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# Electrochemical comparative study of Ti/Ta<sub>2</sub>O<sub>5</sub>/Pt-RuO<sub>2</sub>-IrO<sub>2</sub> and Ti/Ta<sub>2</sub>O<sub>5</sub>/Pt anodes: Stability, service lifetime, and electrooxidation performance

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## Abstract

This work aimed to compare the stability, service lifetime, and electrooxidation performance of Ti/Ta<sub>2</sub>O<sub>5</sub>/Pt-RuO<sub>2</sub>-IrO<sub>2</sub> (PRI) and Ti/Ta<sub>2</sub>O<sub>5</sub>/Pt (Pt) electrodes thermally prepared. The service lifetime study performed under 410 mA/cm<sup>2</sup> in a 9N H<sub>2</sub>SO<sub>4</sub> showed that PRI electrode had six (06) times longer lifetime than the Pt electrode. Bulk electrolysis experiments were carried out on Pt and PRI under 20 mA/cm<sup>2</sup>. COD removal, current efficiency (CE), specific energy consumption (SEC), electrical energy cost, and anode efficiency ( $\eta$ ) were estimated. Both electrodes lead to the conversion of the parent compounds. However, the Pt electrode was best suited for amoxicillin (AMX) electrooxidation with 36.89% by COD removal in KClO<sub>4</sub> 0.1 M. Besides, the PRI electrode provided the best performances for the AMX electrooxidation (8.15%) and telebrix (TLX) (29.28%) in HClO<sub>4</sub> 0.1 M and KClO<sub>4</sub> 0.1 M, respectively. The presence of NaCl enhanced significantly the organic compound electrooxidation in terms of COD removal, CE, SEC, electrical energy cost, and  $\eta$  on the both electrodes. This is probably because of the co-action of direct and indirect (by active chlorine) oxidations. But the PRI electrode presented the best performance in the presence of chloride ions. In summary, the experimental conditions can determine the performance of an anode.

## KEYWORDS

dimensionally stable anode, electrooxidation, energy consumption, life time, pharmaceuticals compounds, Pt electrode

## 1 | INTRODUCTION

Nowadays, most of environmental problems are due to water pollution. Agricultural activities, urban wastewater, waste discharge at landfill, industrial wastewater, and hospital wastewater are considered important releasing sources of pollutants in the water.<sup>1–5</sup> Among the wide variety of pollutants present in wastewater, hospital wastewater containing pharmaceutical compounds

receives special attention. Their presence in wastewater not only affects water quality but also leads to potential long-term negative effects on the ecosystems and human health.<sup>6</sup> In Ivory Coast, an investigation carried out by our laboratory showed that the Treichville University Hospital has a wastewater treatment plant for the treatment of its wastewater before discharge. Unfortunately, this wastewater treatment plant has not been functional since 1975.<sup>7</sup> Consequently, the wastewater from various



services has been directly and continuously discharged into the Ebrié lagoon. This situation could represent a real risk of public health. Our survey has also showed that the antibiotics are regularly prescribed to the hospitalized patients and among these, amoxicillin. In addition, iodinated contrast products such as Omnipaque and Telebrix are also used there for scanners. Thus, these pharmaceutical compounds (amoxicillin, Telebrix, etc.) could have been found in surface waters and lead to serious consequences for the aquatic and human population.<sup>6,8,9</sup> Therefore, it's imperative to develop techniques to remove efficiently pharmaceutical compounds in wastewater.

The main wastewater treatment process is the biological treatment.<sup>10,11</sup> However, this technique is not suitable to remove efficiently pharmaceutical compounds in wastewater because of their generally nonbiodegradable character.<sup>12,13</sup> Due to the limitations of biological wastewater treatment processes, alternative processes (only or combined) have been pursued, such as ozonation, irradiation, Fenton, and photocatalysis.<sup>14–18</sup> In fact, the choice of the process of treatment depends on its cost, reliability, and efficiency. Thus, electrochemical methods appear to be very attractive for the wastewater treatment containing pharmaceuticals. Indeed, these methods are based on the in situ generation of hydroxyl radicals ( $\cdot\text{OH}$ ) which are very powerful and unselective oxidizing species. Electrooxidation is one of the methods commonly used for the degradation of organic compounds.<sup>19–22</sup> This technique has many advantages: it is friendly to the environment, it requires little or no addition of chemicals, it works with simple equipment, and the reaction can be easily stopped by turning off the power.<sup>23,24</sup> However, its effectiveness depends on various operational parameters such as the material used at the anode, temperature, initial organics concentration, supporting electrolyte, pH, current density, and others.<sup>25</sup>

Our previous works on the treatment of wastewater containing amoxicillin (1 g/L) have been carried out on different material anodes (BDD and  $\text{RuO}_2$ ). Under the same experimental conditions, we have showed that with the BDD, more than 40% of the COD abatement rate is reached after 4 h of electrolysis against 4.53% on  $\text{RuO}_2$  after 10 h.<sup>26,27</sup> Flamur et al studied the electrooxidation of amoxicillin on several electrode materials such as carbon felt, carbon fiber, carbon graphite, platinum, lead dioxide, dimensionally stable anode (DSA) ( $\text{Ti}/\text{RuO}_2\text{-IrO}_2$ ), and BDD.<sup>28</sup> In this study, Sopaj et al showed that the current density is a key parameter in the performance of the electrodes used at the anode because the efficiency of the electrodes increased with the current density. However, the BDD electrode exhibited the better performance in degrading amoxicillin than DSA. For a density of  $20.83 \text{ mA}/\text{cm}^2$ ,

the degradation rate was almost 100% on a BDD electrode against 40% on the DSA. The BDD electrode allows complete mineralization of amoxicillin to be achieved after 6 h compared to less than 25% on DSA for the same duration of treatment and at the same current density. The classification of the electrodes in increasing order of anodic oxidation efficiency was as follows:  $\text{DSA} < \text{felt carbon} < \text{carbon fiber} < \text{Platinum} < \text{BDD}$ . Platinum electrode exhibited better efficiency for amoxicillin anodic oxidation than DSA electrode. Likewise, Sondas et al<sup>29</sup> evaluated the performance of BDD,  $\text{RuO}_2$ ,  $\text{IrO}_2$ , and Pt electrodes for the treatment of urine wastewaters that contained many inorganic ions, the most important of which are sulphates, phosphates, nitrates, ammonium, and chlorides. It has been proven, in this study, that all these electrodes lead to remove completely the *Escherichia coli* present in urine wastewaters at low applied electric charge ( $1.34 \text{ Ah dm}^{-3}$ ). However, complete depletion of COD and TOC can be obtained during electrolysis with BDD anode at applied electric charge of 4 and  $8 \text{ Ah dm}^{-3}$ , respectively. With the  $\text{RuO}_2$  anode, 82% and 100% of the TOC and COD removal rate, respectively, and 100 was reached after  $29 \text{ Ah dm}^{-3}$  against 73% of TOC removal and 100% of COD removal for the  $\text{IrO}_2$  anode. The platinum anode exhibited the lowest performance in terms of COD and COT with 13% and 58% of COT and COD removal, respectively, at applied electric charge of  $44 \text{ Ah dm}^{-3}$ . Another researcher group, Ozge et al<sup>30</sup> investigated on the electrochemical reduction of iohexol using  $\text{Ti}/\text{RuO}_2$ ,  $\text{Ti}/\text{Pt}$ ,  $\text{Ti}/\text{IrO}_2\text{-RuO}_2$ ,  $\text{Ti}/\text{IrO}_2\text{-Ta}_2\text{O}_5$ ,  $\text{Ti}/\text{Ta}_2\text{O}_5\text{-SnO}_2\text{-IrO}_2$ , and  $\text{Pt}/\text{SnO}_2$  as anodes. The results obtained showed that the  $\text{Ti}/\text{RuO}_2$  electrode allows better degradation of iohexol with more than 99% of the degradation rate, followed by the  $\text{Ti}/\text{IrO}_2\text{-RuO}_2$  electrode (79%).  $\text{Ti}/\text{Pt}$  electrode having the third lowest compound removal rate with about 40% of degradation rate. Marcela et al<sup>31</sup> studied the electrooxidation of methyl red (100 mg/L) on  $\text{Ti}/\text{Pt}$  and  $\text{Ti}/\text{Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$  (DSA) anodes in sulfuric acid medium (0.25 M). For this purpose, the influence of the applied current density and the temperature were investigated. With regard to the current density, it emerged from this work that the Pt electrode is more efficient in terms of rapid coloration and COT removals than the DSA. On the other hand, the influence of temperature showed that on the DSA, the decoloration times required were lower in comparison on the Pt anode but had a lower TOC removal rate than Pt anode. Besides, in the presence of NaCl, the highest TOC removal efficiencies are achieved at  $\text{Ti}/\text{Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$  compared to the  $\text{Ti}/\text{Pt}$  electrode. As we can see, the performance of the anodic oxidation process depends on several factors. And except the BDD electrode which is recognized as the most



efficient for the treatment of any type of pollutant, the electrochemical performance of the other anodes can be linked to the experimental conditions.

The goal of this work is to investigate on the electrochemical performance of two active anodes that are Ti/Ta<sub>2</sub>O<sub>5</sub>/Pt and Ti/Ta<sub>2</sub>O<sub>5</sub>/Pt-RuO<sub>2</sub>-IrO<sub>2</sub> thermally prepared. The influence of some experimental parameters on the efficiency of these two electrodes will be studied. To do this, we studied the stability, service time, and the lifetime of each electrode under drastic conditions. The electrochemical stability and the longer life of an electrode are the main concerns of electrochemical processes. For its very prolonged use, the service life of the electrode must be determined. Unfortunately, this parameter seems to be neglected in many works which compare the performance of electrodes. The effect of the supporting electrolyte, the influence of chloride ions, and the effect of pharmaceutical compounds will also be examined. To our knowledge, no comparative study on the performance of anodic oxidation had yet been the subject of a scientific publication.

## 2 | EXPERIMENTAL

### 2.1 | Chemical

In this study, all chemicals used were reagent grade or higher and were used as received without any further purification. Potassium perchlorate (KClO<sub>4</sub>), perchloric acid (HClO<sub>4</sub>), sodium chloride (NaCl), and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) were obtained from Fluka and amoxicillin (C<sub>16</sub>H<sub>19</sub>N<sub>3</sub>O<sub>5</sub>S) tablets and a vial of 100 ml of Télébrix 35 (TLX) were purchased from a pharmacy in Abidjan. TLX is an injectable iodine contrast product whose active substances are meglumine ioxitalamate (C<sub>19</sub>H<sub>28</sub>I<sub>3</sub>N<sub>3</sub>O<sub>10</sub>) and sodium ioxitalamate (C<sub>12</sub>H<sub>10</sub>I<sub>3</sub>N<sub>2</sub>NaO<sub>5</sub>). All the solutions used in the current work were prepared with distilled water. All the electrochemical experiments were made at ambient temperature of 25°C.

### 2.2 | Preparation of electrodes

The electrodes used as anodes in this work were thermally prepared in our laboratory at 400°C on a sandblasted titanium substrate. The coating precursors were prepared from RuCl<sub>3</sub>, xH<sub>2</sub>O (ALDRICH), H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (SIGMA-ALDRICH), TaCl<sub>5</sub> (Aldrich), and H<sub>2</sub>IrCl<sub>6</sub>·xH<sub>2</sub>O (SIGMA-ALDRICH). The solvent used is isopropanol (PANREAC). The commercial products were used as received without any further treatment. The dimension of the titanium substrate is

1.6 cm × 1.6 cm × 0.5 cm for voltammetry and service life investigations. For the preparative electrolysis investigation, the titanium substrates have the following dimension: 5.0 cm × 5.0 cm × 0.5 cm.

The surface of each titanium substrate was sandblasted in order to roughen the surface to ensure good adhesion of the deposit on it. They were rinsed with distilled water to remove the grains of sand that remained on their surface after sandblasting. These substrates were then rinsed in isopropanol using an ultrasonic bath ( $f = 35$  kHz) for approximately 30 min. They are then removed from the isopropanol and dried in an oven for 15 min at 80°C. After that, the precursor was applied using the technique of painting with a brush on cleaned titanium (Ti) substrate then put in an oven (Salvis) for 15 min at 80°C to allow the evaporation of the solvent. Then after, it is put in a furnace (ZYH-10) at 400°C for 15 min to allow the decomposition of the precursor. These steps were repeated until the desired weight of the coating is reached. Finally, all the electrodes were treated by a thermal process at 400°C for 1 h in a furnace.

### 2.3 | Electrochemical system for anodic oxidation

Bulk electrolysis was performed in an undivided electrochemical reactor under a galvanostatic regime. The system worked under a batch operation mode. The simulated wastewater containing organic compound was fed with a peristaltic pump into the electrochemical reactor. The flow rate was 2.08 ml s<sup>-1</sup>. All the experiments of electrolysis were conducted at room temperature (22°C–25°C) in an open, cylindrical, and undivided glass cell of 250-ml capacity equipped with a magnetic stirrer to keep the wastewater well mixed. The solution tank is completely covered with aluminum foil to avoid the penetration of light rays into the solution. Ti/Ta<sub>2</sub>O<sub>5</sub>/Pt and Ti/Ta<sub>2</sub>O<sub>5</sub>/Pt-RuO<sub>2</sub>-IrO<sub>2</sub> electrodes were used as anode, and Zirconium (Zr) plates were used as cathode. The electrodes were square, and the geometric area of each of them was 16 cm<sup>2</sup> (active area). The current density was held constant for each series of experiments. During each experimental run, samples of 2 ml were drawn from the reactor at defined time intervals and analyzed in terms of COD. The experimental mounting is presented on Figure 1.

### 2.4 | Electrode service life

The service life of the newly prepared electrodes lifetimes was measured by accelerated life tests. The life

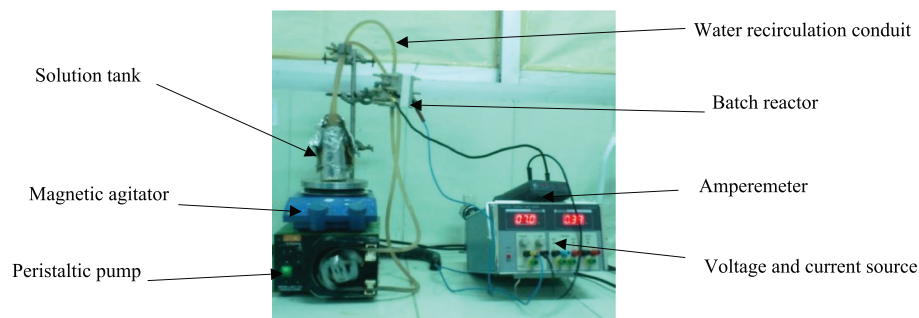


FIGURE 1 A picture of experimental mounting<sup>19</sup>

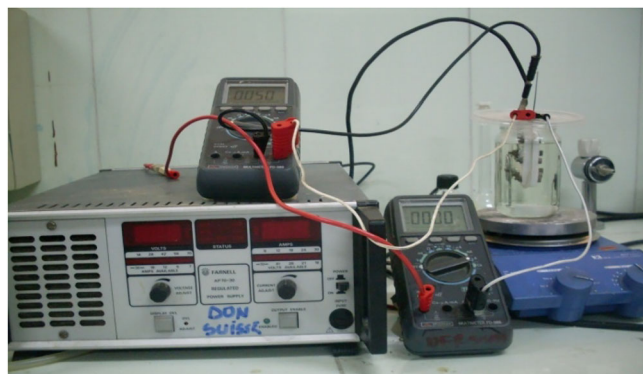


FIGURE 2 The assembly carried out for the lifetime test, anode (the prepared electrodes: Pt or PRI) in  $\text{H}_2\text{SO}_4$  9N, cathode: platinum wound,  $T = 25^\circ\text{C}$

of the electrode is a very important parameter in choosing an electrode. As part of this work, the lifetime test was investigated in a 9N sulfuric acid solution under a current density of  $410 \text{ mA/cm}^2$ .<sup>32</sup> The assembly carried out for the lifetime test, presented on Figure 2, is composed of a beaker containing the prepared material mounted in a teflon-based cage which constitutes the anode (positive terminal of the generator) and of the platinum wire used at the cathode (negative terminal generator), all immersed in 150 ml of 9N sulfuric acid. The solution is constantly stirred to remove gas bubbles formed on the surface of the working electrode which would increase the resistance of the cell. This test requires the use of two multimeters. One consists in imposing exactly the desired current density and the other in order to follow the evolution of the potential during the lifetime test. All measurements were made at  $25^\circ\text{C}$ . The electrode is deactivated when its potential increases significantly up to 10 V. The evolution of the potential and that of the voltammetric charges are recorded over time. The geometric area of the working electrode that is in contact with the supporting electrolyte is  $1 \text{ cm}^2$ .

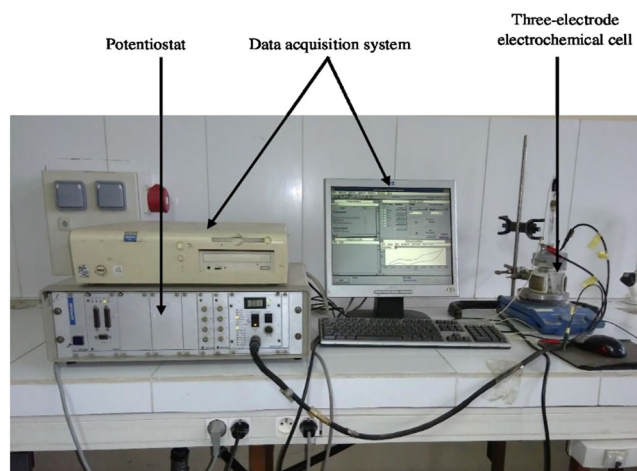


FIGURE 3 Experimental device for voltammetry measurements

## 2.5 | Cyclic voltammetry

Cyclic voltammetry (CV) was performed in a conventional three electrode cell using a computer-controlled Autolab potentiostat ECHOCHEMIE (PGSTAT 20).  $\text{Ti}/\text{Ta}_2\text{O}_5/\text{Pt}$  and  $\text{Ti}/\text{Ta}_2\text{O}_5/\text{Pt-RuO}_2\text{-IrO}_2$  electrodes were used as the working electrode, saturated calomel electrode  $\text{Hg}/\text{Hg}_2\text{Cl}_2/\text{KCl}$  as reference electrode, and Pt wire as counter electrode. The geometric area of the working electrode that is in contact with the supporting electrolyte is  $1 \text{ cm}^2$ . The reference electrode is a saturated calomel electrode. The electrode reference is put in a Luggin capillary whose end is placed very close to the working electrode in order to reduce the ohmic drop. The potential of the electrode was reported relative to the saturated calomel electrode (SCE). The experimental device is shown on Figure 3.

## 2.6 | Analytical methods

The experiments were followed by determining the chemical oxygen demand (COD), a global parameter. The COD corresponds to the oxygen consumption necessary



for the complete oxidation of the organic matter and of certain oxidizable inorganic compounds contained in the sample analyzed. During the experiments, 2 ml of the samples are taken at well-defined time intervals and introduced into HACH tubes already predosed. These tubes are then heated in a digester at 150°C for 120 min. After cooling, the COD value is read directly on the DR600 spectrophotometer. COD abatement rate is determined using this formula:

$$\Delta(\text{COD}) = \frac{\text{COD}_0 - \text{COD}_t}{\text{COD}_0} * 100, \quad (1)$$

where  $\text{COD}_0$  and  $\text{COD}_t$  are, respectively, the initial COD and the final COD ( $\text{mgO}_2/\text{L}$ ).

The current efficiency (CE) which can be defined as the part of the current directly used for the oxidation of the organic compounds has been determined in this work according to Equation 2.<sup>33</sup>

$$\text{CE}(\%) = \frac{FV(\text{DCO}_0 - \text{DCO}_t)}{8I\Delta t} * 100, \quad (2)$$

where  $\text{DCO}_0$  and  $\text{DCO}_t$  are, respectively, the COD ( $\text{g O}_2/\text{L}$ ) at times 0 and time ( $t$ ) (s), respectively;  $F$  is Faraday's constant ( $96458 \text{ C/mol}$ );  $V$  is the volume of the solution ( $\text{dm}^3$ );  $I$  is the current (A); and 8 is the equivalent weight of oxygen ( $32\text{gO}_2/4 \text{ g e}^- \text{ O}_2$ ).

The specific energy consumption (SEC) per unit of mass of COD (SEC,  $\text{kWh kg COD}^{-1}$ ) was determined using Equation 3.<sup>34</sup>

$$\text{SEC} (\text{kWh Kg COD}^{-1}) = \frac{UIt}{1000V(\text{COD}_0 - \text{COD}_t)}, \quad (3)$$

where  $U$  is the average potential difference between the anode and cathode during electrolysis (V),  $I$  is the applied electrolysis current (A),  $t$  is the electrolysis time (h),  $V$  the wastewater volume (L), and  $\text{DCO}_0$  and  $\text{DCO}_t$  are, respectively, the COD ( $\text{Kg O}_2 \text{ L}^{-1}$ ) at times 0 and time ( $t$ ).

The cost of wastewater treatment to degrade 1 kg of COD was assessed. In Côte d'Ivoire, the electrical energy cost of a kWh for an industrial unit is worth on average 94.23 CFA francs, or US \$0.17.

### 3 | RESULTS AND DISCUSSIONS

#### 3.1 | Service life and electrochemical characterization of electrodes

Although electrodes must be highly efficient for degradation of pharmaceutical compounds, the determination of

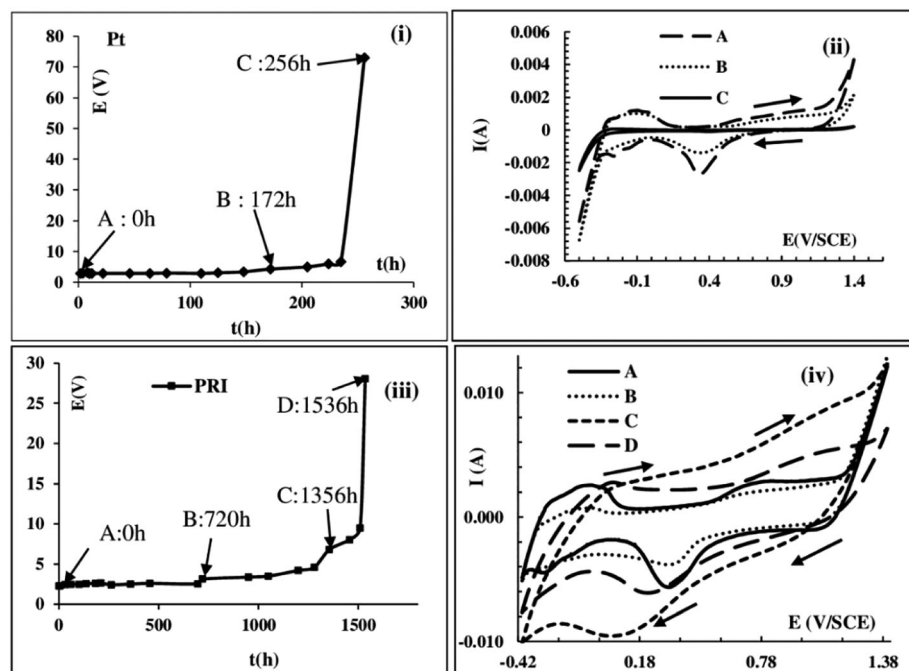
their stability in different media and their lifetime are essential.

Figure 4 shows the evolution of the potential as a function of the polarization time of the  $\text{Ti}/\text{Ta}_2\text{O}_5/\text{Pt}$  and  $\text{Ti}/\text{Ta}_2\text{O}_5/\text{Pt}-\text{RuO}_2-\text{IrO}_2$  electrodes. These two electrodes have been physically characterized in our previous work.<sup>19,35</sup>

The curve of the potential as a function of the polarization duration of the Pt electrode (Figure 4i) can be divided into three parts: the first part is characterized by an almost constant potential; it is between 0 to 125 h with a potential around 3 V. The second part is between 125 to 235 h. In this part, there is a slight increase in the potential which goes from 3 to 6.7 V. As for the third part, it is located after 235 h and is characterized by a very rapid increase in the potential which reaches 73 V after 256 h of polarization. This increase in potential reflects the deactivation of the  $\text{Ti}/\text{Ta}_2\text{O}_5/\text{Pt}$  electrode, probably due to a detachment of the Pt deposit.

Points A, B, and C marked in Figure 4i are associated with the cyclic voltammetry recorded during the polarization of this electrode which are presented in Figure 4ii. The voltammetric curve A corresponds to the curve of the newly prepared  $\text{Ti}/\text{Ta}_2\text{O}_5/\text{Pt}$  electrode. This curve has the same characteristics as that of pure platinum as described in acidic media by Kambire et al<sup>36</sup> with adsorption and desorption peaks located between  $-0.3$  and  $0.1$  V followed by the double layer domain characterized by an almost zero current which is between  $0.1$  and  $0.5$  V. The anode wave characterizing the formation of platinum oxide is between  $0.5$  and  $1.20$  V in the forward direction of potential in scanning. The reduction of platinum oxide characterized by a reduction peak in the potential reverse direction in scanning is located around  $0.34$  V. The oxygen evolution range starts from  $1.20$  V characterized by a rapid increase in current. The evolution of hydrogen begins at the potential of  $-0.3$  V. Curve B corresponds to the voltammogram recorded after 172 h of polarization; a voltammetric load is lower than that of voltammogram A. This observation would indicate a slight decrease in the activity of the electrode. After 256 h, the recorded voltammogram (curve C) has a very low charge compared to curves A and B. This would mean that after 256 h, we see the deactivation of the  $\text{Ti}/\text{Ta}_2\text{O}_5/\text{Pt}$  electrode.

According to previous work carried out by our research team,<sup>32</sup> the deactivation of the  $\text{Ti}/\text{Pt}$  electrode occurs after 72 h of polarization due to the detachment of the platinum deposit from the surface of the titanium support. Compared to the  $\text{Ti}/\text{Pt}$  electrode,  $\text{Ti}/\text{Ta}_2\text{O}_5/\text{Pt}$  electrode lasts 3.28 times longer. The difference observed would be mainly due to the presence of  $\text{Ta}_2\text{O}_5$ , used as a



**FIGURE 4** (i) Potential evolution against the time in  $H_2SO_4$  9N with anode:  $Ti/Ta_2O_5/Pt$  and cathode: Pt wire; (ii) voltammogram in 0.1-M  $H_2SO_4$  at points A, B, and C; WE:  $Ti/Ta_2O_5/Pt$ , CE: Pt wire,  $T = 25^\circ C$ ; (iii) potential evolution against the time in  $H_2SO_4$  9N with anode:  $Ti/Ta_2O_5/Pt-RuO_2-IrO_2$  and cathode: Pt wire; (iv) voltammogram in 0.1-M  $H_2SO_4$  at points A, B, and C; WE:  $Ti/Ta_2O_5/Pt-RuO_2-IrO_2$ , CE: Pt wire,  $T = 25^\circ C$

precoat, which significantly improves the resistance of the platinum electrode in very corrosive conditions.

In our literature search, we did not find any work on the  $Ti/Ta_2O_5/Pt$  or  $Ti/Pt-Ta_2O_5$  electrode. However, the  $IrO_2$  electrode combined with  $Ta_2O_5$  on a titanium substrate ( $Ti/IrO_2-Ta_2O_5$ ) and prepared by thermal decomposition has been the subject of several works.<sup>37–39</sup> For Yan et al.,<sup>38</sup> without  $Ta_2O_5$ , a rapid dissolution of  $IrO_2$  would be observed. In addition, he showed that the number of layers is also a significant factor in the durability of the electrode. Tantalum used in combination or as a precoat has the effect of improving the stability of the electrode.<sup>40</sup>

The presence of  $Ta_2O_5$  would slow the detachment of the Pt deposit from the surface of the support.

Figure 4iii presents the life test of the  $Ti/Ta_2O_5/Pt-RuO_2-IrO_2$  electrode. The curve of the evolution of the potential as a function of the polarization time can also be divided into three (03) parts. The first part, between 0 and 696 h, is characterized by a constant potential which is close to 2.54 V. It is followed (second part) by a slight increase in the potential which goes from 2.54 to 9.54 V at polarization times 696 and 1510 h. The last part is marked by a sudden increase in the potential which reaches a value of 28 V after 1538 h of polarization. This abrupt increase reflects the deactivation of the electrode. According to these findings, the  $Ti/Ta_2O_5/Pt-RuO_2-IrO_2$  electrode is more stable under very drastic conditions than the  $Ti/Ta_2O_5/Pt$  electrode. Its lifetime is six times longer than that of the  $Ti/Ta_2O_5/Pt$  electrode under our experimental conditions. This could be explained by the presence of the precursor of  $IrO_2$  in the surface of this

thermally prepared electrode. Pohan et al.<sup>32</sup> showed that the platinum electrode combined with  $IrO_2$  had a longer life than the pure  $Ti/Pt$  electrode. Likewise, Fahad et al.<sup>41</sup> had shown that adding  $IrO_2$  to the  $RuO_2 + TiO_2$  electrode can improve the stability of the electrode in an acidic environment. During the lifetime study of the  $Ti/Ta_2O_5/Pt-RuO_2-IrO_2$  electrode, voltammetric measurements were realized. The points A, B, C, and D of the figure are associated with the voltammograms of Figure 4iv. The voltammetric curve A corresponds to the voltammogram of the  $Ti/Ta_2O_5/Pt-RuO_2-IrO_2$  electrode freshly prepared thermally. This voltammogram shows the characteristics of the pure platinum electrode and the oxides ( $RuO_2$  and  $IrO_2$ ). Indeed, the hydrogen adsorption and desorption zone between  $-0.42$  and  $0.07$  V is noted. The double layer domain is observed between  $0.07$  and  $0.55$  V. Though, the current is not zero attesting to the presence of oxides ( $IrO_2$  and  $RuO_2$ ) on the surface of the electrode. This area is followed by the formation of platinum oxide. The reduction peak of the platinum oxide is located around  $0.33$  V in the cathodic sweep direction. The voltammetric curve B recorded after 720 h of polarization has a lower charge than the voltammetric curve A with a progressive disappearance of the zone of adsorption and desorption of hydrogen as well as the decrease of the reduction peak of platinum oxide. This shows a gradual departure of platinum from the surface of the electrode. In addition, the voltammetric charge of curve C (recorded after 1356 h of polarization) is greater than in A and B. Its shape resembles that of  $IrO_2$  and  $RuO_2$ . This observation would show the total detachment of



platinum from the surface of the Ti/Ta<sub>2</sub>O<sub>5</sub>/Pt-RuO<sub>2</sub>-IrO<sub>2</sub> electrode, thus leading to activation of the DSA (IrO<sub>2</sub> and RuO<sub>2</sub>). At 1536 h of polarization (curve D), the voltammetric charge begins to decrease with an abrupt increase in the potential, attesting the deactivation of the electrode which would be due to a dissolution of the RuO<sub>2</sub> and IrO<sub>2</sub> deposits.

Indeed, the life of an electrode depends on several factors. Among others, we have the pH, the temperature, the method of preparation, and the shape of the electrode and the current density applied. In this work, we investigated the effect of the applied current density on the duration of the Pt electrode deposited directly on a sandblasted titanium support. Current density is one of the most important parameters in electrooxidation. It controls the transfer of electrons and the generation of oxidative species in solution. The current densities applied vary from 20 to 100 mA/cm<sup>2</sup> for the degradation of 1 g/L of amoxicillin. The supporting electrolyte is sulfuric acid (0,1 M). The potential was monitored at well-defined time intervals during the electrolysis. The results obtained are presented in Figure 5.

This figure shows an almost constant evolution of the potential for low current densities, that is to say at 20 and 50 mA/cm<sup>2</sup> with potential values equal to 4.2 and 6.7 V, respectively. The Ti/Pt electrode would be stable at low current density. However, at 100 mA/cm<sup>2</sup>, the potential increases slowly up to 7 h of electrolysis, going from 11.2 to 24.9 V. After 7 h, there is a sudden increase in the potential up to 10 h of electrolysis reaching 51.6 V. This sudden increase would reflect the deactivation of the platinum electrode. Prolonged use of the electrode under very high current density may cause the electrode to deactivate.

Microphotos of the sandblasted titanium (a) and platinum electrode before (b) and after (c) deactivation were taken. The surface of sandblasted titanium is rough

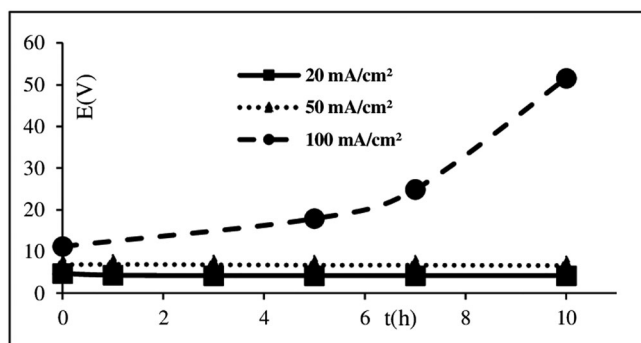


FIGURE 5 Evolution of the potential during the electrodegradation of 1 g/L AMX in H<sub>2</sub>SO<sub>4</sub> 0.1 M. Anode: Ti/Pt; cathode: Zr; T = 25°C

(Figure 6a). This has the effect of facilitating good adhesion during the deposition of the precursor. Before deactivation (Figure 6b) the pure platinum (Pt) electrode has a smooth, compact, and almost homogeneous surface, and after deactivation (Figure 6c), it has a rough surface that closely resembles the surface of sandblasted titanium. This would involve the detachment of the platinum (Pt) deposit from the titanium substrate. This detachment would be caused by a lack of adhesion which originates from the nature of the “deposit–titanium” interface which is characterized by a mechanical adhesion of the platinum layer on the rough surface of the titanium.<sup>31</sup> There is therefore no real chemical bond between the deposit and the substrate. Under high current densities, the electrolyte penetrates the pores of the electrode and oxidizes the surface of the titanium to insulating titanium oxide. The formation of this oxide increases the resistance of the substrate/deposition interface. Increasing this resistance could contribute to the deactivation of the electrode.

### 3.2 | Effect of chloride ions

Electrooxidation of pollutants can be done in different ways. The organic compound can undergo direct and/or indirect electrochemical oxidation. In addition, peroxide, Cl<sub>2</sub>, Fenton's reagent, hypochlorite, and so forth are powerful oxidative species which can be electrochemically produced. These oxidizing agents are capable of oxidizing any type of organic compound that can cause their complete degradation to CO<sub>2</sub>, H<sub>2</sub>O, and other inorganic compounds. The most widely used oxidizing agent is probably chloride ions, due to the ubiquitous character of the chloride in real wastewater, and because of their very efficient action.

In this work, the study was carried out in the absence and the presence of 400-mM chloride ions in 0.1-M KClO<sub>4</sub> medium. The electrode materials used at the anode are Pt and PRI and at the cathode Zirconium has been used. The applied current density is 20 mA/cm<sup>2</sup>. The results obtained are presented in Figure 7.

Figure 7i shows the influence of the electrodes on the change in COD removal during electrooxidation of amoxicillin in the absence of NaCl. It can be seen that the decrease in COD depends on the electrode. The decrease in COD is much rapid on the Ti/Ta<sub>2</sub>O<sub>5</sub>/Pt electrode than on the platinum electrode combined with RuO<sub>2</sub> and IrO<sub>2</sub> (Ti/Ta<sub>2</sub>O<sub>5</sub>/Pt-RuO<sub>2</sub>-IrO<sub>2</sub>). On the PRI electrode, the change in COD is almost stationary (insert of Figure 7i). The COD reduction rates obtained after 10 h of electrolysis are 0.83<sup>19</sup> and 36.89% respectively on PRI and Pt. According to these results, these two electrodes lead



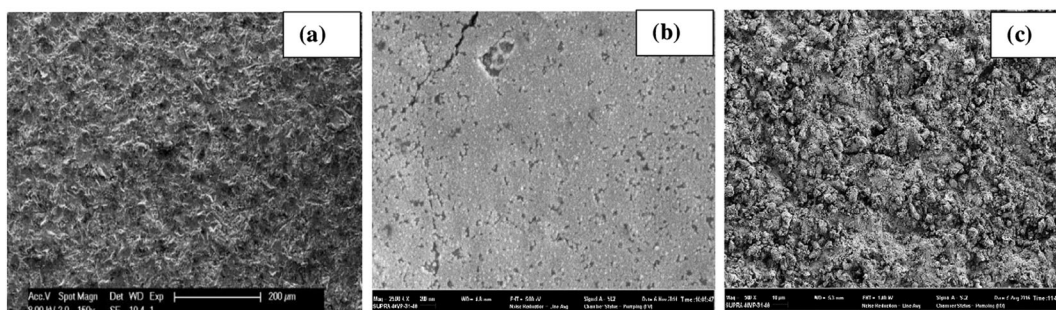


FIGURE 6 Microphotographs of sandblasted titanium (a), platinum before (b) and after (c) deactivation

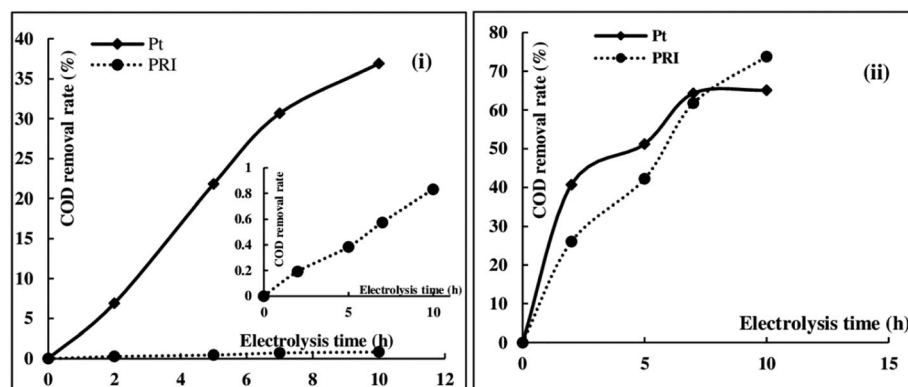
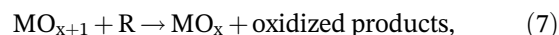
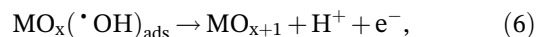
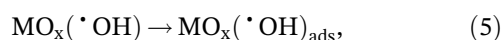


FIGURE 7 Electrolysis of AMX = 1 g/L on Ti/Ta<sub>2</sub>O<sub>5</sub>/Pt and Ti/Ta<sub>2</sub>O<sub>5</sub>/PRI electrodes in 0.1-M KClO<sub>4</sub> at 20 mA/cm<sup>2</sup> in the absence (i) and in the presence of 400 mM (ii) of NaCl; cathode: zirconium; *T* = 25°C; *t* = 10 h. Insert: Electrolysis of AMX = 1 g/L on Ti/Ta<sub>2</sub>O<sub>5</sub>/PRI electrode in 0.1-M KClO<sub>4</sub> at 20 mA/cm<sup>2</sup> in the absence of NaCl

to the conversion of amoxicillin into other intermediate compounds.

The relatively low COD abatement rates obtained with the two electrodes are related to their nature. Pt and DSA electrodes are so-called active electrodes. On this type of electrode, the hydroxyl radicals are chemisorbed on the surface of the electrode and, thus, participate in the partial degradation of the organic compounds.<sup>42</sup> In addition, partial degradation of organic compounds can occur via the upper oxide of DSAs. In fact, the adsorbed hydroxyl radical can react with the oxygen present in the oxide by transferring oxygen from the adsorbed radical to form the upper oxide (Equations 4–7) which partially degrades organic compound. The results obtained under our experimental conditions attest that Pt and PRI electrodes lead to the conversion of the parent compound into intermediate compounds. Indeed, the coloration of amoxicillin, initially colorless, takes a dark yellow color after 10 h of electrolysis on PRI electrode<sup>19</sup> which suggests that some part of amoxicillin was degraded to other organic matter. The same observation was made during the amoxicillin degradation on the Pt electrode under a current density of 20 mA/cm<sup>2</sup> in 0.1-M KClO<sub>4</sub>.



where MO<sub>x</sub> is the DSA electrode and MO<sub>x+1</sub> is the upper oxide that can react with the organic compound (R). RO is the by-product of R.

During the degradation of organic compounds, side reactions such as the evolution of oxygen can take place simultaneously. The CE applied for the electrochemical treatment of simulated wastewater containing amoxicillin determined according to Equation 2 gave 0.34% and 13.98% for the PRI electrode and the Pt electrode, respectively. The percentage of the applied current used for the degradation of amoxicillin is very low and is less than 15% for the two electrodes used in this work. Most of it, over 85% of the applied current, is used for the undesirable reaction such as the oxygen evolution reaction which takes place simultaneously with the degradation of amoxicillin. This shows that the CE strongly depends on the anode material. However, with the PRI electrode, it would appear that almost all of the applied current is used for side reactions. From the above, it appears that the Pt electrode would appear to be more electrocatalytic for the degradation of amoxicillin in terms of COD removal rate and CE.



It should be noted, however, that less than 50% of the COD removal rate was obtained at the end of the experiment regardless of the type of anode material used.

The findings of the investigations performed on the degradation of amoxicillin in the presence of 400-mM NaCl on the Pt and PRI electrodes are presented in Figure 7ii. This figure shows that the COD elimination curves constructed as a function of the electrolysis time of the different electrodes have practically the same appearance for the both electrodes. The increase in the COD removal rate in the presence of NaCl is much faster than in the absence of NaCl. After 10 h of electrolysis, the various COD removal rates obtained on the PRI and Pt electrodes are 73.79%<sup>19</sup> and 65.16%, respectively, which are greater than 50%. This results shows that, in the presence of NaCl, the electrochemical degradation of amoxicillin on PRI electrode must occur mainly via indirect process by active chlorine. Contrariwise, on the Pt electrode, the great enhancement of the amoxicillin degradation would be due of the co-action of direct and indirect (by active chlorine) oxidations. The presence of NaCl significantly accelerates the degradation of amoxicillin. In the presence of NaCl, the PRI electrode becomes more electrocatalytic for amoxicillin degradation than the Pt electrode. In solution, the chloride ions can promote the formation of large amounts of active chlorine ( $\text{Cl}_2$ ,  $\text{HClO}$ , and  $\text{ClO}^-$ ) formed in the reaction mixture depending on the pH of the medium,<sup>19,42</sup> concentration, and applied current, that seems to successfully attack the organic compound. DSAs are more active in forming the oxidative species of chlorine.<sup>43,44</sup> Although the presence of NaCl results in a consequent improvement in the elimination of COD, we cannot conclude on a reaction mechanism in this work because further investigations are required. However, Ravneet et al<sup>45</sup> proposed a possible reaction mechanism of the amoxicillin electrooxidation (200 mg/L) at Ti/RuO<sub>2</sub> electrode with 2 g/L of NaCl, in which he showed the aliphatic acids; CO<sub>2</sub>, SO<sub>4</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup> and H<sup>+</sup> were the products obtained at the end of the reaction.

The CE determined in the presence of NaCl are 54.90% and 47.57% on PRI and Pt electrodes, respectively. These CEs are much higher than those obtained in the absence of NaCl. On average, more than 51% of the applied current is used for the degradation of

the organic compound. The presence of chloride ions allows a very significant reduction in loss of the electric current.

Furthermore, the SEC for the degradation of 1 kg of COD of organic compound in the absence and presence of NaCl was determined according to Equation 3. The values of the SEC as well as the electrical energy cost of treatment are shown in Table 1.

According to this table, the SEC for the Pt and PRI electrodes in the absence of NaCl gives 187.27 and 7142.86 kWh/kg COD, respectively. The SEC obtained with the Pt electrode is very low compared to that obtained with the PRI electrode. The electrical energy cost for the degradation of 1 kg of COD are \$31.84 and \$1214.29, respectively, for Pt and PRI electrodes. In the absence of NaCl and in KClO<sub>4</sub> medium, the treatment of wastewater containing 1 g/L of amoxicillin on a PRI electrode requires an energy consumption and an electrical energy cost approximately 38 times greater than on the Pt electrode. In fact, the lower the SEC, the more efficient the electrooxidation process. In our case and our experimental conditions, the oxidation process of amoxicillin in KClO<sub>4</sub> medium and in the absence of chloride ions seems more efficient with a Pt electrode. Likewise, Orhan et al<sup>46</sup> showed that the Pt electrode had the smallest SEC compared to DSAs (Pt-RuO<sub>2</sub>; RuO<sub>2</sub>-TiO<sub>2</sub>; RuO<sub>2</sub>-IrO<sub>2</sub> and IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>) to degrade 1 kg of TOC of bisphenol A regardless of the current density applied (25, 75, and 125 mA/cm<sup>2</sup>) in H<sub>3</sub>PO<sub>4</sub> used as an electrolyte supporting.

In the presence of NaCl, we note, in general, a very significant decrease in the SEC and the electrical energy cost attesting to the efficiency of the electrochemical process for the degradation of amoxicillin. In the presence of chloride ions, a very significant energy gain is achieved regardless of the electrode used at the anode. Indeed, the SEC determined in the presence of NaCl is 6.05 and 266.42 times smaller than that calculated in the absence of NaCl. However, the PRI electrode had the lowest SEC compared to the Pt electrode with 26.81 versus 30.94 kWh kg COD<sup>-1</sup>, respectively. These SECs are lower than that obtained by Chatzisyseon et al<sup>47</sup> after 7.5 h of treatment of total phenolic content (TPh) at 5-mM NaCl and 80°C which was 72 kWh/kg COD removed. Regarding the electrical energy cost, it is also very considerably reduced with \$5.27 and \$4.56, respectively, on Pt and

**TABLE 1** SEC and cost of treatment of amoxicillin on the Pt and PRI electrodes in the absence and presence of NaCl

	KClO <sub>4</sub> (0.1 M) + AMX (1 g/L)		KClO <sub>4</sub> (0.1 M) + AMX (1 g/L) + NaCl (400 mM)	
	SEC (kWh kg COD <sup>-1</sup> )	Cost (\$)	SEC (kWh kg COD <sup>-1</sup> )	Cost (\$)
Pt	187.27	31.84	30.94	5.27
PRI	7142.86	1214.29	26.81	4.56

PRI. In conclusion, the PRI electrode is suitable for the treatment of real wastewater which contains chloride ions because it allows a higher COD removal rate than the Pt electrode with the lower energy cost.

In addition, it should be noted that the PRI surface appears to be dominated by IrO<sub>2</sub> which is not very efficient for the oxidation of amoxicillin as it exhibits similar behavior as the IrO<sub>2</sub> electrode. Indeed, the COD reduction rates after 10 h of electrolysis are substantially the same as those of the IrO<sub>2</sub> electrode (2.47% in the absence and 71.65% in the presence of NaCl) in the same experience conditions.<sup>48</sup>

### 3.3 | Effect of supporting electrolyte

The nature of the supporting electrolyte can significantly influence the degradation kinetics of organic compounds on the electrodes. Electrolytes provide the necessary ionic strength and conductivity for electrolysis. The effect of the different electrolytes on the COD removal rate of amoxicillin on Ti/Ta<sub>2</sub>O<sub>5</sub>/Pt and Ti/Ta<sub>2</sub>O<sub>5</sub>/Pt-RuO<sub>2</sub>-IrO<sub>2</sub> electrodes was investigated. The current density of 20 mA/cm<sup>2</sup> was applied, and decimolar solutions of KClO<sub>4</sub> and HClO<sub>4</sub> were selected as supporting electrolytes. The COD removal rates determined after 10 h of electrolysis are showed in Figure 8.

By comparing the COD removal rate on the two electrodes in the two supporting electrolytes, a strong influence of the support medium is observed on the process of electrodegradation of amoxicillin for each electrode. This observation is in agreement with our previous work.<sup>19</sup> For the Pt electrode, the COD abatement rate determined in HClO<sub>4</sub> medium is very negligible (1.74%) compared to that obtained in 0.1-M KClO<sub>4</sub> medium (36.89%). Under our experience conditions, Ti/Ta<sub>2</sub>O<sub>5</sub>/Pt seems more

electrocatalytic for the degradation of AMX in 0.1-M KClO<sub>4</sub> medium. While on the Ti/Ta<sub>2</sub>O<sub>5</sub>/Pt-RuO<sub>2</sub>-IrO<sub>2</sub> electrode, AMX degradation seems to be better in HClO<sub>4</sub> medium (8.15%) than in KClO<sub>4</sub> medium (0.83%). According to the results, it appears that the Pt electrode is more electrocatalytic for the degradation of amoxicillin in 0.1-M KClO<sub>4</sub>, while PRI is better for the degradation of amoxicillin in 0.1-M HClO<sub>4</sub> in terms of COD removal rate.

The CE have been determined. It appears that the Pt electrode has a higher CE in KClO<sub>4</sub> medium (13.98%) than in HClO<sub>4</sub> medium (0.68%). Regarding the PRI electrode, the CE is smaller in KClO<sub>4</sub> medium (0.34%) than in HClO<sub>4</sub> medium (3.14%). Regardless of the electrolyte medium, the CEs are very low. This translates that parasitic reactions are predominant on the electrodes used in this work. Indeed, Aquino et al<sup>49</sup> showed that the effective current obtained at the DSA for the treatment of real wastewater in the absence of chloride ions was very low because the oxygen evolution reaction (OER) is the predominant side reaction. Otherwise, the SEC was also determined as well as the cost of electrical energy to degrade 1 kg of COD of amoxicillin. In KClO<sub>4</sub> medium, the smallest SEC is obtained on the Pt electrode (187.27 kWh kg COD<sup>-1</sup>) unlike the PRI electrode where it is 7142.86 kWh kg COD<sup>-1</sup>. The cost of electrical energy to treat 1 kg of COD are, respectively, 31.84 US \$ and 1214 US \$ for Pt and PRI electrodes. The electrooxidation process of amoxicillin appears to be more efficient on the Pt electrode in potassium perchlorate medium. On the other hand, in HClO<sub>4</sub> medium, the SEC calculated after 10 h of electrolysis is 468.75 kWh kg COD<sup>-1</sup> on PRI and 2163.46 kWh kg COD<sup>-1</sup> on the Pt electrode. The cost of electrical energy associated with the treatment of simulated wastewater containing amoxicillin are US \$79.69 and US \$367.79 for PRI and Pt electrodes. From the above, the PRI electrode appears to lead to a better efficiency of the degradation process of amoxicillin in perchloric acid medium.

The anode efficiencies have been calculated in this work on both electrodes and supporting electrolytes according to Equation 8.<sup>34</sup>

$$\eta(\text{g COD/Ah m}^2) = \frac{(\text{COD}_0 - \text{COD}_t)V}{I * t * S}, \quad (8)$$

where COD<sub>0</sub> and COD<sub>t</sub> are the COD values at time = 0 and time = t, V is the volume of solution (L), I is the current applied (A), t is the electrolysis time (h), and S is the anode area (m<sup>2</sup>).

The anode efficiencies calculated for 0.1-M KClO<sub>4</sub> gave 26.07 g COD/Ah m<sup>2</sup> and 0.68 g COD/Ah m<sup>2</sup>, respectively, for Pt and PRI electrodes. On the other hand, the

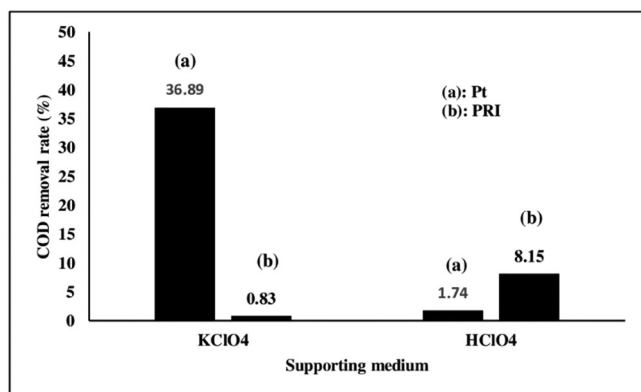


FIGURE 8 Amoxicillin COD abatement on Ti/Ta<sub>2</sub>O<sub>5</sub>/Pt and Ti/Ta<sub>2</sub>O<sub>5</sub>/Pt-RuO<sub>2</sub>-IrO<sub>2</sub> in KClO<sub>4</sub>, HClO<sub>4</sub> 0.1 M. Cathode: zirconium; T = 25°C; t = 10 h



anode efficiencies in 0.1-M HClO<sub>4</sub> medium for the Pt and PRI electrodes are 1.27 g COD/Ah m<sup>2</sup> and 5.86 g COD/Ah m<sup>2</sup>. According to these observations, it appears clearly that the anode efficiency depends on the anode used and also the supporting electrolyte medium in our experimental conditions. In addition, the anode efficiencies for the Pt electrode in KClO<sub>4</sub> medium (26.07 g COD/Ah m<sup>2</sup>) and PRI in HClO<sub>4</sub> medium (5.86 g COD/Ah m<sup>2</sup>) are within the range of anode efficiencies determined by Ukundimana et al<sup>34</sup> for DSA.

### 3.4 | Effect of organic compound

The effect of the organic compounds on the performance of Pt and PRI electrodes has been investigated in 0.1-M KClO<sub>4</sub> using as supporting electrolyte under current density of 20 mA/cm<sup>2</sup>. The electrodes have the same active area (16 cm<sup>2</sup>). The model compounds chosen are amoxicillin and Telebrix. The results obtained are presented in Figure 9. This figure shows a difference in reactivity of organic compounds on the electrodes. Such observations have been made by Rosimeire M. Farinos and Luís A.M. Ruotolo.

Figure 9i shows the change in COD\* as a function of the electrolysis time of AMX on the Pt and PRI electrodes. The change in COD\* over time of amoxicillin electrolysis remains almost constant during degradation of amoxicillin at the PRI electrode. With the Pt electrode, the curve of the COD\* as a function of time decreases during electrolysis, reflecting oxidation of amoxicillin during treatment. The COD abatement rates ( $\Delta(\text{COD})$ ) determined after 10 h of electrolysis are 0.83% for the PRI electrode<sup>19</sup> and 36.89% for the Pt electrode (insert Figure 9i). According to these results, Pt electrode is most efficient for the amoxicillin oxidation. Figure 9ii presents the curves of the COD normalized (COD\*) as a function of time produced during the electrolysis of TLX on the

electrodes of Pt and PRI. The degradation kinetics of TLX are faster on the PRI electrode than on the Pt electrode. The COD abatement rates determined after 10 h of electrolysis are 9.79% and 29.28%, respectively, on the electrode of Pt and electrode of PRI. Similar results were found by Ozge et al<sup>30</sup>; the DSA (Ti/RuO<sub>2</sub>) electrode has been found to be more efficient at degrading iohexol, an iodine contrast product like TLX, than the platinum electrode. TLX is an iodine contrast product; it would release I<sup>-</sup> ions which would in turn oxidize in (I<sub>2</sub>). The iodine (I<sub>2</sub>) produced would not adsorb on the surface of PRI unlike Pt where one could have adsorption of I<sub>2</sub> on its surface. In view of these results, the performance of an electrode used at the anode may depend on the compound to be degraded. Kenova et al<sup>50</sup> showed that the degradation rate of Eriochrome Blue on BDD was more than 43 times that of aniline. According to them, this observation could be probably explained by the aniline ability to polymerize in the course of direct oxidation on the anode surface.

The values of the CE determined for the TLX electrooxidation attests that parasitic reactions such as that of the release of oxygen are also preponderant during electrolysis as in the case of the amoxicillin degradation. However, these reactions are less prominent on the PRI electrode (CE [%] = 15.44%) compared to the Pt electrode (CE = 4.72%). The SEC for the degradation of 1 kg of COD of TLX is 173.56 kWh kg COD<sup>-1</sup> and 568.89 kWh kg COD<sup>-1</sup> on the PRI and Pt electrodes, respectively. Regarding the anode efficiency of Pt and PRI electrodes for the TLX electrooxidation, we have obtained 8.80 and 28.81 g DCO/Ah m<sup>2</sup>, respectively. From all of the above, the PRI electrode appears to be more efficient for TLX degradation in terms of COD, electrical energy cost, and anode efficiency than the Pt electrode. Indeed, a low value of the anode efficiency indicates the difficulty of the electrode in degrading an organic compound. In summary, we can say that the

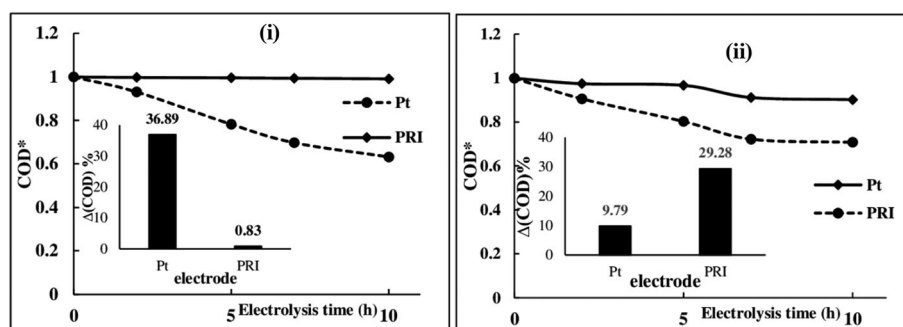


FIGURE 9 (i) Electrolysis of AMX = 1 g/L on Ti/Ta<sub>2</sub>O<sub>5</sub>/Pt and Ti/Ta<sub>2</sub>O<sub>5</sub>/PRI electrodes in 0.1-M KClO<sub>4</sub> at 20 mA/cm<sup>2</sup>. Cathode: zirconium;  $T = 25^{\circ}\text{C}$ ;  $t = 10$  h. Insert: COD abatement rate of the AMX degradation on Ti/Ta<sub>2</sub>O<sub>5</sub>/Pt and Ti/Ta<sub>2</sub>O<sub>5</sub>/PRI electrodes.

(ii) Electrolysis of TLX = 1 g/L on Ti/Ta<sub>2</sub>O<sub>5</sub>/Pt and Ti/Ta<sub>2</sub>O<sub>5</sub>/PRI electrodes in 0.1-M KClO<sub>4</sub> at 20 mA/cm<sup>2</sup>; cathode: zirconium;  $T = 25^{\circ}\text{C}$ ;  $t = 10$  h. Insert: COD abatement rate of the TLX degradation on Ti/Ta<sub>2</sub>O<sub>5</sub>/Pt and Ti/Ta<sub>2</sub>O<sub>5</sub>/PRI electrodes



efficiency of the electrooxidation process of an organic compound depends on the anode material used in our experimental conditions.

## 4 | CONCLUSION

This work aimed to show that the efficiency of an anode can depend on experimental conditions. To do this, the shelf life, the effect of chloride ions, the effect of the support medium, and the influence of the organic compound were investigated. COD removal, CE, SEC, electrical energy cost, and anode efficiency ( $\eta$ ) were evaluated. The electrochemical characterization allowed us to show that the Ti/Ta<sub>2</sub>O<sub>5</sub>/Pt-RuO<sub>2</sub>-IrO<sub>2</sub> electrode exhibits the characteristics of platinum and oxides (RuO<sub>2</sub> and IrO<sub>2</sub>). In addition, it has a service life six times longer than that of Ti/Ta<sub>2</sub>O<sub>5</sub>/Pt. The deactivation of the Pt electrode is manifested by detachment of the platinum from the titanium. In the case of the deactivation of the PRI electrode, it manifests itself, first, by a departure of the platinum from the surface of the electrode which would be followed by the dissolution of the oxides. In bulk electrolysis, both electrodes lead to the conversion of the parent compounds. However, the Pt electrode was best suited for amoxicillin (AMX) electrooxidation with 36.89% by COD removal, CE of 13.98%, SEC of 187.27 kWh/kg COD, and an electrical energy cost of 31.84 US \$ in KClO<sub>4</sub> 0.1 M. In the same experimental conditions, PRI electrode allowed to 0.83%, 0.34%, 7142.86 kWh/kg COD, and 1214.29 US \$, respectively, of COD removal rate, CE, SEC, and electrical energy cost. Besides, the PRI electrode provided the best performances for the AMX electrooxidation (8.15%) and Télébrix (TLX) (29.28% and  $\eta = 5.86$  g COD/Ah m<sup>2</sup>) in HClO<sub>4</sub> 0.1 M and KClO<sub>4</sub> 0.1 M, respectively. The presence of NaCl enhanced significantly the organic compound electrooxidation in terms of the COD removal, CE, SEC, cost energy, and  $\eta$  of the both electrodes. This is probably because of the co-action of direct and indirect (by active chlorine) oxidations. But the PRI electrode presented the best performance, in the presence of chloride ions, because it has the highest COD removal rate (73.79%), the highest CE (54.90%), the lowest SEC (26.81 kWh/kg COD), and the lowest electrical energy cost (4.56 US \$). In conclusion, the experimental conditions can determine the performance of an anode.

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