

Electro-oxidation of tetracycline in methanol media on DSA[®]-Cl₂

Rodrigo de Mello^a, Manuel A. Rodrigo^b, Artur J. Motheo^{a,*}

^(a) São Carlos Institute of Chemistry, University of São Paulo, P.O. Box 780, CEP 13560-970, São Carlos, SP, Brazil

^(b) Department of Chemical Engineering, Faculty of Chemical Sciences & Technologies, Universidad de Castilla - La Mancha, Campus Universitario s/n, 13071 Ciudad Real, Spain

*Corresponding author

Phone: +55 16 33739932

E-mail: artur@iqsc.usp.br

Abstract

The electro-oxidation of tetracycline (TeC) in methanol medium containing chloride or sulfate ions was evaluated using a DSA[®]-Cl₂ in a flow reactor and compared with BDD. The results show that after 30 min of electrolysis no TeC is detected by liquid chromatography when chloride is used as supporting electrolyte. On the other hand, after 90 min of electrolysis using a BDD anode only 61% of TeC was removed from solutions with chloride, but in the presence of sulfate the removal reaches 94%. This evidences that the oxidizing species generated during electrochemical oxidation control the process and the mechanism of degradation of the TeC. Besides that, it was possible to infer that only a small amount of methanol might convert to formaldehyde or formic acid, although they were not detected according to the nil changes in the FTIR spectra or in the HPLC chromatograms recorded.

Keywords

Electrochemical oxidation; tetracycline; methanol; DSA[®]

1. Introduction

With the development of new techniques increasingly sensitive to the detection of substances, new contaminants have been found in water bodies, whether continental or oceanic, and in atmospheric air. Scientific community knows these contaminants as Emerging Pollutants (EP's). They have concentrations in the order of $\mu\text{g L}^{-1}$ and include a wide variety of compounds, such as pharmaceuticals, microplastics, surfactants, pesticides, personal care products, plasticizers and preservatives and food additives (Petrović et al., 2003). Even being found in low concentrations, EP's can reach the environment from several ways, but the most part of them reach water bodies from domestic sewage treatment plants, hospital wastewater, livestock and agriculture activities (De la Cruz et al., 2012).

Among the pharmaceuticals, the antibiotics are the group of most worries by scientific community, because of their wide use by humans and animal to treat infections (Santos et al., 2020). The human and animal body is not capable of metabolize completely the antibiotics, so they are eliminated by feces and urine, and reach the environment via domestic sewage (Parra et al., 2016). Their fate in water bodies and their bioaccumulation is an increasing environmental and human health concern (Desbiolles et al., 2018). Tetracyclines have a wide spectrum of antimicrobial activity and have been used to treat various types of bacterial infections, besides being used in food preservation, and microbial control of fermentation (Parra et al., 2016).

Conventional water treatment plants are not able to remove EP's completely and, besides that, organic contaminants with high toxicity can inhibit the action of microorganisms and even destroy bacterial cultures during biological treatment (Diez, 2010). Among the methods for removing contaminants, electrochemical processes have gained a lot of attention due to the advantages over traditional methods and have proved to be efficient in removing pesticides (Malpass et al., 2012; Santos et al., 2014, 2015; Souza et al., 2016; de Mello et al., 2018; Muñoz-Morales et al., 2019a), pharmaceuticals (Parra et al., 2016; Hussain et al., 2017; Garcia-Segura et al., 2018; García-Espinoza and Nacheva, 2019), personal care products (Gomes et al., 2016; Frontistis et al., 2017;

Steter et al., 2018; Ding et al., 2019; Dionisio et al., 2019), textile residues (Rajkumar and Kim, 2006; Malpass et al., 2007, 2008; Alves et al., 2010) and another contaminant classes (Fornazari et al., 2012; Souza et al., 2014a, 2014b). In this process, the properties of electrode material are very important, and the use of highly efficient and stable electrocatalytic electrodes makes electrochemical methods even more attractive. As examples of this type of electrodes, one can mention the commercial dimensionally stable anode (DSA[®], a type of mixed metal oxide electrode (MMO) used widely on chlor-alkali industry) and the boron-doped diamond (BDD). The first stands out for the electrochemical generation of substances with high oxidative power from the anions contained in the solution (Martínez-Huitle et al., 2015), being specially relevant for the production of chlorine species (Tomcsányi et al., 1999). Besides that, it can produce hydroxyl radicals, which are strongly adsorbed on the surface, making these electrodes very active for O₂ evolution and leading to selective oxidation of contaminants. On the other hand, the BDD anode has a high capacity for generating hydroxyl radicals poorly adsorbed and it presents higher oxygen evolution overpotential. These characteristics favor the oxidation of organic compounds and are lower effective for O₂ evolution (Pelskov et al., 1987; Cominellis, 1994).

Despite that, the electrochemical treatment of wastes with low concentration of contaminant is commonly inefficient because of diffusional limitations that occurred in the electrochemical cell and the high energetic costs (Sirés et al., 2014; Martínez-Huitle et al., 2015; Muñoz-Morales et al., 2019a). It is because the electrolysis of diluted wastes fits well with the first order kinetics so, it is required the same applied electric charge to reduce a given percentage of the initial concentration, regardless of the initial concentration value (Muñoz-Morales et al., 2019a).

Thus, an alternative to improve the efficiency of the electrochemical process is to pre-concentrate the contaminant. Some methods have been shown to be viable, such as electrocoagulation for colloid concentration (Muñoz et al., 2017) and the use of electrodialysis to ionic species concentration (Raschitor et al., 2017). The adsorption process is interesting to be used, once it presents low initial cost, high flexibility, simplicity, easy operation and high efficiency, being

widely employed in water treatment plants. The mechanisms of adsorption can be physical, chemical or competitive. Van der Waals or dispersion force drives the first one. The chemical adsorption is related with the chemical reaction, which occur between surface functional groups of adsorbent and adsorbate molecules (Zhu et al., 2020). The main advantage of the chemical adsorption is the higher selectivity than physical adsorption. In this case, it is very important that the substance adsorbed being removed with an appropriate solvent, and more than that, this solvent must have properties that enable it to be used in electrochemical oxidation processes. As far as we know, electrolysis performed in non-aqueous media is a new issue and there is just a few works in the literature (Ayata et al., 2013; Saravanan et al., 2013). Other works include electro reduction (Farzinnejad et al., 2005; Wain et al., 2006; Chanique et al., 2013) or the organic synthesis (Inprakhon et al., 2017; Suresh et al., 2018) were studied.

Taking into account this background, the aim of the present work has been to evaluate the possibility of using DSA[®] as anode in the electrochemical oxidation of tetracycline hydrochloride in methanol or methanol/water solutions. These types of solutions are expected to be produced during the pre-concentration procedure carried out by a sequential adsorption onto GAC and desorption using methanol as solvent as reported elsewhere (Muñoz-Morales et al., 2019a, 2019b, 2020) in combined processes in which diamond electrolysis was successfully combined with this pre-concentration stage. Because of that, the electrolysis of the resulting solution was also carried out using BDD anode to compare the efficiency of both electrodes in the presence of some amount of NaCl or H₂SO₄. Besides that, the behavior of methanol was analyzed. Finally, a possible mechanism of degradation in this medium was proposed.

2. Experimental

2.1. Chemical products

Tetracycline hydrochloride (TeC, C₂₂H₂₄N₂O₈ · HCl, >95%) was supplied from Sigma-Aldrich. Methanol HPLC grade (99.9% - Panreac Química, Brazil) was used as solvent and mobile phase

in HPLC, along with acetonitrile HPLC grade (99.98% - J.T. Baker) and oxalic acid P.A. (99.5 – 102.5% - Synth) 0.01 M. Deionized water (Millipore Milli-Q system, resistivity: 18.2 M Ω cm⁻¹ at 25 °C) was used when necessary. All the chemicals were used as received without further purification.

2.2. Analytical techniques

The voltammetric response for both DSA[®] and BDD electrodes was evaluated at 50 mV s⁻¹ using a PGSTAT128N potentiostat/galvanostat (Metrohm Autolab B.V., The Netherlands), controlled by the software Nova 2.0. An Ag/AgCl electrode was used as reference. The measurements were performed in four different electrolytes: methanol with 0.05M of NaCl. Methanol with 0.05M methanol and 100 mg L⁻¹ of TeC, methanol with 0.017 M of H₂SO₄ and methanol with 0.017 M H₂SO₄ and with 100 mg L⁻¹ of TeC. The different concentration of sodium chloride and sulfuric acid were chosen in order to keep the same ionic strength.

The concentration of TeC during electrooxidation experiments was monitored by high-performance liquid chromatograph (HPLC, Shimadzu, LC-10AD VP) with UV detector (Shimadzu, SPD-10A VP). Stationary phase was Ascentis[®] C-18 reversed phase column (Supelco, 3 μ m, 150 mm x 4.6 mm). The eluent was a mixture of methanol, acetonitrile and oxalic acid 0.01 M, at isocratic mode, in a volumetric proportion 40:5:55, operating with flow of 0.5 mL min⁻¹, with detection wavelength at 360 nm and the furnace temperature was kept in 40 °C.

Analysis of the reaction products of methanol electrochemical oxidation were performed using HPLC (Shimadzu, LC-10AD VP) with an ion exchange column Aminex[®] (Bio-Rad, HPX-87H, 9 μ m, 300 mm x 7.8 mm) as described elsewhere (Malpass and Motheo, 2001; Batista et al., 2004).

The eluent was H₂SO₄ 3.33 M operating with flow of 0.6 mL min⁻¹, with detection in a UV detector (Shimadzu, SPD-10A VP) at λ =210 nm followed by a refractive index detector (RID-10A VP).

The first one was used to detect the carboxylic acid and the second for methanol and aldehyde.

The products were identified by comparing the retention times against reference chemicals. The

concentration of oxidants produced during the electrolysis process was determined by iodometric titration (Andrade, 2018).

The infrared spectra of the samples were measured by attenuated total reflection-Fourier transform infrared (ATR-FTIR). It was used a FTIR spectrometer VERTEX 70 (Bruker Corporation, Germany) coupled with a diamond crystal ATR. The spectra were taken at a spectral resolution of 4 cm^{-1} , and to each measurement 32 scans were performed.

2.3. Experimental set-up

To determine the removal efficiency of TeC in methanol or water medium and in methanol “contaminated” with water (2.5%, v/v), solutions with 100 mg L^{-1} of TeC and 0.050 M NaCl or 0.017 M H_2SO_4 (supporting electrolyte) were prepared. The different concentrations were used to maintain the ionic strength in 0.050 M .

The differences between a Ti/Ru_{0.3}Ti_{0.7}O₂ (DSA[®]) anode (supplied by DeNora S.A., Brazil) and a Boron-Doped Diamond (BDD) anode (supplied by CONDIAS GmbH, Germany) were studied in a single-compartment filter-press flow cell. In the case of the DSA[®] anode, a titanium cathode was used, with an apparent geometric area of 14.81 cm^2 , separated by Viton[®] and Teflon[®] spacers, as described elsewhere (Gomes et al., 2011). For the BDD system, it was used one stainless-steel cathode, both with an apparent geometric area of 80 cm^2 , and ethylene propylene diene monomer spacer/sealer. In both cases, the treatment of 0.7 L of solution was carried out in flow regime using a jacketed reservoir with 0.7 L of capacity and a peristaltic pump (Solar – model SL-64) at flow rate of $42\text{ dm}^3\text{ h}^{-1}$. The temperature of the reservoir was kept at $21 \pm 2\text{ °C}$ using a thermostatic bath. The applied current density was 10 mA cm^{-2} during 1 h and it was provided by a power supply (Missipa - MPL-3303). This current density was chosen, since in a previous test at 20 mA cm^{-2} , the removal of TeC was very fast, which made it impossible to determine the kinetic behavior.

Prior to use, for both system setup, the anode was polarized for 20 min in H₂SO₄ 0.05 M solution at 40 mA cm⁻² to remove any impurities from its surface. For chromatographic analyses, 2 mL aliquots were taken from the reservoir at different times during the electrolysis process.

3. Results and discussion

3.1. Electrochemical oxidation of TeC

Fig. 1 shows the voltametric response of DSA[®] (Fig. 1a) and BDD (Fig. 1b) electrodes in different methanol solutions, which contain chlorides or sulfates anions, alone and with 100 mg L⁻¹ of TeC. As it can be seen, intensities are much higher in the case of the DSA[®], pointing out a higher electrochemical response than that of BDD in the four electrolytes tested. Also important to note that with both electrodes, intensities recorded in sulfate are higher than those obtained in chloride containing electrolytes, despite electrolytes had the same ionic strength. Similar to what occurs in aqueous supporting electrolytes [1], there is a large electrochemical window using BDD electrode in methanol medium. This was also confirmed in a previous work focus on the same technology (Muñoz-Morales et al., 2019a) and means that oxidants can be produced more efficiently with diamond electrodes. The addition of TeC to the sulfate and chloride methanol solutions leads to an increase in the current produced, indicating that TeC is oxidized on the electrode surface with both electrodes. However, changes are more relevant with the BDD electrode, pointing out that direct electrolysis is also more significant in the electrolysis made with this anode. In addition, an oxidation peak in the nearness 0.5 V is observed when TeC is present, showing that TeC is oxidized at this potential on the BDD anode surface. This peak is masked by the decomposition of the electrolyte in the voltammetries made with DSA[®].

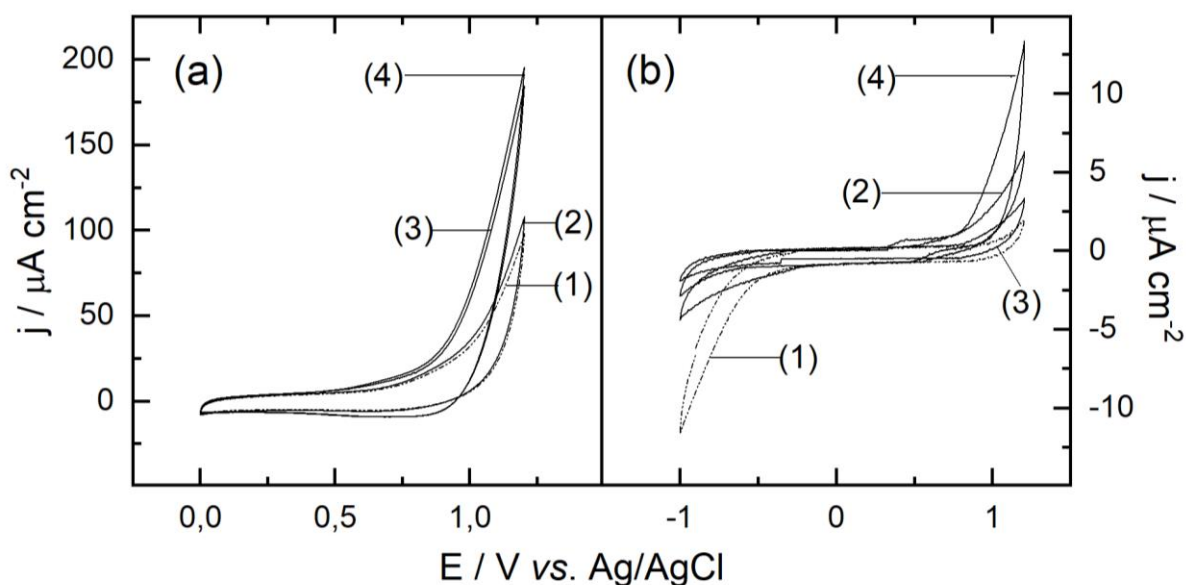


Fig. 1. Cyclic voltammograms for (a) DSA[®] and (b) BDD electrodes with different electrolytes: (1) methanol/NaCl; (2) methanol/NaCl with 100 mg L⁻¹ of TeC; (3) methanol/H₂SO₄; and (4) methanol/H₂SO₄ with 100 mg L⁻¹ of TeC (4). Auxiliary electrode: Ti plate for DSA[®] and stainless-steel for BDD; Reference electrode: Ag/AgCl. Scan rate: 50 mV s⁻¹.

Fig. 2 shows the electrochemical oxidation of TeC solutions (100 mg L⁻¹) carried out in methanol, water and a mixture of 97.5% methanol and 2.5% water, using the DSA[®] (Fig. 2a) and BDD (Fig. 2b). TeC was completely removed from all solutions using the active one. During the first 10 min, the removal rate of TeC was practically the same, regardless of the solvent, with 0.05 Ah L⁻¹ of electric charge being sufficient to remove 92% and 98% of TeC from solutions containing methanol or water, respectively, and 91% from solution composed of the solvent mixture. On the other hand, electrolysis performed with BDD anode showed less removal of the contaminant from methanol solution, as can be seen in Fig. 2b, and after 90 min of electrolysis it was still possible to detect the presence of TeC. In this case, after applying an electric charge of approximately 2.0 Ah L⁻¹, only 61% of TeC were removed from the methanol solution and 55% from the methanol-water mixture solution. In an aqueous media, 0.38 Ah L⁻¹ were required to remove about 97% of TeC. This amount of electric charge is almost ten times greater than that needed to remove

the same percentage of TeC using the DSA[®]. Besides that, in the first few minutes of electrolysis, a quick removal of TeC occurs: in 10 min, about 90% of TeC was already removed. For comparison purposes, the theoretical decrease for a 100% current efficiency is also shown in Figure 2 considering complete mineralization of the antibiotic (90 mmol e⁻/ mmol TeC). As seen, the decays observed experimentally are faster than those required for mineralization confirming the production of intermediates that are more refractory than the parent TeC.

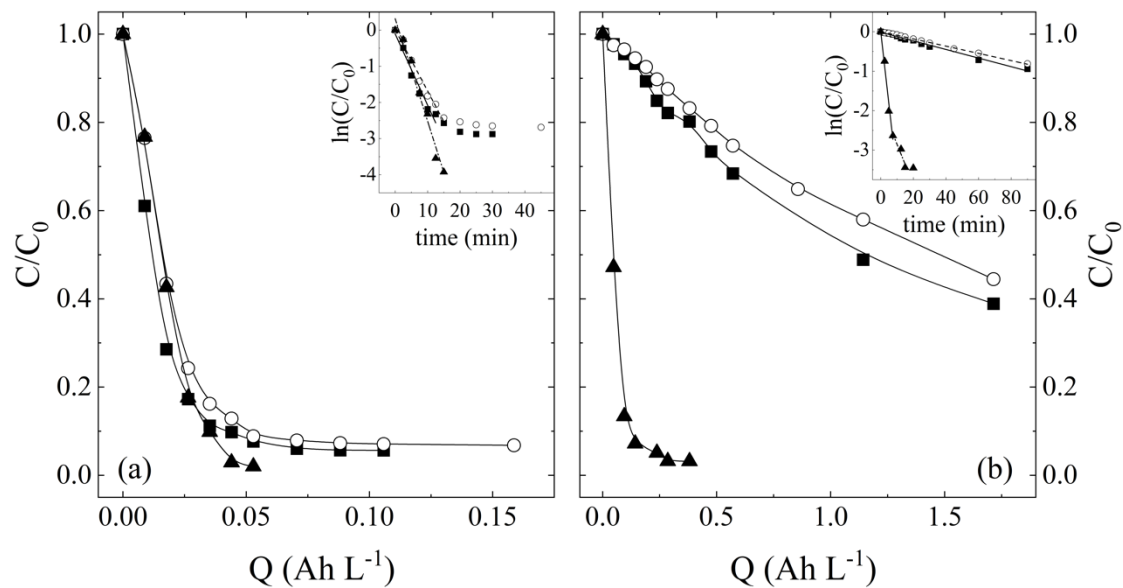


Fig. 2. Electrochemical removal of TeC (100 mg L⁻¹), as the function of the instant applied electric charge, from solutions of (■) 100% methanol, (○) 97.5% methanol + 2.5% water and (▲) 100% water as solvent. Anode: (a) DSA[®] and (b) BDD. Supporting electrolyte: NaCl 0.050 M. Applied current density: 10 mA cm⁻². Inset: kinetic analysis considering a pseudo-first order reaction.

Fig. 3 shows the concentration of oxidants produced during the electrolysis processes. In aqueous media, both electrodes produce higher concentration of oxidants than in methanol media. This fact impacts directly on electrochemical oxidation of TeC. As observed, TeC was removed faster when water was used as solvent. Besides that, using BDD, it can be verified a maximum concentration of oxidants production at around 150 min of electrolysis, while with DSA increase the concentration of oxidants continuously on that solutions. It's very important to take in mind that

the oxidants produced by each electrode are different: DSA[®] electrodes are very active for active chlorine species (e.g., Cl₂, HClO and ClO⁻) when Cl⁻ is present in the solution and these species are the mainly responsible for indirect oxidation (Tomcsányi et al., 1999; Dionisio et al., 2020); on the other hand, BDD produces higher amount of perchlorate by oxidation of chloride (Brillas and Martínez-Huitle, 2015). In addition, the oxidation power of these species may play an important effect on TeC removal and this can be an important drawback for it, even in methanol media. As can be observed, in methanol media, both electrodes produce almost the same concentration of oxidants. However, due the different species generated by each electrode, values for TeC removal are very different. Note that, in water, BDD produces a higher quantity of hydroxyl radicals than DSA[®] (Comninellis, 1994)^[2-4] and that explains why, in that case, the contaminant removal is higher and faster using BDD than DSA[®]. Finally, ruthenium electroactive from Ti/Ru_{0.3}Ti_{0.7}O₂ may act as catalyst in the electro-oxidation of organic contaminants, although in this case its contribution to TeC removal is expected to be negligible once when Cl⁻ are present, these anions occupy the active sites of the DSA[®] electrode.

Figure 4 shows the concentration of oxidants agents produced during the electrolysis process. As can be observed, in aqueous media, there was a great number of oxidants being produced. As expected, using BDD as an anode, a large amount of hydroxyl radical can be produced, and this production was confirmed by the high concentration determined. In the case of DSA[®], chlorinated species can be produced in larger quantities than in BDD. It is important to remember that DSA[®] can produce active chlorine species (Cl₂, HClO and ClO⁻) that are the mainly responsible for indirect oxidation (Dionisio et al., 2020). When chloride is present in the solutions, BDD produces higher amount of perchlorate and this can be an important drawback for TeC removal (Brillas and Martínez-Huitle, 2015). In addition, the oxidation power of the species may play an important effect on TeC removal: in water, for example, there is a higher production of hydroxyl radical with BDD than with DSA[®] anodes, which has a standard reduction potential of 2.80 V/SHE (García-Segura et al., 2018), with a high oxidative power, involving in a faster removal of the contaminant.

In methanol media, the situation reverses: BDD does not have this advantage, while DSA[®] promotes the more efficient formation of the active chlorine species. In addition, ruthenium electroactive from Ti/Ru_{0.3}Ti_{0.7}O₂ may act as catalyst in the electro oxidation of organic contaminants, although in this case its contribution to TeC removal is expected to be negligible once when Cl⁻ are present, these anions occupy the active sites of the DSA[®] electrode.

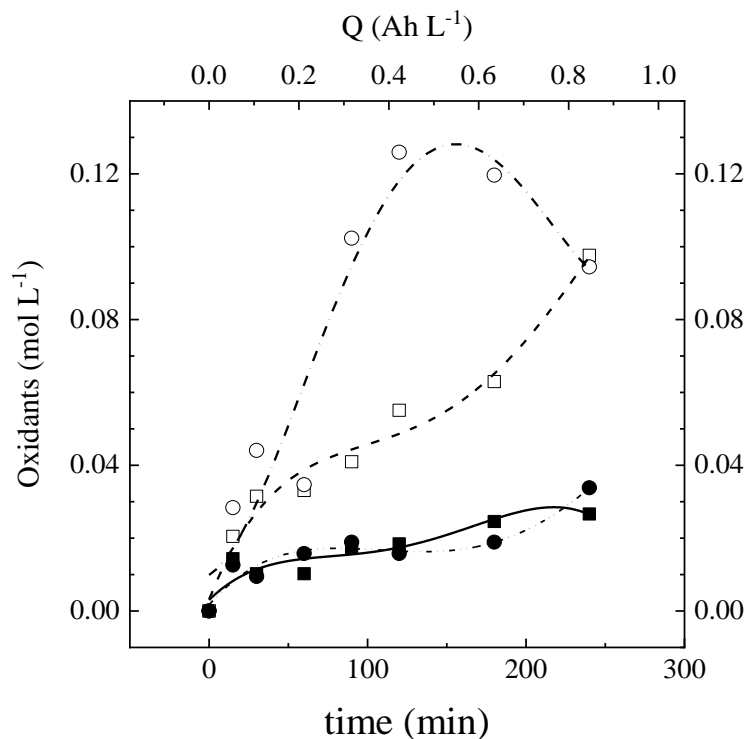


Fig. 3. Concentration of oxidants produced during the electrolysis in methanol (●, ■) and aqueous medium (○, □) using DSA[®] (square) and BDD (circle). Electrolyte: 0.050 M NaCl.

The electrolysis was also performed in the presence of sulfate anions (sulfuric acid solutions). As can be seen in the Fig. 4, a much higher removal was promoted when BDD was used. When using DSA[®] less than 25% of TeC was removed with a kinetic constant of $0.0358 \pm 0.0008 \text{ s}^{-1}$, while with BDD, almost 95% of the contaminant was degraded with a kinetic constant of $0.405 \pm 0.004 \text{ s}^{-1}$. It indicates that the oxidizing species produced during the electrolysis control the removal of TeC in methanol media, once that BDD is able to convert sulfate to persulfate, promoting the contaminant removal and DSA[®] does not. (Brillas and Martínez-Huitle, 2015).

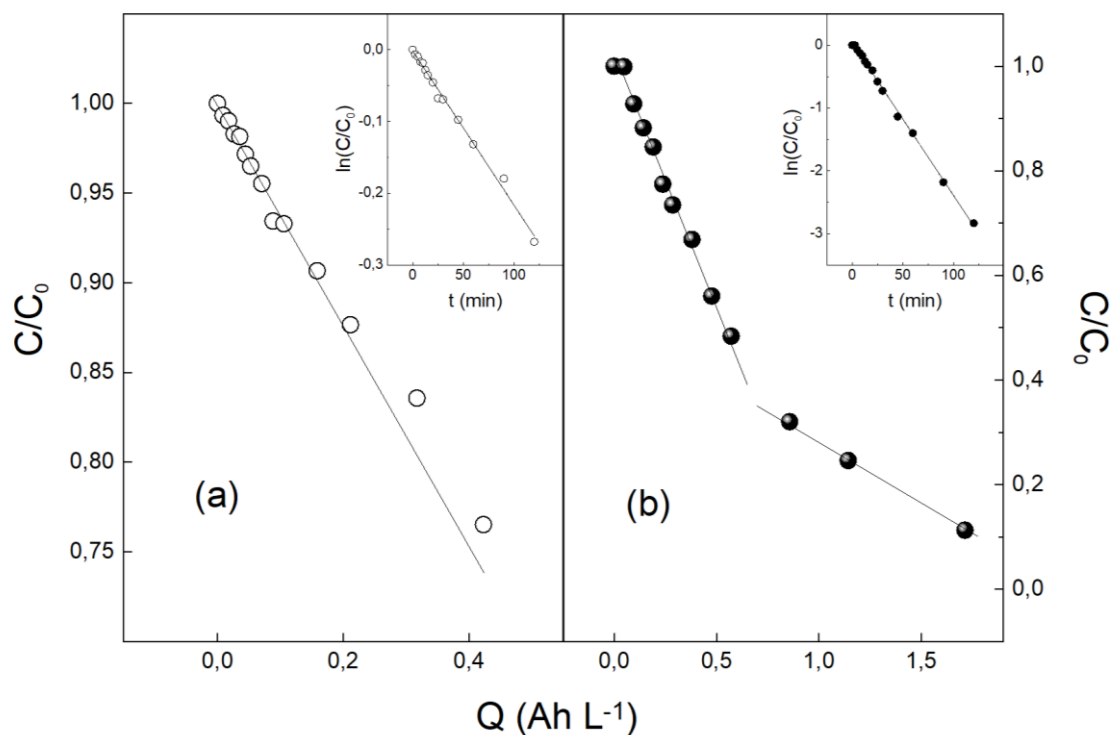


Fig. 4. Electrochemical removal of TeC (100 mg L⁻¹), as the function of the instant applied charge, from solutions of 100% methanol using DSA[®] (a) and BDD (b) as anode. Supporting electrolyte: H₂SO₄ 0.017 M. Applied current density: 10 mA cm⁻². Inset: kinetic analysis considering a pseudo-first order reaction.

Electrochemical oxidation processes are dependent on the nature of the electrode material (Brillas and Martínez-Huitle, 2015). The BDD is characterized as inert and presenting physio-adsorption and, therefore, in aqueous media, a large part of the hydroxyl radical is produced from water and organic oxidation is mediated by these radicals, which can result in reaction products totally oxidized (Marselli et al., 2003; Brillas and Martínez-Huitle, 2015). Thus, the lower removal of TeC in methanol when BDD is used, may be related only to the prevention in the formation of strongly oxidizing radicals due to the absence of water, but also to the direct oxidation on the anode surface. Furthermore, the formation of methanoate radicals is possible (Muñoz-Morales et al., 2020) even in low quantity. However, further analysis will be necessary for confirmation.

On the other hand, DSA[®] electrodes in chloride medium are capable to generate chlorine oxidative species, in particular, hypochlorous acid and hypochlorite ion (Santos et al., 2020b) even when methanol was used as solvent. Meanwhile, perchlorate ions are predominant when BDD is used and the chloride anion is oxidized to non-useful oxochlorine compounds such as perchlorate, for example, when the non-active anode is used (Sánchez-Carretero et al., 2011; Santos et al., 2020c). When H₂SO₄ was used as supporting electrolyte the performance of BDD increased. It shows that the supporting electrolyte play an important role in the mechanism for TeC removal.

3.2. Kinetic analysis

It is important to note that for both in methanol (with or without the presence of water) and in aqueous media, the concentration decay of TeC with both anodes obeys a first order kinetics. This behavior is very common in the removal of organic compounds by electrochemical oxidation in aqueous medium (Malpass and Motheo, 2001; Vedenyapina et al., 2008; Parra et al., 2016; Santos et al., 2020a). The values for the first order kinetics constants are shown in the Table 1. In methanol/NaCl, with and without water, the kinetics constants present very close values in both cases, DSA[®] and BDD. Furthermore, there is no statistical difference between the constants for the electrochemical oxidation performed using the active anode. For the processes performed in aqueous medium, the values for the constants are higher than for methanol solutions, as expected, since the large production of chlorinated oxidants, in the case of the DSA[®], and hydroxyl radicals for the BDD. Comparing the kinetic constants for methanol/H₂SO₄ and methanol/NaCl is possible to observe the large difference in the performance of DSA[®] anode.

Solvent		DSA [®]		BDD	
		k (10 ⁻³ s ⁻¹)	R ²	k (10 ⁻³ s ⁻¹)	R ²
100% methanol	NaCl	3.28 ± 0.31	0.966	0.182 ± 0.006	0.990
	H ₂ SO ₄	0.0358 ± 0.0008	0.993	0.405 ± 0.004	0.998

97.5% methanol + 2.5% water	NaCl	2.82 ± 0.16	0.985	0.153 ± 0.002	0.998
100% water	NaCl	4.72 ± 0.32	0.977	6.12 ± 0.55	0.984

Table 1. First-order kinetic constants of TeC electrolysis in methanol-water solutions

The electrolysis carried out using the BDD electrode shows a different behavior, dependent on the solvent. In the case of the experiments performed in methanol media there was no peak associated to intermediate products, as can be observed in chromatograms presented in the [Fig. SM-1a](#) and [SM-1b](#). This can occur because of the instantaneous oxidation of intermediates, as soon as they are formed. It was also verified for electrochemical oxidation of lindane in the study carried out by Muñoz-Morales et al. (Muñoz-Morales et al., 2019a). For TeC removal in aqueous media, the intermediates are not removed as fast, as can be seen in the [Fig. SM-2](#), and were detected by HPLC ([Fig. SM-1c](#)). Nevertheless, as can be seen in the [Fig. 5](#), after 15 min of electrolysis they were no longer detected. As previously said, in the first 10 min of electrolysis about 90% of TeC was removed. This causes two different kinetic behaviors, as can be seen in the inset of [Fig. 2b](#). At first, a kinetic constant of 6.12 s^{-1} was found, and after 10 min this constant was reduced to 1.70 s^{-1} . This behavior was also observed by Dionisio et al. (2019) and it may be related with a change in the oxidation mechanism during the electrolysis.

On the other hand, when DSA[®] was used, a wide variety of intermediates was detected ([Fig. SM-3](#), [SM-4](#), [SM-5](#) and [SM-6](#)). Most of them were detected in very low concentration and they were oxidized very quickly. In methanol media, after 45 min of electrolysis, the intermediates were no detected. Meanwhile, in aqueous medium they were detected up to 60 min of experiment ([Fig. 5](#)). The largest peak area of intermediates was found in the first 5 min of electrolysis in the case of the experiments carried out in methanol media using DSA[®] and in aqueous medium using BDD. In the case of aqueous medium using DSA[®], it can be found after 7.5 min. It is important to note that, in this case, TeC was detected only up to 15 [min](#) of electrolysis, but the intermediates remained in the solution for up to 60 [min](#). In the methanol media used, TeC was no longer detected after 25

min and the intermediates remained up to 45 min. Since all organic compounds (TeC + oxidation products) have been completely removed in methanol, it is possible that complete TeC mineralization has occurred. Unfortunately, it is not possible to determine the removal of TOC, due to the large amount of methanol present as a solvent, which masks any changes in the antibiotic or intermediates.

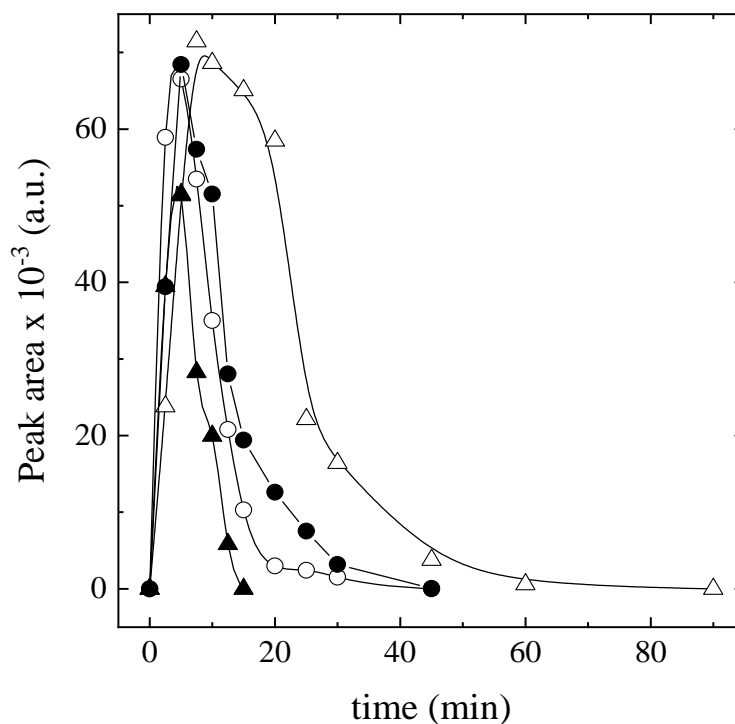


Fig. 5. Peak area of the intermediates detected as function of electrolysis time of (○) 100% methanol (DSA[®]), (●) 97.5% methanol + 2.5% water (DSA[®]), (△) 100% water (DSA[®]) e (▲) 100% water (BDD) solutions containing TeC.

3.3. Effect of solvent electrolysis

Experiments using methanol without the contaminant were performed to verify if the solvent changes during the electrolysis. Some studies have shown that methanol electrooxidation occurs via parallel pathways forming HCHO, HCOOH and CO₂ (Ota et al., 1984; Malpass and Motheo, 2001; Batista et al., 2003, 2004). In this case, methanol was used as a solvent, it is extremely important to ensure that this substance is not consumed or altered during the experiments.

From the analysis of the FTIR spectra in the **Fig. 6**, it was possible to see the characteristics IR absorption for alcohols associated with both the O-H (a broad and strong band) and the C-O stretching vibrations, located in the region 3500-3200 cm^{-1} and 1260-1050 cm^{-1} , respectively. C-H stretch was also detected in the region 3000-2700 cm^{-1} . Results are according with Doroshenko et al. (Doroshenko et al., 2013) and the NIST library. As can be seen, there is no significant difference between the spectra over electrolysis time.

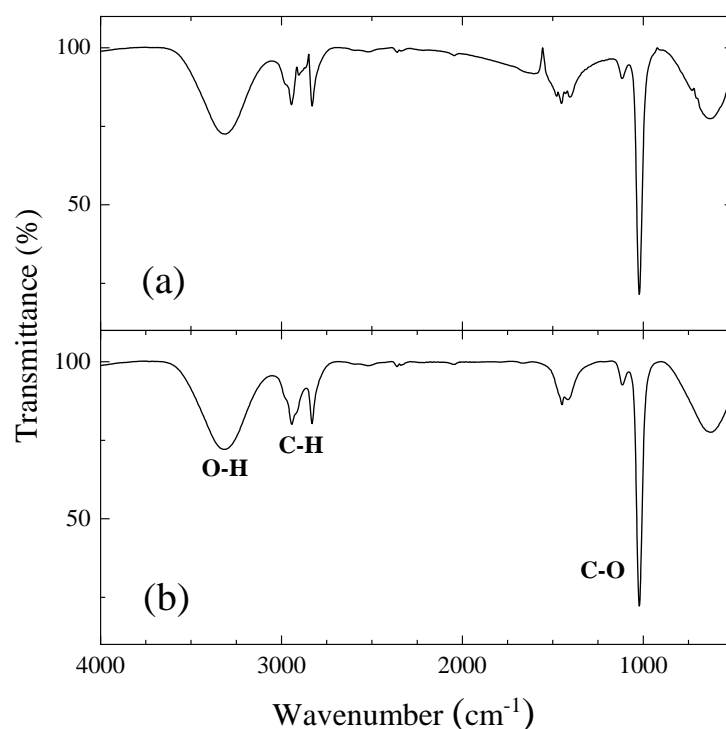


Fig. 6. FTIR spectra for the methanol electrochemical oxidation using DSA[®]. Samples taken at (a) 0 and (b) 240 min.

Fig. SM-7 shows the UV-vis spectra for those samples. As can be observed, the absorbance increases in the wavelength from 320 to 200 nm. This result can be related an increase in the formaldehyde and formic acid concentration. These substances present a retention time of 13.6 min for the aldehyde and 14.2 min for the acid by the HPLC method. As can be seen in the **Fig. SM-8**, both substances were not detected. Therefore, it can be concluded that the substances are produced in a very low concentration, which can evaporate during handling, and does not change the nature of the solvent, despite the increase in absorbance verified by UV-vis.

4. Conclusions

This study shows that it is possible to remove organic compounds using electrochemical oxidation in methanol media. Using DSA[®] as anode, complete removal was achieved in 1 h with solutions containing chloride ions, even in the presence of 2.5% of water. On the other hand, while with chloride-supporting electrolyte the removal of TeC was about 60% with the use of BDD anode, using sulfate-supporting electrolyte the performance of this anode reaches 94% being higher than the efficiency of the DSA[®]. This shows that the oxidant agents produced during the electrolysis control the process and the mechanism of degradation of TeC. It was possible to observe that methanol does not change during electrolysis and only a small amount of formaldehyde or formic acid were suspected to be formed, although they were not detected according to the negligible changes in the FTIR spectra or the nil variations in the HPLC chromatograms recorded.

Acknowledgments

Financial support from the São Paulo Research Foundation (FAPESP, Brazil) [2017/10118-0, 2017/20444-1, 2018/16308-8 and 2020/03052-5] and from the Spanish Ministry of Economy, Industry and Competitiveness, European Union through project PID2019-107271RB-I00 (AEI/FEDER, UE) are gratefully acknowledged. The authors would also like to thank Embrapa Instrumentation, Brazil.

References

- Alves, P.A., Malpass, G.R.P., Johansen, H.D., Azevedo, E.B., Gomes, L.M., Vilela, W.F.D., Motheo, A.J., 2010. Photo-assisted electrochemical degradation of real textile wastewater. *Water Sci. Technol.* 61, 491–498. <https://doi.org/10.2166/wst.2010.870>
- Andrade, J.C. de, 2018. Determinações iodométricas. *Rev. Chemkeys* 1–6. <https://doi.org/10.20396/chemkeys.v0i2.9623>
- Ayata, S., Stefanova, A., Ernst, S., Baltruschat, H., 2013. The electro-oxidation of water and alcohols at BDD in hexafluoroisopropanol. *J. Electroanal. Chem.* 701, 1–6. <https://doi.org/10.1016/j.jelechem.2013.03.024>
- Batista, E.A., Malpass, G.R.P., Motheo, A.J., Iwasita, T., 2003. New insight into the pathways of methanol oxidation. *Electrochem. Commun.* 5, 843–846. <https://doi.org/10.1016/j.elecom.2003.08.010>
- Batista, E.A., Malpass, G.R.P., Motheo, A.J., Iwasita, T., 2004. New mechanistic aspects of methanol oxidation. *J. Electroanal. Chem.* 571, 273–282. <https://doi.org/10.1016/j.jelechem.2004.05.016>
- Brillas, E., Martínez-Huitle, C.A., 2015. Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods. An updated review. *Appl. Catal. B-Environ.* 166–167, 603–643. <https://doi.org/10.1016/j.apcatb.2014.11.016>
- Chanique, G.D., Arévalo, A.H., Zonn, M.A., Fernandez, H., 2013. Electrochemical reduction of patulin and 5-hydroxymethylfurfural in both neutral and acid non-aqueous media. Their electroanalytical determination in apple juices. *Talanta* 111, 85–92. <https://doi.org/10.1016/j.talanta.2013.02.041>
- Cominellis, C., 1994. Electrocatalysis in the electrochemical conversion/combustion of organic pollutants for waste water treatment. *Electrochim. Acta* 39, 1857–1862.

[https://doi.org/10.1016/0013-4686\(94\)85175-1](https://doi.org/10.1016/0013-4686(94)85175-1)

- De la Cruz, N., Giménez, J., Esplugas, S., Grandjean, D., De Alencastro, L.F., Pulgarín, C., 2012. Degradation of 32 emergent contaminants by UV and neutral photo-fenton in domestic wastewater effluent previously treated by activated sludge. *Water Res.* 46, 1947–1957. <https://doi.org/10.1016/j.watres.2012.01.014>
- de Mello, R., Santos, L.H.E., Pupo, M.M.S., Eguiluz, K.I.B., Salazar-Banda, G.R., Motheo, A.J., 2018. Alachlor removal performance of Ti/Ru_{0.3}Ti_{0.7}O₂ anodes prepared from ionic liquid solution. *J. Solid State Electr.* 22, 1571–1580. <https://doi.org/10.1007/s10008-017-3700-6>
- Desbiolles, F., Malleret, L., Tiliacos, C., Wong-Wah-Chung, P., Laffont-Schwob, I., 2018. Occurrence and ecotoxicological assessment of pharmaceuticals: Is there a risk for the Mediterranean aquatic environment? *Sci. Total Environ.* 639, 1334–1348. <https://doi.org/10.1016/j.scitotenv.2018.04.351>
- Diez, M.C., 2010. Biological aspects involved in the degradation of organic pollutants. *J. Soil Sci. Plant Nut.* 10, 244–267. <https://doi.org/10.4067/S0718-95162010000100004>
- Ding, J., Bu, L., Zhao, Q., Kabutey, F.T., Wei, L., Dionysiou, D.D., 2019. Electrochemical activation of persulfate on BDD and DSA anodes: Electrolyte influence, kinetics and mechanisms in the degradation of bisphenol A. *J. Hazard. Mater.* 121789. <https://doi.org/10.1016/j.jhazmat.2019.121789>
- Dionisio, Dawany, Motheo, A.J., Saez, C., Canizares, P., Rodrigo, M.A., 2019. Competitive anodic oxidation of methyl paraben and propylene glycol: Keys to understand the process. *ChemElectroChem* 6, 771–778. <https://doi.org/10.1002/celec.201801332>
- Dionisio, D., Motheo, A.J., Sáez, C., Rodrigo, M.A., 2019. Effect of the electrolyte on the electrolysis and photoelectrolysis of synthetic methyl paraben polluted wastewater. *Sep. Purif. Technol.* 208, 201–207. <https://doi.org/10.1016/j.seppur.2018.03.009>

- Dionisio, D., Santos, L.H.E., Rodrigo, M.A., Motheo, A.J., 2020. Electro-oxidation of methyl paraben on DSA[®]-Cl₂: UV irradiation, mechanistic aspects and energy consumption. *Electrochim. Acta* 338, 135901. <https://doi.org/10.1016/j.electacta.2020.135901>
- Doroshenko, I., Pogorelov, V., Sablinskas, V., 2013. Infrared absorption spectra of monohydric alcohols. *Dataset Pap. Chem.* 2013, 329406. <https://doi.org/10.7167/2013/329406>
- Farzinnejad, N., Beigi, A.A.M., Fotouhi, L., Torkestani, K., Ghadirian, H.A., 2005. Electrochemical behavior of some triazine derivatives at glassy carbon electrode in non-aqueous media. *J. Electroanal. Chem.* 580, 245–254. <https://doi.org/10.1016/j.jelechem.2005.03.032>
- Fornazari, A.L.T., Malpass, G.R.P., Miwa, D.W., Motheo, A.J., 2012. Application of electrochemical degradation of wastewater composed of mixtures of phenol-formaldehyde. *Water. Air. Soil Poll.* 223, 4895–4904. <https://doi.org/10.1007/s11270-012-1245-y>
- Frontistis, Z., Antonopoulou, M., Venieri, D., Dailianis, S., Konstantinou, I., Mantzavinos, D., 2017. Solar photocatalytic decomposition of ethyl paraben in zinc oxide suspensions. *Catal. Today* 280, 139–148. <https://doi.org/10.1016/j.cattod.2016.06.008>
- García-Espinoza, J.D., Nacheva, P.M., 2019. Degradation of pharmaceutical compounds in water by oxygenated electrochemical oxidation: Parametric optimization, kinetic studies and toxicity assessment. *Sci. Total Environ.* 691, 417–429. <https://doi.org/10.1016/j.scitotenv.2019.07.118>
- García-Segura, S., Ocon, J.D., Chong, M.N., 2018. Electrochemical oxidation remediation of real wastewater effluents — A review. *Process Saf. Environ.* 113, 48–67. <https://doi.org/10.1016/j.psep.2017.09.014>
- Gomes, F.E.R., de Souza, N.E., Galinaro, C.A., Arriveti, L.O.R., de Assis, J.B., Tremiliosi-Filho, G., 2016. Electrochemical degradation of butyl paraben on platinum and glassy carbon

electrodes. *J. Electroanal. Chem.* 769, 124–130.
<https://doi.org/10.1016/j.jelechem.2016.03.016>

Gomes, L., Miwa, D.W., Malpass, G.R.P., Motheo, A.J., 2011. Electrochemical degradation of the dye reactive orange 16 using electrochemical flow-cell. *J. Brazil. Chem. Soc.* 22, 1299–1306.
<https://doi.org/10.1590/S0103-50532011000700015>

Hussain, S., Steter, J.R., Gul, S., Motheo, A.J., 2017. Photo-assisted electrochemical degradation of sulfamethoxazole using a Ti/Ru_{0.3}Ti_{0.7}O₂ anode: Mechanistic and kinetic features of the process. *J. Environ. Manage.* 201, 153–162. <https://doi.org/10.1016/j.jenvman.2017.06.043>

Inprakhon, P., Wongthongdee, N., Amornsakchai, T., Pongtharankul, T., Sunintaboon, P., Wiemann, L.O., Durand, A., Sieber, V., 2017. Lipase-catalyzed synthesis of sucrose monoester: Increased productivity by combining enzyme pretreatment and non-aqueous biphasic medium. *J. Biotechnol.* 259, 182–190. <https://doi.org/10.1016/j.jbiotec.2017.07.021>

Malpass, G.R.P., Miwa, D.W., Machado, S.A.S., Motheo, A.J., 2008. Decolourisation of real textile waste using electrochemical techniques: Effect of electrode composition. *J. Hazard. Mater.* 156, 170–177. <https://doi.org/10.1016/j.jhazmat.2007.12.017>

Malpass, G.R.P., Miwa, D.W., Mortari, D.A., Machado, S.A.S., Motheo, A.J., 2007. Decolorisation of real textile waste using electrochemical techniques: Effect of the chloride concentration. *Water Res.* 41, 2969–2977. <https://doi.org/10.1016/j.watres.2007.02.054>

Malpass, G.R.P., Miwa, D.W., Santos, R.L., Vieira, E.M., Motheo, A.J., 2012. Unexpected toxicity decrease during photoelectrochemical degradation of atrazine with NaCl. *Environ. Chem. Lett.* 10, 177–182. <https://doi.org/10.1007/s10311-011-0340-4>

Malpass, G.R.P., Motheo, A.J., 2001. Galvanostatic oxidation of formaldehyde-methanol solutions on Ti/Ru_{0.3}Ti_{0.7}O₂ electrodes using a filter-press cell. *J. Appl. Electrochem.* 31, 1351–1357. <https://doi.org/10.1023/A:1013814831777>

- Marselli, B., Garcia-Gomez, J., Michaud, P.-A., Rodrigo, M.A., Comninellis, C., 2003. Electrogeneration of hydroxyl radicals on boron-doped diamond electrodes. *J. Electrochem. Soc.* 150, D79. <https://doi.org/10.1149/1.1553790>
- Martínez-Huitle, C.A., Rodrigo, M.A., Sirés, I., Scialdone, O., 2015. Single and coupled electrochemical processes and reactors for the abatement of organic water pollutants: a critical review. *Chem. Rev.* 115, 13362–13407. <https://doi.org/10.1021/acs.chemrev.5b00361>
- Muñoz-Morales, M., Sáez, C., Cañizares, P., Rodrigo, M.A., 2020. Improvement of electrochemical oxidation efficiency through combination with adsorption processes. *J. Environ. Manage.* 262. <https://doi.org/10.1016/j.jenvman.2020.110364>
- Muñoz-Morales, M., Sáez, C., Cañizares, P., Rodrigo, M.A., 2019a. Enhanced electrolytic treatment for the removal of clopyralid and lindane. *Chemosphere* 234, 132–138. <https://doi.org/10.1016/j.chemosphere.2019.06.059>
- Muñoz-Morales, M., Sáez, C., Cañizares, P., Rodrigo, M.A., 2019b. A new electrochemically-based process for the removal of perchloroethylene from gaseous effluents. *Chem. Eng. J.* 361, 609–614. <https://doi.org/10.1016/j.cej.2018.12.119>
- Muñoz, M., Llanos, J., Raschitor, A., Cañizares, P., Rodrigo, M.A., 2017. Electrocoagulation as the key for an efficient concentration and removal of oxyfluorfen from liquid wastes. *Ind. Eng. Chem. Res.* 56, 3091–3097. <https://doi.org/10.1021/acs.iecr.7b00347>
- Ota, K.I., Nakagawa, Y., Takahashi, M., 1984. Reaction products of anodic oxidation of methanol in sulfuric acid solution. *J. Electroanal. Chem.* 179, 179–186. [https://doi.org/10.1016/S0022-0728\(84\)80286-7](https://doi.org/10.1016/S0022-0728(84)80286-7)
- Parra, K.N., Gul, S., Aquino, J.M., Miwa, D.W., Motheo, A.J., 2016. Electrochemical degradation of tetracycline in artificial urine medium. *J. Solid State Electr.* 20, 1001–1009.

<https://doi.org/10.1007/s10008-015-2833-8>

Pelskov, Y. V., Sakharova, A.Y., Krotova, M.D., Bouilov, L.L., Spitsyn, B. V., 1987.

Photoelectrochemical properties of semiconductor diamond. *J. Electroanal. Chem.* 228, 19–27. [https://doi.org/10.1016/0022-0728\(87\)80093-1](https://doi.org/10.1016/0022-0728(87)80093-1)

Petrović, M., Gonzalez, S., Barceló, D., 2003. Analysis and removal of emerging contaminants in wastewater and drinking water. *TrAC – Trend. Anal. Chem.* 22, 685–696. [https://doi.org/10.1016/S0165-9936\(03\)01105-1](https://doi.org/10.1016/S0165-9936(03)01105-1)

Rajkumar, D., Kim, J.G., 2006. Oxidation of various reactive dyes with in situ electro-generated active chlorine for textile dyeing industry wastewater treatment. *J. Hazard. Mater.* 136, 203–212. <https://doi.org/10.1016/j.jhazmat.2005.11.096>

Raschitor, A., Llanos, J., Cañizares, P., Rodrigo, M.A., 2017. Novel integrated electro-dialysis/electro-oxidation process for the efficient degradation of 2,4-dichlorophenoxyacetic acid. *Chemosphere* 182, 85–89. <https://doi.org/10.1016/j.chemosphere.2017.04.153>

Sánchez-Carretero, A., Sáez, C., Cañizares, P., Rodrigo, M.A., 2011. Electrochemical production of perchlorates using conductive diamond electrolyses. *Chem. Eng. J.* 166, 710–714. <https://doi.org/10.1016/j.cej.2010.11.037>

Santos, G.O.S., Eguiluz, K.I.B., Salazar-Banda, G.R., Saez, C., Rodrigo, M.A., 2020a. Photoelectrolysis of clopyralid wastes with a novel laser-prepared MMO-RuO₂TiO₂ anode. *Chemosphere* 244. <https://doi.org/10.1016/j.chemosphere.2019.125455>

Santos, G.O.S., Eguiluz, K.I.B., Salazar-Banda, G.R., Sáez, C., Rodrigo, M.A., 2020b. Understanding the electrolytic generation of sulfate and chlorine oxidative species with different boron-doped diamond anodes. *J. Electroanal. Chem.* 857, 113756. <https://doi.org/10.1016/j.jelechem.2019.113756>

- Santos, G.O.S., Gonzaga, I.M.D., Eguiluz, K.I.B., Salazar-Banda, G.R., Saez, C., Rodrigo, M.A., 2020c. Improving biodegradability of clopyralid wastes by photoelectrolysis: The role of the anode material. *J. Electroanal. Chem.* 864. <https://doi.org/10.1016/j.jelechem.2020.114084>
- Santos, J.P.T. da S., Tonholo, J., de Andrade, A.R., Del Colle, V., Zanta, C.L. de P. e. S., 2020. The electro-oxidation of tetracycline hydrochloride in commercial DSA[®] modified by electrodeposited platinum. *Environ. Sci. Pollut. R.* <https://doi.org/10.1007/s11356-020-09919-2>
- Santos, T.É.S., Silva, R.S., Carlesi Jara, C., Eguiluz, K.I.B., Salazar-Banda, G.R., 2014. The influence of the synthesis method of Ti/RuO₂ electrodes on their stability and catalytic activity for electrochemical oxidation of the pesticide carbaryl. *Mater. Chem. Phys.* 148, 39–47. <https://doi.org/10.1016/j.matchemphys.2014.07.007>
- Santos, T.É.S., Silva, R.S., Eguiluz, K.I.B., Salazar-Banda, G.R., 2015. Development of Ti/(RuO₂)_{0.8}(MO₂)_{0.2} (M=Ce, Sn or Ir) anodes for atrazine electro-oxidation. Influence of the synthesis method. *Mater. Lett.* 146, 4–8. <https://doi.org/10.1016/j.matlet.2015.01.145>
- Saravanan, K., Selvamani, V., Kulangiappar, K., Velayutham, D., Suryanarayanan, V., 2013. Regioselective anodic α -methoxylation of 2-oxazolidinone on boron doped diamond in acidic methanol medium. *Electrochem. commun.* 28, 31–33. <https://doi.org/10.1016/j.elecom.2012.12.002>
- Sirés, I., Brillas, E., Oturan, M.A., Rodrigo, M.A., Panizza, M., 2014. Electrochemical advanced oxidation processes: Today and tomorrow. A review. *Environ. Sci. Pollut. R.* 21, 8336–8367. <https://doi.org/10.1007/s11356-014-2783-1>
- Souza, F.L., Aquino, J.M., Irikura, K., Miwa, D.W., Rodrigo, M.A., Motheo, A.J., 2014a. Electrochemical degradation of the dimethyl phthalate ester on a fluoride-doped Ti/ β -PbO₂ anode. *Chemosphere* 109, 187–194. <https://doi.org/10.1016/j.chemosphere.2014.02.018>

- Souza, F.L., Aquino, J.M., Miwa, D.W., Rodrigo, M.A., Motheo, A.J., 2014b. Photo-assisted electrochemical degradation of the dimethyl phthalate ester on DSA[®] electrode. *J. Environ. Chem. Eng.* 2, 811–818. <https://doi.org/10.1016/j.jece.2014.02.003>
- Souza, F.L., Saéz, C., Lanza, M.R.V., Cañizares, P., Rodrigo, M.A., 2016. The effect of the sp³/sp² carbon ratio on the electrochemical oxidation of 2,4-D with p-Si BDD anodes. *Electrochim. Acta* 187, 119–124. <https://doi.org/10.1016/j.electacta.2015.11.031>
- Steter, J.R., Brillas, E., Sires, I., 2018. Solar photoelectro-Fenton treatment of a mixture of parabens spiked into secondary treated wastewater effluent at low input current. *Appl. Catal. B-Environ.* 224, 410–418. <https://doi.org/10.1016/j.apcatb.2017.10.060>
- Suresh, S., Reddy, I.A.K., Venkatathri, N., 2018. Synthesis of SAPO-16 molecular sieve in non-aqueous medium by microwave method using Hexamethyleneimine as a template. *Micropor. Mesopor. Mat.* 263, 275–281. <https://doi.org/10.1016/j.micromeso.2017.12.008>
- Tomcsányi, L., De Battisti, A., Hirschberg, G., Varga, K., Liszi, J., 1999. The study of the electrooxidation of chloride at RuO₂/TiO₂ electrode using CV and radiotracer techniques and evaluating by electrochemical kinetic simulation methods. *Electrochim. Acta* 44, 2463–2472. [https://doi.org/10.1016/S0013-4686\(98\)00381-8](https://doi.org/10.1016/S0013-4686(98)00381-8)
- Vedenyapina, M.D., Eremicheva, Y.N., Pavlov, V.A., Vedenyapin, A.A., 2008. Electrochemical degradation of tetracycline. *Russ. J. Appl. Chem.* 81, 800–802. <https://doi.org/10.1134/S1070427208050145>
- Wain, A.J., Drouin, L., Compton, R.G., 2006. Voltammetric reduction of perinaphthenone in aqueous and non-aqueous media: An electrochemical ESR investigation. *J. Electroanal. Chem.* 589, 128–138. <https://doi.org/10.1016/j.jelechem.2006.01.025>
- Zhu, L., Shen, D., Luo, K.H., 2020. A critical review on VOCs adsorption by different porous materials: Species, mechanisms and modification methods. *J. Hazard. Mater.* 122102.

- [1] G. Foti, D. Gandini, C. Comninellis, A. Perret, W. Haenni, Oxidation of organics by intermediates of water discharge on IrO₂ and synthetic diamond anodes, *Electrochemical and Solid State Letters*, 2 (1999) 228-230.
- [2] P. Canizares, C. Saez, J. Lobato, R. Paz, M.A. Rodrigo, Effect of the operating conditions on the oxidation mechanisms in conductive-diamond electrolyses, *Journal of the Electrochemical Society*, 154 (2007) E37-E44.
- [3] P. Canizares, F. Martinez, M. Diaz, J. Garcia-Gomez, M. Rodrigo, C. Comninellis, M. Doyle, J. Winnick, Electrochemical oxidation of aqueous phenol wastes using active and non-active electrodes, *Energy and Electrochemical Processes For a Cleaner Environment, Proceedings2001*, pp. 59-71.
- [4] M.A. Rodrigo, P.A. Michaud, I. Duo, M. Panizza, G. Cerisola, C. Comninellis, Oxidation of 4-chlorophenol at boron-doped diamond electrode for wastewater treatment, *Journal of the Electrochemical Society*, 148 (2001) D60-D64.