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Investigating the Oxidative Degradation of Amoxicillin on Pt-RuO₂ Electrodes: Insights into Surface Stability and Halide Effects

Foffié Thiery Auguste Appia¹, Jean-Claude Meledje¹, Konan Martin Koffi², Lassiné Ouattara^{1,*}

¹Laboratoire de Constitution et Réaction de la Matière, UFR SSMT, Université Félix Houphouët-Boigny of Cocody, Abidjan, 22 BP 582 Abidjan 22, Côte d'Ivoire

² UFR Environnement, Université Jean Lorougnon Guédé, Daloa, Côte d'Ivoire

Abstract: This study investigated the electrochemical oxidation of amoxicillin using a platinum-ruthenium oxide (Pt-RuO₂) electrode in various supporting electrolytes: KClO₄, HClO₄, H₂SO₄, and NaOH. The Pt-RuO₂ electrode exhibited a robust electrochemical response across all tested media, with higher catalytic activity observed in acidic environments. A surface inhibition effect was observed with increasing amoxicillin concentration, limiting the availability of active sites on the electrode. Additionally, the pH of the medium impacted the reduction peaks, with a consistent decline in intensity correlating with increased acidity. Chloride ions (C Γ) further improved the oxidation peak, indicating a catalytic role in the oxidation process. These findings provide insights into optimizing the electrochemical degradation of amoxicillin and highlight the importance of medium composition in influencing electrode performance. Chronoamperometry confirmed the formation of an inhibitory surface layer. These results underscore the role of medium composition in optimizing electrochemical degradation efficiency.

Keywords: Electrochemical oxidation, pharmaceuticals, DSA, surface inhibition, chloride ions.

1. Introduction

The discovery and widespread use of antibiotics, including amoxicillin (AMX), have greatly improved public health by effectively treating common bacterial infections such as skin, respiratory, and urinary tract infections ^{1,2}. However, a significant portion of administered AMX is excreted in an unmetabolized form, which leads to environmental contamination of water resources ^{3,4}. This contamination poses substantial toxicological risks to aquatic ecosystems and, through bioaccumulation, to humans ⁵.

The persistence of AMX in the environment also promotes the spread of antibiotic-resistant bacteria, a serious concern for public health, as these resistances can transfer from animals to humans ^{5,6}. Recognizing these risks, the European Union has added AMX to its watch list of emerging contaminants due to its ecological impact potential ⁷.

To monitor AMX presence, various analytical methods, such as high-performance liquid chromatography and electrochemical techniques, have been developed to detect this molecule at trace levels in water samples^{8,9}. Electrochemical methods, in particular, provide cost, speed, and sensitivity advantages for in situ analysis¹⁰. Recent

*Corresponding author: Lassiné Ouattara Email address: <u>ouatlassine@yahoo.fr</u> DOI: <u>http://dx.doi.org/10.13171/mjc02505151829ouattara</u>

advancements in electrode modification, using nanocarbon materials like graphene, graphite, and carbon nanotubes, have enhanced the electrochemical signals for AMX, offering a promising solution for accurate analysis ^{11,12}. Combining these nanomaterials with metallic nanoparticles (such as gold and palladium) further improves electrode sensitivity and stability, enabling reliable detection even in complex matrices like milk and urine ^{9,13,14}.

Despite these advancements, conventional wastewater treatment methods remain ineffective at entirely removing AMX ¹⁵. This highlights the need for novel treatment approaches, such as advanced oxidation processes and adsorption, and the development of electrochemical solutions using nanomaterials to mitigate the impact of AMX on the environment and human health ¹⁶.

In addition to electrode modifications ¹⁷, halide ions, particularly chloride ions (Cl⁻), have gained attention in electrochemical oxidation processes ¹⁸. Halide ions can enhance the electrochemical oxidation of organic pollutants by forming reactive intermediates, such as active chlorine or hypochlorite ions, which can effectively degrade pharmaceutical compounds like AMX ^{19,20}. Chloride ions are beneficial due to their widespread availability, low cost, and ability to form

Received January 29, 2025 Accepted April 18, 2025 Published May 15, 2025 strong oxidants that accelerate the degradation of antibiotics, making them a valuable tool in environmental remediation efforts ²¹. However, controlling the concentration of chloride ions is critical, as excessive levels may lead to undesirable byproduct formation and electrode corrosion ²².

Given these considerations, this study aims to investigate the electrochemical oxidation of AMX on a Pt-RuO₂ electrode across different supporting media, chloride ion concentrations, and pH levels. These investigations will provide insight into optimizing electrochemical conditions for AMX degradation and highlight the potential of halide ions as catalytic agents in the electrochemical treatment of pharmaceutical contaminants.

2. Materials and methods

2.1. Reagents and chemicals

Amoxicillin tablets made by Bailly-Creat were obtained from a pharmacy in Abidjan using its commercial formula. The tablets were crushed before use. H_2SO_4 , $HCIO_4$, $KCIO_4$, and NaCl were purchased from Fluka. Chemicals were used as received from suppliers. Experiments were performed at a laboratory temperature of 25°C, and distilled water was used for all solution preparation. pH was adjusted by H_2SO_4 (1M) and NaOH (1M).

2.2. Electrochemical measurements

The electrochemical oxidation of AMX was performed in a three-electrode cell (100 mL) with the Platinum (Pt) combined to ruthenium dioxide (RuO₂) as a working electrode (WE), a saturated calomel electrode (SCE) as a reference electrode (RE) and Platinum wire as a counter electrode (CE). Cyclic voltammetry measurements and chronoamperometry were performed using a Voltalab PGP 201 potentiostat, which was connected by the interface to a computer to collect the data. The measuring program is Voltmaster 1. Before each experiment, we electrochemically cleaned the electrode by cyclic voltammetry in 1 M sulfuric acid solution until a reproducible voltammogram was obtained. To minimize the ohmic drop, the reference electrode was mounted in a luggin capillary and placed close to the working electrode.

3. Results and Discussion

3.1. Pt-RuO₂ electrode and electrochemical response

A platinum electrode modified with ruthenium oxide (Pt-RuO₂) was developed and tested for the electrochemical oxidation of amoxicillin in different supporting electrolytes, specifically KClO₄, HClO₄, H2SO₄, and NaOH (Figure 1).

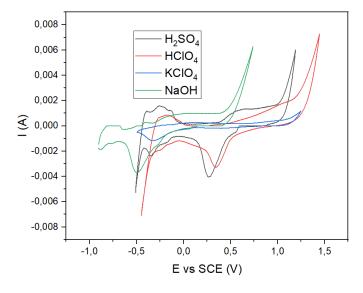


Figure 1. Electrochemical response of Pt-RuO₂ electrode in various electrolyte supporting (H₂SO₄, HClO₄, KClO₄, NaOH), in the absence of organic compounds. Scan rate v=480 mV/mn; CE: Platinum wire; ER: ECS; T=25°C.

The results reveal that the Pt-RuO₂ electrode exhibits a good electrochemical response in each supporting electrolyte, though with notable variations. In the neutral KClO₄ medium, the electrode demonstrates adequate stability and sensitivity, allowing for reproducible measurements. However, no clear hydrogen or oxide formation regions were observed. This behavior may be attributed to the influence of the RuO₂ component, which probably dominates the surface response under these conditions. In highly acidic media such as HClO₄ medium, distinct anodic and cathodic features are observed, with a broader potential window and the onset of oxygen evolution occurring at higher potentials. This suggests a higher electrochemical activity and stability of the electrode in this medium ²³. In H₂SO₄, the cyclic voltammogram shows well-defined hydrogen adsorption/desorption peaks and platinum oxide formation, although

interactions with sulfate ions may slightly influence the current response. The overall current response in the basic NaOH medium is less structured, and the oxygen evolution reaction occurs at lower potentials. These results indicate good catalytic activity of the Pt-RuO₂ electrode, with optimized performance in acidic media, particularly in HClO₄, opening prospects for tailored electrochemical oxidation applications based on specific degradation needs.

3.2. Electrode Reproducibility and Stability in the Presence of Amoxicillin

To evaluate the reproducibility and stability of the Pt-RuO₂ electrode's electrochemical response, cyclic voltammetry (CV) experiments were conducted by varying the scan rate in the presence of amoxicillin (AMX) (Figure 2.A). As expected, an increase in the scan rate led to a rise in the oxidation peak currents, consistent with theoretical predictions for electrochemical systems dominated by surface processes ²⁴. This behavior is commonly associated with the capacitive or adsorption-controlled nature of the electrode surface, wherein higher scan rates facilitate rapid charge transfer, thus enhancing the peak currents²⁵.

To isolate the effect of the scan rate on the electrode's we normalized the peak current values by removing the scan rate contribution (Figure 2.B). Upon normalization, the oxidation peaks aligned closely, indicating consistent electrode response and validating the stability and reproducibility of the Pt-RuO₂ surface across a range of experimental conditions. This reproducibility is crucial for electrochemical detection applications, as it suggests that the Pt-RuO₂ electrode maintains its active surface properties and provides reliable data across multiple scans and varying operational conditions ²⁶.

Such findings support the robustness of Pt-RuO₂ in electrochemical applications, particularly for the detection and degradation of pharmaceutical contaminants, where stable and reproducible performance is essential. The electrode's reliable response at different scan rates suggests minimal surface fouling or degradation, which is often a concern in the electrochemical oxidation of organic compounds like AMX. This characteristic may be attributed to the synergy between Pt and RuO₂, where Pt provides excellent conductivity while RuO₂ contributes chemical stability, minimizing electrode surface passivation ^{19,21}

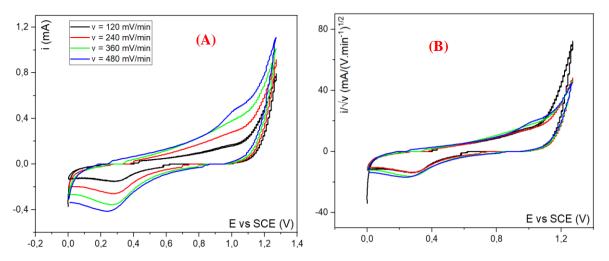


Figure 2. (A) Cyclic voltammetry curves recorded at Pt-RuO₂ electrode in 0.1 M KClO₄ electrolyte containing 1 g/L amoxicillin at several potential scan rates (120-480 mV/mn), CE: Platinum wire; ER: ECS; T=25°C; (B) Cyclic voltammograms obtained after peak normalization.

3.3. Influence of Amoxicillin Concentration

The electrochemical behaviour of the Pt-RuO₂ electrode was further investigated by gradually increasing the concentration of amoxicillin in various supporting electrolytes (Figure 3). In all cases, the oxidation peak current of amoxicillin initially increased with concentration, suggesting enhanced interaction between the amoxicillin molecules and the active sites on the Pt-RuO₂ surface. However, a marked decrease in the oxidation peak current was observed after reaching a specific threshold concentration, despite continued increases in amoxicillin concentration. This behavior indicates a potential surface inhibition phenomenon, where high

concentrations of amoxicillin likely lead to a saturation of active sites on the electrode surface, restricting further oxidation. Such inhibition can occur due to the adsorption of amoxicillin molecules or their intermediates on the electrode, blocking the accessibility of active sites, a phenomenon supported by studies on other pharmaceuticals in electrochemical systems ²⁷.

Further supporting this hypothesis, a progressive decrease in the reduction peak current was observed, ultimately leading to the disappearance of the reduction peak. This effect could be attributed to forming an adsorbed layer or film of reaction intermediates on the Pt-RuO₂ surface, a behavior

This pattern aligns with findings from similar studies where electrochemical inhibition was observed at high substrate concentrations, impacting the efficacy of electrodes modified with metal oxides or other catalysts ²⁹. Such studies emphasize the importance of optimizing concentration ranges to balance high catalytic activity with preventing surface inhibition.

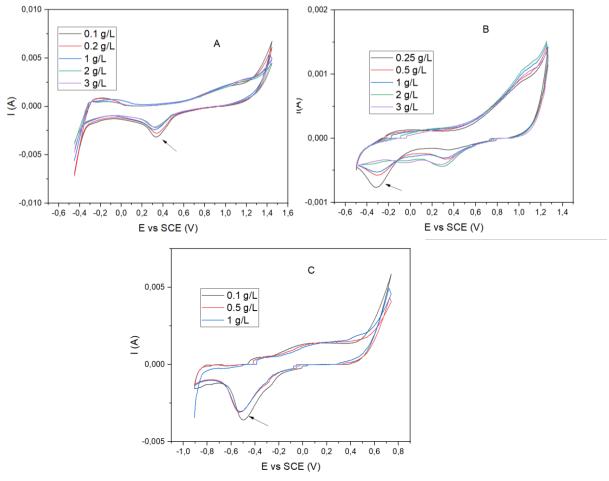


Figure 3. Cyclic voltammetry curves of various concentration of AMX at Pt-RuO₂ electrode for various concentrations recorded in 0.1 M of electrolyte supporting (HClO₄ (A), KClO₄ (B) and NaOH (C)) under the potential scan rate: 480 mV/mn, CE: Platinum wire, RE: SCE, T= 25°C.

3.4. Influence of pH on the Electrochemical Oxidation of Amoxicillin

The effect of the support medium's pH was investigated by varying this parameter in the electrochemical oxidation

tests of amoxicillin on the Pt-RuO₂ electrode. Regardless of the pH values applied (2.4, 5.2, 6.9, 9.3, and 11.7) (Figure 4), a similar trend was observed in the reduction currents, with a gradual decrease in the intensity of reduction peaks until they disappeared completely. This observation suggests an inhibition of the Pt-RuO₂ electrode surface, likely caused by the adsorption of reaction intermediates or amoxicillin molecules that block active sites required for electron transfer. This inhibition phenomenon, welldocumented in the literature on electrochemical systems containing organic compounds ²⁷, can be intensified by pH variations that alter the electrode surface state, the adsorption properties of amoxicillin, and its degradation byproducts ²⁴. Notably, the reduction peaks completely disappeared at pH 11.7, indicating possible fouling or increased passivation of the electrode surface. This supports the hypothesis that extreme or high pH conditions favor the formation of persistent adsorption layers, thereby limiting the electrocatalytic activity of Pt-RuO₂. These results confirm that the electrode's performance in amoxicillin degradation depends not only on concentration but also on the pH of the medium, underscoring the need to select optimal conditions to avoid surface inhibition.

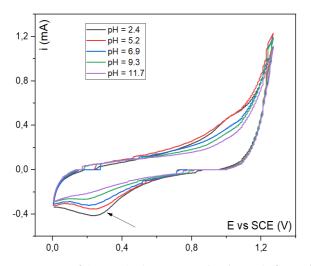


Figure 4. Cyclic voltammetry curves of AMX (1 g/L) at Pt-RuO₂ electrode for various pH (2.4-11.7) recorded in 0.1 M of electrolyte supporting (KClO₄) under the potential scan rate: 480 mV/mn, CE: Pt wire, RE: SCE, T= 25°C.

3.5. Effect of Chloride Ions (Cl⁻) on the Oxidation of Amoxicillin

Electrochemical tests conducted at a fixed concentration of amoxicillin revealed a significant increase in the oxidation peak when the chloride ion (Cl⁻) concentration was gradually increased from 100 to 5800 mg/L in KClO₄. This behavior could be attributed to the catalytic Effect of Cl⁻ ions on the Pt-RuO₄ electrode surface, a phenomenon observed in several studies on the electrochemical oxidation of organic compounds in the presence of halides. Chloride ions can promote the generation of reactive species at the electrode surface, such as active chlorine or chlorinated radicals, capable of oxidizing amoxicillin or accelerating its decomposition. This increase in the oxidation peak may also result from a synergistic effect between Cl⁻ ions and the electrode's active sites, facilitating electron transfer. Additionally, increased Cl⁻ concentration could alter electrochemical double layer, the affecting interactions between amoxicillin molecules and the electrode ²³. These findings suggest that adding Cl⁻ at optimal concentrations could enhance the efficiency of amoxicillin's electrochemical oxidation; however, excessively high concentrations risk promoting electrode corrosion or producing undesirable byproducts ³¹

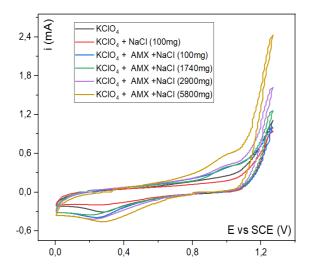


Figure 5. Cyclic voltammetry curves of AMX (1 g/L) at Pt-RuO₂ electrode for various concentrations of NaCl recorded in 0.1 M of electrolyte supporting (KClO₄) under the potential scan rate: 480 mV/mn, CE: Pt wire, RE: SCE, T= 25°C.

3.6. Inhibitory Layer Formation in Chronoamperometry

The results of the chronoamperometry experiment conducted at a potential of 1000 V vs SCE show an

initial rise in current during the first 30 seconds, followed by a gradual decrease. This behavior suggests the formation of an inhibitory layer on the electrode surface, which reduces charge transfer and limits the flow of electroactive species to the surface. Such phenomena are often observed in systems where a passivating layer, typically oxidized or adsorbed products, develops on the electrode surface ³².

In these systems, the current decrease over time can be attributed to the adsorption of species generated by the oxidation of analytes or electrolyte components, forming a barrier on the electrode surface that restricts access of electroactive species to the reaction site. This behaviour is well-documented in anodic oxidation studies of various organic compounds and contaminants, where the formation of secondary products or oxidized byproducts reduces the electrode's electrochemical activity. This progressive passivation could also result from the precipitation of oxides or other surface deposits, as observed in similar electrochemical degradation experiments where high potentials induce the formation of thin layers of metal oxides ³¹.

These observations support the hypothesis of an inhibitory layer or passivating effect on the electrode during high-potential application. Future studies could investigate the properties of this inhibitory layer through complementary techniques, such as electrochemical impedance spectroscopy or atomic force microscopy, to better understand the mechanisms of passivation and their impact on analyte degradation.

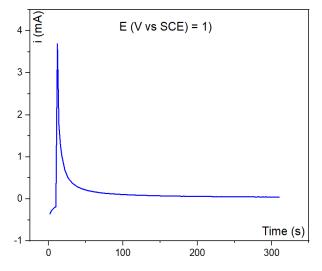


Figure 6. Chronoamperometric was recorded for the oxidation of amoxicillin (1 g/L) on the Pt-RuO₂ electrode in KClO₄ (0.1M) for 300 s at 1000 mV. CE: platinum wire; ER: SCE; $T = 25^{\circ}$ C.

4. Conclusion

In conclusion, the electrochemical oxidation of amoxicillin using the Pt-RuO2 electrode demonstrated significant potential for effective degradation in various media. Acidic conditions improved catalytic performance, while amoxicillin concentration influenced oxidation efficiency, with surface inhibition observed at higher levels. The enhancing effect of chloride ions highlights the role of supporting electrolytes in optimizing the degradation process. Chronoamperometry experiments exhibited the formation of an inhibitory layer on the electrode surface. Future research should focus on exploring the mechanistic pathways of amoxicillin oxidation and investigating the long-term stability of the Pt-RuO₂ electrode in real-world applications, such as wastewater treatment. Overall, these findings contribute to a better understanding of the pharmaceutical of electrochemical behavior compounds and the potential for using modified electrodes in environmental remediation efforts.

Declaration

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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