Electrooxidation of amoxicillin on a Ti/Ta$_2$O$_5$/Pt-RuO$_2$-IrO$_2$ electrode

Foffié Thiery Auguste Appia, Mohamed Berté, Lassiné Ouattara*

Laboratoire de constitution et de réaction de la matière, UFR SSMT, Université Félix Houphouët Boigny de Cocody, Abidjan, 22 BP 582 Abidjan 22, Côte d’Ivoire

Abstract:
This paper has investigated the electrooxidation of amoxicillin (AMX) on a dimensionnally stable electrode (DSA) thermally prepared. The electrode prepared at 400 °C is composed of Pt combined with ruthenium oxide and iridium oxide. The microphoto of the surface of this electrode has characteristics similar to those of platinum and DSA's (RuO$_2$ and IrO$_2$). A non-zero current observed in this zone attests to the presence of the oxides (RuO$_2$ and IrO$_2$) in the surface of the new prepared electrode. Within a strongly protonated medium, the voltammetric charge of the PRI electrode is higher than that in a weakly protonated medium. Moreover, the oxidation of amoxicillin on the PRI electrode can occur directly by electron exchange at the electrode/solution interface and/or through oxidative species produced in solution. In addition, chlorine ions affect the mechanism of the oxidation of amoxicillin on the PRI electrode. In the absence of chloride ions, the oxidation process of amoxicillin on the PRI electrode is essentially controlled by diffusion. But, in the presence of chloride, a mixed diffusion-adsorption process occurs during the oxidation of amoxicillin.

Keywords: Amoxicillin; DSA; Platinum; Cyclic voltammetry.

1. Introduction
Antibiotics are drugs generally used to treat or prevent some types of bacterial infectious diseases. These pharmaceutical compounds can quickly and effectively eliminate infections, causing human beings to feel better [1, 2]. Widely used in general medicine, the antibiotics such as Penicillin were able to stop infectious pathogens such as Staphylococcus aureus [3]. However, the increasing consumption of antibiotics, in general, leads to their accumulation in the environment causing the development of antibiotic resistance bacteria [4, 5] making them to be inefficient to treat some infectious diseases [6, 7]. This constitutes a real human and aquatic organism health concern. Amoxicillin, a semi-synthetic penicillin belonging to the group of β-lactam antibiotics, is one of the widely used drug in the world and it has been detected in many countries such as Ghana [8], Australia [9], United Kingdom and France [10, 11]. The treatment of waters containing antibiotics such as amoxicillin is difficult to occur by conventional biological treatment due to its non-biodegradable character. In this condition, and because of its ability to degrade non-
biodegradable organics i.e. to oxidize completely the non-biodegradable compound by the intermediate of extremely reactive and unselective hydroxyl radical, electrochemical techniques have been chosen for such an investigation [12-14]. This method does not require any addition of toxic chemical reagents and does not induce the production of hazardous compounds but its performance depends on the electrode. In fact, in this method, the anode material plays an important role because the electrochemical oxidation of the organics could proceed via various reaction routes such as via direct electron transfer at the anode surface and/or via mediated oxidation with °OH or other oxidative species formed from water or other species discharge at the anode surface. In this context, the boron doped diamond, a non-active electrode, has been found to be a good candidate to treat organic compounds because it interacts very weakly with physisorbed BDD (°OH) and promotes a much greater O₂-overpotential than other conventional anodes like Pt, DSA (dimensionally stable anode) [15-17]. But, because of its high cost, a focus was paid on the dimensionally stable electrodes (DSA). In this way and from many studies dealing with the electrochemical treatment of the organic compounds, many anode materials have been tested. In particular, the use of dimensionally stable anodes (DSA) for wastewater treatment has led to technological developments, thus reducing operational and investment costs. In this case, a new DSA made of the mixture of platinum, ruthenium and iridium oxides (Pt-RuO₂-IrO₂ or PRI) was thermally prepared at 400°C and used to investigate voltammetrically the oxidation amoxicillin in aqueous solutions.

2. Materials and methods

The electrode of Pt-RuO₂-IrO₂ (PRI) used in the present work was prepared in our laboratory with appropriate metallic precursor. The coating precursors were prepared from H₂PtCl₆, 6H₂O (Fluka), RuCl₃·xH₂O (Fluka) and H₂IrCl₆·6H₂O (Fluka). The precursor was dissolved in pure isopropanol (Fluka) used as solvent. The commercial products were used as received without any further treatment. The titanium substrate on which the electrode films were deposited has the following dimension 1.6cm×1.6cm×0.5cm for the voltammetric investigation. The surface of each substrate was sandblasted to ensure good adhesion of the deposit on it. After sandblasting, the substrate was washed vigourously in water and then in isopropanol to clean their surface from residual sands. The substrate was then dried in an oven at 80°C and weighed. After that, the precursor was applied by a painting procedure on cleaned titanium (Ti) substrate then put in an oven for 15 min at 80°C to allow the evaporation of the solvent. Then after, it is put in a furnace 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. A final decomposition of 1 h was done at 400°C.
The deposit loading was about 5 g m\(^{-2}\) on each Titanium substrates.

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

The voltammetric measurements were performed on the prepared electrode 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). All the potential in the voltammetric measurements were reported against SCE in the whole text.

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\(^2\).

The chemicals used in this work are composed of H\(_2\)SO\(_4\) (Fluka), HClO\(_4\) (Fluka), KClO\(_4\) (Fluka), NaCl (Fluka) and Amoxicillin tablets (from a pharmacy in Abidjan). All the chemicals have been used as received without any further treatment for the experiment. All the solutions used in the current work have been prepared with distilled water. All the experiments were made at ambient temperature of 25°C.

3. Results and discussion

3.1 Physical characterization of the thermally prepared electrode

The characterization of the surface morphology of unblasted titanium, sandblasted titanium as well as the Pt-RuO\(_2\)-IrO\(_2\) electrode prepared thermally was carried out by scanning electron microscopy (SEM). The results obtained are presented in Figure 1.

*Fig. 1.* Scanning electron micrograph of (a) smooth titanium, (b) sandblasted titanium and (c) PRI electrode.
Figure 1 presents the micrograph of the uncoated titanium (Figure 1a, b) and coated titanium (Figure 1c). In Figure 1a, the microphoto of the uncoated of titanium presents a smooth surface with a uniform and continuous structure. In Figure 1b., the surface of the sandblasted titanium looks to be different to the surface of the uncoated titanium. The surface of the sandblasted titanium seems to be rough. The roughness surface of the sandblasted titanium can facilitate the deposits of the precursors. Figure 1c shows the surface of the prepared electrodes consisted in depositing Pt-RuO$_2$-IrO$_2$(PRI). It appears from the comparison of the three microphotos that the titanium surface in figure 1c was totally covered by the deposit. The surface of the PRI electrode is rough and shows cracks with various sizes. In fact, the sizes of the cracks of this deposit are thinner than that is generally observed at such magnification for pure DSAs possibly due to the presence of the platinum in the deposit [19]. This electrode presents the characteristics of platinum and DSA’s electrodes [18, 19]. This finding indicates that the surface of the PRI electrode is composed by the platinum, ruthenium dioxide and iridium dioxide [18, 20]. The microphoto of the surface of the PRI electrode presents similar characteristics to that DSA type electrodes reported previously in literature both by our group [20, 21] or by other researchers [22, 23].

3.2 Electrochemical characterization of the prepared electrode in H$_2$SO$_4$ medium

Figure 2 presents the cyclic voltammogram of the thermally prepared PRI electrode realized in 0.1 M of sulfuric acid under a scan rate of 20 mV/s. The cyclic voltammogram of this electrode showed the usual feature generally observed with polycrystalline platinum electrode in acidic media indicating that the surface of PRI electrode is partially composed of platinum clusters [19]. However, the adsorption and desorption peaks observed on the PRI electrode voltammogram are not very marked as those of Pt electrodes. Moreover, the current density, in the double layer region, is not zero contrary to the electrode Pt where it is generally characterized by an almost zero current. These differences are due to the presence of metal oxides (RuO$_2$ and IrO$_2$) on the surface of PRI electrode.

![Fig. 2. Cyclic voltammogram of PRI electrode prepared thermally at 400°C in 0.1M sulfuric acid under a potential scan rate of 20 mV/s. CE: Platinum wire, T=25°C.](image-url)
3.3 Effect of supporting electrolyte

The effect of the supporting electrolyte was investigated on the PRI electrode in perchloric acid and potassium perchlorate medium 0.1M under a potential scan rate of 8 mV/s. The obtained results are illustrated in Figure 3.

In this figure, a clear difference in the behaviour of the electrode in these two supporting electrolytes is observed. The voltammetric charge in perchloric acid is higher than that in potassium perchlorate medium. This difference is related to H$^+$ and K$^+$ ions in the two types of solutions. The current, in absolute value, decreases with the molar concentration of protons H$^+$. That observation suggested that protons H$^+$ contribute significantly in the reduction of the ohmic drop of the electrolyte by increasing the conductivity of the supporting electrolyte. Similar observations have been made with other electrodes in previous work [24].

![Fig. 3. Cyclic voltammograms on PRI electrode in KClO$_4$ 0.1M (A) and in HClO$_4$ 0.1M. CE: platinum wire, RE: SCE, 8 mV s$^{-1}$, T = 25 °C.](image)

3.4 Electrochemical investigation of oxidation of amoxicillin on PRI electrode in KClO$_4$ medium

Figure 4 presents the voltammetric curves recorded on PRI electrode under a potential scan rate of 20 mV/s in 0.1M of potassium perchlorate with or without various concentrations of amoxicillin.

In the absence of amoxicillin (curve in blue), the oxygen evolution reaction started at 1.14 V by a rapid increase of the current density. In the presence of various concentrations of amoxicillin, the current increases rapidly around 0.8 V. This finding indicates that the oxidation of amoxicillin starts to this potential (0.8 V) in the domain of water stability via certainly a direct electron transfer between PRI electrode and amoxicillin. Within the high potential domain, the current density decreases in the presence of amoxicillin suggesting that the oxidation of amoxicillin takes also place via oxidative species in the reaction medium. The gap of the potential $|\Delta E| = |E - E_0|$ recorded between the onset of the oxygen evolution reaction (OER) potential in the presence (E) and in absence (E$_0$) of amoxicillin for a given current density of 0.0012 A.cm$^{-2}$ is reported in the Table 1. In this table, the shift of the oxygen evolution over potential in the negative direction became important as the concentration of the amoxicillin increases. This result suggests that the intermediates resulted from water decomposition are involved in the amoxicillin oxidation in that domain.
Fig. 4. Cyclic voltammetry curves recorded on PRI electrode in several concentrations of amoxicillin containing 0.1 M KClO₄ electrolyte under the potential scan rate: 20 mV/s, CE: PRI, RE: SCE, T= 25°C.

| Concentration of amoxicillin (g/L) | |ΔE| = |E - E₀| |
|-----------------------------------|--|--|
| 0.0                               | 0.00 |
| 0.1                               | 0.12 |
| 0.25                              | 0.13 |
| 0.5                               | 0.16 |
| 1                                 | 0.17 |
| 2                                 | 0.19 |

Table 1
ΔE against amoxicillin concentration (E₀ = 1.03 V)

Figure 5 presents the cyclic voltammograms recorded on the PRI electrode in a 0.1M KClO₄ of various concentrations of amoxicillin and corrected from the capacitive charge. Anodic peaks are observed at around 1.14 V in the forward potential scan. These anodic peaks are characteristic of the oxidation of amoxicillin. At this potential (1.14 V), the current density recorded increases as the concentration of the amoxicillin increases. These current densities plotted against the concentration of amoxicillin showed a linear evolution (insert of Figure 5) indicating that the appearance of those current densities was directly related to the amoxicillin oxidation.

According to the obtained results, amoxicillin can be degraded on PRI electrodes via a catalytic oxidation mechanism that involved a direct oxidation of the amoxicillin on the electrode surface and/or by an indirect oxidation via species from in situ redox species [24].
Fig. 5. Cyclic voltammetry ohmic correction on the PRI electrode in 0.1M KClO₄ medium containing different concentrations of amoxicillin. \( v = 20 \) mV/s, EC: PRI, RE: SCE, \( T = 25^\circ C \). Inset: Evolution of anodic waves current density against amoxicillin concentration at \( E=1.14V \)

3.5 Investigation of the potential scan rates

The potential scan rates were studied on the voltammetric responses of the prepared electrodes in 0.1 M KClO₄ containing 1g/L of amoxicillin (Figure 6). This figure shows that the oxidation wave of amoxicillin increases with the potential scan rates. The current density recorded at 1.14 V and plotted against the potential scan rates is presented in the Figure 7.

Fig. 6. Cyclic voltammetry curves recorded on PRI electrode in 1 g/L amoxicillin containing 0.1 M KClO₄ electrolyte at several potential scan rates (8-250 mV/s), CE: PRI, \( T= 25^\circ C \), RE: SCE.
The curve obtained in Figure 7A is not linear. This result indicates that the oxidation of the amoxicillin process does not occur via adsorption for the potential scan rates explored. Moreover, plotting the current recorded at 1.14 V against the square root of the potential scan rates (Fig.7B) leads to a linear relationship between current density and square root with the following equation:

\[ J_p = 0.0002 \sqrt{v} + 0.2437 \]

and coefficient of determination of \( R^2 = 0.9926 \). This result indicates that the oxidation process of amoxicillin is a diffusion controlled process.

The logarithm of the current as a function of the logarithm of the potential scan rates recorded at 1.14 V is presented in Figure 7C. The obtained straight line is characterized by the equation

\[ \ln(J_p) = 0.454 \ln(v) + 1.982 \]

with a coefficient of determination of \( R^2 = 0.996 \). The slope of the straight lines is 0.454 close to 0.5 indicating that the oxidation process of the amoxicillin is controlled by diffusion. Indeed, when the slope is close to 1, this indicates an oxidation controlled by adsorption. Otherwise, if the slope is close to 0.5 that means a diffusion-controlled process [25, 26]. According to these results, the oxidation of amoxicillin is controlled only by diffusion.

Fig.7. (A): Evolution of the oxidation wave current density at 1.14 V against the scan rate of potential. (B): Evolution of the oxidation wave current density at 1.14 V against the square root of potential. (C): Evolution of the logarithm of the oxidation wave current at 1.14 V against the logarithm of the scan rate of potential.
3.6 Effect of chloride ions

Figure 8 shows the cyclic voltammograms performed in 0.1 M KClO$_4$ solutions containing different concentrations of NaCl. In this Figure, a rapid increase in the current density after 1.05 V is observed for 10 and 20 mM NaCl (presence of NaCl) whereas for 0 mM NaCl (absence of NaCl), this rapid increase in the current density starts at 1.14 V. The increase of the current at the 1.05 V potential is related to the evolution of chlorine (Cl$_2$) while that observed at 1.14 V reflects the evolution of oxygen (O$_2$). According to the previous work performed in our laboratory [27] on RuO$_2$ and Pt-RuO$_2$, it has been obtained that the chlorine evolution reaction (CER) occurs before the oxygen evolution reaction (OER) in 1M HClO$_4$ medium. These results show that the oxidation of chloride to Cl$_2$ is faster than that the discharge of H$_2$O to O$_2$ on the PRI electrode. Indeed, from a thermodynamic point of view, the evolvement of Cl$_2$ should occur after that of O$_2$ because the standard potential of the O$_2$/H$_2$O (0.97V/ECS) is inferior to that of the Cl$_2$/Cl$^-$ (1.1V/ECS). The catalytic activity that has enhanced the CER kinetic could be related to local reaction if the pores of the electrodes due to its roughness.

In this Figure, a localized peak is observed around 1.01 V in the backward of the potential sweep. This peak, absent for 0 mM NaCl appears in the presence of chloride. Moreover, its height increases as the concentration of NaCl increases. This peak characterizes the reduction of Cl$_2$. The current density plotted against the NaCl concentration (Figure 9) shows a straight line of equation $J_p = 6 \times 10^{-5} C + 0.0021$, with a coefficient of determination $R^2 = 0.9977$.

![Graph](image)

**Fig. 8.** Cyclic voltammetry of the PRI electrode in KClO$_4$ 0.1M containing various concentrations of NaCl; $v = 20$ mV/s, CE: platinum wire, RE: SCE, T = 25°C.
The effect of chlorine is studied in the presence of 1 g/L of amoxicillin in KClO₄ 0.1M. The cyclic voltammograms recorded are presented in figure 10. The current density increases when the concentration of NaCl. The rapid increase of the current intensity observed at around 0.88 V, in the domain of supporting electrolyte stability, is linked to a direct oxidation of amoxicillin through an electronic charge transfer reaction. In the high potential domain, the current density recorded in the absence of NaCl is lower than the current density recorded in the presence of NaCl. This current density increases with the concentration of NaCl. In the presence of NaCl, chloride ions contribute to the oxidation of amoxicillin. The obtained results clearly show that chlorides contribute in enhancing the kinetic of the amoxicillin oxidation. In fact, the higher current density recorded in the presence of chlorides could result from the oxidation between Cl₂ and the amoxicillin leading to the generation of oxidized by product on the electrode surface.

Jₚ plotted as a function of the NaCl concentration for a potential set at 1.06 V gives a straight line with R² = 0.9957 (insert of the Figure 10).

The effect of the potential scan rate on the PRI electrode in the presence of 100 mM NaCl was investigated. The obtained results were shown in Figure 10. This figure shows some peaks in the forward direction of the potential scan in the potential domain between -0.5 and 0 V. These peaks increase with the potential scan rate and a slight shift of the potential towards positive direction is observed. In the backward potential scan and in the potential domain -0.1 V to -0.8 V, there is presence of peaks which intensities increase with the potential scan.
It is also observed a slightly shift of the gas evolving potential in the negative direction. These peaks are related to the reduction of species formed during the oxidation processes of the amoxicillin. The currents densities related of the anodic and cathodic peaks have been plotted against the potential scan rate (insert Figure 10). The curves $J_{pa} = f (v)$ and $J_{pc} = f (v)$ are linear and the respective coefficients of determination are $R^2 = 0.9972$ and 0.9606. These results suggest a diffusion-controlled mechanism in that domain of potential.

Figure 11 showed that, in the presence of 100 mM of NaCl, the voltammetric charge increases also with the potential scans rates. To determine the adsorbent or diffusive character of the electrooxidation of amoxicillin, $\ln(J_p)$ was plotted as a function of $\ln(v)$ (Figure 12). Thus, the current density recorded at 0.95 V led to $\ln(J_p) = 0.8043\ln(v)+3.4419$ with $R^2 = 0.9937$.

This indicates that the oxidation process of amoxicillin on the PRI electrode in the presence of 100 mM NaCl occurs by adsorption and diffusion. The current density plotted as a function of the potential scan rate and current density versus the square root of the potential scan rate (insert of the Figure 12) led to straight lines with coefficients of determination $R^2 = 0.9917$ and 0.9977 respectively indicating that a mixed control process such as adsorption and diffusion occurs during the oxidation of amoxicillin on PRI electrode in the presence of NaCl.

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**Fig. 10.** Cyclic voltammetry of the electrode in KClO$_4$ 0.1 M + amoxicillin 1g /L and in KClO$_4$ 0.1 M + amoxicillin 1 g/L containing NaCl 20; 50 and 100 mM; v= 20mV/s, CE: platinum wire, RE: SCE, T=25°C. Insert: Evolution of the oxidation wave current density 1.06 V against the concentration of NaCl.
Fig. 11. Cyclic voltammetry curves recorded on PRI electrode in 1 g/L amoxicillin containing 100 mM NaCl in 0.1 M KClO$_4$ electrolyte at several potential scan rates (10-100 mV/s), CE: PRI, T= 25 °C, RE: SCE.

Fig. 12. Evolution of logarithm of the oxidation wave current at 1.1 against logarithm of the scan rate of potential. Insert: (A) Evolution of the oxidation wave current density at 1.1 V against the square root of potential; (B) Evolution of the oxidation wave current density at 1.1 V against the scan rate of potential and against square root of potential.
4. Conclusion

The surface of PRI electrode prepared at 400°C is rough, cracked with the presence of cavities of varying sizes. It presents the characteristics of Platinum and DSA. The cyclic voltammogram obtained in perchloric acid medium has an appearance similar to that of pure platinum. However, this curve has a non-zero current density in the domain of the double layer due to the presence of DSA (RuO$_2$ and IrO$_2$). The oxidation of amoxicillin on the PRI electrode occurred directly via electron exchange at the electrode/solution interface and / or through oxidative species produced in solution. In the absence of chloride ions, the oxidation process of amoxicillin on the PRI electrode is essentially controlled by diffusion. But, in the presence of chloride, a mixed diffusion-adsorption process occurs during the oxidation of amoxicillin. In this domain, diffusion-controlled mechanism takes place.

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References


