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# Electrochemical Oxidation of the Paracetamol in its Commercial Formulation on Platinum and Ruthenium Dioxide Electrodes

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Pt and $RuO_2$ electrodes have been prepared thermally at 400°C on titanium substrates. The physical and electrochemical characterization showed that the surface of the platinum electrode is smooth, compact and almost homogeneous and that of $RuO_2$ is rough with a mud cracked structure. The voltammetric investigations revealed that the oxidation of the paracetamol occurs on both the prepared electrode. That organic oxidation occurs via a process that involves a direct electron transfer at the surface of the electrode and by an indirect oxidation process via $OH^{\cdot}$ species and possibly via other in situ redox species. On both the electrodes, the paracetamol oxidation process is diffusion controlled. In the presence of $Cl^-$, $NO_3^-$ or $PO_4^{3-}$ the oxidation of paracetamol still occurs via a direct electron transfer in the water stability domain and via an indirect oxidation routes in the higher potential domain by oxidative species resulting from the oxidation of $Cl^-$, $NO_3^-$ or $PO_4^{3-}$. The addition of such ions in the electrolyte increases the kinetic of the paracetamol oxidation. This increase is low for all the ions on $RuO_2$ electrode but it is high with $Cl^-$ or $NO_3^-$ on Pt and low with $PO_4^{3-}$. pH studies have revealed that the protonation form of the molecule undergoes a rapid oxidation than the deprotonated form on Pt. On $RuO_2$, the pH influence is very low compared to platinum electrode.

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**Keywords:** platinum, ruthenium dioxide, cyclic voltammetry, paracetamol oxidation.

## 1. INTRODUCTION

Paracetamol or N-acetyl-*p*-aminophenol is used to treat many diseases such as fever cough, cold, headache, toothache, muscular aches, backache, cancer pain, asthma, chronic pain, neuralgia etc. [1-4]. Recently, it was found from many researches that paracetamol can also be used to treat cardiovascular disease and can protect against ovarian cancer [5, 6]. After oral administration of paracetamol, it undergoes a quick absorption and distribution in the whole body and can also be rejected easily through urine [7]. Thus, the paracetamol is found in the environment, in the domestic wastewaters and in the hospitals wastewaters. The presence of the pharmaceuticals in the wastewater decreases the water quality and consequently causes a negative impact on the ecosystems and the human health [8-10]. For the oxidation or degradation of the pharmaceuticals, many techniques like biological degradation processes, Fenton reaction, ozonation, photocatalysis, sonication, irradiation or their combinations were used [11-14]. The choice of the type of the wastewater treatment to be used depends on the economics, the reliability and the treatment efficiency. Electrochemical methods have gained a great interest in that area because of the increased efficiencies that they can achieve. From literature, it appears that many works have been performed on the determination of paracetamol in various media using various electrodes [15-21] but less works have been performed on its degradation. Some attempts have been carried out such as that realized on zinc oxide modified glassy carbon where the electrode has shown good sensitivity response for paracetamol [22]. Platinum which is one on the most used electrodes in electrochemistry due to its high electrical conductivity and its chemical inertness [23] is generally used for pharmaceuticals determination. Very scarce works dealing with the oxidation of the paracetamol on platinum was found. The use of the dimensionally stable anodes (DSA) for the wastewater treatment has contributed in some works in reducing the operational and investment costs. Moreover, DSA electrodes presents high electrocatalytic activity, high stability against anodic corrosion and also a very high mechanical stability but its use for paracetamol oxidation is very scarce. Among DSAs, $RuO_2$ electrodes have shown good electrocatalytic activity for the oxidation of various organics. But its use for the paracetamol oxidation does not exist by our knowledge. In the current work, Pt and $RuO_2$ anode materials have been prepared thermally for the electrochemical oxidation of the paracetamol because such a technique leads to highly active catalysts [24]. The prepared electrodes have been physically and electrochemically characterized and applied in the following to the paracetamol degradation.

## 2. EXPERIMENTS

The electrodes used in the following work were all prepared in our laboratory with the appropriate metallic precursors. The coating precursors were prepared from $H_2PtCl_6,6H_2O$ (Fluka) and $RuCl_3,xH_2O$ (Fluka). All the precursors were dissolved separately in 10 mL of pure isopropanol (Fluka) used as solvent. The commercial products were used as received without any further treatment.

The titanium substrates, on which the deposit were performed, have the following dimension 1.6 cm x 1.6 cm x 0.5 cm. The surface of each substrate was sandblasted to ensure good adhesion of the deposit on it. After sandblasting, all the substrates were washed vigourously in water and then in isopropanol to clean their surface from residual sands. The substrates were then dried in an oven at 80 °C and weighed. After that, the precursor was applied by a painting procedure on the titanium substrate then put in an oven for 10 min at 80 °C to allow the solvent to evaporate. Then after, it is put in a furnace at 400 °C for 15 min to allow the precursor to decompose. These steps were repeated until the desired weight of the coating is reached. A final decomposition of 1 h was done at 400 °C. The electrodes prepared by this technique are platinum (Pt) and ruthenium dioxide ($RuO_2$) electrodes. The deposit loading was about 5 $g/m^2$ on each titanium substrate.

The physical characterization of the electrodes were performed using a scanning electronic microscopy (SEM, ZEISS, SUPRA 40VP) device.

The voltammetric measurements were performed on the prepared electrodes in a three-electrode electrochemical cell using an Autolab PGStat 20 (Ecochemie). The counter electrode (CE) was a platinum wire and the reference electrode (RE) was a saturated calomel electrode (SCE). To overcome the potential ohmic drop, the reference electrode was mounted in a luggin capillary and placed close to the working electrode by a distance of 1 mm. The apparent exposed area of the working electrode was 1 $cm^2$.

Products such as $KClO_4$ (Fluka), KCl (Fluka), $H_2KO_4P$ (Fluka) and $KNO_3$ (Prolabo) were used as received. All the solutions used for the electrochemical investigations in the current work have been prepared with distilled water.

## 3. RESULTS AND DISCUSSION

### *3.1. Physical Characterization of the prepared electrodes*

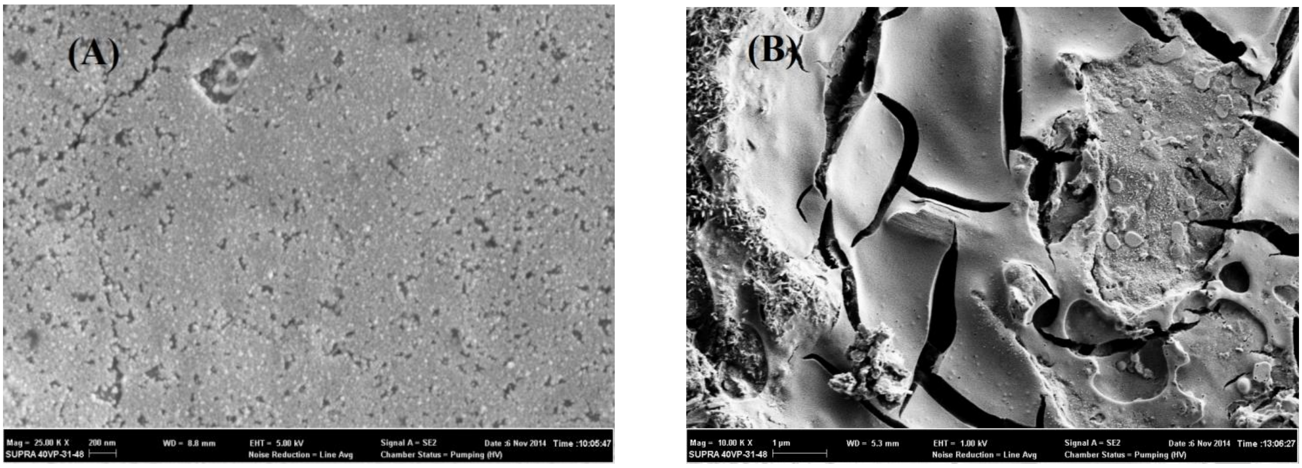


**Figure 1.** Scanning electron micrographs of (A) Pt and (B) $RuO_2$ electrodes

Figure 1 presents the micrographs of the prepared electrodes by the thermal decomposition of the appropriate metallic precursors indicating that the titanium substrate seems to have its surface totally covered by the deposit. The surface of the platinum electrode is smooth, compact and almost homogeneous. The surface of the $RuO_2$ electrode is rough with a mud cracked structure. That observation is similar to that is generally observed for thermally prepared $RuO_2$ electrode [25]. Pores are also present on the deposit. The cracks observed on the electrodes surfaces occur during the cooling of the deposit because of the thermal shock to which these deposits are subjected during their retreat from the furnace.

### *3.2. Electrochemical characterization of the prepared electrodes in $KClO_4$ medium*

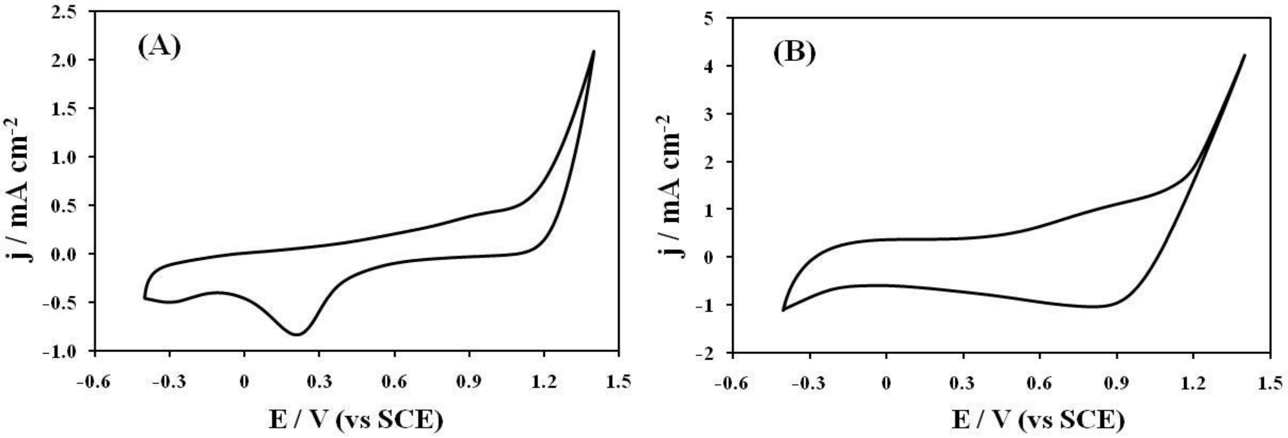


**Figure 2**. Cyclic voltammograms of (A) Pt and (B) $RuO_2$ in 0.1 M $KClO_4$ at the potential scan rate: 20 mV/s, CE: Pt, RE: SCE, T = 25°C

In Figure 2, the voltammograms realized in 0.1 M potassium perchlorate electrolyte under a potential scan rate of 20 mV/s on the prepared electrodes were presented. Figure 2A showed the usual feature generally observed with polycrystalline platinum in neutral media. The double layer region is characterized by an almost zero current in the forward potential scan followed by a weak oxide formation domain (0.7 V-1.12 V). An oxide reduction peak at 0.24 V (backward potential scan) is observed. A rapid increase in the current density related to oxygen evolution reaction started at 1.12 V. In figure 2B, the voltammograms recorded on $RuO_2$ electrode in $KClO_4$ 0.1 M showed that the current density is almost constant from - 0.2 to 0.4 V in the forward potential scan. From 0.4 to 1.1 V an increase of the current density is observed. The oxygen evolvement was observed by the rapid increase in the current density after 1.1 V. From those results, it appears that the reversible redox transition peaks usually observed in the acidic electrolytes in the potential domain starting from 0.15 V to 0.4 V are absent. Therefore, the presence of the anodic wave around 0.78 V is characteristic of an irreversible surface transition process. This finding reveals that protons play an important role in the reversibility of the electrode surface redox transition processes.

### *3.3. Effect of varying paracetamol concentrations*

Figure 3 presents the voltammetric curves recorded on Pt electrode under a scan rate of 20 mV/s in potassium perchlorate free or containing various concentrations of paracetamol.

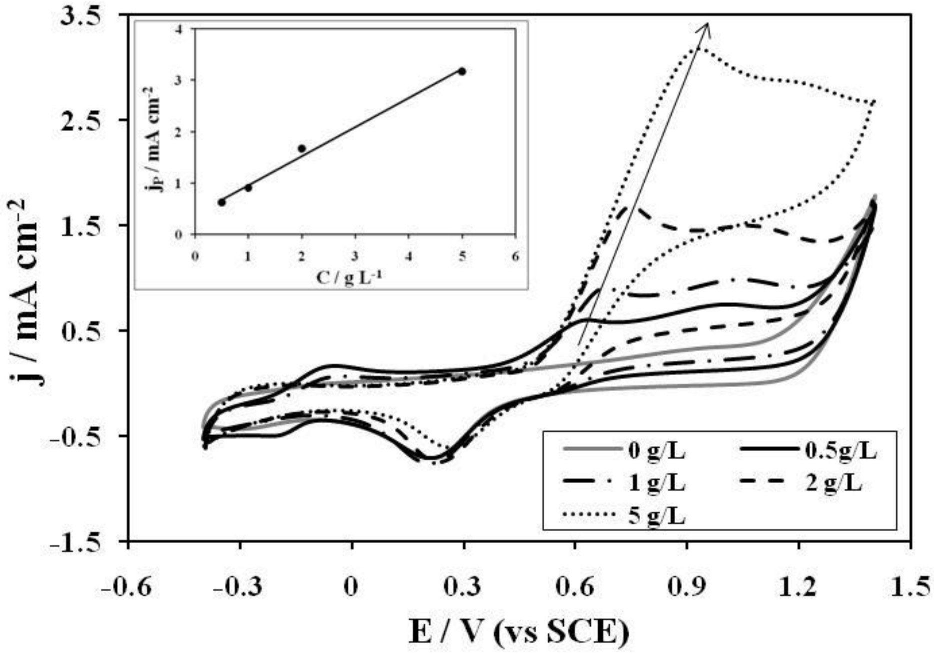


**Figure 3**. Cyclic voltammetry curves recorded on Pt electrode in several concentrations of paracetamol containing 0.1 M $KClO_4$ electrolyte under the potential scan rate: 20 mV/s, CE: Pt, RE: SCE, T= 25 °C. Inset: plot of current density of the first paracetamol oxidation peak versus paracetamol concentrations

In the presence of paracetamol which concentration was varied from 0.5 g/L to 2 g/L, a fast increase of the current density is observed around 0.42 V followed by two anodic peaks at 0.61 V and 1 V under 20 mV/s. Indeed, the fast increase of the current density and the appearance of the anodic peaks are characteristic of the oxidation of the paracetamol. That oxidation occurs in the domain of water stability via probably a direct electron transfer between platinum and paracetamol. As the concentration of the paracetamol increases, the oxygen evolution reaction potential is found to be higher than that recorded in the absence of the paracetamol. Moreover, in the higher potential domain, the recorded current intensity is lower in the presence of the paracetamol than in its absence. Such results revealed the involvement of species resulting from water discharged in the oxidation of paracetamol [26] in the higher potential domain. In figure 3, the paracetamol oxidation peaks appear in the potential domain where platinum oxide is formed. Thus, the oxidation of the paracetamol could result from the participation of adsorbed hydroxyl radicals $OH^{\circ}$ in the process. The current density of the first oxidation peak was studied according to the paracetamol concentration. The obtained results are presented in the inset of the figure 3. A straight line with a correlation coefficient of 0.992 was obtained. Such a result indicates that this electrode can be used to determine paracetamol quantitatively [27]. The second peak following the first oxidation peak could result from the oxidation of an intermediate that was produced at around 0.61V. According to the obtained results, one can indicate that paracetamol can be degraded via a catalytic oxidation mechanism that involved a direct oxidation of the paracetamol on the electrode surface i.e a direct electron transfer at the electrode surface and by an indirect oxidation via $OH^{\circ}$ species and possibly via other in situ redox species.

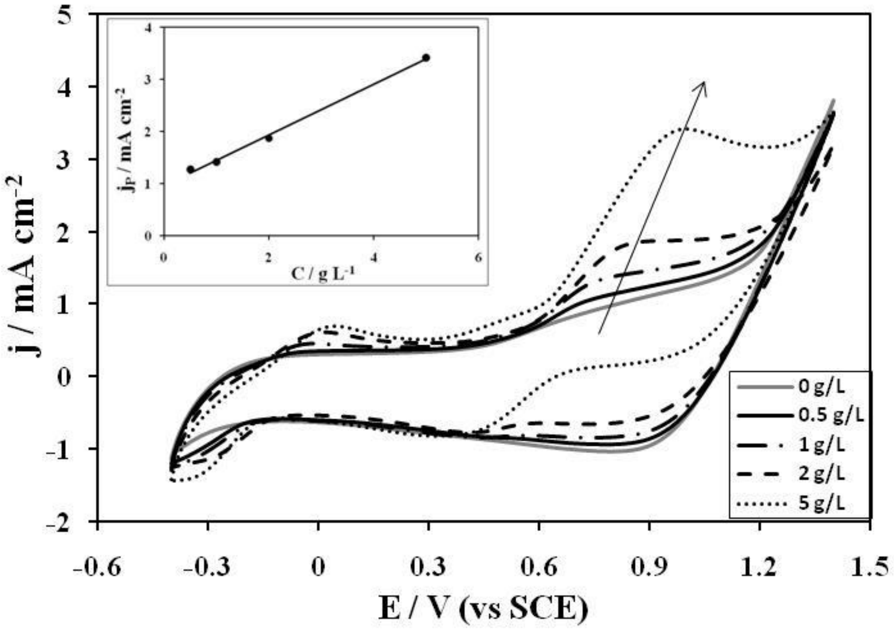


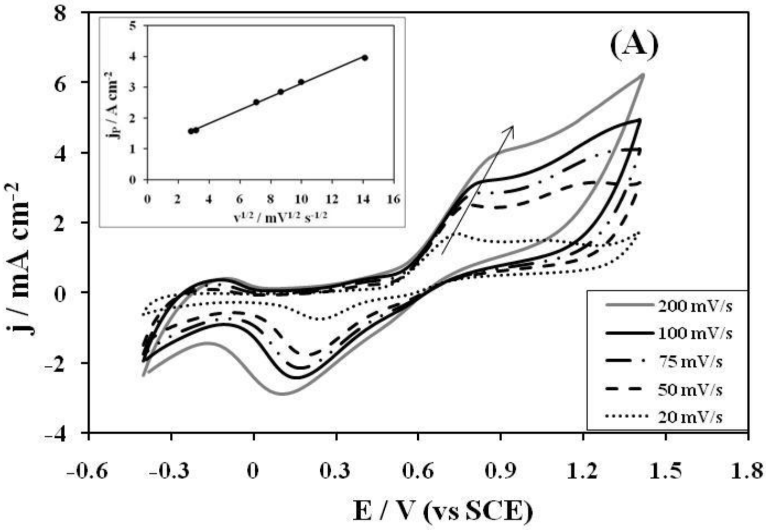
**Figure 4.** Cyclic voltammetry curves recorded on $RuO_2$ electrode in several concentration of paracetamol containing 0.1 M $KClO_4$ electrolyte at the potential scan rate: 20 mV/s, CE: Pt, T= 25 °C, RE: SCE. Inset: Plot of current density of the paracetamol oxidation peak versus paracetamol concentrations.

In the presence of paracetamol, a fast increase of current density is observed after 0.5 V on $RuO_2$ electrode (Figure 4). That increase of the current is followed by an oxidation wave in the forward potential scan. The waves observed for the low concentration become a peak as the concentration of paracetamol reaches 5 g/L in this work. On the $RuO_2$ electrode, it is also observed as in the case of the platinum electrode that the onset of the oxygen evolution reaction potential increases as paracetamol is added to the electrolyte indicating the involvement of water discharged species in the oxidation process. Figure 4 also shows that the oxidation current density wave increases with the paracetamol concentration. In the inset of figure 4, the oxidation current densities of the waves recorded at the shoulder at the beginning of the waves were plotted against the concentration of paracetamol. One observes a linear relationship of the current versus concentration (j vs. *C*) curve. This result showed that the oxidation waves observed are linked to paracetamol oxidation. Moreover, the smaller the concentration of the paracetamol, the quicker the diffusion control process is reached on such an electrode. The oxidation of paracetamol starts in the potential domain of water stability indicating a direct paracetamol oxidation process on $RuO_2$ electrode surface. In the higher potential domain, as the concentration of the paracetamol increases, a decrease of the current density is observed. That current decay could indicate the oxidation of paracetamol in this potential domain. Moreover, it could also highlight the competition between a direct and an indirect oxidation process of the paracetamol via the in situ formed adsorbed $OH^{\circ}$ radicals. According to the obtained results, one can indicate that the paracetamol can be degraded on $RuO_2$ electrodes via a catalytic oxidation mechanism that involved a direct oxidation of the paracetamol on the electrode surface and by an indirect oxidation via $OH^{\circ}$ species and possibly via some other in situ redox species.

Both the investigated electrodes seem to behave in the same manner. But Pt oxide seems to be more active than $RuO_2$. Under the investigated conditions, water undergoes discharged over the $RuO_2$ electrode surface leading to the formation of highly adsorbed hydroxyl radicals that immediately contribute to the oxidation of the $RuO_2$ surface forming a higher oxide $RuO_3$ [11]. On the investigated electrodes, in the backward of the potential scan, one notices the presence of a peak at around 0.28V related to the reduction of the paracetamol or its intermediate on Pt and the absence of such a peak on $RuO_2$. Such findings showed that the paracetamol oxidation process is quasireversible on Pt due to the high gap between the anodic and cathodic peaks and totally irreversible on $RuO_2$.

### *3.4. Effect of varying potential scan rates*

The effect of the potential scan rates were examined on the voltammetric responses of the prepared electrodes in 0.1 M $KClO_4$ containing 2 g/L of paracetamol (figure 5). This figure showed that the voltammetric charge increases with the potential scan rates for all the prepared electrodes. The oxidation peak current density of the paracetamol increases with the potential scan rate too. The paracetamol oxidation peak current density plotted against the square root of the potential scan rates are presented in the inset of figures 5AB. A linear evolution was obtained for both the Pt and $RuO_2$ electrodes. The slopes of the straight lines are about $2.15\times10^{-4}$ $mA.cm^{-2}.mV^{-1/2}.s^{1/2}$ with $R^2 = 0.998$ and $3.86\times10^{-4}$ $mA.cm^{-2}.mV^{-1/2}.s^{1/2}$ with $R^2 = 0.999$ for Pt electrode and the $RuO_2$ electrode respectively. That linear evolution of the $j_p$-$v^{1/2}$ curves indicate that the process is diffusion controlled [28, 29]. In case of platinum, in the backward of the potential scan, a peak located around 0.2 V increases as the potential scan rate increases. The presence of such a peak at around 0.2V indicates that the produced intermediates are reduced on the prepared platinum electrode as the potential is reversed. Moreover, the gap between the peaks is higher than 60 mV indicating the irreversibility character of the oxidation process. In case of $RuO_2$, in the backward of the potential scan, no reduction peak is observed but the cathodic current intensity increases with the potential scan rate. Such result indicates that the irreversibility of the paracetamol oxidation process is more pronounced on $RuO_2$.



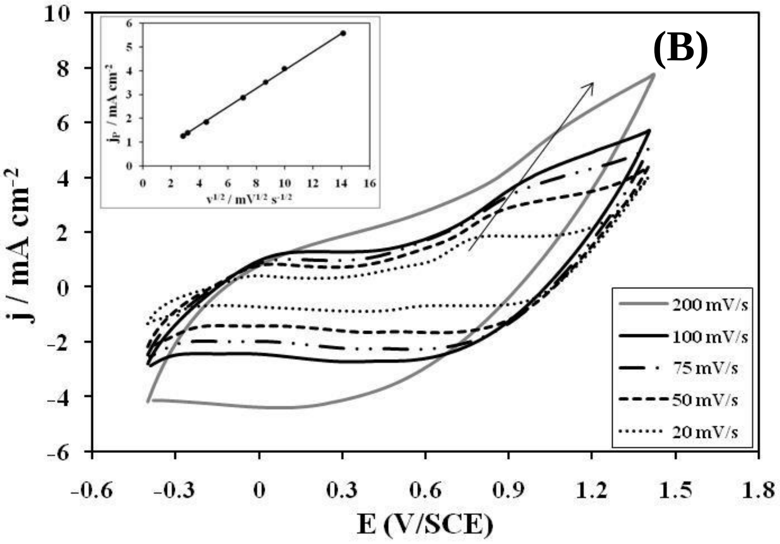
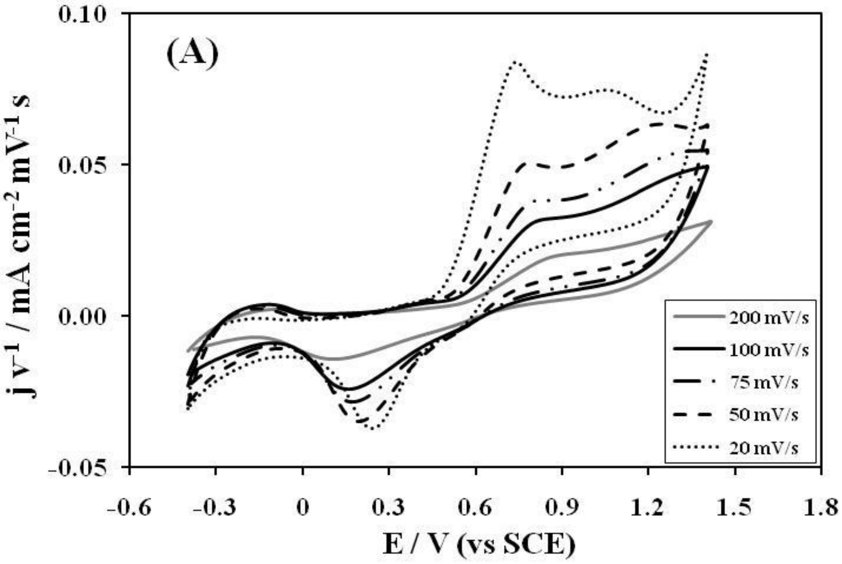


**Figure 5**. Cyclic voltammetry curves recorded on (A) Pt and (B) $RuO_2$ electrodes in 2 g/L paracetamol containing 0.1 M $KClO_4$ electrolyte at several potential scan rates (20-200 mV/s), CE: Pt, T= 25 °C, RE: SCE. In the inset: Evolution of the peak of current density against the square root of the potential scan rates.

In Figure 6, normalized current density, obtained through the ratio of the current density over the potential scan rates, were plotted against the applied potential on Pt and $RuO_2$ electrodes. In these figures 6A and 6B, as the potential scan rates increase, the capacitance decreases indicating that for the low potential scan rates, more electrode active sites intervene in the surface processes. It appears from those results that, on both the electrodes, for the high potential scan rates, few actives sites mainly those located at the electrode surface are involved in the pharmaceutical oxidation process. As the potential scan rate decreases, more actives sites, composed by those at the electrode surface and those in the pores, cracks of the electrode, are involved in the process.



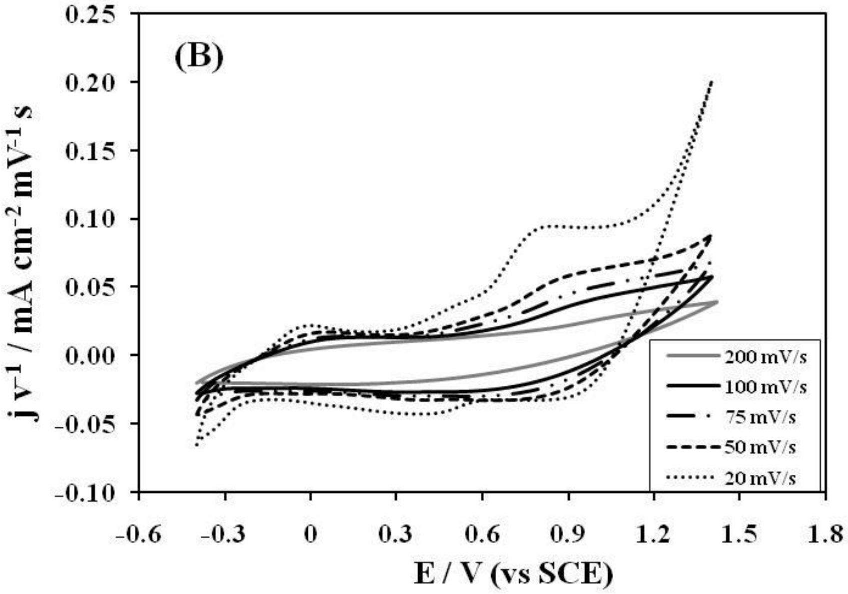


**Figure 6**. Normalized current density of the cyclic voltammetry measurement recorded on (A) Pt and (B) $RuO_2$ in 0.1 M $KClO_4$ containing 2 g/L paracetamol with the potential scan rates (20-200 mV/s) versus applied potential (j/v vs. E); CE: Pt, RE: SCE, T = 25°C.

### *3.5. Effect of temperature*

The effect of the temperature was studied on the oxidation process of the paracetamol on the prepared electrodes, Pt and $RuO_2$. The results are presented in Figure 7. The current density of the paracetamol oxidation peak increased gradually as the temperature is varied from 25 °C to 70 °C for each electrode. In the inset of Figures 7A and 7B, the logarithm of the current density of the paracetamol oxidation peak was plotted against the reciprocal of the temperature of the electrolyte. The obtained results show an almost linear evolution of $\ln(j_p)$ vs. 1/T. The characteristics of the straight lines are presented in Table 1:

**Table 1.** The characteristics of the straight lines $\ln(j_p)$ vs. 1/T

| Electrode | $\lvert Slope \rvert$ (K) | Ordinate (-) | $R^2$ |
|---|---|---|---|
| Pt | 1905 | 0.194 | 0.967 |
| $RuO_2$ | 1202 | 1.946 | 0.997 |

From those results, it appears that the kinetic of the paracetamol oxidation increases with the temperature on Pt and $RuO_2$. The activation energy determined are 229, 12 J/mol and 144, 57 J/mol on Pt and $RuO_2$ respectively. The figure 7 shows that the onset of the oxygen evolution reaction potential decreases when the temperature increases indicating an acceleration of that process with temperature. In fact, the increase of the oxidation process of paracetamol can be explained by the activation of more surface active sites for direct oxidation and also by the production of much more $OH^{\circ}$ radical in the high potential domain.

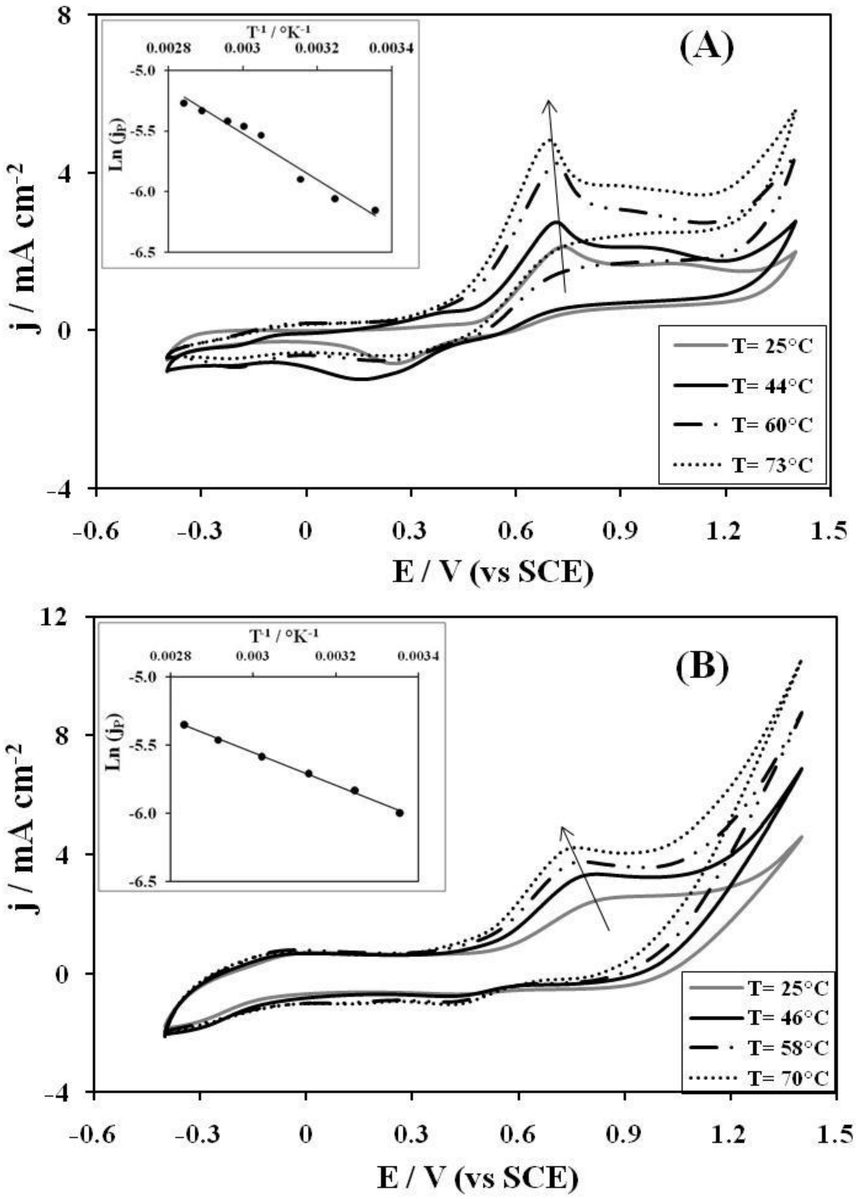


**Figure 7**. Cyclic voltammetry curves recorded on Pt and $RuO_2$ electrodes in 2 g/L of paracetamol containing 0.1 M $KClO_4$ electrolyte at several temperatures, CE: Pt, potential scan rate: 20 mV/s, RE: SCE. In the inset: Evolution of the current density peak against reciprocal of electrolyte temperature for the prepared electrodes.

### *3.6. Effect of* $Cl^-$, $NO_3^-$ *or* $PO_4^{3-}$

Figure 8 presents the results of the cyclic voltammetry measurements realized on Pt and $RuO_2$ electrodes in paracetamol containing $KClO_4$ electrolyte with $Cl^-$, $NO_3^-$ or $PO_4^{3-}$.

On the Pt electrode, one observes the presence of the paracetamol oxidation peak around 0.7 V/ECS in the absence of $NO_3^-$; $PO_4^{3-}$; $Cl^-$ and in their presence. In the higher potential domain, a rapid increase of the current occurs in the presence of $Cl^-$while only a slight increase was observed in the presence of $NO_3^-$; $PO_4^{3-}$.

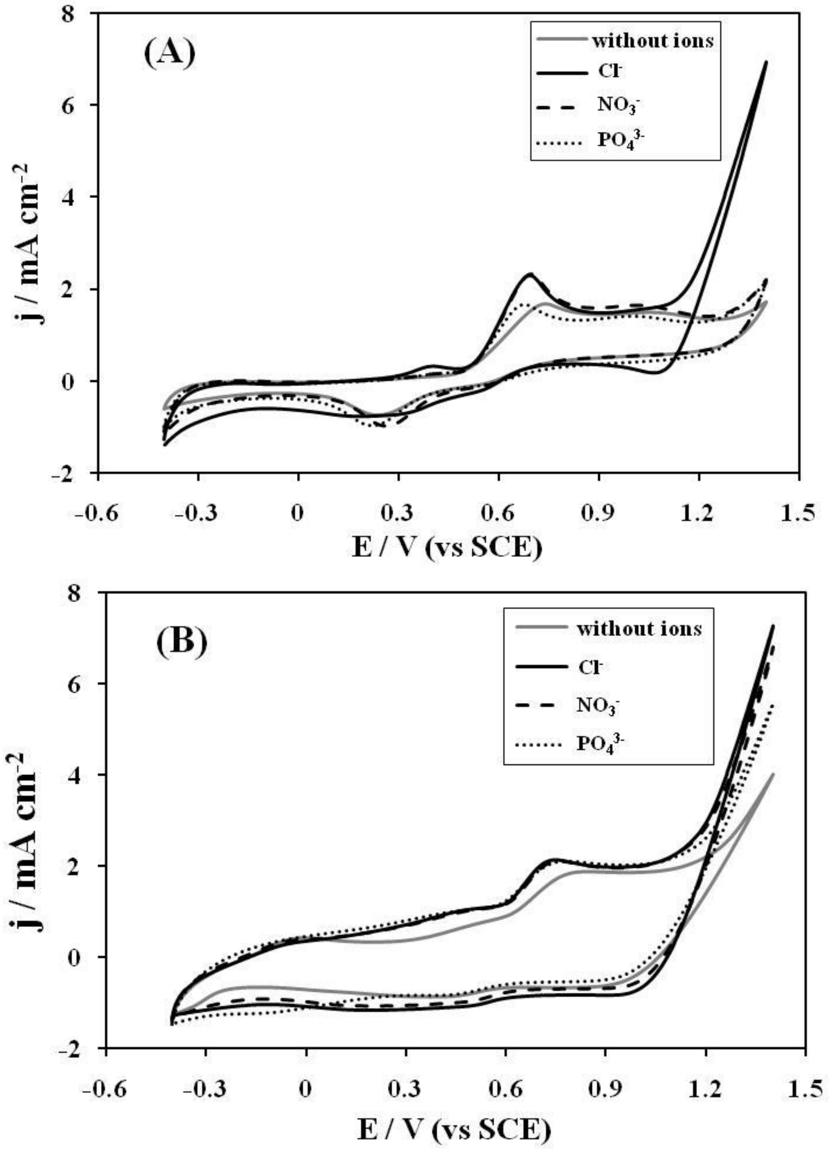


**Figure 8**. Cyclic voltammetry curves recorded on (A) Pt and (B) $RuO_2$ electrodes in 2 g/L of paracetamol containing 0.1 M $KClO_4$ electrolyte in the absence and in the presence of 0.1 M $Cl^-$, 0.1 M $NO_3^-$ or 0.1 M $PO_4^{3-}$, CE: Pt, RE: SCE, potential scan rate: 20 mV/s, T = 25°C

These results indicate that the paracetamol oxidation process occurs via a direct electron transfer process and indirectly via oxidative species resulting from those ions oxidation. On platinum, species resulting from the oxidation of chloride seem to contribute highly in the oxidation of the paracetamol. In fact, in the presence of chloride, local acidification at the electrode surface led to chloride formation at lower overpotential [28]. On $RuO_2$ electrode, all the three ions have almost the same effect on the paracetamol oxidation since the recorded voltammograms are superimposed in the domain of water stability. In the higher potential domain, the current density increases in the presence of each of the ions in the paracetamol containing electrolyte. The obtained results show that the oxidation of the paracetamol occurs via a direct electron transfer in the presence of the used ions in the domain of water stability and via an indirect oxidation process involving species resulting from the ions oxidation.

### *3.7. Effect of pH*

The pH was varied from pH 4 to 12 to determine its effect on the catalytic oxidation of paracetamol on the platinum and ruthenium dioxide electrodes. The results are presented in Figure 9. Figure 9A shows that the oxidation current density of the paracetamol decreases as the pH is increased. This figure shows also that the potential of the first paracetamol oxidation peak decreases when the pH increases. The current density of the first paracetamol oxidation peak current density decreases when the pH increases on Pt electrodes. The potential of the first paracetamol oxidation peak was studied according to the pH (inset of figure 9A). A linear trend was obtained with a correlation coefficient $R^2$=0.967.

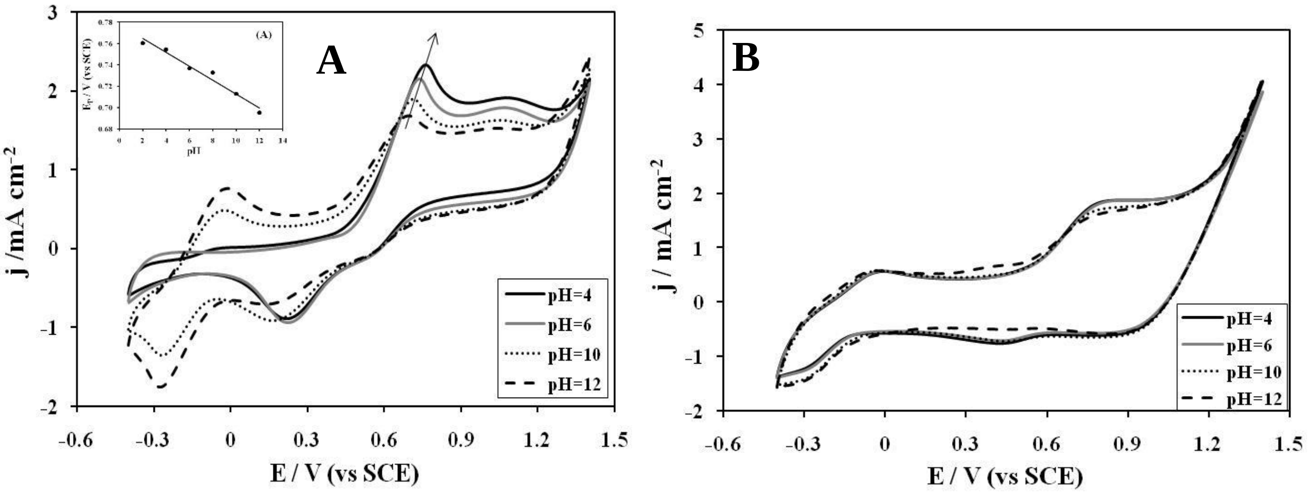


**Figure 9**. Cyclic voltammetry curves recorded on Pt electrode (A) and on $RuO_2$ electrode (B) in 2 g/L paracetamol containing 0.1 M $KClO_4$ electrolyte at various pH, potential scan rate: 20 mV/s, CE: Pt, RE: SCE, T = 25°C. In the inset (A) of figure 9 A: The first oxidation potential peak in $KClO_4$ 0.1 M containing 2 g/L paracetamol against the electrolyte pH (A) against the electrolyte pH.

In figure 9B, the effect of the pH on the catalytic oxidation of paracetamol at the $RuO_2$ electrode was studied. Figure 9B shows that at a given potential around 0.8V, the current density related to the oxidation of the paracetamol decreases as the pH is increased. So is the case of the potential at a given current density around 1.8 mA/cm$^2$. Such results indicate that pH influences the oxidation of paracetamol. It appears that protonated species are oxidized easily on platinum than the deprotonated one whereas on $RuO_2$, that effect is not well pronounced indicating that the oxidation routes seems to be almost the same independently of the pH of the electrolyte.

## 4. CONCLUSION

Pt and $RuO_2$ developed in this work by a thermal decomposition technique showed respectively smooth, rough surface and mud cracked structure. These deposits cover totally the titanium substrate. The obtained results showed that paracetamol can be degraded on both the prepared electrodes. The degradation of the paracetamol occurs on both the electrodes via a catalytic oxidation mechanism that involved a direct electron transfer on the electrode surface and by an indirect oxidation routes via $OH^{\cdot}$ species and possibly via other in situ redox species. The paracetamol oxidation process is diffusion controlled. In the presence of $Cl^-$, $NO_3^-$ or $PO_4^{3-}$ an increase of the paracetamol oxidation kinetic is observed. This work showed that for both the electrodes used, the paracetamol oxidation decreases as the pH is increased although this change is lower on the $RuO_2$ electrode than the platinum electrode.

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