Electrochemical treatment of real petrochemical effluent: current density effect and toxicological tests
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ABSTRACT
This work aims to investigate the electrochemical treatment of petrochemical industry effluents (from the northwest region of Brazil) mediated by active chlorine species electrogenerated at ruthenium-titanium oxide supported in titanium (Ti/Ru0.3Ti0.7O2) and boron doped diamond (BDD) anodes by applying 15 and 45 mA cm⁻². Chemical oxygen demand (COD) determinations and toxicity analyses were carried out in order to evaluate the process extension as well as the possible reuse of the wastewater after treatment. Toxicity was evaluated by assessing the inhibition of lettuce (Lactuca sativa) stem growth, seed germination, and the production of nitrite (NO₂⁻) and nitrate (NO₃⁻) species. Results clearly showed that the best COD reduction performances were reached at the BDD anode, achieving almost 100% of removal in a short time. Degradation of nitrogen-organic compounds generated NO₂⁻ and NO₃⁻ which act as nutrients for lettuce. Toxicity results also indicated that the electrogenerated active chlorine species are persistent in the effluent after the treatment, avoiding the stem growth, and consequently affecting the germination.

Key words | indirect electrochemical oxidation, Lactuca sativa, produced water, water disinfection

HIGHLIGHTS
- Ti/Ru0.3Ti0.7O2 and BDD anodes were used for treating petrochemical effluent.
- BDD anode promotes the production of active chlorine.
- Toxicity was evaluated by assessing the inhibition of Lactuca sativa growth.
- Nitrite and nitrate are produced during effluent treatment.
- Toxicity results indicated that the electrogenerated active chlorine species are persistent.

INTRODUCTION
Effluent contamination with organic or chemical pollutants is often present in the 21st century environment (Li et al. 2014; Reddy et al. 2019a). These contaminants affect the water quality, which have a direct impact in the human health via different infections such as diarrhea, cholera, typhoid fever, amoebiasis, and schistosomiasis (Brito et al. 2015b; Reddy et al. 2019a). An intense urbanization and industrialization causes the increase of pollutant sources, which are responsible for spreading these problems to several countries around the world, independently of their development level (Martínez-Huitle & Brillas 2008; Brito et al. 2015b).

The variety of industrial effluents and the presence of complex organic compounds require further studies into the development of treatments capable of reducing the impact of these diverse sources of pollutants (Baird & Cann 2011; dos Santos et al. 2014; Kamali et al. 2019a). The process selection requires that the removal of contaminants has the least environmental impact possible (Freire et al. 2000; Kamali et al. 2019a). As a disinfection agent,
chlorine is the most common reagent for water disinfection (Johnston 1979; Bazzoli 1993; Martínez-Huitle & Brillas 2008). The inactivation of microorganisms occurs with the rupture of cell membranes or enzyme transformation when chlorine species bond with viruses and bacterial structures and substituting the hydrogen atoms with chlorine atoms (Martínez-Huitle & Brillas 2008). The hypochlorous acid (HClO), a neutral covalent compound, is predominant at pH 5.5–7.5 and destroys microorganisms due to its rapid penetration through protective layers where it subsequently promotes the rupture of molecular bonds inside the cells (Martínez-Huitle & Brillas 2008). At higher pH, around 8.0, the hypochlorite ion (OCl⁻) is the predominant chlorine species, which is responsible of microorganism inactivation. However, OCl⁻ is less likely to penetrate the cell due to its electrical charge, which inhibits the pathogen reproduction (Erren et al. 1997; Li et al. 2004).

A disadvantage of chlorine is the production of organochloride byproducts from the reaction of chlorine with organic components of the treated effluents, which are hazardous compounds due to their carcinogenic potential (Martínez-Huitle & Brillas 2008) (e.g. haloacetic acids, haloacetonitriles, trichloromethanes chlorofrom, and dichloroactic acid). Alternatives to using chlorine include ultraviolet radiation, ultrasound, electric field pulses, radiation, filtration, magnetic disinfection, and microwaves (Almquist et al. 2017; Yang et al. 2020); ozone, silver, copper, iron, iodine, bromine, hydrogen peroxide, chlorine dioxide and potassium per-manganate (Hyung et al. 2017); photocatalysis (Serrão Sousa et al. 2017; Mishra et al. 2019; Navakoteswara Rao et al. 2019; Reddy et al. 2019b, 2019c, 2020b, 2020c), photoelectrochemical disinfection (Serna-Galvis et al. 2017); membranes (Jyothi et al. 2019; Kamali et al. 2019c; Zandi et al. 2019; Esfahani et al. 2020); activated sludge (Kamali et al. 2019b); electrochemical treatments (Ganiyu et al. 2018), and nanoparticles (Villegas-Guzman et al. 2017; Reddy et al. 2020a). Among these alternatives, ozone, ultraviolet radiation, and electrochemical disinfection are the most promising, providing both primary (microorganisms inactivation) and residual (microbiological residues prevention) disinfection (Serrão Sousa et al. 2017; Trigüeiro et al. 2017).

Different electrochemical systems and anodes have been employed for treating wastewaters aiming for the elimination of microorganisms (Martínez-Huitle & Brillas 2008) and organic matter (Ferreira et al. 2013; Isarain-Chávez et al. 2013; Martínez-Huitle et al. 2015; Martínez-Huitle & Panizza 2018). The efficacy of these technologies is directly related to the selected anode material, electrolytes composition, reactors, temperature, and mediators (Brillas & Martínez-Huitle 2015; Solano et al. 2016; Clematis et al. 2017; Ganiyu et al. 2018, 2020; Klidi et al. 2018; Martínez-Huitle & Panizza 2018; Abidi et al. 2019; Ganiyu & Martínez-Huitle 2019; Esclona-Durán et al. 2020). Among them, electrochlorination can be highlighted because it significantly reduces the pollutants loading in the industrial effluents. This approaches generates in situ oxidizing species, such as chlorine (Cl₂(dissolved)), HClO, chlorine dioxide (ClO₂), OCl⁻, which are able to induce both electrochemical disinfection of the effluents and reduction of the organic load, avoiding problems related to the accumulation of chlorine in the system and reducing the organic matter along the process (Martínez-Huitle & Brillas 2008; De Moura et al. 2014a). These oxidative species can be produced at the anode according to the following reactions (Liang et al. 2005; Martínez-Huitle & Brillas 2008; Ganiyu et al. 2018, 2020):

\[
2\text{Cl}^- \rightarrow \text{Cl}_2(aq) + 2e^- \quad (1)
\]
\[
\text{Cl}_2(aq) + \text{H}_2\text{O} \leftrightarrow \text{HClO} + \text{Cl}^- + \text{H}^+ \quad (2)
\]
\[
\text{ClO}^- + \text{H}_2\text{O} \rightarrow \text{ClO}_2 + 2\text{H}^+ + 2e^- \quad (3)
\]
\[
\text{ClO}_2^- + \text{H}_2\text{O} \rightarrow \text{ClO}_3^- + 2\text{H}^+ + 2e^- \quad (4)
\]

Nowadays, petroleum refinery and petrochemical plants are one of the major contributors to toxic and recalcitrant organic polluted water (due to the genotoxic, phytotoxic, and carcinogenic contaminants), which has become a significant concern in the field of environmental engineering. Different biological processes have been used to treat these effluents, achieving chemical oxygen demand (COD) removals ranging from 60% to 90%, and a retention time usually from 10 to 100 days (dos Santos et al. 2014a; de Oliveira Campos 2018; Jain et al. 2020). These methods have not been efficient in removing petroleum hydrocarbons present in these wastewaters. However, a significant number of advanced oxidation processes have achieved the same COD removal efficiency in a few hours and were able to break down recalcitrant organic compounds (dos Santos et al. 2014a; Jain et al. 2020). Among them, electrochemical advanced oxidation processes can be considered as an alternative for the prevention of water pollution, and intensive research has been performed to discover more efficient technologies (dos Santos et al. 2014a; Martínez-Huitle et al. 2015). Electroreduction, electroflotation, electrocoagulation (Jain et al. 2020), electrochemical oxidation, or electrooxygenation with different anodes (dos Santos et al. 2014a; Jain
et al. 2020), and indirect electrooxidation with active chlorine are the main methods for treating petrochemical wastewaters (PW) (dos Santos et al. 2014a; Escalona-Durán et al. 2019). The treatment by emerging technologies such as electro-Fenton (Jain et al. 2020) and photoassisted systems like photoelectro-Fenton and photoelectrocatalysis has also recently received much attention (dos Santos et al. 2014a).

Therefore, the main objective of this work is to apply an electrochemical approach to treat a real petrochemical industrial effluent, investigating parameters such as anode material, applied current density ($j$), and liquid medium. The indirect electrochemical oxidation process was indicated because of the chloride (Cl$^-$) content, which favors electrochlorination. Toxicological analyses were carried out to the best experimental conditions to understand the efficient reduction of the organic load, achieving lower energy requirements and, consequently, lower treatment costs.

MATERIALS AND METHODS

Wastewater characteristics

A real industrial effluent (PW) was obtained with lower organic load (262 ppm) in terms of COD and was subjected to filtration prior to treatment to eliminate suspended solids. Wastewater characteristics are listed in Table 1. The effluent conductivity was increased with the addition of 7% (m/v) of sodium sulfate (Na$_2$SO$_4$) during the electrochemical treatment.

Chemicals and analytical methods

Chemicals were of the highest quality commercially available and were used without further purification. All solutions were prepared with ultrapure water. Linear polarizations curves were carried out using AutoLab 302N. Ruthenium-titanium oxide supported in titanium (Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$) and boron doped diamond (BDD) anodes (2 cm$^2$ of exposed area), silver/silver chloride (Ag/AgCl) (3 M) and platinum wire were used as working, reference and counter electrodes, respectively. Quasi-steady polarization curves were registered at a scan rate of 10 mV s$^{-1}$ and a 0.45 mV step potential in PW sample or in solution containing 750 ppm of sodium chloride (NaCl) using Milli-Q water. COD was determined using a COD reactor (HANNA HI 839800, Brazil) and direct reading spectrophotometer (HI 83099, Brazil). The analysis of nitrate (NO$_3$) concentration was performed using a multiphotometer (HANNA HI 83099, Brazil) and the nitrate (NO$_3$) measurements was determined through colorimetric method of salicylate (Vendrell & Zupancic 1990). The produced active chlorine species during electrolysis, Cl$_2$ (dissolved), chlorite (ClO$_2$), ClO$_2$, and chlorate (ClO$_3$) were determined based on a sequence of iodometric titrations, as schematized by Equations (5)–(10) (Brito et al. 2015a):

$$2\text{ClO}_2 + 2\text{I}^- \rightarrow \text{I}_2 + 2\text{ClO}_2$$

(5)

$$\text{ClO}_2 + 4\text{H}^+ + 4\text{I}^- \rightarrow 2\text{I}_2 + \text{Cl}^- + 2\text{H}_2\text{O}$$

(6)

$$\text{Cl}_2 + 2\text{I}^- \rightarrow \text{I}_2 + 2\text{Cl}^-$$

(7)

$$\text{ClO}_3^- + 6\text{KBr} + 6\text{HCl} \rightarrow 3\text{Br}_2 + 6\text{KCl} + 3\text{H}_2\text{O} + \text{Cl}^-$$

(8)

$$3\text{Br}_2 + 6\text{I}^- \rightarrow 3\text{I}_2 + 6\text{Br}^-$$

(9)

$$\text{I}_2 + 2\text{S}_2\text{O}_5^{2-} \rightarrow 2\text{I}^- + \text{S}_4\text{O}_6^{2-}$$

(10)

Experimental apparatus and procedure

The electrochemical treatment of 1 L of effluent was performed in a flow system (Figure 1) using BDD and Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$ as anodes (area 63.6 cm$^2$) and applying 15 and 45 mA cm$^{-2}$ (with a MINIPA MPL-3305 power supply). Ti was used as the cathode in all cases (with and without electrolyte – 7% Na$_2$SO$_4$). Samples were subjected to chemical analysis of pH, conductivity, and toxicity assays. Bioassays of acute toxicity with lettuce (Lactuca sativa) seeds were performed following the methodology of Sobrero & Ronco (2004). Assays were performed in duplicate for each current density with PW effluent before and after treatment.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD (ppm)</td>
<td>262 ppm</td>
</tr>
<tr>
<td>Chloride (ppm)</td>
<td>741 ppm</td>
</tr>
<tr>
<td>pH</td>
<td>7.89</td>
</tr>
<tr>
<td>Conductivity</td>
<td>4.29 mS cm$^{-1}$</td>
</tr>
<tr>
<td>Elements (ppm):</td>
<td></td>
</tr>
<tr>
<td>Al (0.26), B (0.604), Fe (0.39), Mn (0.115), Zn (0.027), Na (593.3), Ba (0.83), Sr (3.252)</td>
<td></td>
</tr>
</tbody>
</table>
Energy requirements and cost

To justify the electrochemical treatment as an alternative for treating PW, it is important to determine energy consumption requirements (in kWh m$^{-3}$), which are directly associated with operating conditions:

\[
\text{Energy consumption} = \frac{[E_C \times I \times t]}{1,000 \times V_s} \quad \text{(11)}
\]

where $I$ is the electrolysis current (A), $t$ is the time of electrolysis (h); $V_s$ is the sample volume (L), and $E_C$ is the average cell voltage (V). Costs were also estimated based on energy requirements and Brazilian electrical energy price per kWh (R$ 0.625, excluding taxes), which was then converted into US$.

RESULTS AND DISCUSSION

Evaluation of the catalytic activity of anode materials at different current densities

Anodic oxidation process, oxidants production, and energy consumption depend on the electrode nature and, for this reason, it is important to characterize the potential window and anodic oxygen evolution reaction using electrochemical measurements (polarization curves) for all electrodes used (Kapalka et al. 2010; De Moura et al. 2014b). Figure 2 shows the linear polarization curves registered at Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$ and BDD electrodes in the PW effluent, as well as in a solution containing 750 ppm of NaCl (concentration of NaCl was chosen to mimic the amount of dissolved salt in the PW). Polarization curves indicated that the potential for the oxygen evolution reaction (o.e.r.) is shifted from 1.1 to 1.6 V versus Ag/AgCl due to the electrocatalytic material and the tested solution used.

Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$ presents lower oxygen overpotential than BDD, highlighting its better electrocatalyst character for o.e.r. Comparing the polarization curves obtained, the polarization curves at Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$ have less positive potentials (Figure 2) due to the importance of the Cl$_2$/H$_2$O system, as indicated in a previous work (De Moura et al. 2014b). As a direct consequence of this occurrence,
the anode potential in the region of applied current densities values used for electrochemical incineration of organics reached more than 2.0 V (in bulk electrolysis). At these polarization levels, the number and reactivity of hydroxyl radicals, adsorbed at the electrode surface, could lead to fast incineration of a number of organic substrates due to the coexistence of active chlorine species (dos Santos et al. 2014b), often assumed as intermediates in the chlorine evolution reaction. Considering the fact that, in the case of chloride mediation, incineration reactions should be a set of volume rather surface reactions, the change from Ti/Ru0.3Ti0.7O2 to BDD should not involve dramatic changes in the incineration mechanism (Martínez-Huitle et al. 2005, 2008; Sales Solano et al. 2013). In fact, the polarization curve for PW sample shifted to less positive potentials, indicating that the production of active chlorine species is favored together with the elimination of organic matter (Figure 2, dashed curves). Nevertheless, the efficiency of indirect oxidation depends on the diffusion rate of oxidants in the solution and on pH value (Martínez-Huitle & Ferro 2006; Brillas & Martínez-Huitle 2015; Martínez-Huitle et al. 2015), as well as other solution effects (Martínez-Huitle et al. 2015).

**Electrochemical treatment efficiency of real PW**

To evaluate the treatment efficiency to remove COD using Ti/Ru0.3Ti0.7O2 (Figure 3(a)) and BDD (Figure 3(b)) anodes, different current densities (15 and 45 mA cm⁻²) were applied. The effluent conductivity was increased with the addition of 7% (m/v) of Na₂SO₄ and compared to the as-received PW effluent. Results clearly showed that COD removal is strongly influenced by the anode material (see Figure 3). For Ti/Ru0.3Ti0.7O2 (Figure 4(a)), ~10% or less of COD was removed at the end of the treatment, in all cases, by adding, or not, sulfate. This behavior suggests that the o.e.r. and/or the production of Cl₂ were favored when sulfate was added in the PW effluent. Results clearly showed that COD removal is strongly influenced by the anode material (see Figure 3). For Ti/Ru0.3Ti0.7O2 (Figure 4(a)), ~10% or less of COD was removed at the end of the treatment, in all cases, by adding, or not, sulfate. This behavior suggests that the o.e.r. and/or the production of Cl₂ were favored when sulfate was added in the PW effluent. Decreasing the organic oxidative process. Conversely, complete COD removal was achieved at the BDD anode independently of the applied current density by adding, or not, sulfates. This anode favors the electrogeneration of a larger concentration of oxidizing species compared to Ti/Ru0.3Ti0.7O2, which mainly favored the production of O₂ and Cl₂. In the presence of sulfate, the BDD anode also promotes the electrogeneration of additional oxidizing species such as the sulfate radical and persulfate (Equations (12)–(14)) (Rocha et al. 2012; Escalona-Durán et al. 2020; dos Santos et al. 2013):

\[
2\text{SO}_4^{2-} \rightarrow \text{S}_2\text{O}_8^{2-} + 2e^- \tag{12}
\]

\[
\text{BDD}^{*}\text{(OH)} + \text{SO}_4^{2-} \rightarrow \text{BDD(SO}_4^{*}) + \text{HO}^- \tag{13}
\]

\[
\text{BDD(SO}_4^{*}) + \text{SO}_4^{2-} \rightarrow \text{S}_2\text{O}_8^{2-} + e^- \tag{14}
\]

The amount of produced active chlorine species drastically exceeds the sulfate oxidizing species (Escalona-Durán et al. 2020) and, consequently, their contribution during the organic matter oxidation could almost be negligible. At the start of the treatment, a higher Cl⁻ concentration was present in the PW effluent, enabling the BDD to efficiently produce active chlorine species (Brito et al. 2015a).

During the electrochemical process, pH variation was mainly attributed to the buffering behavior by H⁺ and OH⁻ species as well as the chlorine active species. The predominance of the electrogenerated oxidative species, such as...
as active chlorine species, is closely dependent on the pH of the solution. Therefore, the pH evolution was determined along the electrochemical treatment of PW using both anodes by applying 15 mA cm\(^{-2}\) (black symbols) and 45 mA cm\(^{-2}\) (red symbols) by adding, or not, sulfate in the PW (Figure 4). Initial values of pH were around 7.9, which in most cases changed slightly during electrolysis between pH 7.5 and pH 8.5 and remained stable during the whole process. Based on these results, we can assume that the electrochemical/chemical reactions regarding the active chlorine production are preferentially favored rather than the o.e.r or production of hydroxyl radicals (Sales Solano et al. 2013; Ganiyu & Martínez-Huitle 2019). In this case, it is possible to infer that Cl\(_2\), OCl\(^-\), ClO\(_2\), ClO\(_3\), and ClO\(_2\) species could be electrochemically generated under these experimental conditions (De Moura et al. 2014b; de Moura et al. 2015; Brito et al. 2016). Variations of the pH at 45 mA cm\(^{-2}\) with BDD indicated that the electro-generation of HClO/OCl\(^-\) is favored, with differences in the predominant species according to the pH variations (Figure 4). Hence, with dissolved sulfate in the system, pH rapidly decreased to \(\sim\)pH 3.5, which favored the presence of hypochlorite; while in absence of sulfate, pH slowly increased to pH 10.2, which favored the presence of OCl\(^-\) in solution.

To have better understanding, the Cl\(^-\) concentration in the effluent was quantified after electrochemical treatment by using the electrochemical flow reactor with Ti/Ru\(_{0.3}\)Ti\(_{0.7}\)O\(_2\) and BDD anodes under different applied current densities (Figure 5). Considering the initial chloride concentration (741 ppm, see Table 1), the electrochemical treatment of PW reduced the Cl\(^-\) concentration under all conditions studied. This behavior is attributed to the depletion of Cl\(^-\) because of its conversion of active chlorine species, which oxidize dissolved organic matter in the PW effluent, and the production of chlorine gas. Another interesting feature is that, under all tested conditions, a more significant decrease on the Cl\(^-\) concentration was attained when the BDD anode was used, compared to the decrease of the Cl\(^-\) concentration when Ti/Ru\(_{0.3}\)Ti\(_{0.7}\)O\(_2\) was used. In that case, the higher consumption of chloride could be attributed to the active chlorine production directly at the diamond surface, as well as the scavenger reaction between Cl\(^-\) with the hydroxyl radical (which is efficiently produced by the BDD anode) (Sirés et al. 2014; Brito et al. 2015a).
Similarly, in the presence of sulfate in solution at the BDD anode, in addition to the produced hydroxyl radical, sulfate radical and persulfate are also electrogenerated (Santos et al. 2015; Uranga-Flores et al. 2015; Escalona-Durán et al. 2020), which could rapidly react with Cl\(^-\) of the PW.

Conversely, at Ti/Ru\(_{0.3}\)Ti\(_{0.7}\)O\(_2\) the production of O\(_2\) and Cl\(_2\) could be the reactions preferentially favored, rather than the active chlorine species at lower and higher applied current densities, respectively (Conway et al. 1991).

**Treatment extension and energy consumption**

Toxicity tests were carried out to compare the depollution/disinfection efficacy of electrochemical treatment by using both anodes. Toxicity assessments were carried out by experimental observations of germination seedlings (Figure 6). Figure 6(a) shows the germination process of the different samples: drinking water as reference matrix, untreated PW, and solutions after 300 min of the electrochemical treatment using Ti/Ru\(_{0.3}\)Ti\(_{0.7}\)O\(_2\) and BDD by adding, or not, sulfate in solution. Significant changes can be observed regarding the system studied, indicating variations of the amount of dissolved toxic compounds in the different samples. For a more in-depth interpretation, germinated seeds were quantified and the data were plotted (Figure 6(b)). As can be seen, 16 seeds germinated in the reference matrix. Conversely, a significant decrease in germinated seeds can be observed at PW (eight germinated seeds), demonstrating the toxicity of the effluent. Interestingly, the number of germinated seeds increased for PW samples submitted to the electrochemical treatment with both tested anodes, with numbers reaching the same as the tap water (reference). A negative effect was observed when sulfate was added to the effluent because a significant reduction of germination was attained (three and seven seeds germinated in the PW sample electrochemically treated with Ti/Ru\(_{0.3}\)Ti\(_{0.7}\)O\(_2\)/Na\(_2\)SO\(_4\) and BDD/Na\(_2\)SO\(_4\) system, respectively), indicating that dissolved toxic compounds in the treated effluent inhibited the germination.

Although germinating seedling analyses showed some promising results, when soluble toxic compounds are present in low concentrations, these are not capable of inhibiting the germination process. Therefore, complementary analyses were performed using *L. sativa* bioassays (Figure 7). In this case, tap water was also tested as an extra reference sample. The average stem length of the reference matrices were 1.2 and 2.2 cm for tap and drinking water, respectively. Conversely, PW did not show a measurable stem, showing that even if the PW could allow the germination, it contained toxic compounds that delay or

![Figure 6](image1.png)  
*Figure 6* | Experimental observations of germinating seedlings of drinking water, PW and treated samples using Ti/Ru\(_{0.3}\)Ti\(_{0.7}\)O\(_2\) and BDD anodes at 45 mA cm\(^{-2}\). (a) Germination process evidence; (b) germinated seed counted.

![Figure 7](image2.png)  
*Figure 7* | Stem length when different samples were used: tap water, drinking water, PW, and treated solutions using Ti/Ru\(_{0.3}\)Ti\(_{0.7}\)O\(_2\) and BDD anodes at 45 mA cm\(^{-2}\).*
completely inhibit the elongation processes of the hypocotyl (Martínez-Huitle & Brillas 2008).

Interesting results were obtained for samples after the electrochemical treatments. The seeds cultivated with treated effluent with Ti/Ru0.3Ti0.7O2 showed a longer stem length (1.7 cm) compared with other treated effluents. A high germination factor of 18 seeds (Figure 6(b)) was observed. The effluent treated by BDD electrolysis and drinking water also showed similar germination factors. Conversely, the elongation of the stem was almost completely inhibited when sulfate was added to the effluent and treated using both anodes. The presence of sulfate allowed the pH to remain stable and the active chlorine species remained in the effluent, which attacked the cell wall of the seed (Klidi et al. 2018; Tasca et al. 2020). The germination and regular growth of the plant were prevented, even when high efficacy was attained in removing dissolved organic matter (Figure 3). In this frame, the inhibition in the high efficacy endured when sulfate was added to the effluent and treated using both anodes. The presence of sulfate allowed the pH to remain stable and the active chlorine species remained in the effluent, which attacked the cell wall of the seed (Klidi et al. 2018; Tasca et al. 2020). The germination and regular growth of the plant were prevented, even when high efficacy was attained in removing dissolved organic matter (Figure 3). In this frame, the inhibition in the high efficacy endured when sulfate was added to the effluent and treated using both anodes. The presence of sulfate allowed the pH to remain stable and the active chlorine species remained in the effluent, which attacked the cell wall of the seed (Klidi et al. 2018; Tasca et al. 2020).

As can be seen, no elongation of hypocotyl was observed when the germination was attained using the effluent and electrochemically treated by adding Na2SO4.

Variations of germination or stem length are related to the amount of nutrients in the samples, such as nitrogen-based compounds (Ferro 2012). The quantification of NO2 and NO3 was therefore performed as an indirect measurement of the nitrogen-based compounds in the tested waters (Figure 8). A notable dependence on the applied current densities was observed at Ti/Ru0.3Ti0.7O2 anode, in which the NO3 concentration increased more than four times when applying 45 mA cm−2 rather than 15 mA cm−2. Although NO2 and NO3 contributed to seed development (Ferro 2012), it was not possible to establish a direct relationship between the nitrogen-based compounds and the toxicity results. It was only possible to indicate that the degradation of dissolved organic matter is attained in different extensions.

The possible application of any process is related to the cost and energy consumption of the proposed treatment. Therefore, the energy requirements (Equation (11)), as well as costs, were estimated for the electrochemical treatment of PW by applying 15 and 45 mA cm−2 using Ti/Ru0.3Ti0.7O2 and BDD anodes (Table 2).

In general, it was observed that the energy consumption of Ti/Ru0.3Ti0.7O2 was higher, except when using low current density (15 mA cm−2) with sulfate. Conversely, the BDD electrode required lower energy requirements at 45 mA cm−2 when it was used without sulfate in the effluent. In the absence of the electrolyte, the potential generated is higher and, consequently, the conductivity of the effluent decreased, resulting in higher energy consumption. The conductivity of the effluent is also improved, therefore reducing the energy requirements. The linear polarization curve (Figure 2) shows the favoring of the reactions (O2 and Cl2 evolution) at low potentials at Ti/Ru0.3Ti0.7O2 compared to BDD. These reactions consume a lot of electric energy, whereas the BDD with lower energy consumption values indicates that the applied current is used in organic matter degradation, as well as the electrogeneration of the active chlorine species (Cotillas et al. 2018)

Table: Energy consumption as a function of COD removal and estimated costs during electrochemical oxidation of PW with Ti/Ru0.3Ti0.7O2 and BDD anodes by applying different current densities.
CONCLUSION

Real petrochemical effluent was electrochemically treated using two different anodes (Ti/Ru0.3Ti0.7O2 and BDD). The efficiency of the process was strongly dependent on the anode material and applied current density. No significant effect of the applied current density was observed at Ti/Ru0.3Ti0.7O2 anode regarding the COD removal. Conversely, higher organic matter elimination (≥98%) was reached independently of the applied current density by using BDD electrode.

The electrogeneration of chlorine active species was demonstrated for both anodes; however, different species participated during the decontamination process. Based on the pH variations during electrochemical treatment, the active chlorine production was preferentially favored rather than the o.e.r or production of hydroxyl radicals. In this case, it is possible to infer that Cl2, OCl−, ClO2, ClO3, and ClO2 species were electrochemically generated under these experimental conditions at Ti/Ru0.3Ti0.7O2 and BDD by applying 15 and 45 mA cm−2, adding, or not, sulfates. However, a predominant contribution of HClO and OCl− was identified for the BDD anode at 45 mA cm−2.

The germination seedling analyses shows the environmental risk of untreated PW. Furthermore, the results of the cultivation of L. sativa showed that the toxicity of PW is reduced after the electrochemical treatment at Ti/Ru0.3Ti0.7O2 and BDD by applying 15 and 45 mA cm−2 in absence of sulfates. Despite obtaining a nearly complete degradation of the organic matter by using BDD anode, no seed growth occurred when this effluent was used for the L. sativa tests. Conversely, the effluent electrochemically treated with the Ti/Ru0.3Ti0.7O2 anode allowed germination. This behavior is due to the production of significant concentrations of oxidants that remain in the effluent after treatment with BDD, preventing the germination of L. sativa. The most efficient result in relation to the COD removal and the energy cost was achieved at the BDD anode by applying 15 mA cm−2 and adding Na2SO4 with 6.68 kWh m−3; however, bioassays exhibited the toxicity character of the treated sample. Therefore, based on the investigation, the most promising treatment of real PW is the electrochemical oxidation using an BDD anode. Smart-devices can be designed and constructed for use in the petrochemical industry to depollute the effluents as a pre-treatment technology.

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DATA AVAILABILITY STATEMENT

Data cannot be made publicly available; readers should contact the corresponding author for details.

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