

Chapter

UNDERSTANDING THE EFFICIENCY OF ELECTROCHEMICAL OXIDATION IN TOXICITY REMOVAL

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ABSTRACT

Today's modern society produces a large amount of wastewaters rich in toxic compounds that, if not properly treated, will have deleterious environmental impact. Considering that conventional treatment methods have limitations in the complete removal of some of the most recalcitrant compounds, the need for more efficient treatments becomes imperative.

Over the past decades, electrochemical oxidation as proved to be a powerful remediation process due to its high oxidizing nature and ease of operation.

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However, in recent years, concern for the toxicity evolution of wastewaters, treated by this method, has increased. Therefore, ecotoxicity tests, performed with organisms from different trophic levels, are nowadays an important parameter included in degradation and remediation studies.

The present work seeks to increase the knowledge on the efficiency of the electrochemical oxidation method in toxicity removal of synthetic and real wastewaters. Electrochemical oxidation processes will be characterized from an ecotoxicological perspective. This approach will allow to evaluate the influence of the electrochemical degradation parameters, such as electrode material or type of electrolyte, in the modulation of toxicity under different scenarios. This chapter aims to provide a comprehensive review on the available literature published since its origin, in the 1990s up to the present.

Keywords: electrochemical oxidation; toxicity; risk evaluation; bioassays

INTRODUCTION

Industrialization, fast urbanization and population growth have contributed to numerous environmental problems, including the generation of wastewaters. Proper treatment must be employed to these wastewaters prior to their release into the aquatic ecosystem to minimize potential harmful impacts. Over the last decades, several technologies have been applied to treat these wastewaters, being the processes involving the use of biological reactors the most common. However, depending on the characteristics of the effluent, these conventional treatments may not be sufficient to reach the level of purification needed to eliminate the negative impact on the environment, since the microorganisms employed (bacteria, yeasts, fungi, algae) can be very sensitive towards the effluent toxicity. Given this, new approaches that do not include the use of microorganisms are being pursued. In this line, electrochemical oxidation is considered to be a promising technology.

Electrochemical oxidation (EO) main advantages include high-current efficiency, no secondary pollution, versatility, safety, ease of operation and environmental compatibility. These abilities make EO a promising remediation technology, being extensively studied in synthetic and real wastewaters treatment. EO consists in the oxidation of pollutants in an electrolytic cell via two mechanisms: (i) direct oxidation, occurring directly at the surface of the anode through direct electron transfer (this mechanism yields very poor decontamination) and (ii) chemical reaction with electrogenerated hydroxyl radicals from water discharge at the anode, such as physisorbed and chemisorbed "active oxygen". Indirect oxidation also occurs in bulk solution through mediators such as active chlorine species (Cl^\cdot , Cl_2 , HClO and ClO^\cdot) formed when chloride is electrolyzed (i.e. when chloride is used as support electrolyte or in real effluents with high

concentrations of chloride) [1]. Depending on the type of anode and potential difference of the electrolytic cell, partial or total combustion of the organic compounds can occur. When employing traditional materials such as platinum and even iridium and ruthenium oxides (IrO_2 and RuO_2) as anodes, partial oxidation to compounds such as carboxylic acids usually occurs. However, for BDD and some metal oxides anodes such as PbO_2 and SnO_2 , with higher oxygen overpotentials, a higher current efficiency occurs which can lead to the total combustion of the organic matter, culminating with CO_2 as final product [2].

When dealing with electrochemical oxidation the role of the anode material is extremely important and will dictate the outcomes obtained. Hence, this chapter was organized in terms of anodes categories. For this purpose, six main types of anodes were grouped: i) metal oxides anodes divided in lead dioxide (PbO_2 - Group 1) and dimensionally stable anodes (DSA-Group 2), boron-doped diamond (BDD-Group 3), platinum (Group 4), carbonaceous (Group 5) and others (Group 6). PbO_2 anodes appear separated from the other metal oxide anodes as they are one of the most commonly studied metal oxide anodes, mainly because of its high oxygen overpotential. DSA-type electrodes encompass several materials of a titanium base metal covered by a thin conducting layer of metal oxide or mixed metal oxides of titanium, ruthenium, iridium, tin, tantalum and antimony. In Figure 1, a distribution of the number of publications using each type of anode, involving toxicity assessment, can be visualized, with the most commonly used anodes being DSA-type and BDD.

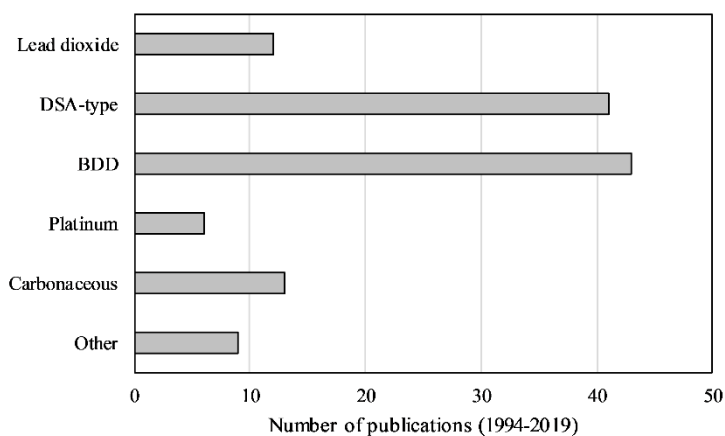


Figure 1. Number of publications reporting on the electrochemical oxidation of synthetic and real effluents, with toxicity assessment, divided by the type of anode

employed (in the period 1994 – 2018). Data retrieved from Web of Science, March 2019.

Electrochemical oxidation has proven to be efficient in the degradation and combustion of several types of compounds and real effluents. Yet, only recently the concern to understand if this technology is also capable of reducing the toxicity of the treated effluents started to emerge as it can be seen in Figure 2. Overall, the number of studies that performed ecotoxicity tests to electrochemically treated (synthetic and real) effluents, increased significantly since 2010, from less than 5 papers per year up to 28 publications in 2018.

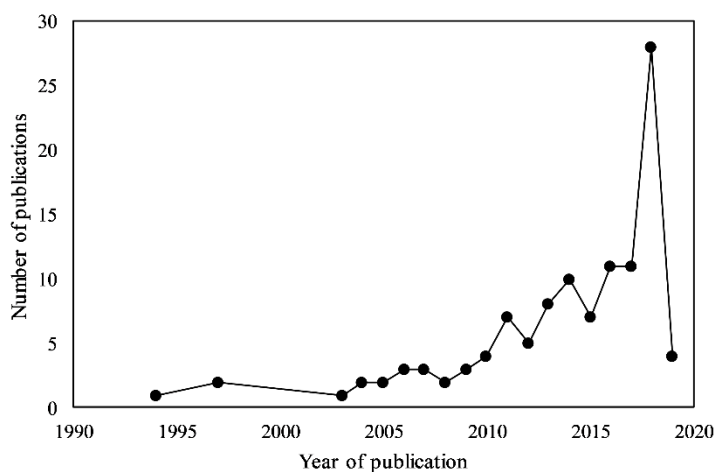


Figure 2. Number of papers published per year until May 2019 regarding electrochemical oxidation treatments that perform toxicity evaluation. Data retrieved from Web of Science, March 2019.

The evaluation of the effluent toxicity can be performed using diverse bioassays that can be used alone or combined. Figure 3 describes the relative use of the different bioassays. Bacteria is overall the most used bioassay to measure the toxicity of the electrochemically treated samples, being used in 55.1% of the publications. This can be attributed to the rapid, reproducible and cost-effective nature of these bacterial assays, with the bioluminescence inhibition assay with *V. fischeri* the most frequently chosen. This was followed by plants (16.3%), fish (9.3%) and crustaceans (6.4%), with organisms belonging to other taxonomic groups (e.g. algae, nematodes, fungi and mammals) employed less frequently. More

recently [3; 4], computational methods to predict toxicities via structural analysis, such as the ECOSAR program and EPIWIN software, are being used.

For each taxonomic group, different species were used to assess the toxicity of the treated effluents. A list of all mentioned species, throughout the review, is presented in Table 1.

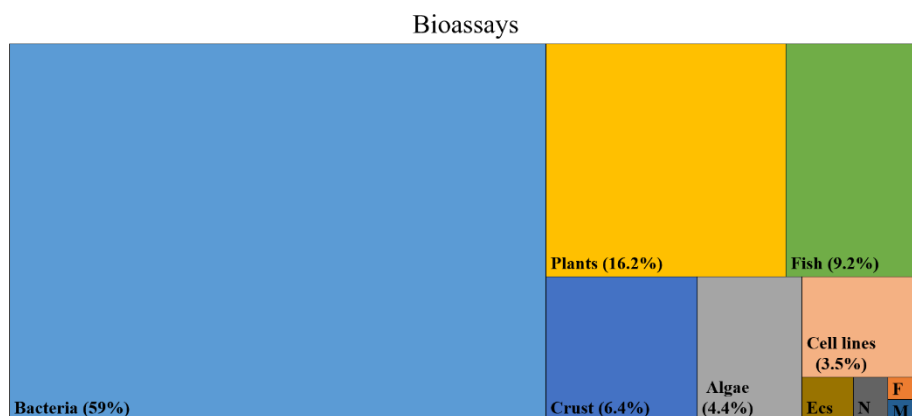


Figure 3. Relative distribution of the different bioassays employed to determine the toxicity of electrochemically treated synthetic and real wastewaters. Crust: crustaceans; Ecs: Ecosar; N: nematodes; F: fungi; M: mammals.

Table 1. List of all species, mentioned in this review, by taxonomic group

Taxonomic group	Species
Algae	<i>S. vacuolatus</i> , <i>D. subspicatus</i> , <i>P. subcapitata</i> , <i>C. vulgaris</i> , <i>S. obliquus</i>
Bacteria	<i>B. cereus</i> , <i>E. coli</i> , <i>P. aeruginosa</i> , <i>S. typhimurium</i> , <i>S. aureus</i> , <i>V. fischeri</i> , <i>V. qinghaiensis</i>
Crustacean	<i>D. similis</i> , <i>D. magna</i> , <i>A. nauplii</i> , <i>A. salina</i>
Fish	<i>D. rerio</i> , <i>O. niloticus</i> , <i>A. panchax</i>
Fungi	<i>S. cerevisiae</i>
Nematode	<i>C. elegans</i>
Plant	<i>L. sativa</i> , <i>V. radiata</i> , <i>V. faba</i> , <i>L. minor</i> , <i>P. sativum</i> , <i>M. sativa</i> , <i>A. cepa</i>

In this chapter, the efficiency in toxicity removal, of synthetic and real wastewaters, by the electrochemical oxidation method, is reviewed, regarding anode materials and operational conditions.

ANODE MATERIAL

Metal oxides anodes – Lead dioxide anodes

Lead dioxide anodes have been used to treat several types of effluents including biocides, dyes, pharmaceuticals and real petrochemical wastewaters. To evaluate the efficiency in toxicity removal using PbO₂ anodes different bioassays from different taxonomic groups and levels of organization are reported in the literature. Overall, most studies used bacteria (37.9%), followed by plants (34.5%), fish (13.8%), cell lines (10.3%) and algae (3.4%).

Biocides

Lead dioxide anodes have been successfully used to remove biocides from effluents. Han et al. [5] prepared a TiO₂-NTs/SnO₂-Sb/PbO₂ anode and studied its efficiency on the removal of fungicides tricyclazole and propiconazole, from aqueous solutions. The nanotubular TiO₂ arrays were the selected substrate, as it increases the electrode surface area, and the number of active sites for the in-situ production of hydroxyl radicals. The electrochemical activity of the anode was tested at an applied current density of 15 mA cm⁻², for 2 hours, achieving COD removals of 58.0% and 70.0% for tricyclazole and propiconazole, respectively. The acute 48-h static toxicity test was performed with zebrafish (*D. rerio*), according to OECD Guideline 203, using effluent collected before and after the treatment. A substantial reduction in the toxicity was observed for the treated tricyclazole effluent, with EC_{50,48h} changing from an initial value of 17.5% to 45.6% after the 2-h treatment. In the case of propiconazole a less significant reduction was observed with an EC_{50,48h} changing from 2.7% to 11.3%. The smaller reduction in the toxicity observed for the latter effluent was attributed to the formation of toxic intermediates, such as 2,4-dichlorophenol and 2,4-dichlorobenzoic acid, identified by GC-MS (gas chromatography-mass spectrometry) and LC-(ESI)-MS/MS (liquid chromatography electrospray ionization tandem mass spectrometry). Another study regarding the degradation of fungicides by electrochemical oxidation in PbO₂ anodes was performed by Liu et al. [6]. In this study, the performance of 3-dimensional ordered microporous PbO₂ filters (3DOM-PbO₂) and flat Ti/PbO₂ was investigated in the degradation of flutriafol, under a current density of 5 mA cm⁻². The toxicity of the effluent was also evaluated using the acute 48-h static toxicity test on zebrafish, for a 2-h degradation assay, with a LC_{50,48h} of 35% for the initial solution. Regarding the test performed with the flat Ti/PbO₂ anode, the LC_{50,48h} value sharply decreased to 15% after the first hour, followed by a gradual increase

to 40% by the end of the 2-h assay. This initial increase in the effluent toxicity to zebrafish was attributed to the formation of toxic intermediates during the first hour such as 2,4'-difluorobenzophenone and o-benzoquinone, identified by GC-MS. These compounds go under further degradation, for the remaining assay time, with the opening of the aromatic rings and formation of low toxic carboxylic acids. In contrast, for the 3DOM-PbO₂ the LC_{50,48h} steadily increases until 70% during the 2-h assay, indicating a higher catalytic activity and more efficient mineralization process when compared with the flat Ti/PbO₂ anode. These studies highlight the positive influence of a high surface area substrate in the catalytic activity of the lead dioxide anode, for both TiO₂-NTs/SnO₂-Sb/PbO₂ [5] and 3DOM-PbO₂ [6]. However, under the applied conditions, the toxic metabolites formed during the electrochemical process are not fully eliminated from the effluent, which contributes to the measured final toxicity values to zebrafish.

Dyes

Dyes are a major contributor to environmental pollution as they are extensively used in several industries, encompassing many fields of up-to-date technology, in e.g., textile industry, leather tanning industry, food, cosmetic, pharmaceuticals, paper production, amongst others. Therefore, many studies focusing on the remediation of dye effluents, through electrochemical degradation, using PbO₂ anodes were reported [7-9]. One study employed PbO₂ coated on mild steel (MS-PbO₂) on the degradation of the azo dye Methyl Orange [7]. The synthetic effluent was treated at a current intensity of 0.12 A, for 7 hours, and both the degradation of the dye and toxicity of the solution were evaluated. The cytotoxicity tests were performed at 1-hour intervals in the human keratinocytes cell line (HaCaT cells). This cytotoxicity assay was chosen by the authors given that after the discharge of the resulting degradation effluent into the water bodies, the epithelial cells are the ones that are mainly exposed to these chemicals. According to the results, methyl orange was found to be less cytotoxic than its degradation intermediates, with an increase in the cytotoxicity after the first hour of electrolysis. During the degradation process, the formation of aromatic amines and diazonium salts was identified, by HPLC-ESI-MS (high-performance liquid chromatography-electrospray ionization tandem mass spectrometry) and attributed as responsible for the initial toxicity increase. As these intermediates were further degraded, the measured cytotoxicity decreased. A different trend was reported by Pillai and Gupta [8], when using a similar type of MS-PbO₂ anode on the electrochemical degradation of malachite green. The assays were run under a current density of 1.91 mA cm⁻², for 4 hours and the toxicity of the effluents before and after was measured

by the inhibition growth effect on *E. coli*. The obtained results indicated that even though the initial effluent possessed some inhibitory effect on the bacteria growth, the sample after electrochemical treatment did not have any inhibitory effect on the *E. coli* culture, indicating that none of the intermediates and end products were toxic to this bacteria strain. Nevertheless, it should be highlighted that these assays evaluate different endpoints and the first one uses only cells whereas the second one uses an entire organism (bacteria) and thus any direct comparison is not possible.

For the degradation of the dye amaranth, Elaissaoui et al. [9] prepared two PbO₂ anodes by coating a SiO_x interlayer through continuous galvanostatic (CG) and pulsed (P) methods (SS/SiO_x/PbO₂-CG and SS/SiO_x/PbO₂-P, respectively). A synthetic effluent, composed by the dye and Na₂SO₄ as support electrolyte, was treated under 25 mA cm⁻², for 5 hours. The resulting aqueous solution underwent phytotoxicity evaluation with the lettuce *L. sativa*, to assess the risk in its possible use for irrigation. The results registered a germination index of 78 and 75% for SS/SiO_x/PbO₂-CG and SS/SiO_x/PbO₂-P, respectively. According to the authors, such results indicate that the electrochemical degradation of this dye with the lead dioxide anodes resulted in non-phytotoxic waters.

A more detailed study on the evolution of the phytotoxicity of a synthetic effluent, electrochemically treated by β-PbO₂ anode, was performed by Ma et al. [10]. In this work, an effluent of quinoline was treated at a current density of 30 mA cm⁻², for 240 min. The phytotoxicity of the solutions was evaluated throughout the oxidation time, and the effects of pH and additional nutrients on the growth parameters of duckweed were also evaluated. Regarding the influence of pH, the solutions were tested without adjustment and with an adjusted pH of 7.5. The content of chlorophyll a (C_a) was significantly higher for the solution with pH 7.5 and it was reported that, after the first 100 min, the observed toxicity to the duckweed was directly associated to the low pH (from 4.3 to 3.8-4.0), caused by the formation of organic acids. However, in the first 60 min a decrease in the C_a was observed, which was related not only to the pH (formation of organic acids) but also to the formation of other toxic degradation intermediates. The same conclusions were drawn from the frond number (FN) parameter. The formation of some toxic intermediates, during the first 60 min of the electrochemical treatment, was further confirmed by the low results obtained during the study of the effect of additional nutrients (at pH 7.5), on both C_a concentration and FN of duckweed. After the 100 min and with the addition of nutrients, the inhibition of the solution on duckweed was not obvious. In the case of the degradation of chlorobenzene by the same type of Ti/β-PbO₂ anode, an overall similar behavior was reported regarding the solution toxicity to *C. vulgaris*, during a 120-min assay [11]. At a

current density of 15 mA cm^{-2} the calculated EC_{50} increased in the first 15 min, decreased slightly from 15 to 30 min and proceed to increase until the 120 min. The increase in toxicity observed during the 15 to 30 min stage was, once again, explained by the formation of more toxic intermediates, like phenol and 1,4-benzoquinone. These intermediates were identified by GC/MS and it was observed that when their concentration started to decrease, and more degradable and less toxic organic acids were formed, the toxicity towards the algae also decreased. A comparable toxicity evolution was reported by Pillai and Gupta [12] on the effluent resulting from the degradation of 2,4-dinitrophenol (2,4-DNP) with MS-PbO₂ anode. The cytotoxicity was assessed on the human keratinocyte cell line (HaCat cells) during the 180 min assay and presented a similar pattern of an initial decrease, followed by an interval of time in which the toxicity increased slightly (from 60 to 120 min) and a final decrease until the end of the assay, at 180 min. It was concluded that the final solution was less toxic than the initial 2,4-DNP effluent, and the observed increase in toxicity at 120 min was explained by the accumulation of some toxic intermediates like catechol (identified by HPLC), classified as a possible human carcinogenic.

Pharmaceuticals

Lead dioxide anodes were also applied in the electrochemical degradation of effluents containing pharmaceutical compounds [13-15]. Wang et al. [13] tested a Ti/SnO₂-Sb/La-PbO₂ anode in the degradation of the antibiotic enrofloxacin under a current density of 8 mA cm^{-2} , for 30 min, obtaining a 95.1% TOC reduction. The toxicity of the effluent was monitored along the time by the luminescence inhibition assay, using *V. fischeri*, and a slight increase from 22.5 to 27.9% inhibition was observed in the first 10 min, followed by a sharp decrease to 6.2% after 15 min. By the end of the electrochemical assay the inhibition effect on the bacteria had completely disappeared. The measured inhibition values coincide with the evolution of the detected intermediates during the assay time (by HPLC-TOF-MS), with an observed accumulation of most of the metabolites at ~10 min, followed by a gradual decrease in their concentration at ~15 min. Therefore, the observed toxicity was attributed to the possibility of some metabolites being more toxic than the initial compound. A similar behavior was observed by the same team [14], when they used a TiO₂ nanotube array intercalated anode (Ti/TNAs*/PbO₂) for the degradation of the antidepressant fluoxetine under 10 mA cm^{-2} , for 30 min. The inhibition (for the bacteria *V. fischeri*) increased dramatically to 100% after 5 min, followed by a decrease, reaching less than 2.2% at the end of the 30 min assay. This

toxicity evolution was also attributed to the formation and accumulation of higher toxic aromatic intermediates and their subsequent degradation.

Chiang et al. [15] tested the efficiency of Ti/PbO₂ anode on the degradation of two high molecular weight organics, lignin and tannic acid, a chelating agent (EDTA) and a pharmaceutical compound, the antibiotic chlortetracycline. The electrochemical treatment was performed for 2 hours, with NaCl as supporting electrolyte and under a current density of 7.5 A dm⁻². The toxicity of each effluent was monitored by *V. fischeri* inhibition assay, before and after electrolysis. Before treatment, lignin is nontoxic, while tannic acid, EDTA and chlortetracycline exhibit substantial toxic effect, with EC_{50,15min} of 6.63, 10.45 and 0.50%, respectively. After the 2-h assays, the EC₅₀ values for all treated effluents increased to more than 100%. Therefore, it was concluded that all remaining organics were nontoxic to the luminescent bacteria.

Real petrochemical wastewaters

The lead dioxide anode was also applied on the degradation of real petrochemical wastewaters produced during crude oil extraction in secondary extraction wells [16]. Ta/PbO₂ anode was employed at a current density of 30 mA cm⁻², for 11 h, obtaining a COD reduction of 84%. The initial wastewater was very cytotoxic to HeLa cells (epithelial cervical cancer cell line), with the treated effluent presenting some inhibitory effects on the human cells' growth in a dose-dependent way. The same study compared these results to those obtained by applying a BDD anode instead of Ta/PbO₂. For a lower electrolysis time (8 h), better results in terms of COD removal were obtained (94% reduction). This higher efficiency was also translated in a less toxic final effluent than the one obtained with the lead dioxide anode. Although the electrochemical application of both anodes resulted in a reduction of the toxicity, the final solutions were still toxic and inhibitory of cell growth.

Metal oxides anodes – Dimensionally stable anodes

Dimensionally stable anodes have been used to treat several types of simulated and real effluents. To evaluate the efficiency in toxicity removal using DSA-type anodes, most studies used bacteria (60.8%), followed by plants (15.7%), crustaceans (7.4%), fungi (7.4%) and cell lines (5.9%). Only 2.0% of the studies used algae and even a lower amount of studies evaluated the toxicity towards fish and mammals (0.5% each).

Synthetic effluents, encompassing several classes of contaminants, such as amines [17; 18], biocides [19; 20], dyes [21-24], pharmaceuticals [25-30], phenolic compounds [31-36], simulated tannery wastewaters [37] and others [38-41], were electrochemically treated with metal-oxide anodes like Ti/RuO₂ [17; 18; 29-32; 35; 38; 39], Ti/IrO₂ [23; 33; 41], Ti/SnO₂ [34; 41], Ti/Ir_{0.1}Sn_{0.9}O₂ [37], Ti/RuO₂-IrO₂ [26; 28; 32], Ti/SnO₂-Sb [27], Ti/Ru_{0.3}Ti_{0.7}O₂ [19; 20; 36], Ti/Ti_{0.66}Ru_{0.34}O₂ [24], Ti/IrO₂-RuO₂-TiO₂ [21; 22], Ti/IrO₂-Ta₂O₅ [32], Ti/Ta₂O₅-SnO₂-IrO₂ [32], Ti/Ce/SnO₂-Sb [25] and some with unspecified mixtures of metal oxides [40].

Amines

Regarding the electrochemical oxidation of the amines n-phenyl-n-isopropyl-p-phenylenediamine (commercial name Flexzone 3P) [17] and p-chloroaniline (PCA) [18], RuO₂ anodes were employed. Flexzone 3P, an aromatic amine used in chemical industries of rubber, antioxidant and antiozonant, was treated with Ti/TiRuO₂, at 0.025 A cm⁻², for 1 h and toxicity evaluation was performed by survival data analysis of fungi *S. cerevisiae*. The initial effluent exhibited a toxic effect that after 5 min decreased, which was in accordance with the 53.8% reduction in the aromatic amine concentration. Similar results were obtained for the electrochemical assays performed with PCA. These tests were performed with an electrochemical Ti/RuO₂ ceramic membrane system (prepared by thermal dip-coating of titanium mesh) operating in two modes: flow-by and flow-through. In the flow-by mode, the peristaltic pumps were turned off, while in flow-through mode, the synthetic effluent was continuously fed into the reactor and pumped out of the reactor through the built-in electrochemical membrane module, at a given membrane flux. After 4 h of hydraulic retention time/electrolysis time a decrease in toxicity (*V. fischeri*) was reported for both experimental conditions, with better results obtained for the flow-through mode, with 14.5% inhibition (from an initial value of 58.0%) and 45.2% of TOC abatement. This behavior was explained by the improved contact of the initial amine and metabolites with the oxidants generated near the membrane surface.

Biocides

The efficiency of Ti/Ru_{0.3}Ti_{0.7}O₂ anodes on the degradation of atrazine and toxicity removal was studied by the same research group [19; 20]. These authors studied the influence of electrolytes NaCl and Na₂SO₄ by performing electrolysis of solutions with only these constituents and observed that after the treatment both presented elevated toxicity to the crustacean *A. nauplii*. Both solutions of atrazine,

with NaCl and Na₂SO₄ as supporting electrolytes, treated electrochemically (10 mA cm⁻²) presented toxic effect, explained by the formation of more toxic metabolites, organo-chlorides in the case of NaCl. They also studied the toxicity evolution towards the lettuce (*L. sativa*) of atrazine solution treated by the same anode, on a current of 0.20 A with NaCl as support electrolyte. After 4 h, the EC₅₀ values for the treated effluent only slightly improved compared to the starting solution, regardless of achieving ~75% TOC removal, and was also linked with the presence of small, toxic, chlorinated by-products.

Dyes

Synthetic dye effluents were electrochemically treated by DSA-type anodes, under different operational conditions, and their toxicity evolution was assessed by plants (*V. radiata* and *L. sativa*) [21; 22; 24] and bacteria (*V. fischeri*) [23].

Aravind et al. [21] studied the performance of Ti/ IrO₂-RuO₂-TiO₂ anodes in the electrochemical oxidation (at 20 mA cm⁻²) of a mixture of two mono-azo reactive dyes (Reactive Red 195 and Reactive Orange 105) and measured the phytotoxicity of the final solutions with the mung bean *V. radiata*. It was assessed that the initial dye mixture was toxic to *V. radiata* and that this response was concentration-dependent (toxicity increased with the increase in the initial dye mixture concentration). However, after treatment, germination indexes of 100% were observed for all initial concentrations (50, 100 and 300 mg L⁻¹) and both plumule and radial lengths were close to those of the control plants, indicating an overall decrease in the solution phytotoxicity. This study also contemplated the application of said anodes in the remediation of real textile wastewater, collected from an effluent treatment collection tank, in India, that receives wastewaters from 70 textile dyeing units. The wastewater had a COD of 1104 mg L⁻¹, high salts concentrations (1500 mg L⁻¹ NaCl and 9730 mg L⁻¹ Na₂SO₄), a biodegradability index of 0.06, and highly inhibited the germination of *V. radiata* seeds (only 44%) with small radical growth values and no observed plumule growth nor chlorophyll. However, after electrochemical treatment, all these parameters improved, with 100% germination and higher values for the others, showing that the resulting waters could be used for irrigation. Sathishkumar et al. [22] used a similar type of anode to electrochemically decolorize methyl red effluents and applied the same plant (*V. radiata*) to assess the toxicity reduction after treatment. A decolorization of 99.96% was achieved at pH 5, NaCl 2 g L⁻¹ and 30 mA cm⁻² applied current density within 10 min, after which the germination increased from 0% to 80%. Through both studies, this anode proves to be able to reduce phytotoxicity of synthetic and real dye effluents. Very different results were reported [24] in the

phytotoxicity evaluation (*L. sativa*) of Basic Blue 99 effluents after electrochemical treatment with Ti/Ti_{0.66}Ru_{0.34}O₂ anode. Although a 100% color reduction was obtained within few minutes of electrolysis (30 mA cm⁻²), the treated solution was more toxic to *L. sativa* germination and growth index than the initial effluent. Given the fact that NaCl was employed as support electrolyte, the final toxicity was explained by the presence of the hypochlorite formed. Increase in toxicity towards bacteria (*V. fischeri*) during electrochemical oxidation of dyes with DSA-type anodes, using NaCl as support electrolyte, was also reported by Wang et al [23]. In this first study, synthetic methylene blue effluent, with 1000 mg L⁻¹ NaCl as support electrolyte, was electrochemically treated with Ti/IrO₂ anodes, at a current density of 428 A m⁻² for 20 min. The treated solution showed 100% light inhibition towards *V. fischeri*, and even with the addition of Na₂S₂O₃ (used to remove chlorine/hypochlorite from the solution) the solution was still highly toxic, with 77% light inhibition. These findings indicate that not only chlorine related species were responsible for part of the toxicity, but also other degradation metabolites, and that even though rapid decolorization was achieved, these waters were not yet suitable for discharge.

Pharmaceuticals

Several studies used DSA-type anodes to treat pharmaceutical effluents and the majority assessed the toxicity evolution using bacteria (*V. fischeri*) [25; 27-30], with exception of Radjenovic et al. [27] which also used algae bioassays (*P. subcapitata*) and Wu et al. [26] that used crustaceans (*D. magna*). The Ti/Ce/SnO₂-Sb [25] anode was able to decrease the concentration of metronidazole by 93.45% after 4 h (under optimal conditions). However, toxicity (*V. fischeri*) increased from a 91.3% bacteria luminescence to 63.7%. This increase in toxicity was attributed to more toxic metabolites formed during the treatment. The production of metabolites with higher toxicities is commonly reported as the main reason for the generation of treated wastewaters with higher toxicity responses than the original effluent. This was observed in two studies that used Ti/RuO₂-IrO₂ anodes in the degradation of pharmaceutical compounds [26; 28]. In one case [26], tetracycline solutions, treated at pH 6 and 1000 A for 8 h, went from immobilizing 20% of the crustaceans *D. magna* to values close to 75% after 6 h, to finally 45% by the end of the assay. Although a small decrease in the immobilization was observed at the end (indicating that the toxicity of the metabolites could be reduced with more electrolysis time) the final solution was still more toxic than the initial. Similarly, Barışçi et al. [28] attributed the increase in the bioluminescence inhibition (*V. fischeri*) of methotrexate solutions from 24.43% to 36.31% by 30-min electrolysis

to the formation of more toxic by-products. In the same study, and under the same experimental conditions (30 mA cm⁻², with Na₂SO₄ electrolyte), a solution of capecitabine was treated and a decrease in toxicity was instead reported. This also shows the influence in the parent compound structure on the generation of toxic metabolites. The same research team of the latter study, performed two other studies [29; 30] comparing the efficiency of Ti/RuO₂ and BDD anodes on the electrochemical oxidation of anti-cancer drugs, with toxicity evaluation (*V. fischeri*). In both, the electrolysis of carboplatin [29] and Imatinib [30], the Ti/RuO₂ presented not only higher drug degradations but also higher toxicity reduction in the final solution. This was attributed to the oxide metal electrode surface behaving as an electron sink, not reacting with the generated OH[•] and contributing to an easier diffusion of the radicals to the bulk solution, where they react with the contaminants.

Radjenovic et al. [27] tested the degradation of metoprolol in a complex matrix of reverse osmosis concentrate (ROC), from an advanced water treatment plant in Australia, by applying a Ti/SnO₂ anode, and evaluated the toxicity using two bioassays, bacteria (*V. fischeri*) and algae (*P. subcapitata*). The toxicity increased substantially in this mixture and for the assay run with the unspiked ROC as well. It was concluded that this increase could be connected to the formation of more toxic metabolites from the degradation of metoprolol or other compounds present in ROC.

Phenolic compounds

Barisçi et al. [32] tested the efficiency of 5 different anodes, Ti/Pt, Ti/IrO₂-Ta₂O₅, Ti/Ta₂O₅-SnO₂-IrO₂, Ti/RuO₂ and Ti/IrO₂-RuO₂, in the degradation of phenol under the same conditions (initial phenol concentration of 100 mg L⁻¹, T = 25 °C, I = 1.1 A, initial pH: 6.82 and with Na₂SO₄ as support electrolyte). The toxicity of the final solution was measured with the bacteria *V. fischeri* at three different exposure times, 5, 15 and 30 min. For the platinum electrode an increase in toxicity was observed in the first 2 h, which correlates with the formation of aromatic degradation products: benzoquinone, hydroquinone and pyrocatechol. These degradation metabolites were monitored by HPLC during the 8-hour assay and it was observed that as their concentration increased and later decreased so did the toxicity to *V. fischeri*. Therefore, it was concluded that the aromatic by-products were more toxic to *V. fischeri* than the parent compound, and that the measured toxicity was directly associated with the concentration of these aromatic molecules in the solution. For the other four metal oxide anodes, a decrease in the solution toxicity was observed, sharply in the first 2 h, remaining constant until the end of

the assays, for Ti/IrO₂-RuO₂ and Ti/RuO₂ anodes and gradually for Ti/IrO₂-Ta₂O₅ and Ti-Ta₂O₅-SnO₂-IrO₂, which is also in accordance with the behavior of the detected metabolites. Other studies [31; 35], contemplating the toxicity evolution (*V. fischeri*) of phenol solutions, treated by electrolysis, were performed with Ti/RuO₂ anodes. In the study performed by Yavuz and Koparal [31], three solutions, with different concentrations of phenol (50, 200 and 500 mg L⁻¹) and Na₂SO₄ as support electrolyte, were treated under a current density of 20 mA cm⁻² and proper toxicity values were obtained in the treated samples. However, for all solutions, an increase of the relative toxicity index was observed in the early stages, due to the formation of the toxic metabolites benzoquinone and hydroquinone. Contrarily, in the study performed by Hurwitz et al. [35], a sharp decrease in the measured toxicity to *V. fischeri* was observed after 2-h electrolysis (at the same current density), not only for the Ti/RuO₂ anode but also with BDD. Given the fact that chloride was present in the initial solution (890 mg L⁻¹), samples were dechlorinated by the addition of sodium thiosulfate prior to toxicity measurements, to eliminate the toxic interference. The difference between the results of both studies could be associated with the electrolyte used.

Chai et al. [34] tested two different anodes, a novel electrode prepared by assembling sieve-like microporous Sb-doped SnO₂ film on vertically aligned TiO₂ nanotubes and a Ti/SnO₂, in the electrochemical oxidation of nitrophenol (at 20 mA cm⁻² and with Na₂SO₄ as support electrolyte). In both assays an increase in the measured toxicity (*V. fischeri*) followed by a decrease, until the 4th hour, was reported. This behavior was in accordance with the evolution of the concentrations of some of the monitored metabolites, such as hydroquinone and benzoquinone. Da Silva et al. [36] applied current densities of 5 and 10 mA cm⁻² in the degradation of another phenolic compound, the commercial surfactant nonylphenol, with Ti/Ru_{0.3}Ti_{0.7}O₂ anode. Acute phytotoxicity was evaluated, before and after the electrochemical treatment, using the lettuce *L. sativa* and the onion *A. cepa*. For the lettuce, both before and after treatment samples were considered toxic. However, for the onion no toxicity was reported for the root growth parameters, mitotic index (cytotoxicity) and chromosomal aberrations (genotoxicity), showing the different sensitivities of both test organisms towards the tested solutions.

Toxicity of untreated and electrochemically treated solution of phenolic acids (3,4-dihydroxybenzoic, 3,4-dimethoxybenzoic, 3,4,5-trihydroxybenzoic, 3,4,5-trimethoxybenzoic, 4-hydroxybenzoic, trans-3-phenylacrylic) usually found in olive mill wastewaters, with Ti/IrO₂, was assessed in mammals by the evaluation of reactive oxygen species (ROS) signals from rat brain slices (obtained from 31 weeks old female Wistar rats) [33]. The results indicated that the treated effluent (at 119 mA cm⁻² and with NaCl as support electrolyte) caused a smaller depression

of the neuronal ROS signal than the untreated sample. However, it led to a potentiation instead of recovery upon washout.

Simulated tannery wastewater

Costa and Olivi [37] studied the effect of chloride concentration on the electrochemical degradation and toxicity evolution towards the daphnid *D. similis* of a synthetic tannery wastewater. A Ti/Ir_{0.10}Sn_{0.90}O₂ anode was applied, at a current density of 20 mA cm⁻², to solutions prepared with 30 compounds used in animal skin processing, with initial chloride concentration of 50, 100 and 500 mmol L⁻¹ and two main results were reported: increasing chloride concentration results in increased toxicity and that electrochemical oxidation is an effective way to decrease the synthetic effluent toxicity.

Other synthetic effluents

A study employing different test organisms to determine the toxicity profiles of solutions of microcystin extracts treated electrochemically by Ti/RuO₂ anode, was performed by Liang et al. [38]. In this, for treated and untreated effluents, acute toxic effects (*V. fischeri*) and genotoxic effects (*V. faba* micronucleus assay and single cell gel electrophoresis assay of mice lymphocytes) were assessed. Electrolysis were carried at 4 mA cm⁻² and three type of electrolytes were tested; 0.02 mol L⁻¹ Na₂SO₄, 0.02 mol L⁻¹ Na₂SO₄ containing 0.5 mmol L⁻¹ NaCl, and tap water, with pH values of 6.2, 6.5 and 7.8, respectively. Results show that 100% degradation of microcystin was achieved for all conditions, after 30-50 min. Acute toxicity (*V. fischeri*) was detected, caused mainly by residual oxidants formed by the electrochemical oxidation reaction, given that once these compounds were eliminated by the reductant Na₂S₂O₃ only weak acute toxicity was observed. For the case of genotoxicity and cytotoxicity of treated samples, the values decreased significantly and, in accordance with the degradation of microcystin, resulting in a final residual toxicity, as the formed metabolites did not induce DNA damage to *V. faba* root tips or mice lymphocytes. A different study [39] employed two test organisms (*V. fischeri* and *D. magna*) to determine the efficiency of the same type of anode, Ti/RuO₂, in the toxicity reduction of electrochemically treated solutions of polycyclic aromatic hydrocarbons in creosote. After treatments of 90 min, at current density of 9.23 mA cm⁻² and with Na₂SO₄ as support electrolyte, toxicity reductions of 91% and 80% were accomplished on *D. magna* and *V. fischeri*, respectively, proving its efficiency.

Del Moro et al. [40] performed the electrochemical degradation of six iodinated contrast media and studied its feasibility, reaction metabolites and toxicity evolution (*V. fischeri*). Five current densities (64, 91, 118, 145 and 182 mA cm⁻²) and the use of two support electrolytes (sodium perchlorate or sodium sulfate) were tested with two DSA electrodes (titanium coated with a proprietary and patented mixed metal oxide solution of precious metals such as iridium, ruthenium, platinum, rhodium and tantalum). Degradations were always above 80% for all conditions and modest toxicity was only found for the lowest applied current density (64 mA cm⁻²), explained by the formation of metabolites that remained for longer periods in the wastewater or could not be further degraded.

Pulgarin et al. [41] performed electrolysis of a solution of 1,4-benzoquinone, with Ti/SnO₂ anode (current density of 50 mA cm⁻², pH 2.5 and Na₂SO₄ as support electrolyte), and compared calculated EC₅₀ values (obtained by the chemical composition of treated samples and the individual EC₅₀ values) with real measured ones by Microtox test (*V. fischeri*). An agreement was found between both and a direct relation between the toxicity of the solution and the concentration of the most toxic component, benzoquinone, was confirmed.

Real effluents

DSA-type anodes were also applied in the electrochemical degradation of real effluents, from different origins, with toxicity being evaluated mostly by bacteria [42-50], followed by plants [21; 51; 52] and crustacean [53], with fewer studies using algae [54] and fish [55].

Textile effluents were the most commonly reported to undergo electrochemical degradation, through DSA-type anodes, accompanied by toxicity monitorization [21; 47; 51; 52; 55]. One of these studies [21] was already mentioned in the previous section given that studies with both simulated dye effluents and real textile wastewaters were performed, and a decrease in toxicity, of the treated wastewater, towards *V. radiata* [21] was observed. A different study [51] reported on the application of a commercial Ti/Ru_{0.3}Ti_{0.7}O₂ anode on the electrochemical oxidation of a real textile wastewater, collected from an effluent mixing tank of a local textile factory. The collected effluent was a mixture of reactive dyes (from the dyeing of cotton fabrics) and auxiliary components, such as fabric softeners, starching agents and sodium chloride. Toxicity (*L. sativa*) of the initial effluent increased from EC₅₀ of 26% to 1.5% after 10 h of treatment (current density 40 mA cm⁻², NaCl as support electrolyte, pH 9). The reason for this increase was associated with the formation of toxic organochloride compounds.

Keenan et al. [47] studied the use of a yeast biosensor (Green Screen EM[®]) in the assessment of changes in toxicity of textile effluents treated by Ti/RuO₂ and BDD anodes, at current densities of 500 and 1000 A m⁻² and different concentrations of NaCl as electrolyte (0, 1 and 2.5%). This biosensor measures the general acute toxicity (cytotoxicity), and genotoxicity, damage to a cell's DNA structure, replication or distribution, caused by mutagenic and/or carcinogenic substances. For all conditions, a rise in cytotoxicity was observed, even for the assays with 0% NaCl, showing that the toxicity observed could not be only attributed to the formation of chlorinated by-products. It was also observed that the lower current density (500 A m⁻²) was more likely to generate cytotoxic metabolites, which was ascribed to be due to a less efficient breaking down of the effluent constituents. Regarding the type of anode used, similar results were obtained, with both producing effluents with similar toxic properties.

Real collected textile industrial wash water (pH 9.6, COD of 843.5 mg L⁻¹ and 1.5 g L⁻¹ chloride) was collected and treated, at a current density of 10 mA cm⁻², in a single cell compartment tubular flow cell, with a mesh Ti/IrO₂-RuO₂-TiO₂ anode [52]. Toxicity test was performed with the aquatic plant *L. minor* (OECD 221), for 7 days, and for the untreated effluent a decrease in frond number was observed, together with phytotoxic effects and sinking of fronds which proved the highly toxic nature of the wastewater. The treated effluent (pH 7, COD of 255 mg L⁻¹ and 0.56 g L⁻¹ chloride) remained toxic, showing chlorosis and necrosis, which was associated with the formation of chlorinated by-products. Similarly, the formation of chlorinated by-products was also associated with the toxic nature of the treated textile wastewater (pH 10, 1156 mg L⁻¹ COD and 1682.5 mg L⁻¹ chloride) collected from a Mink Blanket manufacturing industry in India, and electrochemically treated by Ti/RuO₂ anode (t = 124 min, I = 1.37 A, pH = 5.54 and RT = 157.6 min) [55]. After treatment, reductions of 81 and 92.2% were achieved for COD and color, respectively. However, even with toxicity towards fish (*A. panchax*) decreasing from 100% mortality rate within one minute (initial wastewater) to one hour (treated effluent), the final effluent was still lethal to the aquatic organism, due to the high concentration of chloride in the initial wastewater that leads to the generation of chlorinated by-products during electrolysis.

Ti/IrO₂ anodes were studied in the degradation and toxicity evolution of olive mill wastewater [44] and sediments contaminated with tributyltin (TBT) [54]. The olive mill wastewater was provided by a three-phase olive mill located in Greece and prior to treatment it was strongly toxic (*V. fischeri*), with an EC₅₀ of 9%. After electrochemical oxidation (50 mA cm⁻²) toxicity was completely removed at 43 Ah L⁻¹ with and without 5 mM NaCl. However, for the assay with 25 mM NaCl (and similar conditions) an effluent nearly as toxic as the untreated was obtained. This

was associated with the formation of organochlorinated by-products. For the study with sediments contaminated with TBT, a pilot plant was used, with the material being mixed with water to obtain a pumpable suspension. Toxicity was assessed through three organisms, bacteria (*V. fischeri* and *B. cereus*) and algae (*P. subcapitata*). After treatment, the toxicity results showed to be inconclusive, given that no relation was reported between all toxicity results and the chemical substances investigated in the study. The authors propose further studies to clarify the obtained results, but probably are associated with the endocrine disruptive properties and consequent non monotonic dose responses curves characteristic of endocrine disruptors such as TBT [56].

A tannery wastewater, collected from a equalization tank of a finishing tannery, was electrochemically treated, for 5 h, by three DSA-type anodes at different current densities: Ti/Ru_{0.30}Ti_{0.70}O₂ (20, 50 and 100 mA cm⁻²) Ti/Ir_{0.15}Ru_{0.15}Sn_{0.70}O₂ and Ti/Ir_{0.30}Ti_{0.30}Sn_{0.40}O₂ (20 mA cm⁻²) [53]. For all anodes and conditions, a decrease in toxicity towards daphnids (*D. similis*) was reported, together with the content of total phenolic compounds.

A three-dimensional electrode reactor with Ti/Sb_{0.10}Sn_{0.90}O₂ anode was applied in the degradation of heavy oil refinery wastewater (obtained from a heavy oil refinery of PetroChina) [43]. After 100 min of treatment, at a current density of 30 mA cm⁻², a removal efficiency of 67.2% (of Toxic Units (TU)) was reported. The toxicity (*V. fischeri*) increased in the beginning of the assay, followed by a decrease, which was associated with the conversion of the contaminants in the samples.

Del Moro et al. [46] used a DSA anode (titanium coated with a proprietary and patented mixed metal oxide solution of precious metals such as iridium, ruthenium, platinum, rhodium, tantalum) in the remediation of a landfill leachate (from a landfill used for the disposal of municipal solid waste from 29 municipalities). The initial leachate (3973 mg L⁻¹ COD, 2740 mg Cl⁻ L⁻¹) had an EC₅₀ of 6% (*V. fischeri*) that after being treated at current densities of 33, 83, 133 and 200 mA cm⁻² increased with the current applied to 13, 17, 18 and 22%, respectively.

Two studies reported the treatment of real pharmaceutical wastewaters with DSA-type anodes. One study [45] applied two differently coated (nanocoated and traditional coated) Ti/ RuO₂-IrO₂ anodes in the electrolysis of biologically treated cephalosporin pharmaceutical wastewater and monitored the toxicity evolution (*V. fischeri*). The toxicity of the pharmaceutical wastewater increased in the beginning of the assay and then decreased until the end, indicating the generation of toxic metabolites followed by further degradation and consequent decrease of toxicity. Not so promising results were obtained by Zhan et al. [50] by applying the same type of anode (Ti/RuO₂/IrO₂) in the electrochemical oxidation of a wastewater from a pharmaceutical production plant in China, which produces mainly antibiotics.

After a 6-h treatment at applied current density of 21 mA cm^{-2} , only a slight decrease from the 100% inhibition to *V. fischeri* was obtained.

A titanium tube coated with an oxide layer composed by 70% TiO_2 and 30% RuO_2 (w/w) was used as the cell anode in the electrochemical oxidation of a real industrial wastewater from a chemical industry manufacturer of antioxidant and anti-ozonant substances for rubber (which contained aromatic amines as aniline, diphenylamine and monoamine-diphenylamine; ketones, acetones, xylol, phenol, oil and greases) [48]. After 1-h electrolysis the toxicity towards the bacteria *E. coli* (tested on Hach Toxtrak method 10017, based on the reduction of a redox-active dye by the bacteria respiration) decreased from 64.7 to 6.03%. This was corroborated by the absorbance values to the assessment that no intermediates were formed.

Radjenovic et al. [42] applied $\text{Ti/Ru}_{0.7}\text{Ir}_{0.3}\text{O}_2$ anode on the degradation of reverse osmosis concentrate, from an advanced water treatment plant that receives a mixture of secondary treated effluents from four wastewater treatment plants. It was reported that toxicity determined by the *V. fischeri* luminescence inhibition test (Microtox) increased with higher applied charge during batch and continuous oxidation. This indicates the formation of toxic metabolites, such as chlorinated and brominated organic compounds.

Explosive wastewater (TNT red water), provided by Dongfang Chemical Corporation, was electrochemically treated with a Ti/IrO_2 anode at a current density of 100 mA cm^{-2} and the toxicity evolution was assessed by the luminescence inhibition of bacteria *V. qinghaiensis* [49]. After treatment the acute toxicity decreased 77.5% after electrolysis for 30 h, indicating that the electrochemical treatment can significantly enhance the biodegradability of this type of effluent.

Boron-doped diamond anodes

Several studies (43 papers) used the BDD anode to treat effluents including biocides, dyes, pharmaceuticals, phenolic compounds, other synthetic effluents, real wastewaters and landfill leachates, and evaluated the toxicity removal. Overall, from the 120 toxicity assays performed, most studies used bacteria (56.7%), followed by plants (25.8%) and algae (11.7%). A small percentage of the studies used crustaceans (*D. magna*), nematodes (*C. elegans*), fungi (*S. cerevisiae*) and cell lines to evaluate the toxicity evolution (1.7, 1.7, 1.7 and 0.8%, respectively).

Biocides

Regarding biocides effluents, most studies evaluated the efficiency of BDD anodes on toxicity reduction using bacteria (*V. fischeri* and *V. qinghaiensis*). Alves et al. [57] calculated the reduction on the relative toxicity to *V. fischeri*, of methyl parathion solutions. The relative toxicity ($[(\text{initial EC}_{50}/\text{final EC}_{50}) \times 100]$) decreased from 100% in the initial effluent to 82.15% and 74.06%, after electrochemical treatments at 5 mA cm⁻² and 100 mA cm⁻², respectively. On the degradation of triclosan [58], at 6 mA cm⁻², a 99% relative toxicity reduction (*V. fischeri*) was observed and for acetamiprid [59] the light inhibition on *V. qinghaiensis* decreased from 87% to approximately 22%, after 10 h of electrochemical treatment at 20 mA cm⁻². A decrease in toxicity was also reported by Souza et al. [60], when studying a very toxic initial solution of imazapyr. The authors reported a decrease in toxicity for *V. fischeri* from an EC_{50,15min} of 16.7% to EC_{50,15min} 33.4% after an electrochemical treatment at 50 mA cm⁻². In all these studies, the electrochemical oxidation with BDD anodes resulted in the production of less toxic final solutions. This can be ascribed to formation of less toxic metabolites than the initial compound or formation of more toxic metabolites followed by their further rapid degradation, without accumulation and increase of toxicity values. Contrarily, Landeros et al. [61] reported an increase in toxicity towards bacteria *V. fischeri*, after electrochemical treatment of endosulfan, with BDD anode at a current density of 60 mA cm⁻².

A more comprehensive study of the effect of electrolyte on degradation and toxicity was investigated by Phillips et al. [62], with propanil as a model pollutant. Synthetic effluents of the biocide, with 0.05 N of electrolyte (NaCl, NaNO₃, Na₂SO₄ and NaH₂PO₄), were electrochemically treated at 4.4 A (and, in one case, 8.8 A, for comparison) for 2 h. After the treatment, propanil degradations followed the trend: Na₂SO₄ > NaH₂PO₄ > NaNO₃ > NaCl, from values from 100% to 36%. Regarding the final toxicities, obtained with *V. fischeri*, a different trend was observed: Na₂SO₄ < NaCl < NaH₂PO₄ (quenched with sodium thiosulfate) < NaNO₃ < NaH₂PO₄ (unquenched). For Na₂SO₄ and NaCl final solutions values below 10% were obtained, for NaH₂PO₄ different toxicities were reported for unquenched and quenched solutions, 92 and 23%, respectively, which can be explained by the formation of secondary oxidants, that once quenched with sodium thiosulfate have their impact minimized. The case of NaNO₃ showed an initial increase in the toxicity, followed by a decrease to values close 32%, for both applied currents (4.4 A and 8.8 A). Although, NaNO₃ did not present the best toxicity removal results, it was chosen, by the authors, as the electrolyte to use in the study of the degradation and toxicity evolution of other classes of contaminants. This choice was justified by the inert nature of said electrolyte during electrochemical degradation with BDD anodes, as it does not participate in reactions nor it produces

secondary oxidants. The contaminants include herbicides and pesticides such as propanil, carbofuran, aldicarb, atrazine and cyanazine; flame retardants such as perfluorooctanoic acid (PFOA), diethyl methyl phosphonate (DEMP) and tris(2-chloroethyl) phosphate (TCEP); and pharmaceuticals/contaminants of interest such as bisphenol A (BPA), carbamazepine, and phenylephrine. The toxicity results did not follow the degradation data obtained, showing that for some (carbofuran, carbamazepine, atrazine, and propanil) toxicity increased with time (i.e. production of more toxic metabolites), others (carbofuran and carbamazepine) expressed initial decrease followed by increase of toxicity and lastly aldicarb maintained a similar value throughout the 2 h. A more detailed study about the produced metabolites in each degradation assay was not performed by the authors, which does not allow for a more extensive justification of the reported toxicity results.

Dyes

In the degradation of dyes on BDD anodes, most studies evaluated the toxicity using bacteria (*V. fischeri*) [63-66] and one resorted to plants (*M. sativa*) [67]. Kopal et al. [63] studied the electrochemical oxidation of simulated effluents of Basic Red 29, in a bipolar trickle tower (BTT) reactor using Raschig ring shaped boron-doped diamond (BDD) electrodes, in a recirculated batch mode. A current density of 1 mA cm^{-2} and flow rate of 36.3 mL min^{-1} was employed to the dye solution for 90 min, and the toxicity was established with the short-term luminescent bacteria assay (*V. fischeri*). The relative toxicity decreased rapidly in the first 5 min, to approximately 0.2%, and this value was maintained until the end of the 90-min assay. This rapid decrease in toxicity is in accordance with the fast dye degradation observed in the beginning of the assay, with an observed dye concentration of 0.71 mg L^{-1} after 1 min of electrolysis (from the initial 40 mg L^{-1}).

Abdessamad et al. [67] studied the influence of applying monopolar and bipolar BDD electrodes in the electrochemical oxidation efficiency of Alizarin Blue Black B simulated effluents. The same operational conditions were applied: 40 mA cm^{-2} , $0.1 \text{ M Na}_2\text{SO}_4$, pH 8, 180 min electrolysis time. Toxicities were measured by germination index of the plant *M. sativa*. For both anodes, an increase in the germination index was observed, from highly inhibitory initial effluents to treated solutions that fall in the non-toxic range. Such results open the possibility to use these waters for irrigation.

Yavuz et al. [64; 65] studied the electrochemical oxidation of two dyes (Reactive Black 5 and Basic Blue 3) by BDD anodes and obtained similar results. Both dyes showed high toxicity towards the bacteria *V. fischeri* prior to treatment. Electrolysis at current densities of 1 mA cm^{-2} and 0.875 mA cm^{-2} were performed

to solutions of Reactive Black 5 (RB5) [64] and Basic Blue 3 (BB3) [65], respectively. The simulated effluents toxicity decreased significantly in the first minutes of the degradation assays (5 and 15 min) followed by plateau of the relative toxicity value of 0.333 and 0.051 until the end, for RB5 and BB3, respectively (for 15 min exposure time to the bacteria). These results show the efficiency of the doped diamond anode in the remediation of solutions of dyes, reducing its toxicity, without forming very highly toxic metabolites or efficiently degrading these during the electrochemical oxidation process.

The electrolyte can have an influence in the evolution of the toxicity during the electrolysis time. Vasconcelos et al. [66] studied the toxicity of Reactive Blue 19 dye before and after electrochemical oxidation with BDD anodes, under 100 mA cm^{-2} for 120 min, with $0.1 \text{ M K}_2\text{SO}_4$ as support electrolyte. They also performed electrolysis of a solution containing only the electrolyte, under the same condition. The initial effluent of dye and electrolyte produced 100% inhibition to the bacteria *V. fischeri*, although the solution containing only the electrolyte exhibited no inhibition. These results indicate that the observed toxicity is caused by the dye and not the potassium sulfate used as support electrolyte. However, after the 120-min electrolysis, an inhibition of 95% and 92% was observed for the dye effluent (containing $0.1 \text{ M K}_2\text{SO}_4$) and the electrolyte-only solution, respectively. It was concluded, by the authors, that the toxic effect of the dye byproducts effluent was more associated with the products of the electrolysis of the K_2SO_4 rather than the ones resulting from the dye. This study highlights that the support electrolyte cannot be ignored when studying the toxicity evolution of the electrochemically treated effluents.

Pharmaceuticals

Regarding synthetic pharmaceutical wastewaters, most studies used bacteria (*E. coli*, *S. typhimurium* and *V. fischeri*) [29; 30; 68-74], followed by algae (*D. subspicatus* and *S. vacuolatus*) [69; 75] and plants (*L. minor*) [75; 76] and one study used crustacean (*D. magna*) [77].

The studies regarding the toxicity evaluation of carboplatin [29] and imatinib [30] synthetic effluents treated by electrochemical oxidation on BDD anodes was previously mentioned, as both studies compared the efficiency of this anode with the Ti/RuO_2 anode.

Coledam et al. conducted studies regarding the efficiency of this type of anode in the electrochemical oxidation, and toxicity reduction of antibiotics, cephalexin [70] and norfloxacin [71]. Both studies were performed under 10 mA cm^{-2} , and similar results, regarding growth inhibition of *E.coli* were reported, with a 100%

value for the initial assay hours, followed by a decrease to approximately 0% by the end of electrolysis time. This indicated that the metabolites formed, in the initial hours of treatment, were as toxic as the initial effluent solutions of each antibiotic and that their further degradation resulted in smaller and less toxic compounds, such as carboxylic acids. A similar toxicity evolution was reported by Haidar et al. [72], when applying BDD anode in the electrochemical degradation of the antibiotic sulfachloropyridazine. In this study, three current values were tested (50, 350 and 500 mA) at pH 4.5, for 4 h, and the toxicity of the solution was assessed by the inhibition of the luminescence of *V. fischeri*, after 15 min of exposure. The inhibition increased from close to 40% to approximately 100% in the first minutes of assay, for all three applied currents, and stayed high during some time, followed by a decrease to almost 0% by the end of the electrolysis. Some variation in toxicity during the assay was observed for the times where some toxic by-products, such as 3-amino-6-chloropyridazine and *p*-benzoquinone, present maximum accumulation. These results suggest the formation of more toxic metabolites than the parent compound and their latter degradation into smaller and less toxic compounds, to the luminescent bacteria, resulting in an almost non-toxic solution. A similarly efficient elimination of toxicity was observed [68] after 5-8h of electrochemical oxidation of the anti-inflammatory, diclofenac, under 8 mA cm^{-2} , when tested with the same bacteria.

A study regarding the influence of the type of support electrolyte in the degradation of pharmaceutical compounds, and subsequent variation of toxicity to *E. coli*, was performed by Carneiro et al. [73]. In this study, a simulated effluent containing the antibiotic enrofloxacin and 0.1 M of electrolyte (Na_2SO_4 , NaCl, Na_2CO_3 , NaNO_3 and Na_3PO_4) was electrochemically treated at 10 mA cm^{-2} , for 16 h. After 8 h, only the solution containing NaCl electrolyte presented a decrease in antimicrobial activity. For the other samples, a decrease was only observed after 14 h, with exception of Na_3PO_4 , which only showed a slight reduction in the 16th hour. The authors found a correlation between these results and the concentration of enrofloxacin, with it being completely removed in the first assay hour for the NaCl electrolyte and present in quantities above its minimum inhibition concentration, 0.03 mg L^{-1} , for the other electrolytes. In another study, the NaCl electrolyte employed in the electrochemical oxidation of carbamazepine influenced in the toxicity variation to *V. fischeri* [74]. The inhibition of the bacteria increased significantly with time to TU values of 11.3 and 30.4 at 20 and 90 min, respectively. To assess the contribution of reactive chlorine species in the measured toxicity, experiments with only the electrolyte were performed and values of 8.2 and 28.5 TU were achieved for 20 and 90 min, respectively, showing the toxic nature of these species to *V. fischeri*. These studies highlight the importance in the choice of the

electrolyte, not only for its influence in the degradation of the target pharmaceutical compounds, but also for its possible contribution in the measured toxicity.

Zhu et al. [69] studied the antibacterial activity (*S. typhimurium*) and toxicity change to the green algae *D. subspicatus* of electrochemically treated effluents containing the fluoroquinolone antibiotics: ciprofloxacin, norfloxacin and ofloxacin. Regarding the antibacterial activity, a decrease in this response was observed for all treated solutions, with larger inhibition zones formed by the parent compounds. However, residual antibacterial activity was still observed for these final solutions, which was associated not only with the presence, in small concentrations, of the toxic parent compounds, but also with some toxic intermediates, identified and quantified by HPLC-MS/MS. A different response was obtained in the growth inhibition test performed on the algae *D. subspicatus*. For the treated solutions of ciprofloxacin and norfloxacin, the obtained EC₅₀ values were found to be almost the same as the calculated for the initial effluents (8.8 to 8.7 mg L⁻¹ and 6.8 to 6.7 mg L⁻¹, respectively). However, for the treated solution of norfloxacin, a significant increase was observed, from an initial EC₅₀ 102.7 to 26.8 mg L⁻¹. This study highlights the importance of testing more than one type of organism when assessing the toxicity solutions after electrochemical oxidation, given that the parent compound and metabolites can induce different responses. In this case, the authors associate the high observed growth inhibition to the algae to toxic oxidation products. Another study used algae (*S. vacuolatus*) and aquatic plants (*L. minor*) growth inhibition tests to determine the toxicity evolution of five sulfonamides in BDD anodes [75]. Synthetic effluents of each of the five veterinary antibiotics (sulfadiazine (SDZ), sulfathiazole (STZ), sulfamerazine (SMR), sulfamethazine (SMN) and sulfadimethoxine (SDM)) were electrochemically treated in an undivided electrolytic cell, at a constant current density of 5 mA cm⁻², for 3-h, and both initial and final solutions were evaluated regarding their toxicity. Results showed that the high electrolyte concentration, 6 g L⁻¹ Na₂SO₄, was unsuitable to conduct tests with the fresh water algae, which raises concerns of the impact of high concentration of salts in these treated solutions in freshwater systems, and the choice of the organisms to determine the toxicity of such solutions. The plant, *L. minor*, showed high tolerance towards the high Na₂SO₄ concentration. Three type of responses were obtained: for SMR and SMN a generally high toxicity was observed for both before and after solutions; STZ and SDM exhibited low growth inhibition (35% and 1%) but after electrolysis the value increased to 76% and 32%, respectively; and lastly, the plant was not sensitive to SDZ solutions, before or after treatment. The first two responses showed that *L. minor* is very sensitive to some of the initial antibiotics and degradation products (such as benzoquinone or urea derivatives) even at low concentrations. *L. minor*, was also

used by the same team to evaluate the toxicity evolution of the electrochemical oxidation of five cytostatic drugs ((5-fluorouracil (5-FU), ifosfamide (IF), cyclophosphamide (CF), methotrexate (MTX), imatinib (IMB)) on BDD anodes [76]. The electrochemical oxidations were carried for 6 h at 16 mA cm⁻², with COD and TOC removals above 81% and 65%, respectively. For IMB, the toxicity was initially non-toxic and presented only a slight increase after a few hours, which was explained by the initial concentration of 5 mg L⁻¹ being almost 10 times lower than the drug EC₅₀ of 61.05 mgL⁻¹ and the metabolites being biologically inactive. In the cases of MTX and 5-FU, the initial effluents were quite toxic to *L. minor*, but over time that value decreased, which suggested that the formed intermediates were less toxic than the parent compounds. Lastly, the opposite situation was observed for the final two drugs, CF and IF, where the initial solutions were not inhibitory to the plant, for the same reason as IMB, but contrarily to what was observed for that drug, where the toxicity increased with time. This was associated, according to the authors, to the release of Cl⁻ ions from the drug decomposition and the formation of chlorinated organic metabolites, proved to be toxic even in small concentrations (a concentration lower than 2 mgL⁻¹ of HOCl inhibited 75% of the growth of *L. minor*).

Ouarda et al. [77] studied the electrochemical oxidation of synthetic hospital wastewater fortified with four pharmaceuticals: carbamazepine, ibuprofen, estradiol (at a concentration of 10 mg L⁻¹) and venlafaxine (at 0.2 mg L⁻¹) on BDD anodes for 40 min at a current intensity of 2 A. After treatment, the wastewater was still toxic to *D. magna*, causing a mortality of 100% for dilutions above 20% (v/v).

Phenolic compounds

Phenol is commonly used as a model organic compound for different wastewater treatments, including electrochemical oxidation processes with BDD anodes [78-81; 35]. Moreover, this molecule and related compounds, such as chlorinated phenols (2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, pentachlorophenol) are listed by the U.S. Environmental Protection Agency as priority pollutants [81].

Amado-Piña et al. [78] studied the synergic effect of ozonation and electrochemical oxidation of phenol on BDD anodes. Regarding the electrolysis assays performed, the initial effluent was treated during 2 h, at a current density of 60 mA cm⁻¹, with determination of the germination index of *L. sativa*. The phytotoxicity decreased initially and stayed close to a 50% germination value throughout the 2-h assay, with some fluctuations associated mainly with the formation of oxalic acid. Only for the coupled treatment a full elimination of the

initial toxicity was observed as it was the only process that successfully removed the oxalic acid. In a different study [79], synthetic phenol effluents were treated in a bipolar trickle tower reactor, with BDD anodes, and a decrease in toxicity to bacteria *V. fischeri* was observed, for all tested phenol concentrations. For the initial concentrations of 50, 200 and 500 mg L⁻¹, a COD removal of over 99% was attained at 9, 40 and 60 min of electrolysis, respectively. For these final solutions, EC₅₀ of 99, 67 and 45% (respectively) were achieved from initial 41, 10 and 4% values, which allowed the authors to conclude that this approach was an effective way of reducing toxicity. However, taking in account both studies, and several other examples described in this review, it is important to consider the sensitivities of the chosen organisms in the toxicity assessment and, if possible, more than one organism should be used to provide a wider understating of the toxicity of the solutions.

Saylor et al. [80] understood the complexity of the measurement of the toxicity in effluents and that these values could vary with time. Given this, they performed luminescence inhibition tests, with *V. fischeri*, on electrochemically treated samples over a period of 13 days after the treatment. This study had the purpose to assess and understand changes in the toxicity of the treated effluents over time (13 days) as non-electrochemical reactions could occur, such as hydrolysis, photodegradation, oxidation and polymerization with the organic components after electrolysis. After electrochemical treatment with BDD and graphite anodes at 9.6 and 6.27 mA cm⁻², respectively, samples composition was assessed by HPLC. In the case of BDD anode, the final solution had a measured 15.2 TU, and no phenol was detected, with identified metabolites such as 2-chlorophenol, 4-chlorophenol amongst others. To this final solution no further studies were conducted. However, for the effluent treated by the graphite anode, with a final solution composed of phenol, and metabolites such as catechol, hydroquinone and the very toxic benzoquinone, the time varying study was performed. After electrolysis a TU of 387 was calculated, after 5 days a value of 101 TU was obtained and in by end of the experiment (day 13) a TU of 14.7 was calculated, representing a decrease of 96.2% of the initial toxicity. This was attributed to the conversion of benzoquinone to hydroquinone during time, monitored by HPLC, and given that the first is very toxic (EC₅₀ 0.03 mg L⁻¹) when compared to the latter (EC₅₀ 11.8 mg L⁻¹). The same team also performed a study [81] to determine the influence of anode material and electrolyte in the electrolysis of phenol solutions and its influence in the toxicity to *V. fischeri*. For both effluents treated by BDD and graphite anodes under the same conditions (6.27 mA cm⁻², 0.05 M Na₂SO₄) an increase in toxicity was observed, with higher TU values for the latter anode. Once again, these results were associated with the formation of benzoquinone in higher concentrations at the graphite anode,

without observed further degradation. Given these results, another assay was performed for the BDD anode with 0.05 molL^{-1} NaCl as support electrolyte, where the toxicity increased initially but latter decreased to TU below 5. The effectiveness on the toxicity reduction using NaCl was directly associated with the formation of significant less toxic chlorinated phenols instead of the highly toxic benzoquinone formed when Na_2SO_4 was used. The choice of electrolyte is almost as important as the choice of anode for the reduction of the phenol effluent toxicity in electrochemical oxidation reactions and should be taken in consideration when choosing the operational conditions. As previously mentioned, Hurwitz et al. [35] studied the electrochemical degradation of phenol, with chloride, on BDD and ruthenium oxide on titanium (DSA- Cl_2) and evaluated its toxic effect towards *V. fischeri*. After 6-h, at 20 mA cm^{-2} , the luminescence inhibition decreased from approximately 80% to values below 15%, which is in accordance to other studies, previously mentioned, using chloride in the degradation of phenol.

A comprehensive study of the electrochemical degradation of hydroxybenzenes (including phenol), chlorophenols and nitrophenol, on BDD anodes at 30 mA cm^{-2} , was performed by Cañizares et al. [82]. The toxicity (*V. fischeri*) behaved similarly in each group. For the hydroxybenzenes (phenol, hydroquinone and 1,2,4-trihydroxybenzene) a plateau zone is obtained initially, but the toxicity latter declines to low values by the end. For the chlorophenols (4-chlorophenol and 2,4-dichlorophenol) toxicity increased initially but by the end low values were also obtained. Lastly for the nitrophenols (4-nitrophenol and 2,4-dinitrophenol) the toxicity decreased during time since the beginning of the assay. The different variation in toxicity for each group can be explained by the nature of the phenolic compounds, including the substituent groups in the molecules and formed intermediates.

An electrochemical oxidation of bisphenol A was performed by Li et al. [83], with Cl^- concentration of 40 mM, at current density 15 mA cm^{-2} , for 12 h. For these conditions, the luminous inhibition (*V. fischeri*) increased in the first 5 min, associated with the formation of toxic metabolites such as dichlorophenols and trichlorophenols, followed by a decrease to 1.70% at 4 h, which was maintained until the end of the assay, as some of the metabolites suffered further degradation.

Other synthetic effluents

The bacteria *V. fischeri* was used to assess the toxicity evolution of BDD anodes on the electrochemical oxidation of other type of compounds, such as benzoic acid [84], polycyclic aromatic hydrocarbons (PAHs) [85] and naphthenic acids [86]. For the effluent containing benzoic acid, electrolysis was carried at 14

A, with 0.05 M Na₂SO₄ electrolyte, for 6 h. The toxicity increased with time until the 2nd hour and then slightly decreased but maintained a high inhibition percentage (~80%). With 60% of the initial carbon converted to CO₂ by the 6th hour, the high toxicity of the final solution was explained by the formation of more toxic metabolites than the parent compound. Similar initial evolution was reported for the degradation of the PAH Phenanthrene. The electrochemical oxidation was carried at a current intensity of 1 A and an increase in the inhibition was initially observed (from 45% to 99%) and that high value maintained until the 12th hour, where 60% of mineralization was reached and the toxicity started to decrease, until an inhibition of approximately 60% was achieved by 20th hour. Lastly, the naphthenic acids mixture, treated by 50 mA cm⁻² and with sodium sulfate as electrolyte, had a completely different toxicity evolution during the 6-h assay time, with a decrease up until the 2 h and slight increase of TU (between 4 and 6.8%) by the end of the treatment. It is worth mentioning that the three initial concentrations of chloride were taken into consideration, with the toxicity results being very similar for all. Given such results, the authors proposed further studies to determine if the treatment should be stopped at shorter times (after 2 h the solution was considered non-toxic) or if it should proceed until complete COD removal (6 h) is attained.

Pieczynska et al. [87] used growth inhibition assays with the plant *L. minor* and algae *S. vacuolatus* to evaluate the toxicity evolution of the electrochemical oxidation of imidazolium and pyridinium ionic liquids (1-butyl-3-methyl-imidazolium chloride (IM14 Cl), 1-hexyl-3-methyl-imidazolium chloride (IM16Cl), 1-methyl-3-(2-phenylethyl)-imidazolium chloride (IM1-2Ph Cl), 1-butyl-4-methylpyridinium chloride (Py4-4Me Cl), and 1-butyl-4-(dimethylamino)pyridinium chloride (Py4-4NMe2 Cl)). The electrolysis were performed under a current density of 16 mA cm⁻² for 3.5 h. For the algae *S. vacuolatus* the IM14 Cl had no significant toxic effect neither prior nor after electrochemical oxidation. For IM16 Cl and Py4-4NMe2 Cl a decrease was observed while the contrary was obtained for Py4-4Me Cl, where an increase in growth inhibition was attained. The test using *L. minor* demonstrated the lower sensitivity of this plant given that only the initial solutions of IM16Cl and Py4-4NMe2 Cl caused significant growth inhibition, which decreased in the treated solutions. In the case of IM14 Cl/NaCl mixtures a sharp increase in the toxicity was reported, linked with the formation of chloroorganics, or active chlorine species such as Cl₂ and HClO.

The toxin Microcystin-LR was electrochemically treated under 15 mA cm⁻², for 1 h, and the toxicity was evaluated by the bean *V. faba* root tip cells micronucleus experiment [88]. The micronucleus diminished by 70% by the end of the assay, in accordance with the 68% degradation of the initial compound and

indicates that the measured toxicity was mainly attributed to Microcystin-LR and that the formed intermediates were non-toxic.

Reipa et al. [89] used a completely different type of organism, nematode *C. elegans* to assess the toxicity of electrochemically treated multiwall carbon nanotubes effluents. Before and after electrolysis (at 2 mL h⁻¹, 142 A m⁻²) growth and reproduction of the nematode were assessed and the results showed that the final solutions presented values very similar to the negative control, showing the efficiency of the treatment.

Real effluents

BDD anodes were also applied in the electrochemical degradation of real effluents, such as textile wastewater [47; 63], reverse osmosis concentrate [90], landfill leachates [91; 92], textile [93], food processing wastewaters [94] and real petrochemical wastewater [16], and the toxicity evolution throughout the treatment was further evaluated. In most of these studies, the efficiency in toxicity removal was assessed using bacteria [47; 90; 91; 93], with only three of the studies employing tests with the crustacean *D. magna* [92], the plant *L. sativa* [94] and HeLa cells [16].

Koparal et al. [63], as previously mentioned, performed electrochemical oxidation treatment (under the same conditions of a current density of 1 mA cm⁻² and flow rate of 36.3 mL min⁻¹, employed in the treatment of the synthetic dye effluent) to a textile wastewater, with an initial COD of 566.45 mg L⁻¹ (with this being a more important parameter to evaluate, given that total organics removal is more difficult than dye degradation). With a significantly higher electrolysis time, of 8 h, a final COD concentration of 52.38 mg L⁻¹ was obtained for the tested conditions and a toxicity (*V. fischeri*) close to 0% was observed after 5 h. These results show that the BTT reactor was efficient in the reduction of the toxicity of simulated and real wastewaters containing dyes. Another study, regarding the toxicity evaluation of electrochemically treated real textile wastewater was reported by Keenan et al. [47] and the results obtained suggested an increase in toxicity as detailed previously in the section devoted to “Metal oxides electrodes – Dimensionally stable anodes”, given that a Ti/RuO₂ anode was also studied.

Bagastyo et al. [90] studied the influence of using undivided and divided cell configurations in the electrochemical degradation of reverse osmosis concentrate on BDD anodes. The initial effluent, collected from the concentrate stream of a reverse osmosis unit process at an inland water recycling plant reclaiming a mixture of secondary-treated effluents, had an initial COD of 140 mg O₂ L⁻¹, DOC of 39 mg C L⁻¹ and Cl⁻ concentration of 1391 mg L⁻¹. Complete COD removal was obtained

after 5 Ah L⁻¹ and approximately 70% DOC removal was achieved after 13.4 Ah L⁻¹, for both cell configurations. Toxicity monitoring was performed with Microtox (*V. fischeri*) bioassays. For the undivided cell, an initial sharp increase in toxicity was observed, linked with the formation of more toxic metabolites, although, by the end of the treatments, the measured toxicities were lower than expected, given the formation of organochlorine and organobromine by-products during these assays, reported to be more toxic than their non-halogenated equivalents. The authors hypothesized that this discrepancy had its origin in the poor retention of these halogenated compounds on the SPE (solid-phase extraction) cartridges, during the sample preparation.

Landfill leachate, collected from an intermunicipal sanitary landfill site (Greece), was electrochemically oxidized by Anglada et al. [91]. Initial samples, with COD 3385 mg L⁻¹ and 2587 mg Cl⁻ L⁻¹, were treated at a current of 12 A, for 8 h, after which a removal of ~40% COD was observed. The bacteria *V. fischeri* was used to performed toxicity tests on the landfill leachate samples before and after treatment, with focus in assessing the influence of the initial high chloride concentration in the toxicity of the final sample, considering that it can bring about the formation of toxic chlorinated organic compounds. Results showed an initial EC₅₀ of 18%, which increased to 43% after the 8-h treatment, showing that this process was able to decrease the effluent toxicity even though chlorinated organic compounds were formed. Fernandes et al. [92] used the crustacean *D. magna* to assess the toxicity evolution during the electrochemical oxidation of a landfill leachate from an intermunicipal sanitary landfill facility (Portugal). This treatment (at 700 A m⁻², for 36 h) proved to be very effective in the removal of the organic load (from 11.9 g L⁻¹ to 54 mg L⁻¹) and ammonium nitrogen and at the same time decreasing the acute toxicity to *D. magna* by 59%.

Zhu et al. [93] studied the efficiency of treating biologically-pretreated dyeing wastewater by electrochemical oxidation with BDD anode. The wastewater was collected by the authors from a dye manufactory (China) and, amongst other parameters, presented COD of 532 mg L⁻¹, TOC of 138 mg L⁻¹, 3000 mg Cl⁻ L⁻¹ and pH 7.76. After the 12-h assay, at 20 mA cm⁻², COD decreased to 99 mg L⁻¹ and TOC to a value below 50 mg L⁻¹. Although the assay was able to considerably decrease the COD value, some organic compounds were still present in the treated effluent which could negatively impact the treated wastewater toxicity. The initial dyeing wastewater displayed some toxicity, with an inhibition ratio of luminescence (*V. fischeri*) of 27%, value that increased after 2 h to 68%. This increase was attributed to the formation of chlorinated organic compounds. Though, the inhibition ratio decreased after peaking at 2 h, as the previously formed toxic metabolites were further degraded, and after 6 h negligible values were obtained.

A study regarding the electrochemical oxidation of cashew-nut processing wastewaters was reported by da Costa et al. [94]. These wastewaters are produced during the shelling operation, with the formation of an oil-type of waste denominated cashew-nut shell liquid (CNSL) and it is very hazardous for the environment, as it is rich in organic matter (including phenolic) and toxic, possessing mutagenic potential. The acute toxicity tests were performed, on the initial and final wastewaters, with plant *L. sativa*. Several conditions were tested, including three different current densities (15.5, 25.5 and 35.5 mA cm⁻²), three pH values (3.0, 7.0 and 10.0) and two electrolytes (NaCl and Na₂SO₄). For all conditions (with exception of pH 3) germination index test showed that the effluent was not toxic, favoring the production of nutrients that could promote the growth of some plants, with the authors suggesting a possible reuse of these effluents in the production of biodiesel.

Lastly, the evaluation of toxicity removal from real petrochemical wastewaters treated with BDD anodes was evaluated and the obtained results disclosed a reduction of the toxicity, in spite of the final solutions were still inhibitory of cell growth [16]. Further details on this work can be found in the section “Metal oxides electrodes – lead dioxide electrodes” as this paper compares BDD with lead dioxide anodes.

Platinum anode

A low number of studies (6 papers) used the platinum anode to treat effluents including pharmaceuticals, phenolic compounds and real industrial wastewaters and evaluated the toxicity removal. The efficiency in toxicity removal was assessed using bacteria (87.5%) and plants (12.5%).

Pharmaceuticals

Li et al. [95] performed a study in which Pt anode was not very effective in the degradation of 20 mg L⁻¹ Ibuprofen solutions, reaching only <20% degradation after 120 min, at a current density of 300 mA cm⁻². This was accompanied by an increase in toxicity to *V. fischeri*, from a moderate toxic (20% inhibition) to a highly toxic solution, with a rapid increase to 74% inhibition at 30 min, followed by a gradual rise to 80%, at 120 min. The low degradation values were attributed to the limitation of mass transfer of the molecules to the anode surface and the increase in the bacteria inhibition to the formation of toxic aromatic intermediates. The formation of these intermediates, such as dihydroxyl ibuprofen, 4-ethylphenol, and 1-(4-isobutylphenyl)ethanone (reported to have high toxicity), was monitored through

UPLC-MS (ultra-performance liquid chromatography – mass spectrometry), in which the concentration of aromatic intermediates was shown to increase rapidly in the first 30 min, which corroborates the toxicity results. Therefore, it was concluded that the formed aromatic intermediates were responsible for the increase in the solution toxicity, as they were produced but not effectively destroyed by the electrochemical treatment.

Tu et al [96] tested the efficiency of the Ti/Pt anode in the degradation of 50 mg L⁻¹ berberine solutions, with NaCl as support electrolyte and under acidic conditions. After 60 min, at an applied potential of 2.0 V, the toxicity of the solution decreased from 80% to 14% of *V. fischeri* luminescence inhibition. This was in accordance with the decrease in the initial pollutant concentration and indicates that not only the structure of the berberine molecules was mainly oxidized or destroyed during the electrochemical treatment, by the Pt anode and active chlorines, but also that the formed organic metabolites had lower toxicity and smaller molecular weight.

Phenolic compounds

Barisçi et al. [32] tested the efficiency of 5 different anodes (DSA-type), and Ti/Pt, in the degradation of phenol under the same conditions (initial phenol concentration of 100 mg L⁻¹, T = 25 °C, I = 1.1 A, initial pH: 6.82 and with Na₂SO₄ as support electrolyte). The toxicity was assessed with bacteria *V. fischeri* and the results disclosed different patterns for the different anodes tested, with an increase in the toxicity after 2 h for the platinum electrode and a decrease for the other anodes tested as described in more detail in the section devoted to “Metal oxides electrodes – Dimensionally stable electrodes”.

Real wastewaters

Ribordy et al. [97] tested the efficiency of Pt anodes in the electrochemical treatment of an industrial wastewater from a flavor manufacturing facility after biological treatment by activated sludge. The initial effluent showed low toxicity to the luminescent bacteria *V. fischeri*. However, after the electrochemical treatment, under 150 mA cm⁻², a considerable increase in the toxicity was observed. This increase was linked to the formation of active chlorine species during the process, as the initial Cl⁻ concentration of 400 mg L⁻¹ decreased overtime, and the formation of species, such as HClO and OCl⁻, took place. Once these chlorine species were eliminated by the addition of Na₂SO₃, the toxicity disappeared completely, reinforcing the link between the observed toxicity and their presence in solution.

Torres et al. [98] reported a similar behavior during the degradation of an industrial wastewater containing 5-amino-6-methyl-2-benzimidazolone (AMBI). As the initial concentration of Cl^- (7335 mg L^{-1}) decreased and the possible formation of organic chlorides, and perhaps quinones, took place, the toxicity to *V. fischeri* increased. However, after 3 h, at a current density of 25 mA cm^{-2} , the toxicity started to decline as these intermediates were further degraded. The oxidation of Cl^- occurs promptly on the Pt anode surface to produce chlorine, and depending on the pH, can undergo further oxidation and hydrolysis, resulting in the formation of hypochlorous acid or hypochlorite ion. These species are strong oxidants and help in the degradation of pollutants, although they are known to form organochlorides during the process, known to be highly recalcitrant and toxic, even in small concentrations.

Chakchouk et al. [99] applied an expanded platinized titanium anode in the electrochemical degradation of a real agro industry wastewater, from a Tunisian dairy industry. The toxicity/phytotoxicity of the initial and final solutions (treated at a current density of 140 mA cm^{-2}) was measured through seed germination of *P. sativum* and an increase was reported (from germination index (GI) 151% to 91%). According to the authors, a solution with a seed germination index higher than 70% is considered non-phytotoxic. Given that the results for both solutions, prior and after electrochemical degradation, were $<70\%$, the treatment does not result in the production of an overall toxic wastewater. However, the small reduction of the GI indicates the formation of organic by-products more toxic than the parent compound.

Carbonaceous anodes

Anodes based on carbonaceous compounds have been used to treat some types of synthetic effluents, including biocides, dyes, pharmaceuticals, phenolic compounds and others. The evaluation of toxicity removal was performed using fish (51.7%), bacteria (38.3%) and crustaceans (6.7%). A small percentage of the studies (3.3%) used the ECOSAR Class Program to evaluate the toxicity.

Biocides

One study, employing a carbon felt anode in the electrochemical oxidation of the biocide clopyralid from soil washing effluents (SWE) was reported [100]. In this study, SWE underwent electrolysis, at 5 mA cm^{-2} , during which the toxicity towards bacteria *V. fischeri* initially increased, followed by a decrease for applied charge above 2.5 A h dm^{-3} . The toxicity achieved its highest EC_{50} value (lowest

toxicity) of 143 mg L^{-1} at the maximum applied charge of 3.83 A h dm^{-3} . The initial increase in toxicity was attributed to the formation of toxic metabolites, such as 2,5-dichloropyridine and 2-picolinic acid, that overtime were further degraded into more biodegradable compounds, like acetic acid (all metabolites identified by HPLC and GC-MS).

Dyes

Liu et al. [3] prepared and applied a carbon nanotubes (CNTs)/agarose (AG) membrane deposited on ITO (indium tin oxide conductive glass) on the electrochemical degradation of the dye rhodamine B and calculated the toxicities of the main intermediates through the ECOSAR program and EPIWIN software. This system utilizes the structural information about the compounds to estimate acute toxicities such as LC_{50} values for fish (96 h) and daphnia (48 h); EC_{50} values for green algae (96 h), chronic toxicities for fish (30 d), and daphnia (21 d). For this study, toxicity predictions were performed for the dye and the main degradation products, showing a higher toxicity for the metabolites when compared with the initial dye. These results showed that, although these metabolites can undergo further oxidation into less toxic compounds, the potential risk could be increased before the complete mineralization.

Pharmaceuticals

Regarding synthetic pharmaceutical effluents, the same research team performed several studies with graphite-Poly Vinyl Chloride (PVC) composite anodes on the electrochemical oxidation of simvastatin [101], diclofenac [102], prazosin and levonorgestrel [103], carbamazepine [104] and hydrochlorothiazide [105]. In all cases, bacteria *E. coli* was used to investigate the toxicity evolution throughout the oxidation process, and similar results were attained, with an initial increase in the toxicity (luminescence inhibition), attributed to the formation of toxic metabolites, followed by a decrease until the end of each assay. Most studies were performed with NaCl as support electrolyte except for the electrochemical oxidation of carbamazepine where the influence of used electrolyte was one of the studied parameters. In this study, Al-Qaim et al. [104] performed the electrochemical degradation of the target drug in the presence of NaCl and Na_2SO_4 . In both cases, an increase in toxicity was observed during the assay time, with values later decreasing sharply and very gradually for NaCl and Na_2SO_4 electrolyte, respectively. This showed that, even though more toxic metabolites were formed in both conditions, in the presence of NaCl these by-products were more efficiently

degraded. When NaCl is used as electrolyte there is the possibility of formation of chlorinated by-products, known to be very toxic (as it was extensively reported by several of the studies mentioned in this chapter). However, in the ideal conditions, these toxic metabolites can undergo further electrochemical oxidation, forming less toxic and more biodegradable compounds.

Brito et al. [106] studied the electrochemical oxidation (at 50 mA) of amoxicillin (AMX) effluents on carbon modified with titanium oxide anode (TiO₂@C) and evaluated the toxicity evolution using fish (*D. rerio*) and bacteria (*S. aureus*, *P. aeruginosa* and *E. coli*). The influence of the support electrolyte, on AMX degradation and toxicity, was tested by performing assays with tap water and with solutions of NaCl at 0.01 M and 0.1 M and Na₂SO₄ at 0.1 M, and measured by UV-Vis spectrometry and fish embryo acute and extended toxicity tests with zebrafish (*D. rerio*, OCDE guideline 236). The toxicity towards *D. rerio* early life-stage considering the lethal (egg coagulation, no somite formation, non-detachment of the tail from yolk sac and no heart beating) and sublethal effects (effects on the eye and body pigmentation, absorption of the yolk sac, hatching rate, swimming bladder inflation, otolith, presence of edemas and blood accumulation, tail deformities and body length) was reported as follows: 0.1 M Na₂SO₄ > 0.1 M NaCl > 0.01 M NaCl = tap water. The highest toxicity to zebrafish was reported for the assays with 0.1 M Na₂SO₄ (with 75% AMX removal) and were associated with the intrinsic effects of this electrolyte. For the assays performed with 0.01 M NaCl, a 70% AMX removal was obtained and no acute toxicity for the early-life stages of zebrafish was reported. Given these results, an evaluation of the antimicrobial activity of treated and untreated AMX effluents under the same conditions was performed with microorganisms *S. aureus*, *P. aeruginosa* and *E. coli*, through *broth microdilution technique*. The treated effluent was able to inhibit the antimicrobial activity of AMX, reducing the possibility of inducing bacterial resistance.

Phenolic compounds

Two studies [80; 81], comparing the efficiency of the electrochemical oxidation of phenol with graphite and BDD anodes, were conducted by the same team. An increase in toxicity (*V. fischeri*) was observed for both studies performed with the graphite anode mentioned with more detail in the previous subsection regarding “Boron-doped diamond anodes”.

Another study [4] analyzed the electrochemical oxidation of 2-chlorophenol in a carbon nanotubes/agarose/ITO electrode (CNTs/AG/ITO). The degradation metabolites were identified by HPLC/MS-MS and through these findings their toxicities (and for the parent compound) were calculated using the ECOSAR Class

Program and EPIWIN, previously mentioned [3] as it was used by the same team to assess the toxicities of the degradation of rhodamine B. Overall, similar results were attained, given that some of the identified metabolites manifested higher toxicities than the initial phenolic compound. This demonstrates that the toxicities of the degradation products cannot be ignored as they may increase the effluent toxicity after treatment if not completely mineralized.

Other

Al-Qaim et al. [107] studied the electrochemical oxidation of a caffeine synthetic effluent, using a graphite-PVC composite anode, and the toxicity evolution towards bacteria *E. coli*. The evolution of toxicity was measured during the 200 min of electrolysis (at a constant potential of 6 V and with NaCl as support electrolyte) and during this time an overall initial increase in light inhibition was observed followed by a decrease by the end of the assay. This profile is in accordance with the formation and degradation of the more toxic chlorinated organic by-products.

In a different study [108], a graphite carbon cylinder-based anode modified with PdO and TiO₂ (PdO-TiO₂@Carbon) was applied in the electrocatalytic removal of Nodularin-R (NOD-R), a common cyanotoxin produced by cyanobacteria in algal blooms. The acute toxicity (at 24 h and 48 h) was tested with the brine shrimp *A. salina* for NOD-R effluents treated, at a current of 10 mA, with 10 mmol L⁻¹ NaCl for 20 min and tap water for 60 min. Both conditions resulted in final solutions that did not induce significant toxicity, with 98% and 97% survival rate for NaCl and tap water, respectively. Furthermore, the results disclosed a decrease in the toxicity when compared with the initial wastewater.

Other anode materials

Some studies used other anode materials, that do not belong to any of the former mentioned categories, such as steel [109], iron [110] and titanium [111] anodes, titanium covered with tantalum, platinum and iridium alloy [112-114], titanium oxide (Ti₄O₇) [115-117], and evaluated the toxicity removal. Overall, most of these studies used bacteria (51.5%), crustaceans (24.2%) and fish (18.2%). A small percentage of the studies used algae and the ECOSAR Class Program to evaluate the toxicity (3.0% each).

Dyes

In the study performed by Chatzisyneon et al. [112], a titanium–tantalum–platinum–iridium anode was efficient in the decolorization of a synthetic effluent containing a mixture of 16 dyes, at different experimental conditions, such as pH (3, 6 and 7.5), NaCl concentration (0.5 and 1%) and applied current (5, 10 and 14 A). However, final solutions were found to be very toxic to bacteria (*V. fischeri*), regardless of most of the operational parameters. This overall increase in toxicity (represented as a decrease from the initial EC₅₀ of 4.1%) was attributed to the formation of organochlorinated compounds. Another study, focusing on the electrochemical treatment of synthetic dye effluents (Blue copper) was performed by Mountassir et al. [111]. These authors employed titanium electrodes at a current density of 133.4 A m⁻² with chloride as support electrolyte. Although this treatment successfully removed COD by 92%, the toxicity to the crustacean *D. magna* increased after electrochemical treatment, which was associated with the formation of more toxic degradation metabolites.

Pharmaceuticals

Three studies employed Ti₄O₇ anodes on the electrochemical degradation of antibiotics amoxicillin [115] and tetracycline (TC) [116; 117]. The study regarding the electrooxidation of amoxicillin was performed under current 120 mA and 0.05 M Na₂SO₄ as support electrolyte, and the evolution of toxicity was assessed with the bacteria *V. fischeri*. The toxicity (bioluminescence inhibition) increased in the early stages, linked with the formation of aromatic/cyclic organics, followed by a decrease in toxicity, resulting from the mineralization of the formed by-products. Concerning the studies with TC, Liang et al. [116] applied this type of anode at a current density of 0.5 mA cm⁻² to synthetic effluents of 10 mg L⁻¹ of antibiotic, and assessed the resulting toxicity with bacteria *E. coli* and algae *S. obliquus*. For both bioassays a reduction in toxicity was observed in the final solutions. However, for the percent inhibition of the specific growth rate of the green algae, the value remained high for the initial 4 h with the decrease to a much lower value only being achieved after two more hours (at the final 6-h effluent). This behavior was suggested to be associated with the formation of primary oxidation products with equal or higher toxicity in comparison with TC.

On a different study, Wang et al. [117] treated a synthetic effluent of 5 mg L⁻¹ of TC under a current density of 15 mA cm⁻² and studied the toxicity evolution with bacteria *V. fischeri* and assessed the ecotoxicological potentials of the antibiotic and its intermediates with the ECOSAR program coupled with EPIWIN software. Regarding the toxicity evolution measured with the bacteria, the initial luminescence inhibition increased, slightly until 10 min of treatment, and latter

decreased to much lower values. This was associated with the formation of toxic metabolites and their further degradation, predicted by the ECOSAR program.

Real effluents

Different types of anodes were applied in the electrochemical treatment of real effluents, such as textile [110; 112], olive mill [113; 114] and hospital wastewaters [109], and toxicity evaluation was performed with bacteria (*V. fischeri*) [112; 113], crustacean (*A. salina* and *D. magna*) [109; 113; 114] and fish (*O. niloticus*) [110].

Chatzisyneon et al [112], in a study mentioned in the previous subsection regarding synthetic dye effluents, also applied the titanium–tantalum–platinum–iridium anode in the electrolysis of a real textile wastewater collected from a equalization tank after dyeing process, that consisted of a mixture of residual dyes, NaOH, inorganic salts and several organic components like detergents, softening, dispersing and fixing agents. A similar behavior to the one reported for the synthetic effluent was found, with an increase in toxicity (*V. fischeri*), with a decrease in EC₅₀ from the initial value of 75% to ≤3%, linked with the formation of organochlorinated and other toxic metabolites persistent to further oxidation. Anwar-ul-Haq et al. [110] treated a real textile effluent, from textile industry, in a pilot-scale (70 L) with iron electrodes and toxicity of the solutions before and after treatment was assessed by the mortality of tilapia fish (*O. niloticus*). The results showed that the final solution (after 8 h at 1.0 A) became less toxic to the fish, showing the efficiency of the process in the toxicity reduction.

Two different studies reported on the electrochemical oxidation of olive mill wastewaters (collected from the same three-phase olive mill located in the region of Chania, Greece) on titanium–tantalum–platinum–iridium anodes. Gotsi et al. [113] reported an initial wastewater with 6545 mg COD L⁻¹, and applied a potential of 9 V at a recirculation rate of 0.62 L s⁻¹, with a salinity of 4%. The toxicity of the initial wastewater was quite high towards bacteria *V. fischeri*. However, after 60 min of treatment a slight decrease was observed only to increase by the end of the assay, as prolonged oxidation times leads to the formation of organochlorinated metabolites. Towards *D. magna*, the initial effluent had low toxicity, which increased sharply at the first 60 min and remained high until the end of the assay. Giannis et al. [114] reported an initial wastewater with pH 5.2 and 45.0 g COD L⁻¹. The toxicity of the before and after electrolysis (performed at 18 V) samples was assessed with two crustaceans, *D. magna* and *A. salina*, after undergoing dichlorination by addition of sodium thiosulfate. Both results showed that the treatment was not successful in the reduction of the toxicity and, considering that

all free chlorine had been destroyed, the observed toxicity was attributed to the formation of organochlorinated compounds.

Lutterbeck et al. [109] electrochemically treated effluents generated from a hospital laundry with steel electrodes, at current densities ranging from 15-20 mA cm⁻², and toxicity evolution assessed with crustacean *D. magna*. For both treated samples (collected at two different washing stages of the hospital linens) a significant decrease in toxicity was observed with an increase in the EC₅₀ value after 1-h assay time, showing that for these conditions, the electrochemical treatment proved to be effective in the toxicity reduction (towards *D. magna*).

CONCLUSION

In recent years, toxicological risk assessment has gained more attention as a parameter to include when assessing the efficiency of electrochemical oxidation treatments. Overall, several studies report high toxicities in final effluents when most of the other measured parameters present acceptable values for discharge into the aquatic environment. It is thus of extreme importance to have into consideration the degradation metabolites formed during the electrolysis, as they could avoid further oxidation and possess higher toxicities than the original pollutants. Given this, it is worth mention the use of chloride as a support electrolyte, as it increases the degradation efficiency, but it is also responsible for the formation of active chlorine and other organochlorinated by-products, showed to be very toxic.

Furthermore, it is important to consider the sensitivities of the chosen test organisms in the toxicity assessment, and the employment of a battery of bioassays encompassing different trophic levels is highly encouraged and advised. An evaluation of toxicity with a variety of sensitivities and endpoints gives a more comprehensive information on the ecological risk posed by the effluents to the environment.

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