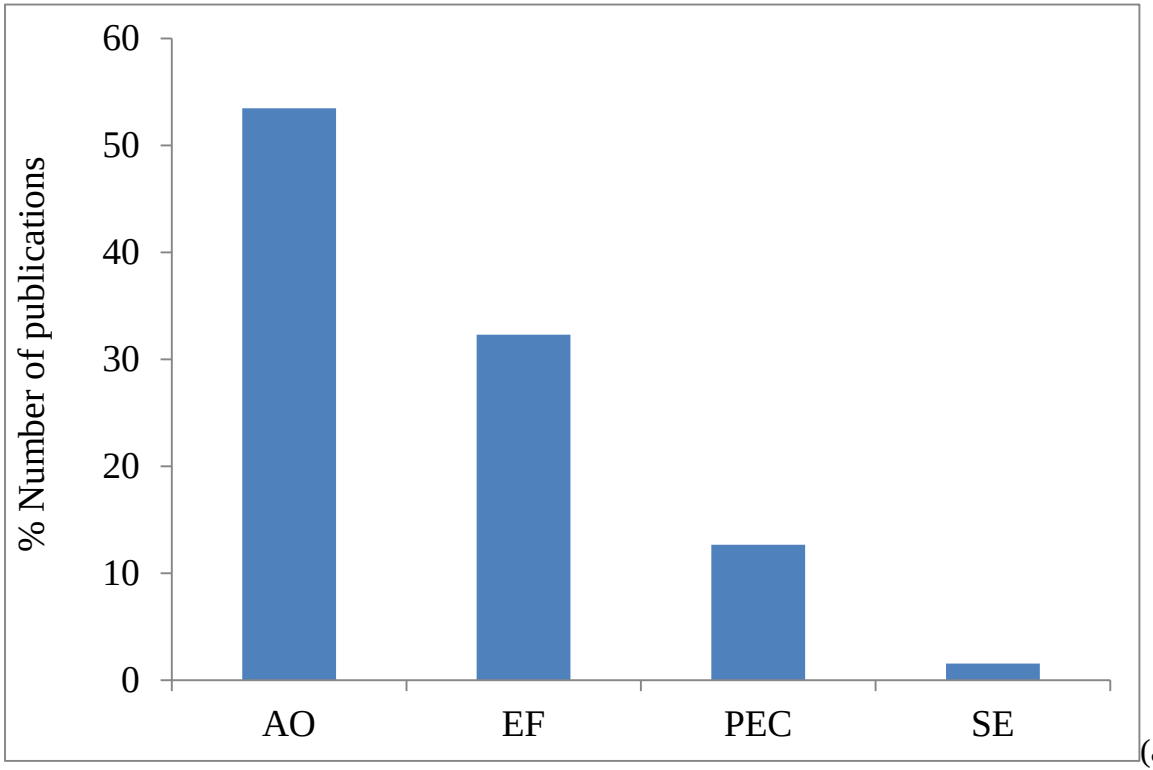


Figure 1


% Number of publications
60
50
40
30
20
10
0
AO
EF
PEC
SE
(a)

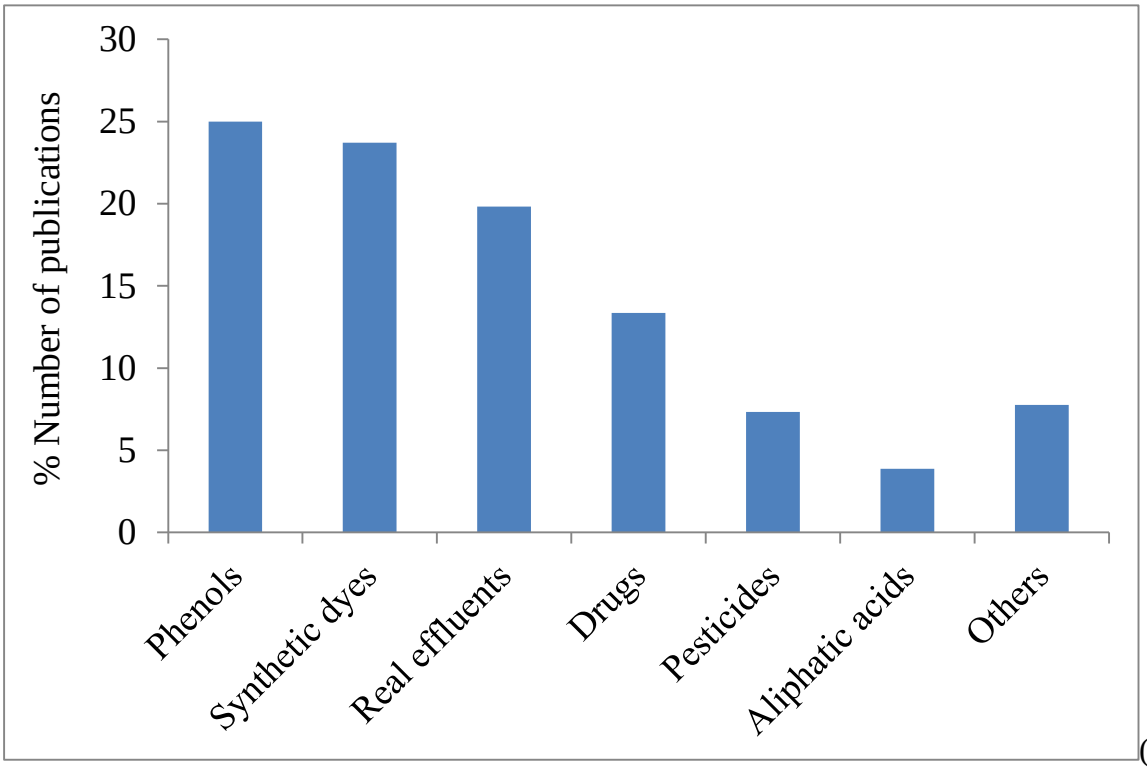

% Number of publications
30
25
20
15
10
5
0
Phenols
Synthetic dyes
Real effluents
Drugs
Pesticides
Aliphatic acids
Others
(b)

Figure 2


DIAMONOX
On-site Generation
Model 40 Cell
Electrochemistry Made Robust

Figure 3

Figure 4

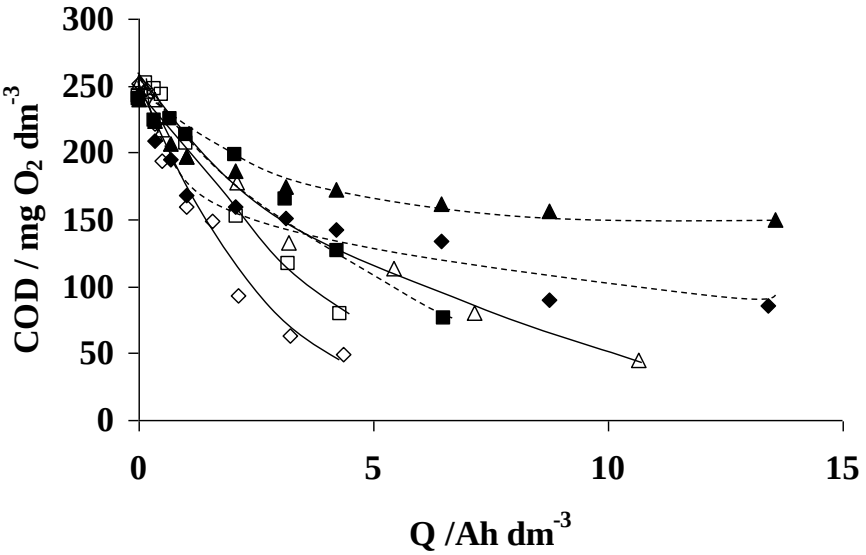


Figure 5

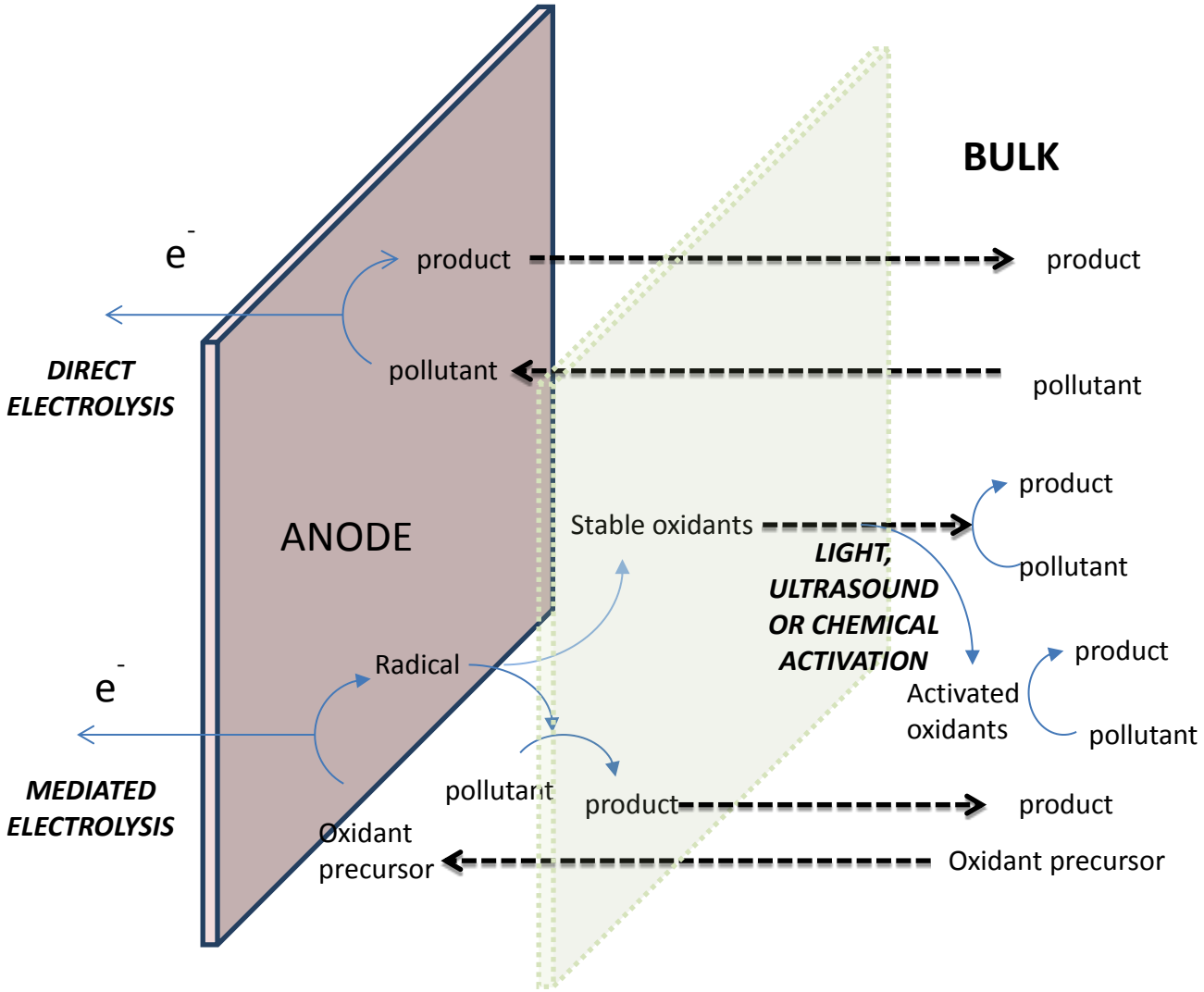

BULK
e-
product
product
DIRECT
ELECTROLYSIS
pollutant
pollutant
ANODE
Stable oxidants
product
pollutant
LIGHT,
ULTRASOUND
OR CHEMICAL
ACTIVATION
Radical
product
Activated
oxidants
pollutant
e-
MEDIATED
ELECTROLYSIS
pollutant
product
product
Oxidant
precursor
Oxidant precursor

Figure 6

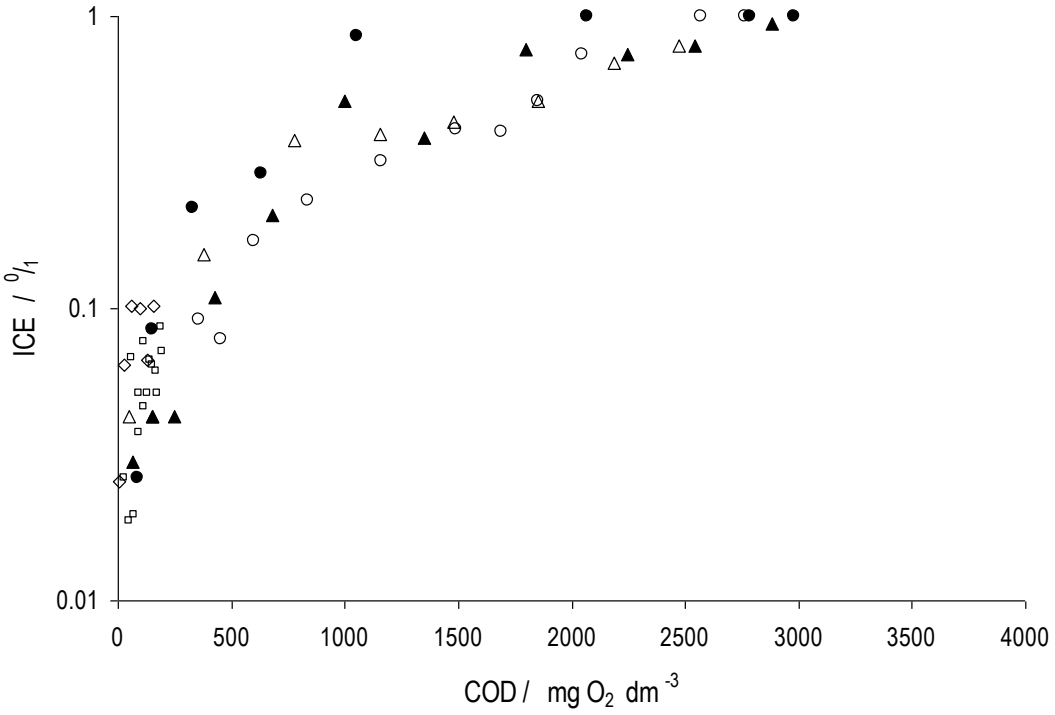

1
0.1
0.01
ICE / %
0
500
1000
1500
2000
2500
3000
3500
4000
COD / mg O2 dm-3

Figure 7

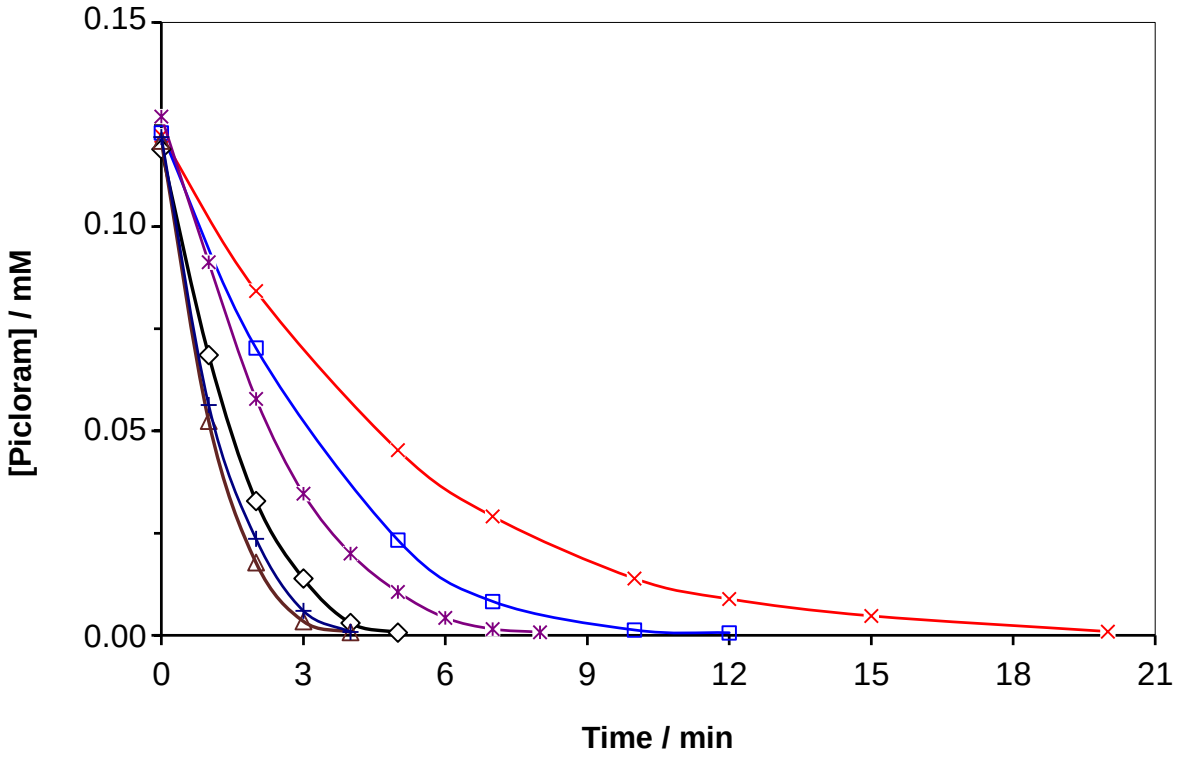


Figure 8

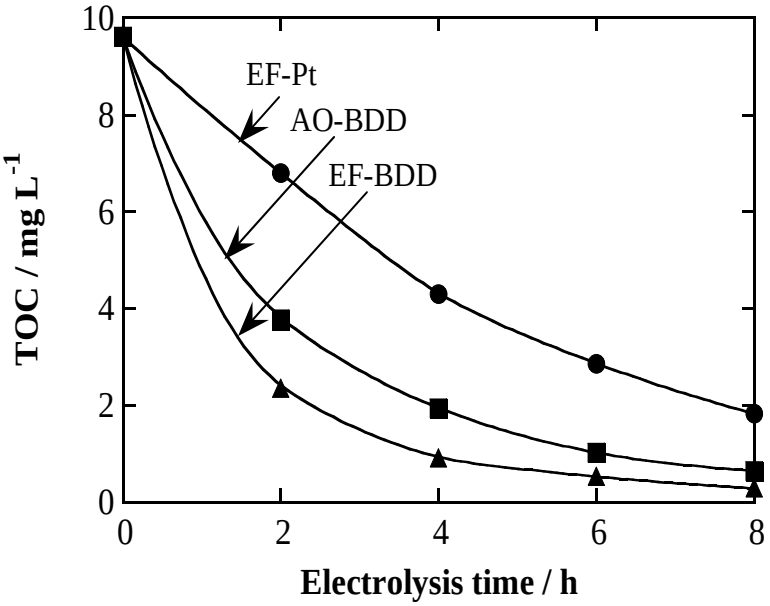

10
8
6
4
2
0
0
2
4
6
8
TOC / mg L-1
Electrolysis time / h
EF-Pt
AO-BDD
EF-BDD

Figure 9

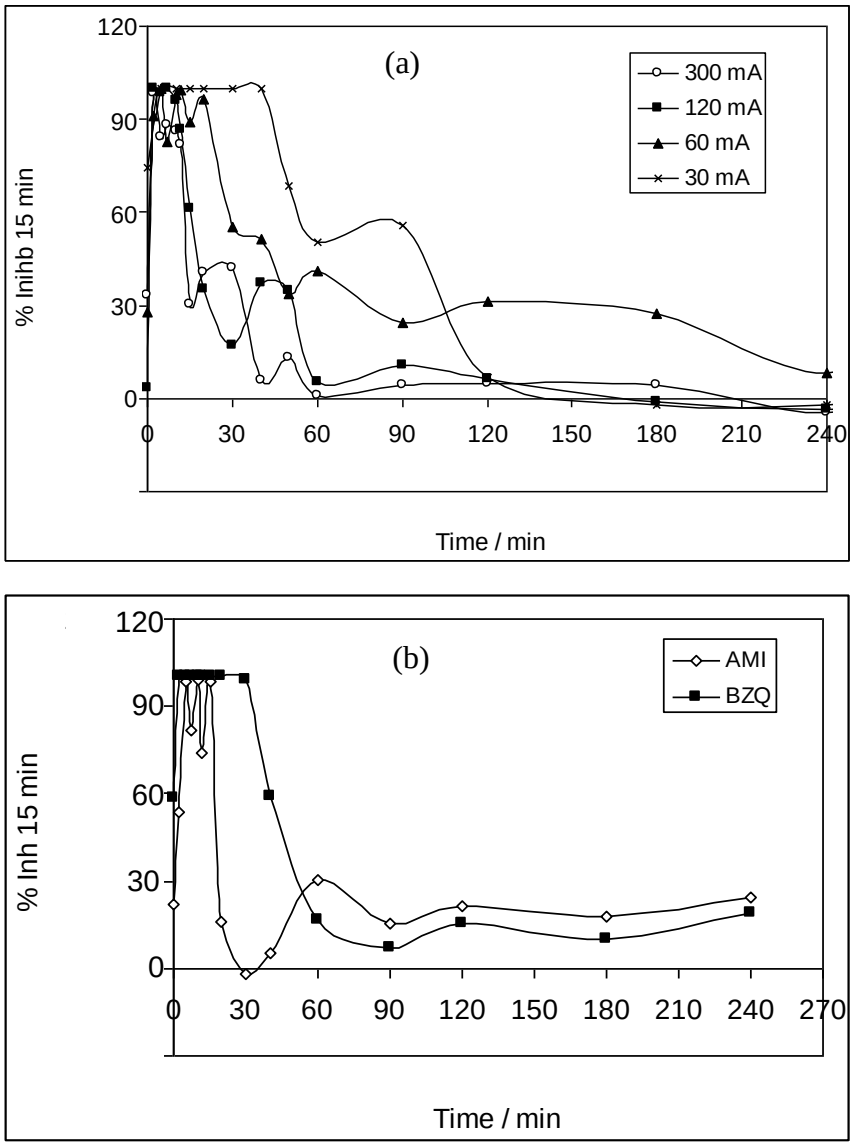

(a)
300 mA
120 mA
60 mA
30 mA
% Inihb 15 min
Time / min
120
90
60
30
0
0
30
60
90
120
150
180
210
240
(b)
AMI
BZQ
% Inh 15 min
Time / min
120
90
60
30
0
0
30
60
90
120
150
180
210
240
270

Figure 10

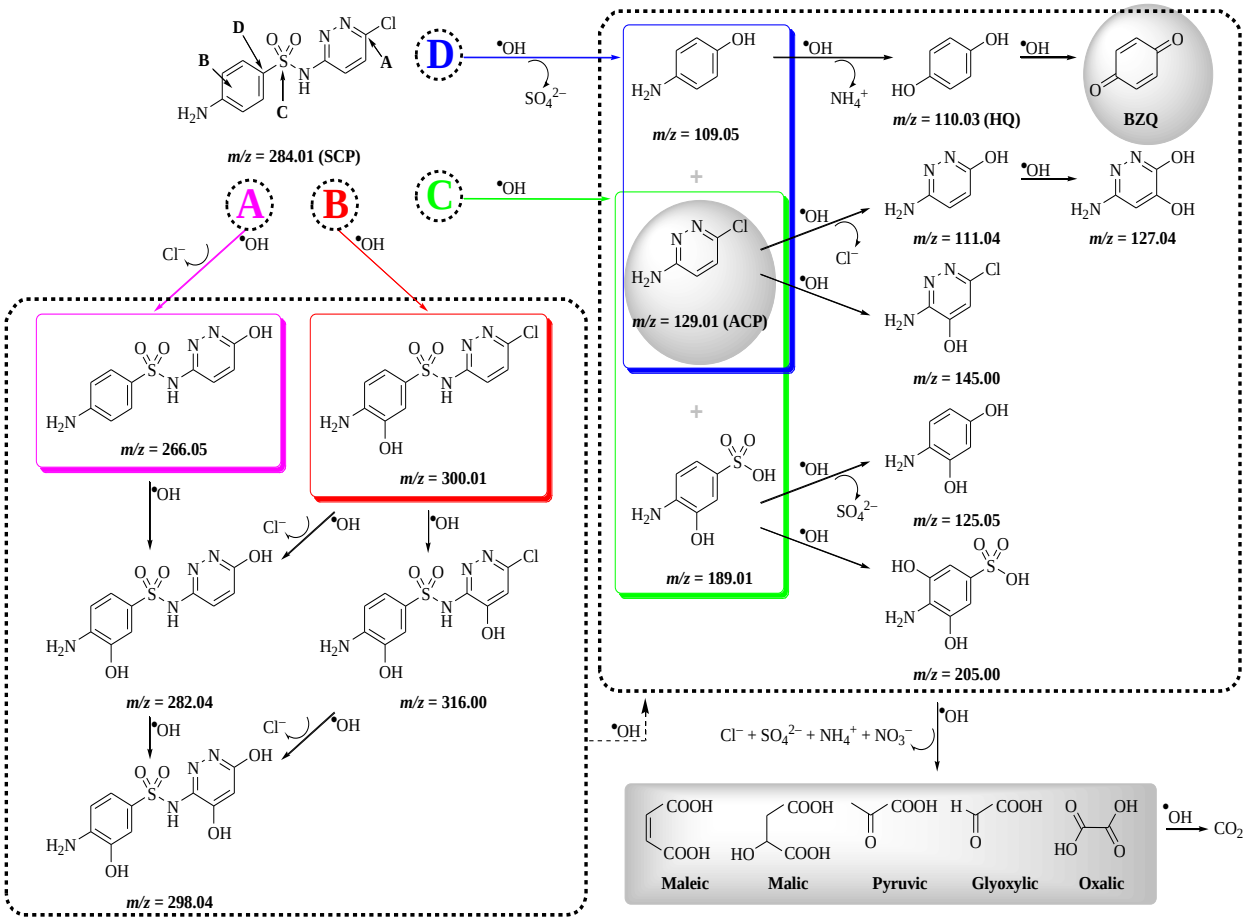

m/z = 284.01 (SCP)
m/z = 109.05
m/z = 110.03 (HQ)
BZQ
m/z = 111.04
m/z = 127.04
m/z = 129.01 (ACP)
m/z = 145.00
m/z = 125.05
m/z = 189.01
m/z = 205.00
m/z = 266.05
m/z = 300.01
m/z = 282.04
m/z = 316.00
m/z = 298.04
Maleic
Malic
Pyruvic
Glyoxylic
Oxalic

Figure 11

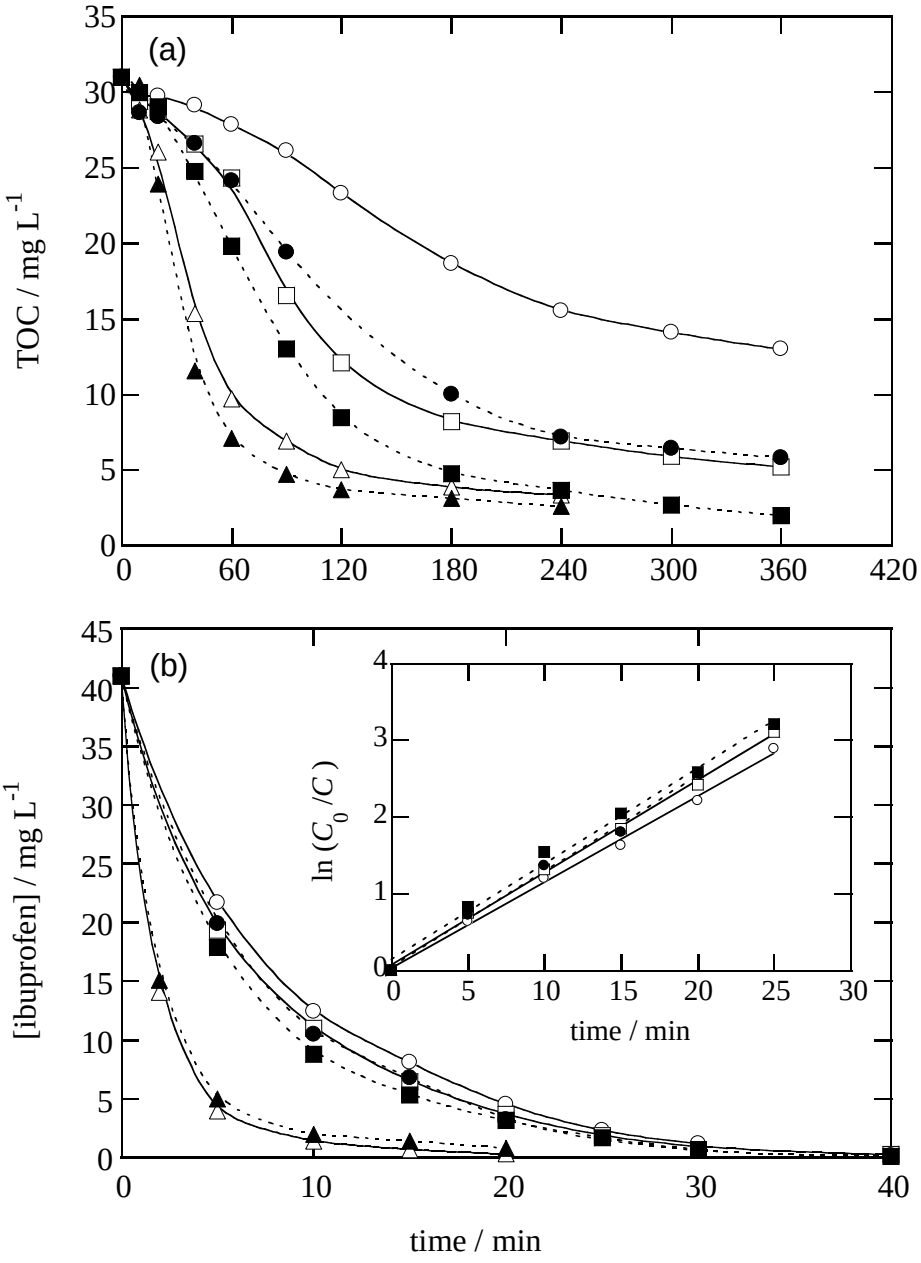

(a)
TOC / mg L-1
0
5
10
15
20
25
30
35
0
60
120
180
240
300
360
420
(b)
[ibuprofen] / mg L-1
ln (C0 /C)
time / min
0
5
10
15
20
25
30
35
40
45
0
1
2
3
4
0
5
10
15
20
25
30
time / min

Figure 12

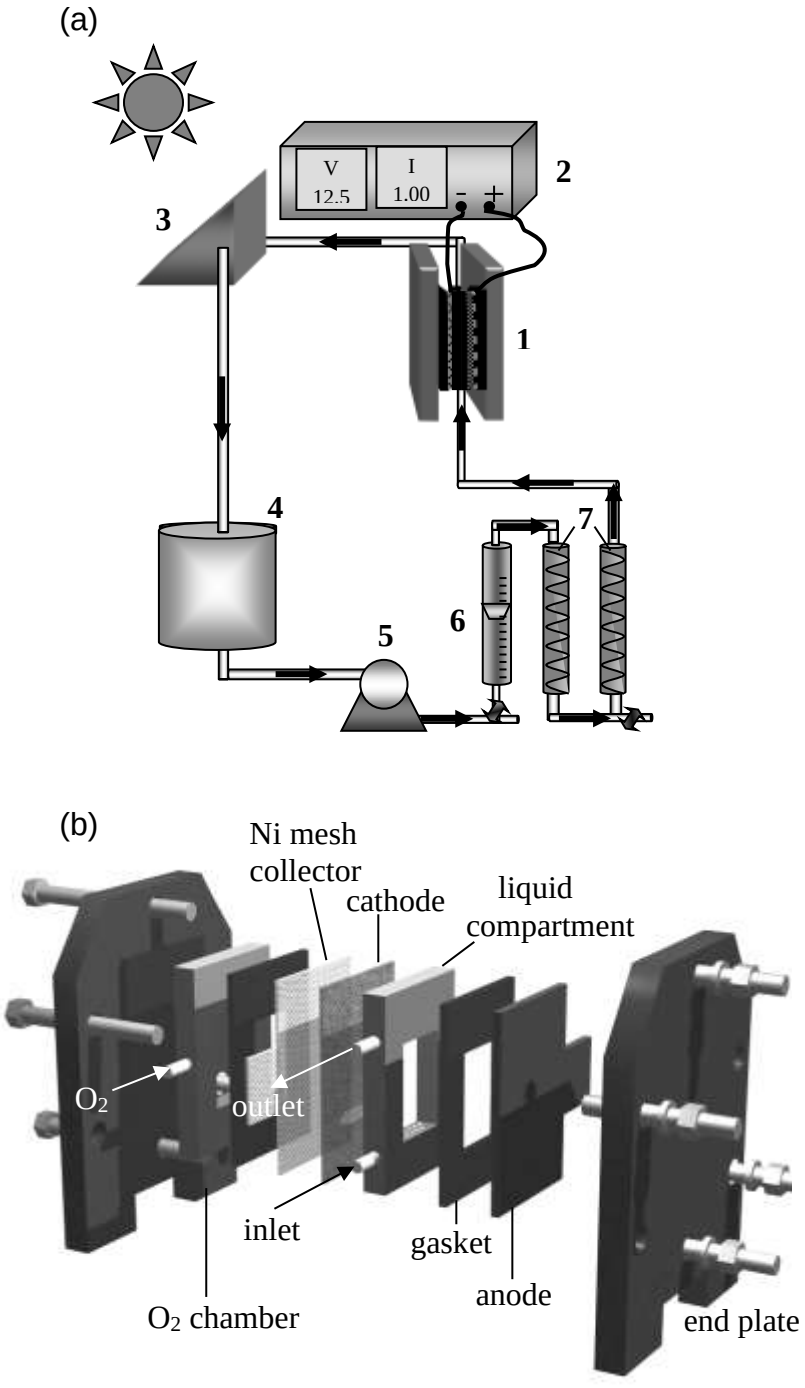

(a)
V
12.5
I
1.00
2
3
1
4
7
6
5
(b)
Ni mesh
collector
cathode
liquid
compartment
O_2
outlet
inlet
gasket
anode
O_2 chamber
end plate

Figure 13

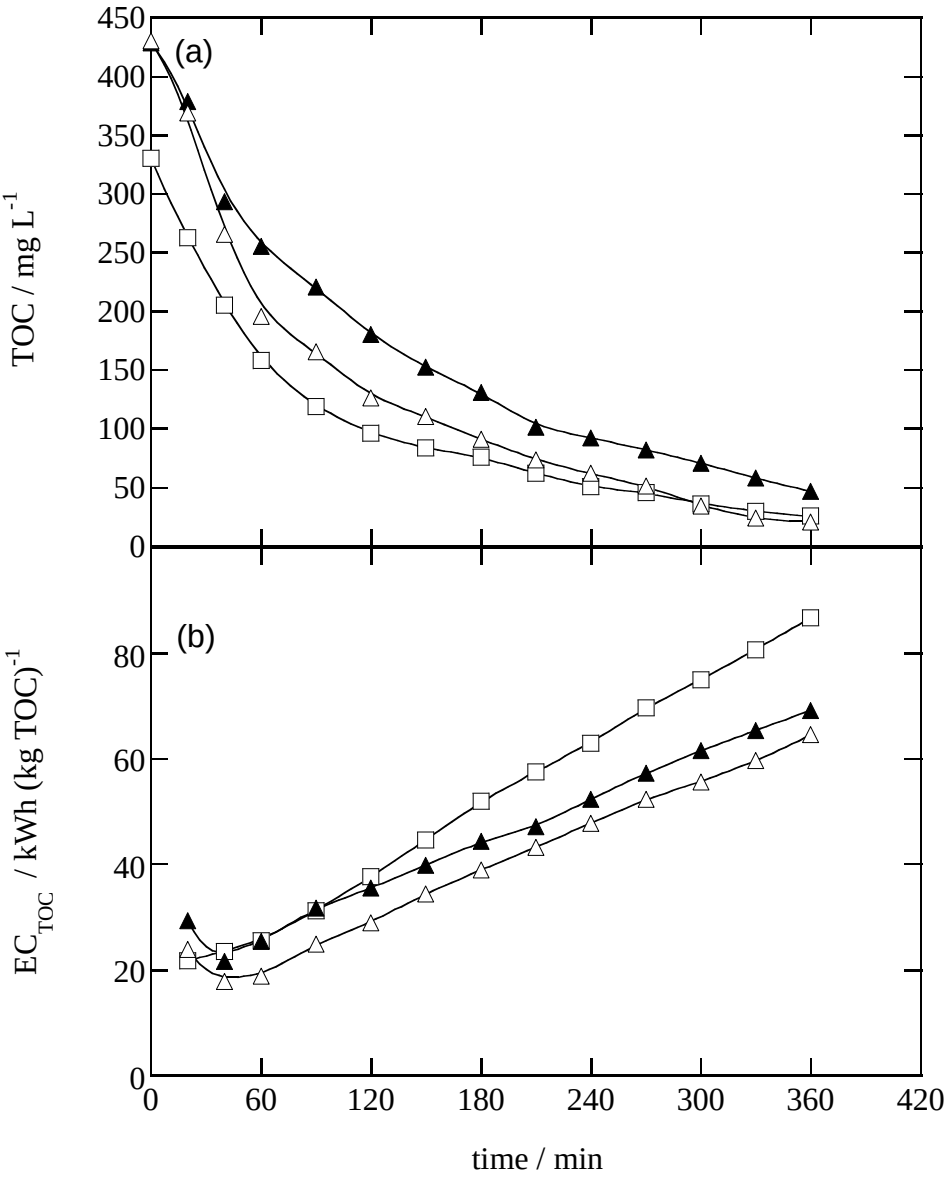

(a)
(b)
TOC / mg L-1
ECTOC / kWh (kg TOC)-1
time / min
0
50
100
150
200
250
300
350
400
450
20
40
60
80
0
60
120
180
240
300
360
420

Figure 14

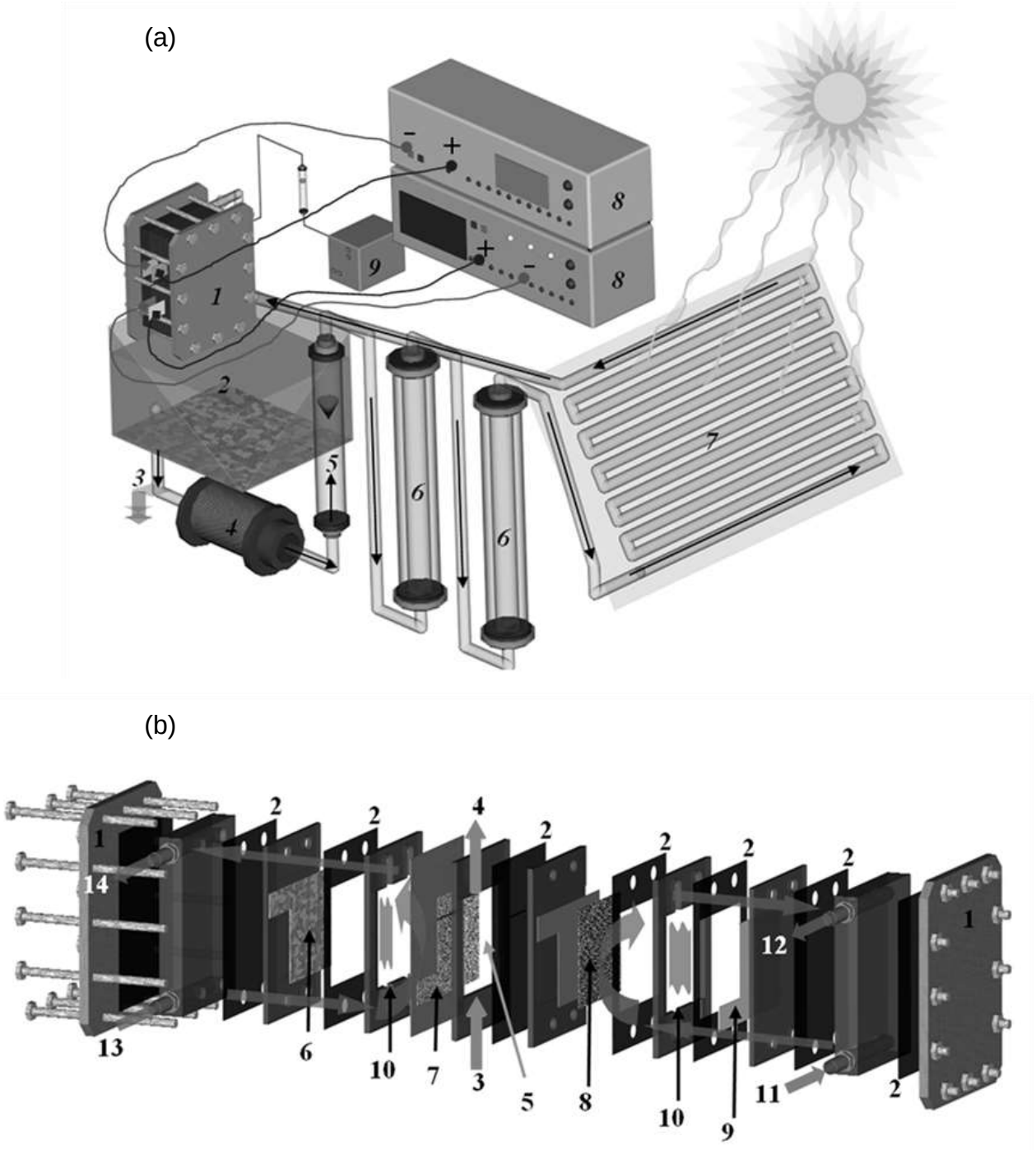


Figure 15

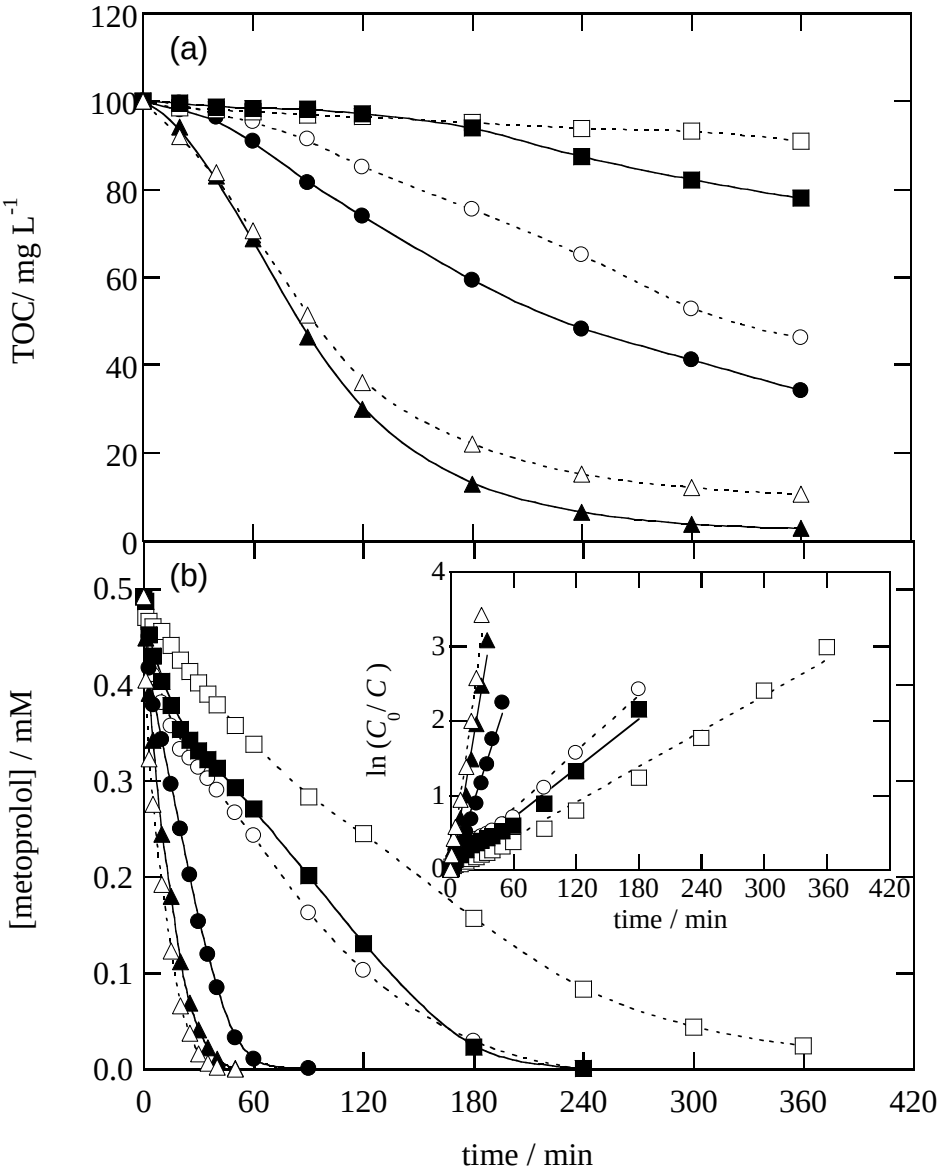


Figure 16

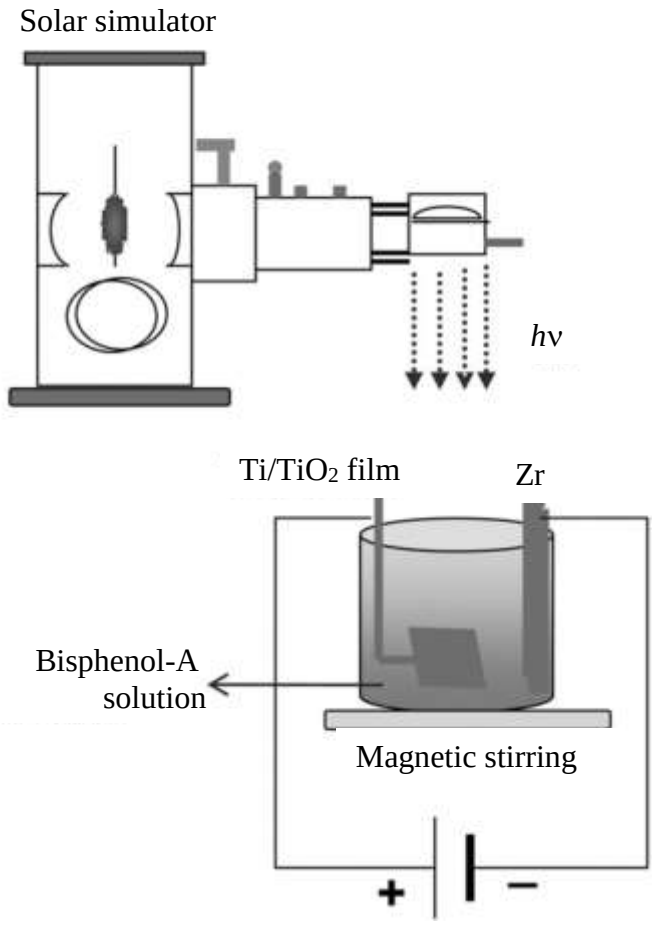

Solar simulator
hν
Ti/TiO2 film
Zr
Bisphenol-A
solution
Magnetic stirring
+
−

Figure 17

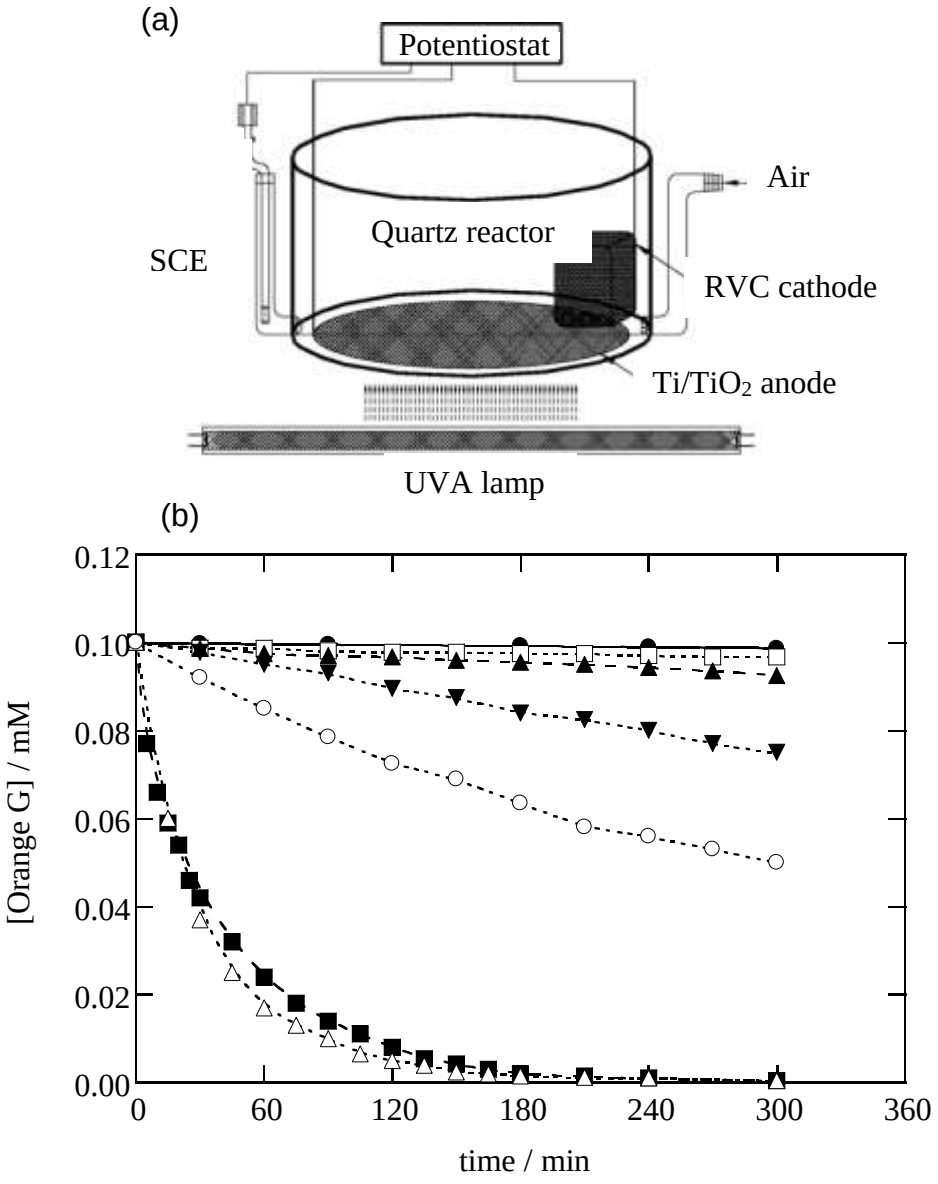

(a)
Potentiostat
Air
Quartz reactor
SCE
RVC cathode
Ti/TiO2 anode
UVA lamp
(b)
[Orange G] / mM
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0
60
120
180
240
300
360
time / min

Figure 18

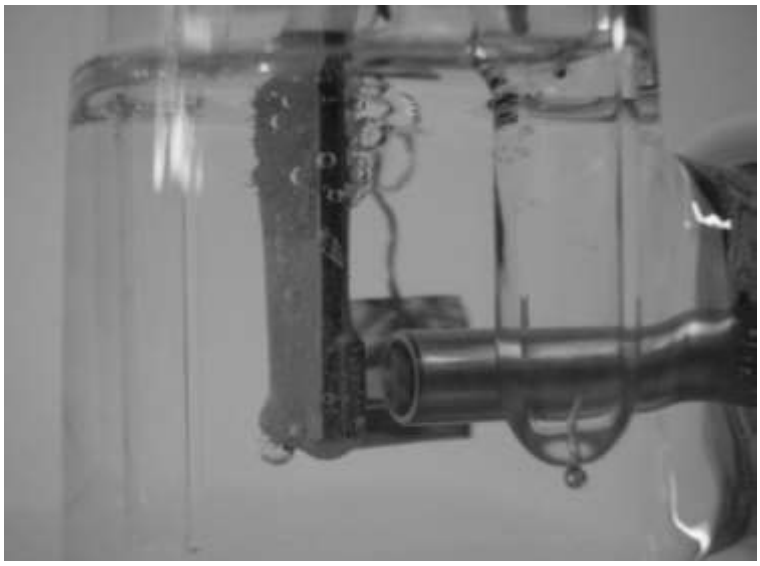


Figure 19

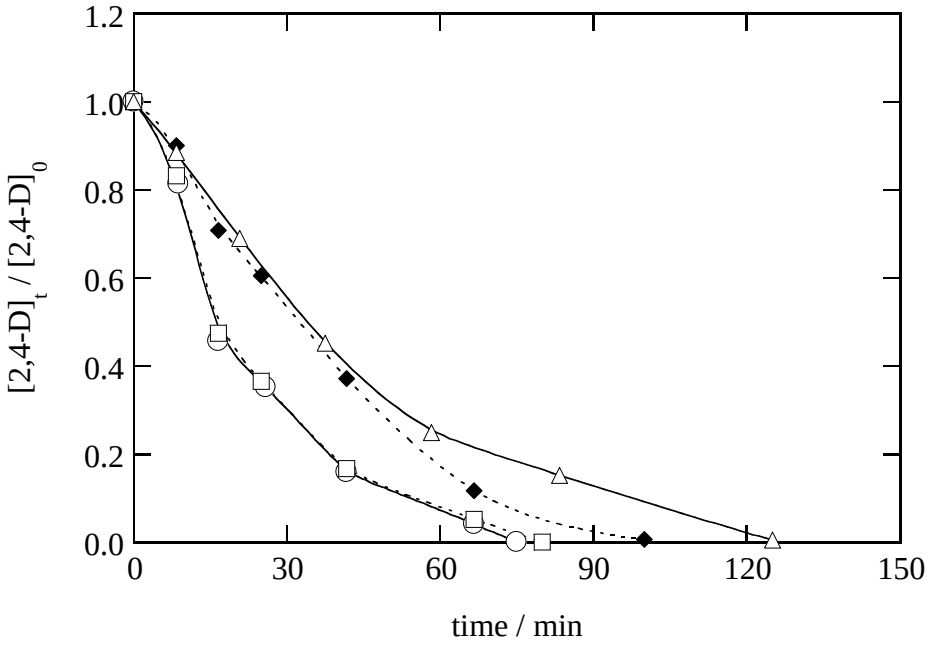


Figure 20