

Electrochemical behavior of paracetamol on Thermally Prepared Ti/Ta₂O₅/50Pt-50RuO₂ Electrode

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Abstract: Paracetamol (PCM), one of the most consumed drugs globally, is found in the environment, domestic wastewater, and hospital wastewater. Our objective is to electrochemically oxidize paracetamol using a ruthenium dioxide modified platinum electrode (Ti/Ta₂O₅/50Pt-50RuO₂). This study was carried out using physical characterization (Scanning electron micrographs) and interpretation of cyclic voltammograms. Platinum (Ti/Ta₂O₅/Pt), ruthenium dioxide (Ti/Ta₂O₅/RuO₂) and platinum – ruthenium dioxide (Ti/Ta₂O₅/50Pt-50RuO₂) electrodes have been prepared thermally at 400°C on sandblasted titanium modified Ta₂O₅ substrate. The scanning electron micrographs characterization showed that Ti/Ta₂O₅/50Pt-50RuO₂ electrode surfaces contain Pt and RuO₂. The surfaces of Ti/Ta₂O₅/Pt and Ti/Ta₂O₅/RuO₂ electrodes contain Pt and RuO₂, respectively. This work shows that PCM degradation was possible on Ti/Ta₂O₅/50Pt-50RuO₂ electrode with the faradic current on the voltammograms presence. In comparison to Ti/Ta₂O₅/Pt and Ti/Ta₂O₅/RuO₂ electrodes, this study showed that Ti/Ta₂O₅/50Pt-50RuO₂ electrode was more electrocatalytic for PCM electrooxidation. These results indicate that PCM degradation on this electrode can occur either by indirect catalytic oxidation involving adsorbed hydroxyl radicals or other oxidizing species produced in situ or by direct electron transfer to the electrode surface. The analysis of the peak currents and the peak potentials has revealed that the PCM electrooxidation process on this electrode attested to an irreversible character. Finally, the results proved that paracetamol electrooxidation on Ti/Ta₂O₅/50Pt-50RuO₂ electrode is associated with mixed control adsorption-diffusion. Oxidation proceeds by adsorption, then the transfer of two electrons to the electrode surface and a chemical transformation. The investigated process proceeded according to the EC mechanism.

Keywords: Platinum; Ruthenium dioxide; Paracetamol; Electrochemical oxidation.

1. Introduction

Paracetamol (N-acetyl-p-aminophenol or acetaminophen), one of the most widely consumed pharmaceuticals in the world, has been widely used to treat arthralgia, headache, fever, and chronic cancer pain ^{1,2}. It is used in various patients, including children, pregnant women, the elderly, and those with osteoarthritis, simple headaches, and non-inflammatory musculoskeletal diseases ^{3,4}. After oral administration of paracetamol (PCM), it undergoes a quick absorption and distribution in the whole body and can also be rejected quickly through urine ^{5,6}. Thus, PCM is found in the environment, domestic wastewaters, and hospital wastewater ^{7,8}. PCM wastewater has substantial negative impacts on human health, which would result in antibiotic-resistant, endocrine disruption, cancer, and several

chronic diseases ⁹. Therefore, wastewater containing PCM requires treatment.

Several methods have been used to remove PCM wastewater, including chemical oxidation ¹⁰, physical adsorption ¹¹ and biodegradation ¹², etc. Physical adsorption can only achieve the enrichment of pollutants rather than decomposition ¹³. Although biological processes are safe and green, high concentrations of PCM can inhibit microbial activity. By contrast, chemical oxidation is relatively fast and efficient for a high concentration of PCM; however, traditional chemical oxidation consumes more chemicals, resulting in secondary pollution ¹⁴. Especially as an environment-friendly advanced oxidation technology with easy implementation, environmental compatibility, and high efficiency, electrocatalytic oxidation technology can generate

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·OH radical in situ. No additional chemical reagent is required, capturing worldwide attention in refractory treatment and harmful organic contaminants¹⁵⁻¹⁷.

The degradation efficiency of organic pollutants in the electrochemical oxidation process strongly depends on the electrode materials^{18,19}. So, exploring a high-performance electrode with low cost, high activity, and excellent stability is crucial. Thus, the platinum electrode (Pt) is the ideal candidate due to its good electrical conductivity and resistance to corrosion^{20,21}. Besides its properties, platinum has efficiently been used in many fields such as electronics, fuel cells, and organic compound oxidation^{21,22}. However, its relatively high cost sometimes limits its use. Also, we have the dimensionally stable anodes (DSA), whose use for wastewater treatment has reduced operational and investment costs⁵. Moreover, DSA electrodes present high electrocatalytic activity, high stability against anodic corrosion, and a very high mechanical strength⁵. In order to solve the problem of the high cost of platinum, it appeared to us necessary to combine it with DSAs. Among DSAs, RuO₂ electrodes have shown good electrocatalytic activity for the oxidation of various organics⁵. For example, according to our previous work, the RuO₂ and Pt electrodes were able to oxidize paracetamol⁵. It was also shown that the mixture of molar ratio of 50% Pt and 50% metallic oxides such as IrO₂ and RuO₂ led to obtaining electrodes with better electrocatalytic activity and higher kinetics for OER (oxygen evolution reaction) and CER (chlorine evolution reaction)^{20,23,24}.

The electrodes properties depend strongly on the technique used in their manufacture. In the literature, methods such as screen-printing, Under Potential Deposition (UPD), current pulse deposition, microemulsion deposition in the water-oil mixture, sol-gel, and application of the precursor by brush followed by a thermal treatment²⁵⁻²⁹. The precursor application by brush followed by a thermal treatment to have a homogeneous dispersion of the deposits on the support. This is the most suitable method to obtain constant electrocatalytic properties on the whole surface of the electrode. Using this technique, we get electrodes with a very rough surface^{30,31}, allowing a large electrode/electrolyte contact surface. Thermal decomposition enables the preparation of anodes with high conductivity, high physical stability, and electrocatalytic anodes for industrial use, this technique was chosen for the electrode preparation^{5,32}.

Thus, our objective is to thermally prepare platinum (Ti/Ta₂O₅/Pt), ruthenium dioxide (Ti/Ta₂O₅/RuO₂), and platinum - ruthenium dioxide (Ti/Ta₂O₅/₅₀Pt - ₅₀RuO₂) electrodes for the electrochemical oxidation of PCM by cyclic voltammetry. Cyclic voltammetry is one of the essential electroanalytical techniques³³⁻³⁵. Its strength lies in the simplicity of its implementation and the richness of the information

collected to study redox processes. Therefore, it will be used in this work for the electrochemical characterization of the electrodes and the study of PCM oxidation.

2. Experiments

2.1. Materials

The electrodes were prepared using a furnace (ZYH-10) and an oven (ARGO LAB TCN 115). Electrodes prepared were characterized by scanning electron microscopy (SEM, ZEISS, SUPRA 40VP) and voltammetry measurements. Voltammetry measurements were performed with a three-electrode electrochemical cell using an Autolab PGStat 20 (Ecochemie). The counter electrode (CE) is a coiled platinum wire, the reference electrode (RE) is a saturated calomel electrode (SCE) and the working electrode is one of the prepared electrodes. The apparent surface area of electrodes in contact with electrolyte is equal to 1 cm². Chemicals such as potassium perchlorate (MERCK), sulfuric acid (SIGMA-ALDRICH), and potassium hydroxide (MERCK) were used in this work. In addition, Paracetamol (Laboratory BAILLY – CREAT) was purchased from a pharmacy in Abidjan. All the solutions used were prepared with distilled water and all the experiments were performed at 25°C.

2.2. Electrode preparation method

In this study, the electrodes were prepared thermally at 400°C. Metal precursor solutions such as H₂PtCl₆.6H₂O (SIGMA-ALDRICH), RuCl₃.3H₂O (ALDRICH) and TaCl₅ (ALDRICH) are dissolved in 10.0 mL of pure isopropanol (PANREAC) used as solvent^{5,20,23,24}. TaCl₅ precursor solution is applied with a brush on the surface of each sandblasted titanium substrate. Then the deposit was oven dried for 10 min at 80°C and then decomposed in a furnace at 400°C for 15 min. These steps were repeated three times so that the surface of titanium substrates was completely covered by Ta₂O₅. Then, the precursor solutions of H₂PtCl₆.6H₂O or/and RuCl₃.3H₂O were applied to the surface of the support with a brush and dried in an oven at 80°C for 10 min. After drying, the deposit was treated in a furnace for 15 min at 400°C. These steps were repeated 3 times to ensure that the deposit covered the entire surface of our support. Finally, a final decomposition is performed at 400°C for 1 h. The dimensions of the titanium support used are 1.6 cm x 1.6 cm x 0.5 cm.

The electrodes prepared in this study are platinum (Ti/Ta₂O₅/Pt), ruthenium dioxide (Ti/Ta₂O₅/RuO₂) and platinum-ruthenium dioxide (Ti/Ta₂O₅/₅₀Pt - ₅₀RuO₂) electrodes. For Ti/Ta₂O₅/₅₀Pt - ₅₀RuO₂ electrode, a mixture of a 50% molar ratio of H₂PtCl₆.6H₂O and RuCl₃.3H₂O was used. The mass of the realized deposit is about 5.0 g/m² for each electrode.

3. Results and Discussion

3.1. Characterization of electrodes

Scanning electron micrographs (SEM) of platinum, ruthenium dioxide and platinum–ruthenium dioxide deposited on sandblasted titanium modified Ta_2O_5 substrate are presented in Figure 1. These images were made with a magnification scale of 5.000. These micrographs indicate that sandblasted titanium-modified Ta_2O_5 substrate seems to have its surface entirely covered by the deposit. SEM of platinum electrode surface shows a relatively smooth and uniform surface with small cracks (Figure 1a). The cracks observed on platinum produced electrodes

during rapid cooling of the deposit. This observation is due to the temperature difference between the inside of the furnace and outside ^{36, 37}.

Ruthenium dioxide electrode surface has cobblestones and high size cracks (Figure 1b). RuO_2 surface also shows cell presence that would increase the porosity of the electrode ³⁸. In Figure 1c, the prepared $_{50}Pt-_{50}RuO_2$ electrode is shown, and its surface has a rough structure and aggregates probably related to platinum. The presence of high size cracks and cobblestones indicates the ruthenium dioxide presence in the deposit. These observations suggest that the surface of the $_{50}Pt-_{50}RuO_2$ electrode is composed of platinum and ruthenium dioxide.

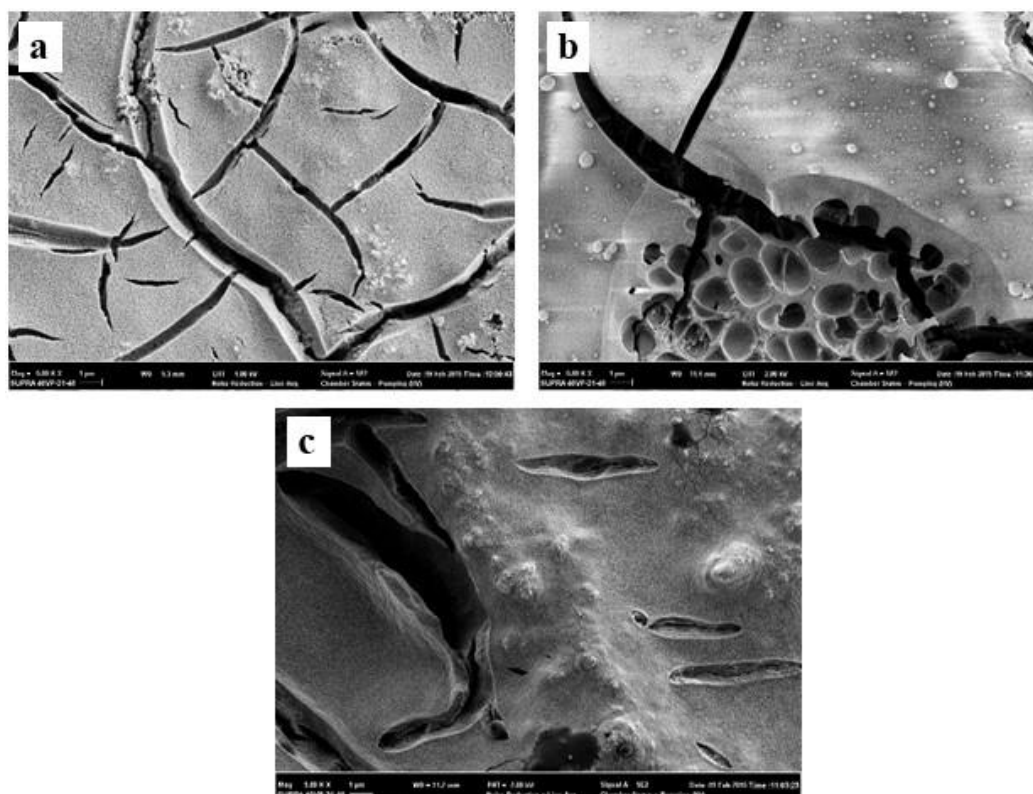


Figure 1. Scanning electron micrographs of Ti/ Ta_2O_5 /Pt (a), Ti/ Ta_2O_5 / RuO_2 (b) and Ti/ Ta_2O_5 / $_{50}Pt-_{50}RuO_2$ (c) electrodes

In Figure 2, the voltammograms realized in 0.1 M potassium perchlorate electrolyte under a potential scan rate of 8 mV/s on the prepared electrodes were presented. The measurement performed on the ruthenium dioxide electrode shows the same shape as that obtained in the literature ⁵. In the potential forward scan, an almost constant current is observed in the range of -0.2 to 0.4 V. Then there is a slow increase in current from 0.4 to 1.1 V, which would be linked to a higher degree of oxide (RuO_3) formation. Compared to Ti/ Ta_2O_5 / RuO_2 electrodes, Ti/ Ta_2O_5 /Pt and Ti/ Ta_2O_5 / $_{50}Pt-_{50}RuO_2$ electrodes have a lower voltammetric charge. This large voltammetric charge observed on Ti/ Ta_2O_5 / RuO_2 electrode is generally characteristic of thermally prepared DSAs ³⁹. The large voltammetric charge of the Ti/ Ta_2O_5 / RuO_2

electrode may be associated with the pseudo-capacitive reactions and the presence of pores and cracked cells observed in the SEM image, which increased the number of active electrode sites on the surface. The voltammograms of Ti/ Ta_2O_5 /Pt and Ti/ Ta_2O_5 / $_{50}Pt-_{50}RuO_2$ electrodes show the same shape. This attests to the presence of platinum in Ti/ Ta_2O_5 / $_{50}Pt-_{50}RuO_2$ deposit. On the other hand, Ti/ Ta_2O_5 / $_{50}Pt-_{50}RuO_2$ electrode has a higher voltammetric charge than Ti/ Ta_2O_5 /Pt. This proves the presence of ruthenium dioxide in the Ti/ Ta_2O_5 / $_{50}Pt-_{50}RuO_2$ layer. OER starts almost at the same potential on Ti/ Ta_2O_5 / RuO_2 and Ti/ Ta_2O_5 / $_{50}Pt-_{50}RuO_2$ (1.1 V/ECS), while it starts at 1.12 V/ECS on platinum.

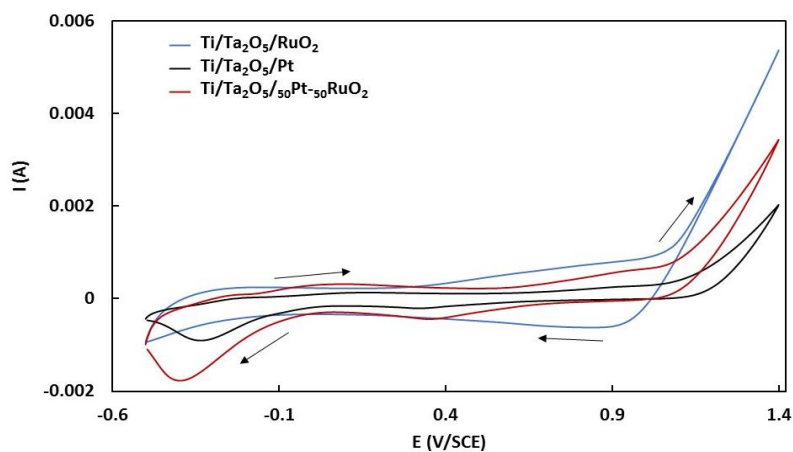


Figure 2. Cyclic voltammograms recorded at various electrodes in 0.1 M KClO_4 at potential scan rate: 8 mV/s, CE: Pt, ER: SCE, $T = 25^\circ\text{C}$

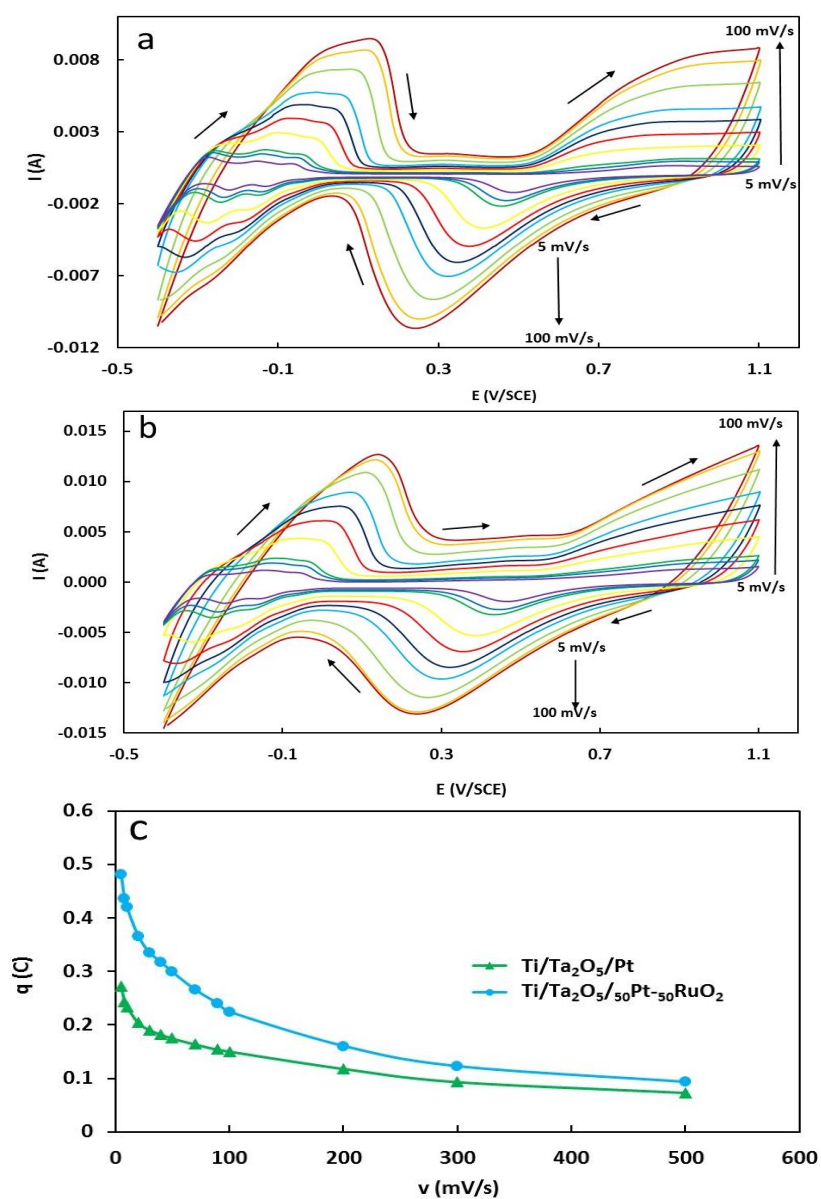


Figure 3. Voltammograms carried out at different potential scan rates in 0.1 M H_2SO_4 on $\text{Ti}/\text{Ta}_2\text{O}_5/\text{Pt}$ (a) and $\text{Ti}/\text{Ta}_2\text{O}_5/_{50}\text{Pt}-_{50}\text{RuO}_2$ electrodes (b). Evolution of the voltammetric charge as a function of the potential scan rate (c)

Voltammetric measurements were also performed on Ti/Ta₂O₅/Pt and Ti/Ta₂O₅/50Pt-50RuO₂ electrodes stabilized by the phenomenon of hydration in the potential domain between -0.4 and 1.1 V/SCE by varying the potential scan rates (5, 8, 10, 20, 30, 40, 50, 70, 90, 100 mV/s). Figures 3a and 3b show the obtained results. The general aspect of the voltammograms is the same, regardless of the potential scan rate

The electrochemical activity of the electrodes was characterized by determining the voltammetric charge *q* between hydrogen evolution and oxygen evolution. The charge *q* is determined by integrating voltammograms between -0.4 and 1.1 V/SCE. Total voltammetric charge *q* is plotted against the potential scan rates (Figure 3c). Figure 3c displays a rapid decrease of voltammetric charge for the low potential scan rates from 5 to 40 mV/s. This rapid decay stabilized at high potential scan rates. The fact could explain the dependence of the voltammetric charge with the potential scan rate of 40. There are some regions of the electrode surface containing active sites that are less accessible than others. The electrolyte gradually reaches these inaccessible active sites when the potential scan rates decrease, causing an increase in voltammetric charge. In fact, the high potential scan rates process taking place at the surface in the outer layer contributes to the voltammetric charge. In contrast, for the low potential scan rates, the process in the deposit's inner and outer layer is involved in the voltammetric charge determined. In the range of potential scan rate (5 to 500 mV / s), it is noted that the platinum–ruthenium dioxide electrode has a higher voltammetric charge than pure platinum. Therefore, Ti/Ta₂O₅/50Pt-50RuO₂ electrode has a higher electrochemical activity than the Ti/Ta₂O₅/Pt electrode. Pt and RuO₂ combination synergistically enhance the electrocatalytic properties of Ti/Ta₂O₅/Pt.

3.2. Electrochemical behavior of paracetamol on prepared electrodes

Figure 4 indicates the cyclic voltammograms obtained on the Ti/Ta₂O₅/50Pt-50RuO₂ electrode in the absence and in the presence of 2.0 g/L PCM at 8 mV/s scan rate in the potential range from -0.5 to 1.4 V/SCE. This figure reveals that only the current onset for the oxygen evolution reaction is visible in a potassium perchlorate medium without PCM. However, in PCM presence, we very clearly distinguish an increase in the current in the potential forward scan and various anodic and cathodic peaks. Indeed, this faradic current with these peaks is characteristic of PCM oxidation on this electrode.

In PCM presence, in the potential forward scan, a slow increase in current with a very low-intensity peak (0.442 mA) is observed in the potential range from -0.1 to 0.45 V/SCE at the potential of -0.02 V/SCE. Then from 0.45 V/SCE, there is a rapid increase in current followed by an oxidation peak at the potential of 0.825 V/ECS with a current intensity of 3.16 mA and an oxidation wave. These peaks are characteristic of the electrochemical oxidation of PCM on Ti/Ta₂O₅/50Pt-50RuO₂⁴¹. As a result, OER starts at a higher potential (1.34 V/SCE) compared to that obtained in PCM (1.1 V/SCE) absence. This increase in the OER potential would probably be linked to a phenomenon of adsorption of the reaction products on the active sites of the Ti/Ta₂O₅/50Pt-50RuO₂ electrode, reducing the kinetics of OER. In the backward potential scan, there is a shift in the platinum oxide reduction peak potential from 0.31 to 0.28 V/SCE. Also, we note an intensity peak presence of -1.07 mA at meager potential (-0.235 V/SCE) on the backward potential scan. This reduction peak could be characteristic of species reduction produced during the oxidation process. It should be noted that the anodic peaks reflecting the oxidation of PCM appear in the stability range of the supporting electrolyte. Therefore, we can deduce that there is a direct electron transfer between Ti/Ta₂O₅/50Pt-50RuO₂ electrode and PCM during paracetamol oxidation.

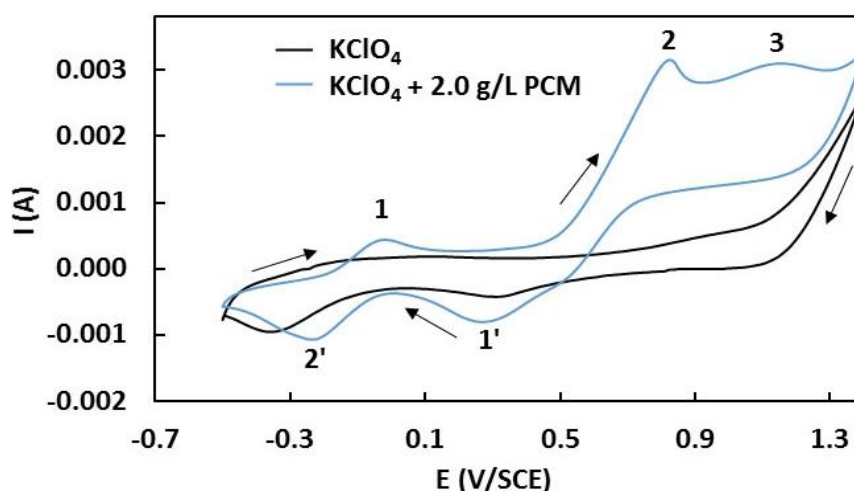


Figure 4. Cyclic voltammograms of Ti/Ta₂O₅/50Pt-50RuO₂ electrode in the absence and the presence of PCM 2.0 g/L in 0.1 M KClO₄ medium under the potential scan rate: 8 mV/s, CE: Pt, RE: SCE, T= 25°C

An effect of electrode material used as the anode for PCM electrooxidation was investigated. Figure 5 shows the voltammograms recorded on the different electrodes (Ti/Ta₂O₅/Pt, Ti/Ta₂O₅/RuO₂, and Ti/Ta₂O₅/50Pt-50RuO₂) in KClO₄ medium in the presence of PCM. In Figure 5, we note that Ti/Ta₂O₅/Pt and Ti/Ta₂O₅/50Pt-50RuO₂ electrodes have similar characteristics against to PCM oxidation. PCM oxidation is easier on pure ruthenium dioxide than on pure platinum, with a higher peak current on ruthenium dioxide than on pure platinum. But this oxidation starts faster on pure platinum ($E_{p2} = 0.740$ V/ECS) than on pure ruthenium dioxide ($E_{p2} = 0.810$ V/ECS).

Indeed, the metal dioxide (RuO₂) addition to platinum seems to improve by a synergistic effect of the

electrocatalytic properties of the Ti/Ta₂O₅/50Pt-50RuO₂ electrode for the oxidation PCM (2.0 g/L). This results in a higher oxidation peak current on Ti/Ta₂O₅/50Pt-50RuO₂ electrode ($i_{p2} = 3.16$ mA) compared to Ti/Ta₂O₅/Pt ($i_{p2} = 1.28$ mA) and Ti/Ta₂O₅/RuO₂ ($i_{p2} = 1.56$ mA). These results are in agreement with the work of Kambiré et al. ²⁴.

For a potential of 1 V/ECS we have recorded the current and represented it as an electrode function (in the inset Figure 5). Therefore, we can classify these electrodes according to the increasing order of the electrocatalytic power for PCM oxidation of Ti/Ta₂O₅/Pt < Ti/Ta₂O₅/RuO₂ < Ti/Ta₂O₅/50Pt-50RuO₂. Thus, the Ti/Ta₂O₅/50Pt-50RuO₂ electrode will be retained for the study of the electrochemical oxidation of PCM.

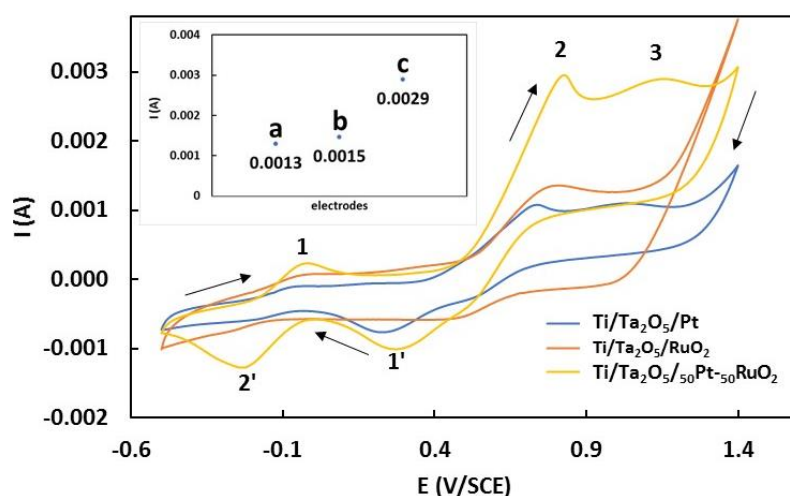


Figure 5. Cyclic voltammograms of PCM (2.0 g/L) recorded at various electrode materials in 0.1 M KClO₄ at 8 mV/s, CE: Pt, ER: SCE, T = 25°C. Inset: current as a function of the electrodes (Ti/Ta₂O₅/Pt (a), Ti/Ta₂O₅/RuO₂ (b) and Ti/Ta₂O₅/50Pt-50RuO₂ (c))

3.3. Influence of paracetamol concentration

Figure 6 shows the voltammetric curves recorded on the Ti/Ta₂O₅/50Pt-50RuO₂ electrode at 8 mV/s in

KClO₄ medium, by varying the paracetamol concentration (0, 0.5, 1.0 and 2.0 g/L).

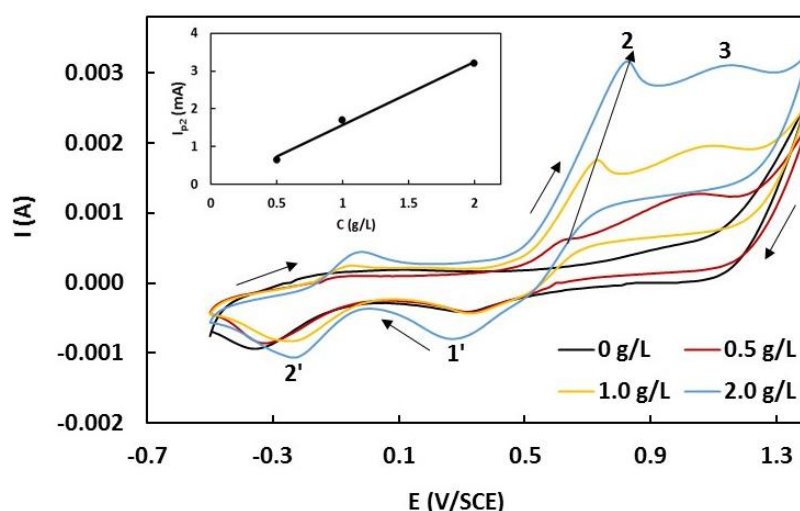


Figure 6. Cyclic voltammetry recorded on Ti/Ta₂O₅/50Pt-50RuO₂ electrode in several concentrations of PCM containing 0.1 M KClO₄ electrolyte at 8 mV/s, CE: Pt, RE: SCE, T = 25°C. Inset: plot of the current density of the second PCM oxidation peak versus PCM concentration

The recorded voltammograms relate the shapes similarly. It is noted that currently recorded PCM presence is low compared to that obtained in PCM absence in the high potential range for low concentrations of PCM (0.5 M). This result indicates the contribution to paracetamol oxidation of oxidative species resulting from the chemical decomposition of water at high potential⁴¹. In Figure 6, peak 2 and the wave of PCM oxidation observed appear in the potential domain where platinum oxide is formed^{20,24}. Hence, PCM oxidation could result from the participation of hydroxyl radicals $\bullet\text{OH}$ adsorbed in the process. Peak current 2 evolution as a function of concentration has been studied. The result obtained is presented in the inset of Figure 6. Peak 2 grows linearly with the concentration while describing a straight line ($R^2 = 0,992$). In this case, the observed peaks are related to the presence of PCM, and this electrode can be used for a quantitative determination of paracetamol in the medium⁴². These results

indicate that PCM degradation on this electrode can occur either by indirect catalytic oxidation involving adsorbed hydroxyl radicals or other oxidizing species produced in situ or by a direct paracetamol oxidation mechanism, i.e., direct electron transfer to the electrode surface. Furthermore, for concentrations up to 2.0 g/L, there is no polymerization of the electrode surface, leading to its partial deactivation.

3.4. Influence of the potential scan rates

The potential scan rate is a significant parameter affecting the electrooxidation of several organic compounds. Thus, the influence of the potential scan rate on PCM electrooxidation was studied. Figure 7 presents the potential scan rate effect on the peaks observed during PCM electrochemical oxidation on Ti/Ta₂O₅/50Pt-50RuO₂ electrode. The measurements were carried out in the potential range from -0.5 to 1.4 V/SCE in the presence of paracetamol (2.0 g/L) in 0.1 M KClO₄.

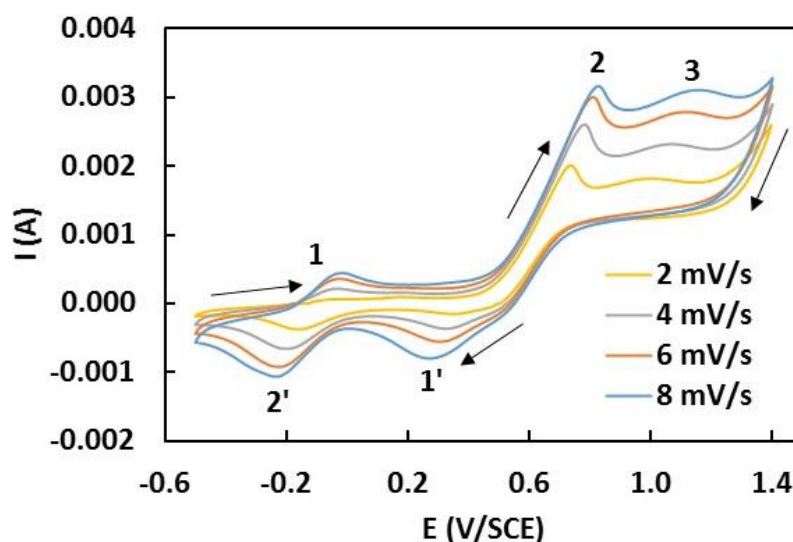


Figure 7. Cyclic voltammetry curves recorded on Ti/Ta₂O₅/50Pt-50RuO₂ electrode in 2.0 g/L PCM containing 0.1 M KClO₄ electrolyte at several potential scan rates, CE: Pt, RE: SCE, T= 25°C

Figure 7 displays that the intensity of the different oxidation peaks increases with the scan rate. It is also noted that the intensity of the reduction peaks observed on the backward scan increases in absolute value with the potential scan rate. The peaks 1 and 2' present in a potential range between -0.5 and 0.2 V/SCE are quasi-symmetric. The evolution of these peaks with scan rate suggests the presence of a redox couple, the benzoquinone/hydroquinone couple, during the oxidation of PCM. The relationships between anodic and cathodic peak potentials with scan rate are shown in Figure 8. If the electrochemical reaction is reversible, so the peak potentials are independent of scan rate. In our study, the oxidation peak potential shifts towards positive values when the scan rate increases, while the reduction peak potential shifts towards negative values. This result shows that the PCM

electrooxidation process on this electrode tends towards a character that is either irreversible or quasi-reversible⁴¹.

For the determination of the limiting step, i.e., the reactions controlled by adsorption, diffusion, or adsorption-diffusion, it is necessary to analyze the dependence: $i_p = f(v^{1/2})$ et $\ln(i_p) = f(\ln v)$. If the reaction at the electrode is controlled by diffusion, so $i_p = f(v^{1/2})$ is linear and intercepts the origin. And if this dependence does not intercept the origin of the axes, the reaction can be controlled by adsorption^{41,43-45}. Moreover, when $\ln(i_p) = f(\ln v)$ is linear, its slope gives us information about the character of the reaction. For a slope equal to 0.5, the response is controlled by diffusion. It is controlled by adsorption if the slope is 1⁴⁵. Figure 9 shows the oxidation and reduction peak currents as a function of the square root of the potential scan rate.

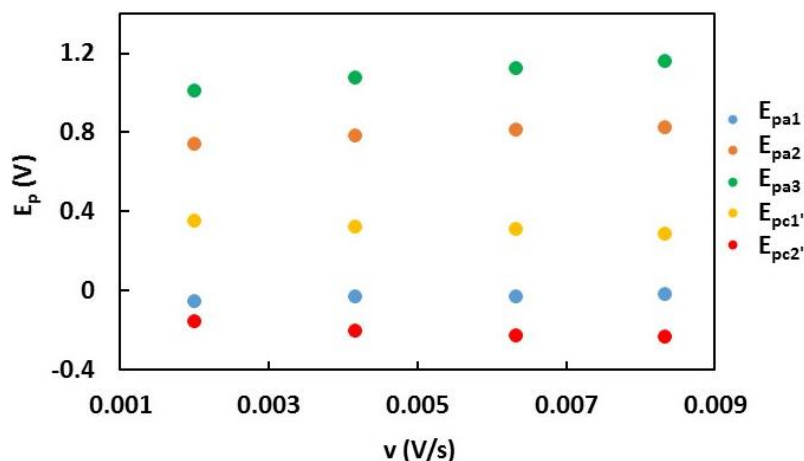


Figure 8. Potential for oxidation (E_{pa}) and reduction (E_{pc}) peaks as a function of potential scan rate (v) for the electrooxidation of 2.0 g/L PCM on Ti/Ta₂O₅/50Pt-50RuO₂ electrode in 0.1 M KClO₄ medium

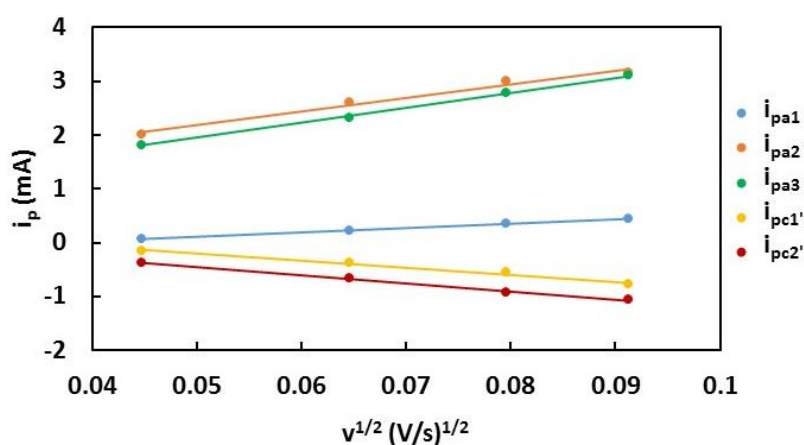


Figure 9. The oxidation peak (i_{pa}) and reduction peak (i_{pc}) currents as a function of the square root of scan rate ($v^{1/2}$) for the electrooxidation of 2.0 g/L PCM on Ti/Ta₂O₅/50Pt-50RuO₂ electrode in 0.1 M KClO₄ medium

It appears in [Figure 9](#) that the anodic and cathodic peak currents recorded during paracetamol

electrochemical oxidation are linearly dependent on the scan rate square root. These peak currents are described by the following equations:

$$i_{pa1} \text{ (mA)} = 8.2891 v^{1/2} \text{ (V/s)}^{1/2} - 0.3095 ; \quad R^2 = 0.9979 \quad (1)$$

$$i_{pa2} \text{ (mA)} = 25.232 v^{1/2} \text{ (V/s)}^{1/2} + 0.9269 ; \quad R^2 = 0.9826 \quad (2)$$

$$i_{pa3} \text{ (mA)} = 27.878 v^{1/2} \text{ (V/s)}^{1/2} + 0.5560 ; \quad R^2 = 0.9986 \quad (3)$$

$$i_{pc1'} \text{ (mA)} = -13.585 v^{1/2} \text{ (V/s)}^{1/2} + 0.4834 ; \quad R^2 = 0.9755 \quad (4)$$

$$i_{pc2'} \text{ (mA)} = -15.162 v^{1/2} \text{ (V/s)}^{1/2} + 0.3072 ; \quad R^2 = 0.9977 \quad (5)$$

The curves of $i_p = f(v^{1/2})$ do not intercept the origin of the axes. Therefore, the reaction at the electrode would be controlled by adsorption. However, the linear dependence of $\ln(i_{pa})$ with $\ln(v)$ described by

the following equations does not confirm this hypothesis. [Figure 10](#) shows that the curves $\ln(i_p)$ as a function of $\ln v$ are straight lines.

$$\ln i_{pa1} \text{ (mA)} = 1.2074 \ln v \text{ (V/s)} + 5.0108 ; \quad R^2 = 0.9994 \quad (6)$$

$$\ln i_{pa2} \text{ (mA)} = 0.3248 \ln v \text{ (V/s)} + 2.7256 ; \quad R^2 = 0.9925 \quad (7)$$

$$\ln i_{pa3} \text{ (mA)} = 0.3761 \ln v \text{ (V/s)} + 2.9253 ; \quad R^2 = 0.9964 \quad (8)$$

The slopes obtained are 1.2074, 0.3248, and 0.3761, respectively, for oxidation peaks 1, 2, and 3. The last two values (0.3248 and 0.3761) being close to 0.5 suggest that the oxidation reaction at peaks 2 and 3 is

diffusion-driven. The value of 1.2074, close to 1 reflects that at peak 1, there is an oxidation reaction controlled by adsorption. Similarly, the evolution of $\ln(i_{pc})$ as a function of $\ln(v)$ translated by the

equations (9 and 10) gives slopes of 1.1509 and 0.7482. These values (1.1509 and 0.7482) show that

the reduction reactions observed at the peaks 1' and 2' are limited by adsorption.

$$\ln i_{pc1'} (\text{mA}) = 1.1509 \ln v (\text{V/s}) + 5.2723 ; \quad R^2 = 0.9983 \quad (9)$$

$$\ln i_{pc2'} (\text{mA}) = 0.7482 \ln v (\text{V/s}) + 3.6744 ; \quad R^2 = 0.9975 \quad (10)$$

These results indicate that an adsorption-diffusion phenomenon occurs during the electrooxidation reaction of PCM⁴⁵. $i_{pa2} / v^{1/2}$ representation of curve

as a function of the potential scan rate (v) allows a more advanced analysis of the electrochemical oxidation of PCM (Figure 11).

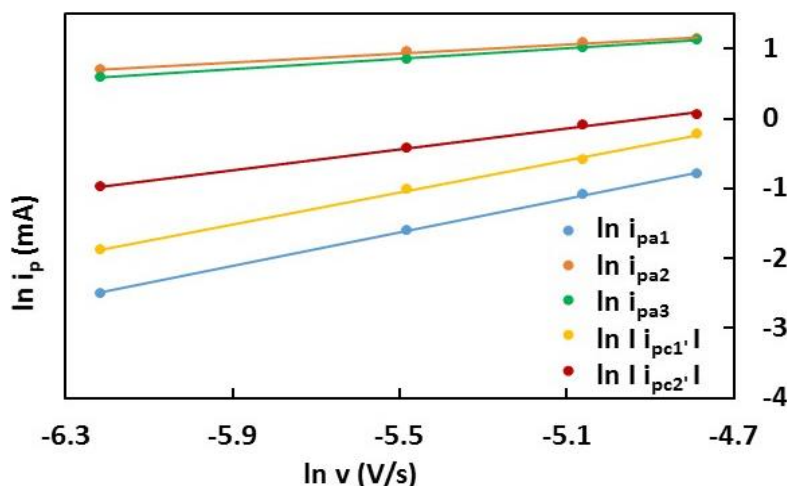


Figure 10. Logarithm of the peak oxidation (i_{pa}) and reduction (i_{pc}) currents as a function of the logarithm of the scan rate ($\ln v$) for the electrooxidation of 2.0 g/L PCM on Ti/Ta₂O₅/50Pt-50RuO₂ electrode in 0.1 M KClO₄ medium

Figure 11 clearly shows that the normalized peak current ($i_{pa2}/v^{1/2}$) depends on the potential scan rate. According to the literature, if an electrochemical process is reversible or irreversible without being preceded or followed by a chemical reaction, this dependence is not observed^{46,47}. The appearance of this graphical representation ($i_{pa2} / v^{1/2} = f(v)$) is

similar to that obtained in the case of an electrochemical-chemical mechanism (EC)⁴⁸⁻⁵¹. The oxidation at peak 2 is an electrochemical process that results in an electronic transfer to the electrode surface followed by the oxidation wave (peak 3), which would be a chemical transformation.

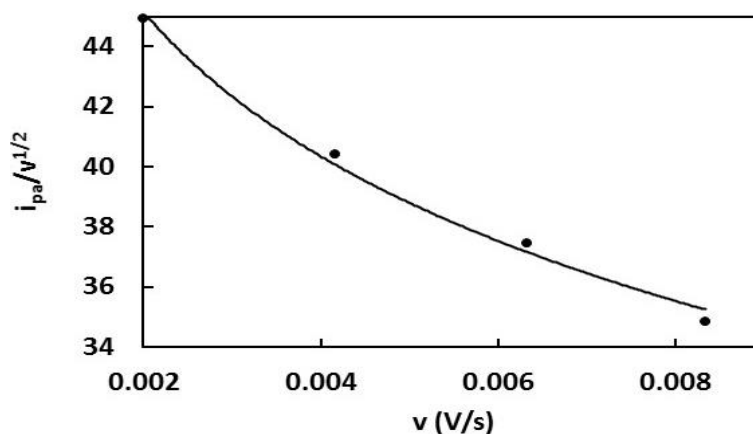


Figure 11. Variation of the scan rate normalized current ($i_{pa2} / v^{1/2}$) with scan rate for the oxidation of 2.0 g/L PCM on Ti/Ta₂O₅/50Pt-50RuO₂ electrode in 0.1 M KClO₄

The relationship between the peak potential E_{pa} and $\ln(v)$ is given by the Lavriron equation (equation 11)^{52,53}

$$E_{pa} = \left(\frac{RT}{\beta n_{\beta} F} \right) \ln v + \text{const} \quad (11)$$

Where E_p is peak potential (V), R -universal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), F -Faraday constant ($96,487 \text{ C.mol}^{-1}$), T -Kelvin temperature (28 K), βn_{β} -anodic transfer coefficient and v -scan rate (V.s^{-1}).

The curve representing E_{pa2} as a function of $\ln(v)$ (Figure 12) is given by the equation 12:

$$E_{pa2} = 0,0597 \ln v + 1,1131 \quad R = 0,9937 \quad (12)$$

By equalizing the slopes of equations 11 and 12 we obtain the anodic transfer coefficient βn_{β} equal to 0.43. According to Bard and Faulkner⁵⁴, we can calculate the electronic transfer coefficient β through the equation 13 :

$$\beta = \frac{47,7}{E_p - E_{p/2}} \text{ mV} \quad (13)$$

Where $E_{p/2}$ is the potential determined at half peak height. At 500 mV/min and for a peak current equal to $I_p = 3.161$ mA, we obtain $E_p = 825$ mV/SCE and $E_{p/2} = 620$ mV/SCE. Thus, the calculation of β leads to a value of 0.233. We can deduce from the calculations of βn_{β} and β that the number of electrons exchanged in the oxidation process equals $1.8 \approx 2$.

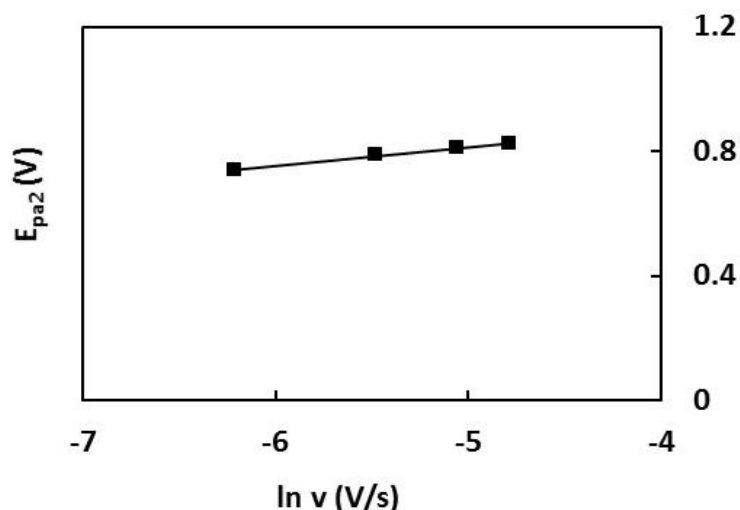


Figure 12. Oxidation peak potential 2 (E_{pa2}) as a function of the logarithm of the scan rate ($\ln v$) for the oxidation of 2.0 g/L PCM on Ti/Ta₂O₅/50Pt-50RuO₂ electrode in 0.1 M KClO₄ medium

4. Conclusion

The physical and electrochemical characterization showed that Ti/Ta₂O₅/50Pt-50RuO₂ electrode surfaces contain Pt and RuO₂. The surfaces of Ti/Ta₂O₅/Pt and Ti/Ta₂O₅/RuO₂ electrodes contain Pt and RuO₂, respectively. The surface of the prepared electrodes is porous and rough with a voltammetric charge which decreases with the scan rate. This study allowed us to show that the degradation of paracetamol is possible on Ti/Ta₂O₅/50Pt-50RuO₂ electrodes with a faradic current on the voltammograms. Compared with platinum and ruthenium dioxide electrodes, this study proved that the Ti/Ta₂O₅/50Pt-50RuO₂ electrode is more electrocatalytic for the electrooxidation of paracetamol. These results revealed that PCM degradation on Ti/Ta₂O₅/50Pt-50RuO₂ electrode could be done by indirect catalytic oxidation involving adsorbed hydroxyl radicals or other oxidizing species produced in-situ by a direct transfer of electrons to the surface of the electrode. Analysis of the peak currents and peak potentials obtained by varying the scan rate shows that the electrooxidation process of paracetamol on this electrode has an irreversible character. It is concluded that the electrooxidation of paracetamol on the Ti/Ta₂O₅/50Pt-50RuO₂ electrode is associated with a mixed adsorption-diffusion control. Oxidation proceeds by adsorption, followed by a transfer of two electrons to the surface of the electrode and a chemical transformation. In addition, the investigated process proceeds according to the EC mechanism.

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