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# Applicability of Electrochemical Technology for Treating a Real Petrochemical Effluent by Electro-generated Active Chlorine Species

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This work aims to investigate the treatment of a real petrochemical effluent (commonly named produced water (PW)) by electro-generated active chlorine species using Ti/$Ru_{0.3}Ti_{0.7}O_2$, Ti/Pt and BDD anodes in a batch cell by applying 45 mA $cm^{-2}$. Chemical oxygen demand (COD) and spectrophotometric measurements were carried out to follow the elimination of organic matter as well as the concentration of active chlorine species was determined at the end of the treatment. Results clearly indicated that, removal efficiencies about 42% and 52%, in terms of COD, were achieved with BDD and Ti/Pt anodes, respectively. Conversely, Ti/$Ru_{0.3}Ti_{0.7}O_2$ anode reached up to 85% of organic matter elimination, as consequence of the efficient production of active chlorine species ($ClO_2^-$, $ClO_2$, $Cl_2$) by the catalytic action of the anode during the electrochemical treatment.

**Keywords:** active chlorine, indirect electrochemical oxidation, mineralization organic matter, produced water.

## 1. INTRODUCTION

Produced water (PW) is created during oil and natural gas exploration and production. Consequently, the volume varies during the extraction process, making PW the largest source of waste in the petrochemical industry [1,2]. The exploration activities aim to maximize oil extraction by injecting water, causing substantial production of PW containing dissolved/suspended solids, organic compounds and heavy metals [3].

Several methods can be applied as treatments for wastewater containing organic pollutants mainly based on physicochemical and biological processes, the use of membranes and, more newly, the advanced oxidation processes (AOPs) [4]. However, the first three abovementioned processes have a major disadvantage related to water salinity ending up into a negative interference that depresses the efficiency of the process [5] when petrochemical effluents are treated. Meanwhile, AOPs based on electrochemical technologies can be highlighted as versatile alternatives given to their possible application in varied medium [6] as well as the probability to be scale up from laboratory to industrial dimensions [7–10].

Electrochemical methodologies are free-chemical agents since the main reagent is the electron, responsible to promote specific reactions at the anode surface and/or in the solution. This characteristic makes the electrochemical processes to have better energetic efficiency compared to other decontamination approaches besides a higher cost-benefit [11,12]. During the electrocatalytic processes, organic pollutants (which are characterized by being recalcitrant, toxics and not biodegradables) are degraded into oxidized products with lower environmental impact and even with biodegradable characteristics [13]. Based on the existing literature, the decontamination efficacy of the electrochemical technologies is highly influenced by the electrocatalytic material in the electrochemical cell [14]. Active and non-active electrodes can be used as anodes, which influence strongly the involved oxidative pathway. In the former, ruthenium oxide ($RuO_2$) and platinum (Pt), favor the partial and selective oxidation of pollutants, while boron doped diamond BDD and lead oxide ($PbO_2$) promote complete combustion of the pollutants, in the latter [11,14,15].

Direct and indirect mechanisms [16] can be favored on anode surface by adsorbing pollutants and a subsequent oxidation via direct electron transfer and/or by producing strong oxidizing species which promote the effective pollutant oxidation in solution [17,18], respectively. In the second case, the existence of an oxidant precursor is necessary in solution, for this reason, electrochemical chloride-mediated oxidation becomes interesting due to the possibility of the electrogeneration of active chlorine species from the chloride ions present in the effluents [19–21].

A limited number of studies have been published concerning the applicability of electrochemical approaches for treating petrochemical effluents. Relevant examples are summarized in Table 1 and the results evidence the great decontamination efficacy attained with different anodes.

**Table 1.** Use of electrochemical processes for the treatment of petrochemical wastewaters.

| Anode used* Wastewater | $C_0$ (mg dm$^{-3}$) | j[d] (mA cm$^{-2}$) | Electrolysis time (h) | Current efficiency (%) | COD decay (%) | Ref. |
|---|---|---|---|---|---|---|
| $Ti/TiO_2$-$RuO_2$-$IrO_2$ | | | | | | |
| Oil refinery | 602[a]<br>141[b]<br>112[c] | 54 | 20 | 7.5 | 92 | [22] |
| Nanometer $TiO_2$ particle | | | | | | |
| Produced water (high salinity) | 645[a]<br>19000[c] | ND | 4 | ND | 47 | [23] |
| $Ti/Ru_{0.34}Ti_{0.66}O_2$ | | | | | | |
| Oil extraction industry | 315[a]<br>887[c] | 100 | 70 | 5 | 57 | [24] |
| Active metal and graphite | | | | | | |

| | | | | | | |
|---|---|---|---|---|---|---|
| Oil field PW | 5800[a]<br>15400[c] | 0,1-2 | 0,17 | ND | 98 | [25] |
| $Ti/RuO_2-TiO_2$ | | | | | | |
| Produced water | 103[g]<br>1.8[b] | 8.6-17.8 | 2 | 65 | 99[h] | [26] |
| Al | | | | | | |
| Oil refinery waste effluent | 80-120[a]<br>13[b] | 0-25 | 2 | 0 | 17<br>92[m] | [27] |
| $Ti/RuO_2$ | | | | | | |
| Creosote oil solution containing PAHs | 2102[a]<br>237[i] | 9-23 | 1.5 | 70 | 61<br>26[j] | [28] |
| $Ti/RuO_2$ | | | | | | |
| Industry waste containing PAHs | 18440-7709[k] | 9-23 | 1.5<br>6.5 | 67<br>100 | 65-95[l] | [29] |
| Amphoteric surfactant solution containing PAHs | 418[k] | 4-13 | 1.5 | 45 | 80-82[l] | [30] |
| Pt/Ir | | | | | | |
| Bilge water (seawater + petroleum pollutants) | 3080[a]<br>23916[b] | 12.8 | 4 | 79 | 85-100 | [31] |
| Nb/BDD | | | | | | |
| Petroleum refinery | 590[a]<br>193[c] | 5 | 1 | 90<br>100 | 96<br>99[m] | [32] |
| Petroleum refinery | 590[a]<br>193[b]<br>1775[c] | 3 | 1 | 90 | 95<br>98[m] | [32] |
| Iron | | | | | | |
| Petroleum refinery | 590[a]<br>193[b] | 1 | 0.25 | 70 | 98<br>75[m] | [32] |
| Ru mixed metal oxide | | | | | | |
| Petroleum refinery | 590[b]<br>193[c] | 20 | 3.5 | 76 | 70<br>94[m] | [32] |
| $Ti/RuO_2–TiO_2–SnO_2$ | | | | | | |
| PW | 20 – 30[a]<br>5[b] | 89 | 0.5 – 2.3 | - | 84-98<br>47-30[m] | [33] |
| Si/BDD | | | | | | |
| Phenolic compounds from the hydrocarbon industry | 3471[b] | 320 | 2 | 70 | 98[j] | [34] |
| Graphite | | | | | | |
| Refinery wastewater | 1021[a]<br>95[b]<br>4730[c] | ND | 1 | 45-100 | 93 | [35] |
| BDD[1]; $Ti/IrO_2–Ta_2O_5$[2] and $Ti/IrO_2–RuO_2$[3] | | | | | | |
| High-salinity reverse osmosis concentrate | 120–190[a]<br>6421[c]<br>25-36[i] | 25<br>50<br>75 | 0.5-2 | 14-26[1]; 33-20[2]; 16-20[3]<br>30-24[1]; 4-8[2]; 14-17[3]<br>25-26[1];2-6[2];13-19[3] | 41-100[1]<br>29-100[2;3] | [36] |
| Ti/Pt[1] and BDD[2] | | | | | | |

| | | | | | | |
|---|---|---|---|---|---|---|
| Produced water | $1588^a$<br>$22.470^c$ | 15<br>30<br>60 | 10 | $56^1$; $100^2$<br>$41^1$; $93^2$<br>$39^1$; $46^2$ | $38^1$; $50^2$<br>$46^1$; $57^2$<br>$87^1$;<br>$400^2$ | [37] |
| | | | $Ti/RuO_2$ | | | |
| Petroleum industry | $712^a$<br>$833^a$<br>$488^c$<br>$514^c$ | 10<br>30 | 2 | $48^{BF}$; $29^{AF}$<br>100 | $87^{BF}$;<br>$96^{AF}$<br>100 | [38] |

$^a$Initial COD (mg $L^{-1}$); $^b$Phenolics initial concentration (mg $L^{-1}$); $^c$Chloride dissolved (mg $L^{-1}$); $^d$Applied current density; $^e$Specific charge passed (Ah $dm^{-3}$); $^f$ND: Not determined; $^g$$NH^{4+}$ concentration; $^h$%$NH^{4+}$ of removal; $^i$initial TOC; $^j$%TOC of removal; $^k$mg Kg of PAHs; $^l$% of PAHs removal; $^m$% of phenol removal; $^{AF}$After flotation; $^{BF}$Before flotation.

A literature analysis indicates that, the use of some non-active anodes produce efficiently active chlorine during electrochemical chloride-mediated oxidation, promoting an effective organic pollutants oxidation [39–41] (more than 50% at the end of the treatment [42–44]). Meanwhile, the real effluent conditions allows to apply the electrochemical chloride-mediated oxidation promoting the electro-synthesis of strong oxidants [19]. Then, this work aims to investigate the applicability of electrochemical chloride-mediated oxidation to treat a real petrochemical effluent, comparing the use of active and non-active anodes. The effect of the electrogenerated active chloride species on the degradation efficiency as well as the energy requirements will be discussed.

## 2. EXPERIMENTAL

### *2.1. Effluent conditions*

PW samples were supplied by a Brazilian petrochemical industry which is located in Rio Grande do Norte (northeast region of Brazil). Suspended solids in the PW were removed by filtration pre-treatment. pH effluent was around 6.7 and electric conductivity around 49.5 mS $cm^{-1}$. It contains with 6200 ppm of chloride and 4.57 ppm of sulfide which were determined by American Public Health Association (APHA) procedures. Chemical oxygen demand (COD) was about 4600 ppm with prior chloride concentration precipitation with $AgNO_3$.

### *2.2. Materials*

Chemicals were of the highest quality commercially available and were used without further purification. All solutions were prepared with ultrapure water. Industrie De Nora SpA (Milan, Italy) provided both $Ti/Ru_{0.3}Ti_{0.7}O_2$ and Ti/Pt electrodes. Adamant Technologies (Switzerland) supplied the BDD electrode.

### *2.3. Electrochemical experiments*

Electrolyzes were performed in galvanostatic conditions in a batch cell (250 mL of capacity (Fig. 1)) with $Ti/Ru_{0.3}Ti_{0.7}O_2$, BDD or Pt/Ti as anodes (surface area of about 18.06 $cm^2$), and a Ti plate as cathode by applying 45 mA $cm^{-2}$ with a DC power supply (MINIPA MPL 3303M, Brazil) at 25°C during 5 h. During the experiments, samples were collected and subjected to COD and spectrophotometric analyses as well as the cell voltage were registered.

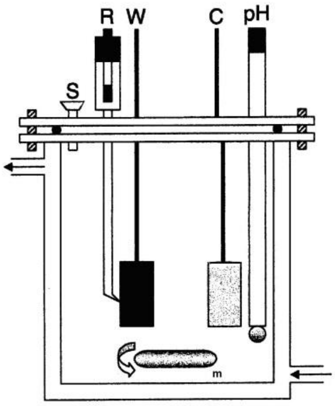

**Figure 1.** Diagram of the electrochemical cell used for studying electrochemical chloride-mediated oxidation of PW: C, counter, R, reference, and W, working electrode ($Ti/Ru_{0.3}Ti_{0.7}O_2$, BDD or Pt/Ti), respectively; pH electrode; S, sample holder; and m, magnetic stirrer.

### *2.4. Analytical methods*

COD was used as parameter to follow the decrease on the organic matter degradation. This analysis was performed with a HANNA HI 83099 multiphotometer after digestion step in the HANNA HI 839800 termo-reactor. Removal efficiencies, in terms of COD, were determined by using the follow equation:

$$\%\ \mathrm{COD\ removel} = \frac{\mathrm{COD_i} - \mathrm{COD_f}}{\mathrm{COD_i}} \times 100 \qquad (1)$$

where initial ($COD_i$) and final ($COD_f$) COD measurements were considered, respectively.

Spectrophotometric analyses were performed in the spectral range of 190-800 nm by using a Specord 210 Plus (Analytik Jena). Also, electrogenerated active chlorine species (chlorine ($Cl_{2(aq)}$), chlorite ($ClO_2^-$), chlorine dioxide ($ClO_2$) and chlorate ($ClO_3^-$)) were determined, based on a sequence of iodometric titrations, as schematized by eq. 2 – 7 [20]:

$$2ClO_2 + 2I^- \rightarrow I_2 + 2ClO_2^- \qquad (2)$$
$$ClO_2^- + 4H^+ + 4I^- \rightarrow 2I_2 + Cl^- + 2H_2O \qquad (3)$$
$$Cl_2 + 2I^- \rightarrow I_2 + 2Cl^- \qquad (4)$$
$$ClO_3^- + 6KBr + 6HCl \rightarrow 3Br_2 + 6KCl + 3H_2O + Cl^- \qquad (5)$$
$$3Br_2 + 6I^- \rightarrow 3I_2 + 6Br^- \qquad (6)$$
$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-} \qquad (7)$$

## 3. RESULTS AND DISCUSSION

### *3.1. Electrochemical chloride-mediated oxidation of PW with different anodes*

As previously indicated, some works have investigated the electrochemical treatment of PW under different experimental conditions, obtaining different removal efficiencies [33,37,45–49], however, the effect of the anodic material on the applicability of electrochemical chloride-mediated oxidation was not completely studied. Figure 2 shows the COD removal after 360 min of electrochemical treatment of PW by applying 45 mA cm$^{-2}$ at Ti/Pt, Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$ and BDD.

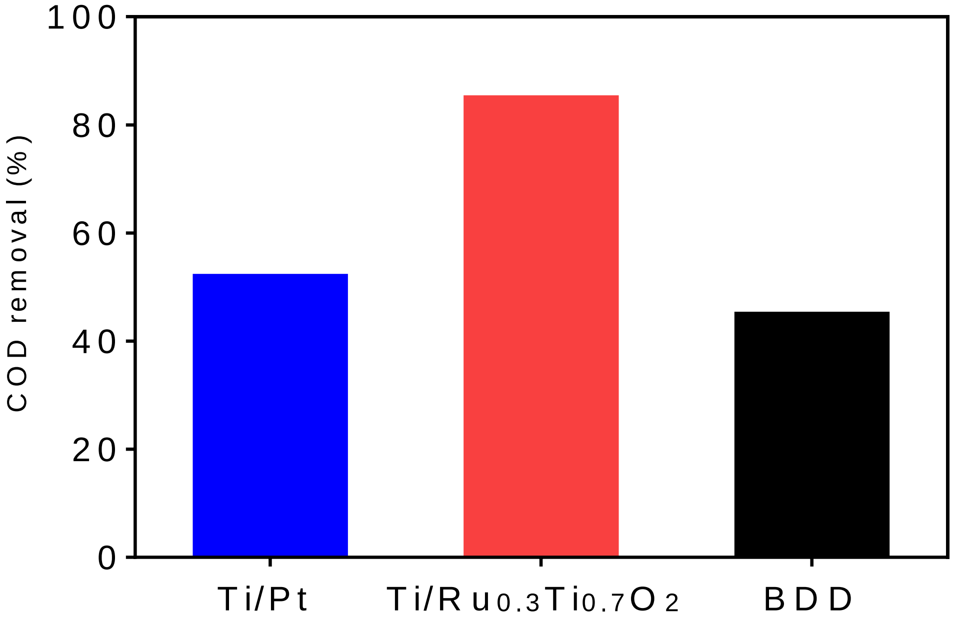

**Figure 2.** COD removal efficiency, as a function of anodic material (Ti/Pt, Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$ and BDD), during electrochemical chloride-mediated oxidation of PW. By applying 45 mA cm$^{-2}$ at 25 °C and 400 rpm of mixing rate.

As can be seen, the use of Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$ anode favors a higher COD removal than the other tested anodes, reaching up 85% of the organic matter elimination while only 52% and 45% were reached by Ti/Pt and BDD electrodes, respectively. Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$ anode is an active electrocatalytic material and its surface (M) interacts strongly with $^{\bullet}$OH and then, a so called higher oxide or superoxide (MO) may be formed (eq. 8):

$$M(^{\bullet}OH) \rightarrow MO + H^{+} + e^{-} \qquad (8)$$

MO acts as a mediator in the oxidation of organics (eq. 9), which competes with the side reaction of oxygen evolution via chemical decomposition of the higher oxide species (eq. 10).

$$MO + \text{organic pollutants} \rightarrow M + RO \qquad (9)$$

$$MO \rightarrow M + \tfrac{1}{2}O_2 \qquad (10)$$

For this reason, active anodes are considered good electrocatalytic materials for oxygen evolution, which consequently limits the degradation of the pollutants present in the effluent. However, in this case, PW sample has a significant concentration of dissolved $Cl^-$ ions (6200 ppm); then, this effluent characteristic favors other electrochemical reactions promoting the formation of strong oxidizing species that could participate on the organic matter degradation [50–54]. According to the literature [50], electrolysis of chloride aqueous solutions in an undivided cell involves the direct oxidation of chloride ion at the anode to yield soluble chlorine:

$$2Cl^- \rightarrow Cl_{2(aq)} + 2e^- \qquad (11)$$

After that, electrogenerated chlorine rapidly is hydrolyzed to be disproportionated to hypochlorous acid and chloride ion:

$$Cl_{2(aq)} + H_2O \rightarrow HClO + Cl^- + H^+ \qquad (12)$$

In the bulk solution HClO is in equilibrium with $ClO^-$:

$$HClO \leftrightarrow ClO^- + H^+ \qquad (13)$$

Depending on the pH conditions in the effluent, the predominant species are: $Cl_{2(aq)}$ until pH near 3.0, HClO in the pH range 3–8 and $ClO^-$ for pH > 8.0. Then, as the electrochemical chloride-mediated oxidation is often performed in alkaline conditions, the general mineralization of organic pollutants is commonly referred to the only chemical action of $ClO^-$ as follows

$$\text{Organic pollutants} + ClO^- \rightarrow CO_2 + H_2O + Cl^- \qquad (14)$$

It is important to remark that, at acidic conditions or higher applied currents, production of chlorine gas can be favored, which is a competitive reaction for producing active chlorine species.

$$2Cl^- \rightarrow Cl_{2(g)} + 2e^- \qquad (15)$$

Meanwhile, only 52% of COD removal was reached when Ti/Pt was used (which is also an active anode). This lower efficiency could be attributed to a limited production of active chlorine species due to the significant production of $O_2$ and $Cl_2$ (eqs. 10 and 15) at Ti/Pt surface; and consequently, a lower catalytic action is attained in solution by the strong oxidizing species with dissolved organic matter compared to $Ti/Ru_{0.3}Ti_{0.7}O_2$ anode.

On the other hand, the non-active anode (BDD) also achieved lower COD removal efficiency (≈45%) compared to $Ti/Ru_{0.3}Ti_{0.7}O_2$ anode. Conversely to active anodes, the surface of a non-active anode, such as BDD, interacts so weakly with $^{\bullet}OH$ that allows the direct reaction of organics with BDD($^{\bullet}$OH) to give fully oxidized reaction products such as $CO_2$ as follows:

$$BDD(^{\bullet}OH) + \text{organic pollutants} \rightarrow BDD + mCO_2 + nH_2O \qquad (16)$$

The mineralization of organics (eq. 16) occurs with physisorbed heterogeneous hydroxyl radicals and it also competes with the side reactions of BDD($^\bullet$OH) such as direct oxidation to $O_2$ (eq. 17) or indirect consumption through dimerization to hydrogen peroxide (eq. 18):

$$\mathrm{BDD}(^\bullet\mathrm{OH}) \rightarrow \mathrm{BDD} + \tfrac{1}{2}\,\mathrm{O_2} + \mathrm{H^+} + \mathrm{e^-} \qquad (17)$$

$$2\mathrm{BDD}(^\bullet\mathrm{OH}) \rightarrow \mathrm{BDD} + \mathrm{H_2O_2} \qquad (18)$$

Although BDD nature favors the formation of hydroxyl radical with a weak surface interaction [55], the organic matter elimination was possibly limited by the promotion of other electrochemical/chemical reactions. Results suggest an inhibition that could be related to the matrix composition and the scavenger action of $Cl^-$ for the produced $^\bullet$OH, which implies to additional reactions allowing to a multi-step oxidative process and turning up into a lowered oxidative process.

For better understanding, the evolution of COD was determined as function of time by the action of the anodic materials tested (Fig. 3). Interestingly, during the first 60 min of treatment, a fast COD removal was observed by using BDD compared to other anodes, which could be related to the participation of $^\bullet$OH. Nevertheless, the organic matter oxidation was limited after this treatment time, reaching only 45% of COD removal at BDD. Then, this behavior is associated to secondary reactions which compete for producing hydroxyl radicals, inhibiting organic matter oxidation. Conversely, significant differences were observed regarding the COD evolution and the processes efficiency at both active anodes. COD decay was constantly attained at Ti/$Ru_{0.3}Ti_{0.7}O_2$, achieving 85% in 180 min of treatment. Meanwhile, no significant COD removal was observed by using Ti/Pt anode after 120 min of treatment, evidencing the major impact of the secondary reactions.

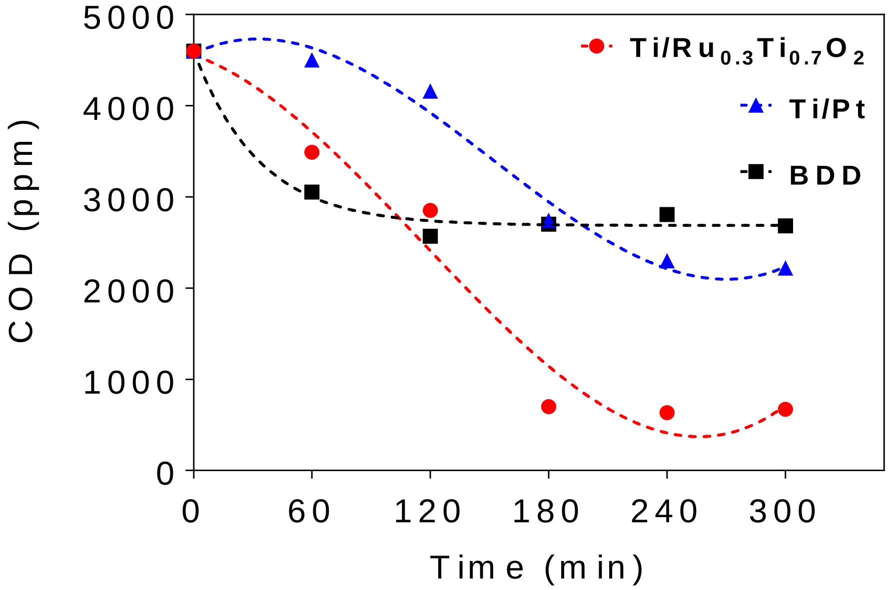

**Figure 3.** COD removal, as a function of time, during the electrochemical treatment of PW using Ti/$Ru_{0.3}Ti_{0.7}O_2$, Ti/Pt and BDD anodes by applying 45 mA $cm^{-2}$ at 25 °C and 400 rpm of mixing rate.

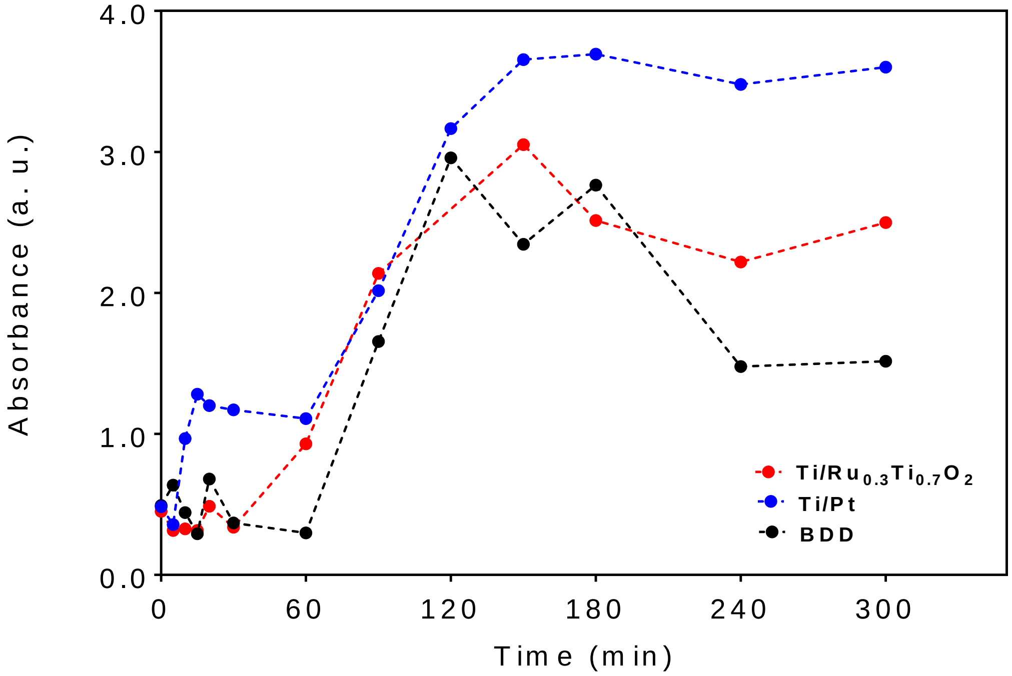

**Figure 4.** Maximum absorbance as a function of the treatment time for the electrodes: $Ti/Ru_{0.3}Ti_{0.7}O_2$, Ti/Pt and BDD at the density 45mA $cm^{-2}$.

The identification of varied degradation routes could imply different organic matter transformations. Therefore, in order to understand the organic matter modifications, the maximum absorbance of samples along the treatments was plotted, as function of electrolysis time (Fig. 4). In all cases, by-products seem to be accumulated after 160 min of treatment, following different tendencies regarding the electrode used. For Ti/Pt, by-products are accumulated during the whole electrochemical treatment, while at $Ti/Ru_{0.3}Ti_{0.7}O_2$ and BDD anodes, the maximum absorbance decreases after 160 and 120 min, respectively, indicating the by-products elimination. These findings suggest that the organic matter oxidation is efficiently promoted by BDD action favoring the by-products degradation. Meanwhile, the formation of intermediates is attained at Ti/Pt, which are not eliminated even after 300 min of treatment. Conversely, $Ti/Ru_{0.3}Ti_{0.7}O_2$ showed to be able to promote the elimination of the by-products formed.

### *3.2. Evaluation of active chlorine species action*

Based on the abovementioned results and discussion, organic matter oxidation depends on the oxidative pathway followed by the electro-catalytic nature of the material. In this sense, indirect oxidation has shown to be a predominant mechanism during the electrochemical treatment of PW under different anodes action. Hence, active chlorine species ($Cl_{2(dissolved)}$, $ClO_2$, $ClO_2^-$) were determined at the end of the electrochemical treatment in order to provide deeper information.

Figure 5 shows active chlorine species concentrations assessed after 300 min of the electrolysis by applying 45 mA $cm^{-2}$ with the three tested anodes.

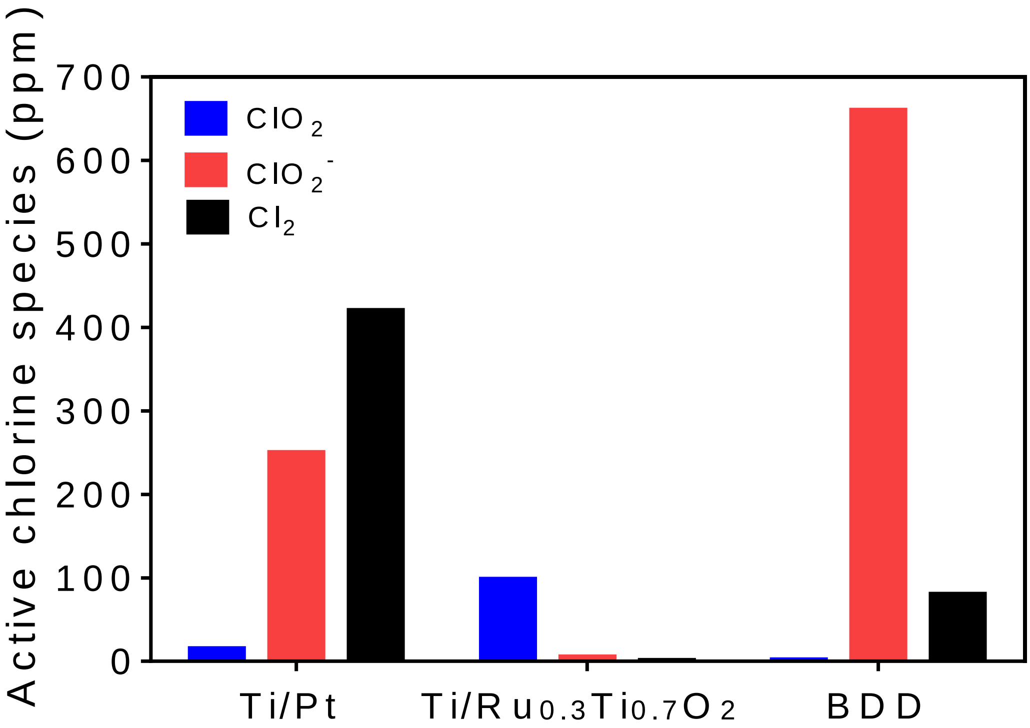

**Figure 5.** Active chlorine species concentrations after electrolysis of PW on each one of the anode used by applying 45 mA cm$^{-2}$ at 25°C.

Notable differences are observed regarding the chlorine species as well as the anode used. In general, lower concentration of the active chlorine species was determined when Ti/$Ru_{0.3}Ti_{0.7}O_2$ anode was used because these are efficiently consumed during the organic matter oxidation. $RuO_2$-based anodes are well known catalysts to perform the $Cl_2$-active mechanism [56] due to their adequate properties (chemical and catalytic) to induce the adsorption-desorption of chlorides ions and charge-transfer. Conversely, a significant concentration of the oxidizing species was determined when the PW was treated with Ti/Pt anode, evidencing the poor efficiency of this system to induce the organic matter mineralization. Produced active chlorine species contribute to the oxidization of organic compounds [16,19,57] but organochlorinated compounds can be feasibly generated and harder to be mineralized. Therefore, by-products are accumulated as well as the electro-generated chlorinated species.

On the other hand, BDD anodes produce large quantities of hydroxyl radicals during electrolysis of aqueous solutions that in the presence of chlorides, they can oxidize to different oxochlorinated compounds. Nevertheless, electrogeneration of active chlorine species by BDD anode [20], seems to be limited by electrocatalytic properties of the anode material. Results showed that $ClO_2^-$ was the predominant specie and its concentration was enlarged (~650 ppm) under the BDD action; fact that could be associated to high instability of the chlorine oxide [58], which undergoes into a disproportionation reaction to produce $ClO_2^-$ (eq. 19).

$$ClO_2 + e^- \leftrightarrow ClO_2^- \qquad (19)$$

It was not possible to chemically analyze the chlorate for this PW sample due to the formation of a precipitate along the titration.

### *3.3. Energy consumption*

So far, it has been exposed the possible applicability of the electrochemical chloride-mediated oxidation for treating PW. Promising results were obtained and significant variations on the efficiency and oxidation routes were observed regarding the anode material. Thus, it is important to determine the electrical requirements. The energy consumption was estimated by using following equation:

$$Energy\ consumption\ (kWh\ m^{-3}) = \frac{V \times A \times t}{V_s} \qquad (20)$$

where $t$ is the time of electrolysis (hours); $V$ and $A$ are the average cell voltage and the electrolysis current, respectively; and $V_s$ is the sample volume ($m^3$). The average energy consumption values at the end of electrochemical treatment were 86, 70 and 115 kWh $m^{-3}$ (Table 2) by using Ti/Pt, Ti/$Ru_{0.3}Ti_{0.7}O_2$ and BDD, respectively. Energy consumption can be expressed in terms of the treatment cost (USD $m^{-3}$), which was estimated using the Brazilian electrical energy price per kWh (BRL 0.625, excluding taxes) and then converted into USD. According to the cost estimation, treatments cost can be described by the following order: Ti/$Ru_{0.3}Ti_{0.7}O_2$ < Ti/Pt < BDD.

**Table 2.** Energy consumption and cost during the electrochemical treatment of PW using different anodes (Ti/Pt, Ti/$Ru_{0.3}Ti_{0.7}O_2$ and BDD) by applying 45 mA $cm^{-2}$.

| **Anode** | **Ti/Pt** | **Ti/$Ru_{0.3}Ti_{0.7}O_2$** | **BDD** |
|---|---|---|---|
| Energy Consumption (kWh $m^{-3}$) | 86 | 70 | 115 |
| Cost (USD $m^{-3}$) | 9.40 | 7.64 | 12.56 |

Based on the obtained information, in general terms, active anodes require lower energy consumption and treatment cost compared to the non-active anode estimations. However, it is important to highlight that the use of the Ti/Pt anode leads to stable by-products that might represent a problem in the application of the technology. In contrast, the use of the Ti/$Ru_{0.3}Ti_{0.7}O_2$ electrode promotes the organic matter oxidation under the lower energy consumption and cost. Extensive studies on scale-up/pilot and field experiments are still needed before the full-scale implementation of the electrochemical chloride-mediated oxidation devices. Most of the studies reported in literature are either bench or pre-pilot scales, as such pilot and field studies are essential before the certification of the process because future developments will rely upon the close collaboration of analytical chemists, engineers and geologists to ensure effective application as well as the exploitation of new electrochemical environmental applications to reduce the costs by using green-energetic technologies [59–62].

## 4. CONCLUSION

The use of electrochemical technology has been assessed during this investigation for treating petrochemical effluent. The process efficiency was evaluated according to the electrocatalytic material used. Three different electrodes were tested, two active anodes (Ti/Pt and $Ti/Ru_{0.3}Ti_{0.7}O_2$) and a non-active anode (BDD). According to the obtained results, the electrochemical chloride-mediated oxidation is promising technology to eliminate organic pollutants from PW. 85% of COD removal) was obtained with $Ti/Ru_{0.3}Ti_{0.7}O_2$ by applying 45 mA $cm^{-2}$ at 25°C, followed to Ti/Pt and BDD achieving 52% and 45% of COD removals, respectively. The enhanced action of the $Ti/Ru_{0.3}Ti_{0.7}O_2$ anode is attributed to a higher production of active chlorine species which are able to promote the organic matter oxidation in the effluent. However, the organic matter transformations determined by the maximum absorbance evolution suggest that some recalcitrant pollutants are present in the effluent even after 300 of electrochemical treatment.

Moreover, the estimated energy consumption as well as the treatment cost were lower when $Ti/Ru_{0.3}Ti_{0.7}O_2$ anode was used. Consequently, the electro-generation of the active chlorine oxidants determined an efficient indirect oxidation pathway for the organic matter by the catalytic action of the $Ti/Ru_{0.3}Ti_{0.7}O_2$ anode turning the electrochemical technology into a viable treatment for the petrochemical industry wastewaters.

## References

1. J. Veil, M.G. Puder, D. Elcock, R.J.J. Redweik, *Argonne Natl. Lab.*, 79 (2004).
2. P. Jain, M. Sharma, P. Dureja, P.M. Sarma, B. Lal, *Chemosphere*, 166 (2017) 96–108.
3. G.T. Tellez, N. Nirmalakhandan, J.L. Gardea-Torresdey, *Adv. Environ. Res.*, 6 (2002) 455–470.
4. R.T. Duraisamy, A.H. Beni, A. Heni, E. W. Elshorbagy and R. K. Chowdhury (Ed.), Water Treat., InTech, (2013).
5. E.V. Santos, J.H.B. Rocha, D.M. de Araújo, D.C. Moura, C.A. Martínez-Huitle, *Environ. Sci. Pollut. Res.*, 21 (2014) 8432–8441.
6. E.V. dos Santos, J.H. Bezerra Rocha, D.M. de Araújo, D.C. de Moura, C.A. Martínez-Huitle, *Environ. Sci. Pollut. Res.*, 21 (2014) 8432–8441.
7. E.I.- Chávez, C. De Rosa, C.A. Martínez, J.M.P.- Hernández, *Int. J. Electrochem. Sci.*, 8 (2013) 3084–3094.
8. M.B. Ferreira, J.H.B. Rocha, J.V. de Melo, C.A. Martinez-Huitle, M.A.Q. Alfaro, *Electrocatalysis*, 4 (2013) 274–282.
9. C.N. Brito, M.B. Ferreira, E.C.M. de Moura Santos, J.J.L. Léon, S.O. Ganiyu, C.A. Martínez-Huitle, *J. Appl. Electrochem.*, 48 (2018) 1321–1330.
10. M. Barbosa Ferreira, F.L. Souza, M. Muñoz-Morales, C. Sáez, P. Cañizares, C.A. Martínez-Huitle, M.A. Rodrigo, *J. Hazard. Mater.*, 392 (2020).
11. C.A. Martínez-Huitle, E. Brillas, *Appl. Catal. B Environ.*, 87 (2009) 105–145.
12. S.O. Ganiyu, M. Zhou, C.A. Martínez-Huitle, *Appl. Catal. B Environ.*, 235 (2018) 103–129.
13. C.A. Martínez-Huitle, M. Panizza, *Curr. Opin. Electrochem.*, 11 (2018) 62–71.
14. C. Comninellis, *Electrochim. Acta*, 39 (1994) 1857–1862.
15. C.A. Martínez-Huitle, S. Ferro, *Chem. Soc. Rev.*, 35 (2006) 1324–1340.
16. C.A. Martínez-Huitle, M.A. Rodrigo, I. Sirés, O. Scialdone, *Chem. Rev.*, 115 (2015) 13362–13407.
17. A. Anglada, A. Urtiaga, I. Ortiz, *J. Chem. Technol. Biotechnol.*, 84 (2009) 1747–1755.
18. M. Panizza, G. Cerisola, *Chem. Rev.*, 109 (2009) 6541–6569.
19. D.C. de Moura, C.K.C. de Araújo, C.L.P.S. Zanta, R. Salazar, C.A. Martínez-Huitle, *J. Electroanal. Chem.*, 731 (2014) 145–152.
20. C.D.N. Brito, D.M. De Araújo, C.A. Martínez-Huitle, M.A. Rodrigo, *Electrochem. Commun.*,

55 (2015) 34–38.
21. S.M. Sanches, C.H.T.P. Silva, E.M. Vieira, *Química Nov. Da Esc.*, 17 (2003) 8.
22. D. Rajkumar, K. Palanivelu, *J. Hazard. Mater.*, 113 (2004) 123–129.
23. G. Li, T. An, J. Chen, G. Sheng, J. Fu, F. Chen, S. Zhang, H. Zhao, *J. Hazard. Mater.*, 138 (2006) 392–400.
24. M.R.G. Santos, M.O.F. Goulart, J. Tonholo, C.L.P.S. Zanta, *Chemosphere*, 64 (2006) 393–399.
25. H. Ma, B. Wang, *J. Hazard. Mater.*, 132 (2006) 237–243.
26. R.M.G. de Lima, G.R. da Silva Wildhagen, J.W.S.D. da Cunha, J.C. Afonso, *J. Hazard. Mater.*, 161 (2009) 1560–1564.
27. O. Abdelwahab, N.K. Amin, E.-S.Z. El-Ashtoukhy, *J. Hazard. Mater.*, 163 (2009) 711–716.
28. L.-H. Tran, P. Drogui, G. Mercier, J.-F. Blais, *J. Hazard. Mater.*, 164 (2009) 1118–1129.
29. L.-H. Tran, P. Drogui, G. Mercier, J.-F. Blais, *J. Hazard. Mater.*, 170 (2009) 1218–1226.
30. L.-H. Tran, P. Drogui, G. Mercier, J.-F. Blais, *J. Appl. Electrochem.*, 40 (2010) 1493–1510.
31. B.K. Körbahti, K. Artut, *Desalination*, 258 (2010) 219–228.
32. Y. Yavuz, A.S. Koparal, Ü.B. Öğütveren, *Desalination*, 258 (2010) 201–205.
33. A.M.Z. Ramalho, C.A. Martínez-Huitle, D.R. da Silva, *Fuel*, 89 (2010) 531–534.
34. A. Medel, E. Bustos, K. Esquivel, L.A. Godínez, Y. Meas, *Int. J. Photoenergy* (2012) 681875.
35. L. Yan, H. Ma, B. Wang, Y. Wang, Y. Chen, *Desalination*, 276 (2011) 397–402.
36. M. Zhou, L. Liu, Y. Jiao, Q. Wang, Q. Tan, *Desalination*, 277 (2011) 201–206.
37. J.H.B. Rocha, M.M.S. Gomes, N.S. Fernandes, D.R. Da Silva, C.A. Martínez-Huitle, *Fuel Process. Technol.*, 96 (2012) 80–87.
38. I.D. Santos, M. Dezotti, A.J.B. Dutra, *Chem. Eng. J.*, 226 (2013) 293–299.
39. C. Comninellis, C. Pulgarin, *J. Appl. Electrochem.*, 23 (1993) 108–112.
40. P.A. Michaud, M. Panizza, L. Ouattara, T. Diaco, G. Foti, C. Comninellis, *J. Appl. Electrochem.* 33 (2003) 151–154.
41. E.V. Dos Santos, C. Sáez, C.A. Martínez-Huitle, P. Cañizares, M.A. Rodrigo, *Electrochem. Commun.*, 55 (2015) 26–29.
42. N. Mohan, N. Balasubramanian, C.A. Basha, *J. Hazard. Mater.*, 147 (2007) 644–651.
43. J. Zou, X. Peng, M. Li, Y. Xiong, B. Wang, F. Dong, B. Wang, *Chemosphere*, 171 (2017) 332–338.
44. J.P.S. Duarte, C.A. Martínez-Huitle, D.R. da Silva, *Sustain. Environ. Res.*, 21 (2011) 329–335.
45. A.J.C. da Silva, E.V. dos Santos, C.C. de Oliveira Morais, C.A. Martínez-Huitle, S.S.L. Castro, *Chem. Eng. J.*, 233 (2013) 47–55.
46. B. Gargouri, O.D. Gargouri, B. Gargouri, S.K. Trabelsi, R. Abdelhedi, M. Bouaziz, *Chemosphere*, 117 (2014) 309–315.
47. C.C. de Almeida, P.R.F. da Costa, M.J. de M. Melo, E.V. dos Santos, C.A. Martínez-Huitle, *J. Mex. Chem. Soc.*, 58 (2014) 276–286.
48. P.R.F. da Costa, D.R. da Silva, C.A. Martínez-Huitle, S. Garcia-Segura, *J. Electroanal. Chem.*, 763 (2016) 97–103.
49. C.A. Martínez-Huitle, D.C. De Moura, D.R. Da Silva, *Chem. Eng. Trans.*, 41 (2014) 373–378.
50. E. Brillas, C.A. Martínez-Huitle, *Appl. Catal. B Environ.*, 166–167 (2015) 603–643.
51. A. Uranga-Flores, C. De La Rosa-Júarez, S. Gutierrez-Granados, D.C. De Moura, C.A. Martínez-Huitle, J.M. Peralta Hernández, *J. Electroanal. Chem.*, 738 (2015) 84–91.
52. S.M.L. de O. Marcionilio, D.M. Araújo, T. de V Nascimento, C.A. Martínez-Huitle, J.J. Linares, *Electrochem. Commun.*, 118 (2020) 106792.
53. G.O.S. Santos, K.I.B. Eguiluz, G.R. Salazar-Banda, C. Sáez, M.A. Rodrigo, *J. Electroanal. Chem.*, 857 (2020) 113756.
54. D. Zhi, Y. Lin, L. Jiang, Y. Zhou, A. Huang, J. Yang, L. Luo, *J. Environ. Manage.*, 260 (2020) 110125.
55. E.V. dos Santos, C. Sáez, C.A. Martínez-Huitle, P. Cañizares, M.A. Rodrigo, *J. Hazard. Mater.*,

300 (2015) 129–134.
56. S. Trasatti, *Electrochim. Acta*, 45 (2000) 2377–2385.
57. C. Do Nascimento Brito, D.R. Da Silva, S. Garcia-Segura, D.C. De Moura, C.A. Martínez-Huitle, *J. Electrochem. Soc.*, 163 (2016) E62–E69.
58. M.M. Huber, S. Korhonen, T.A. Ternes, U. von Gunten, *Water Res.*, 39 (2005) 3607–3617.
59. F. Escalona-Durán, P. Villegas-Guzman, E.V. dos Santos, D.R. da Silva, C.A. Martínez-Huitle, *J. Electroanal. Chem.*, 832 (2019) 453–458.
60. S.O. Ganiyu, C.A. Martínez-Huitle, M.A. Rodrigo, *Appl. Catal. B Environ.*, 270 (2020) 118857.
61. S.O. Ganiyu, C.A. Martínez-Huitle, *Curr. Opin. Electrochem.* (2020). https://doi.org/10.1016/j.coelec.2020.07.007
62. F. Escalona-Durán, D. Ribeiro da Silva, C.A. Martínez-Huitle, P. Villegas-Guzman, *Chemosphere*, 253 (2020) 126599.