Electrooxidation of simulated wastewater containing pharmaceutical amoxicillin on thermally prepared IrO₂/Ti electrode

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Abstract: The electrooxidation of amoxicillin (AMX) on the iridium oxide electrode thermally prepared (400°C) has been investigated by cyclic voltammetry and preparative electrolysis. Physical characterization by Scanning Electron Microscopy (SEM) showed that the IrO_2 electrode has a rough surface with pores' presence. In cyclic voltammetry, the oxidation of AMX occurs directly at the anode's surface or via the higher degree oxide of iridium oxide (IrO_3). It is noted that the oxidation process of AMX can be controlled by diffusion combined with the phenomenon of adsorption. In preparative electrolysis, the effect of several parameters has been investigated. These are the current density, the support medium, the initial pH. The findings obtained show a weak degradation of amoxicillin. The Chemical Oxygen Demand (COD) reduction rate is less than 11% under our experimental conditions, indicating that the IrO_2 electrode leads to the parent compound's conversion. Also, the degradation of the organic compound is favored in a very acidic medium.

Furthermore, the effect of inorganic ions such as SO_4^{2-}, PO_4^{3-}, NO_3^-, Cl^- was evaluated. Investigations show that these ions' effects are diverse, with COD reduction rates ranging from 2.47%; 2.68%; 7.7%; 16.41%, and 71.65%, respectively, in the absence and the presence of SO_4^{2-}, PO_4^{3-}, NO_3^-, Cl^- ions. SO_4^{2-} have virtually no effect on enhancing the degradation of amoxicillin. PO_4^{3-} ions provide a slight improvement in amoxicillin degradation. As for nitrate ions, their influence is 2.31 times than that of phosphate ions. Chloride ions improve the performance of the electrooxidation of amoxicillin on IrO_2 very significantly. The presence of chloride ions makes it possible to go from 2928.35 (absence of inorganic ions) to 33.19 kWh per Kg of COD. This represents an energy gain of over 98%.

Keywords: Amoxicillin; wastewater treatment; antibiotic; DSA; active chlorine.

1. Introduction

The treatment of hospital wastewater before its release into the environment is a real problem in Côte d'Ivoire. Indeed, the wastewater from the teaching hospital of Treichville in Abidjan is directly discharged into the lagoon without any treatment. The said center has a wastewater treatment plant that has not been operating since 1975. According to a survey conducted by our laboratory in this great hospital, the actual wastewater from its various services contains inorganic ions, including chloride, sulfate, nitrate, and phosphate ions [1]. It has also shown that amoxicillin is one of the most prescribed antibiotics for hospital patients after ceftriaxone and augmentin. However, it has been proven that the body partially metabolizes most antibiotics administered to patients, and 25-75% of the antibiotic fractions are released into the environment via urine and feces [2,3] in unchanged form after administration. The continued rejection of these pharmaceutical compounds can pose a real threat to the aquatic ecosystem and human health in the long term [4,5].

Some authors have shown residues of pharmaceutical compounds, particularly antibiotics, in the soil, urban wastewater, groundwater, and surface water [6-8] at concentrations ranging from ng/L to μg/L [9]. The presence and accumulation of many antibiotics in the environment can have adverse effects on aquatic and terrestrial organisms, such as changes in behavior, reproduction, and growth, and this, at low concentrations. For example, amoxicillin released into the environment can cause, among other things, drug allergy and toxicological problems [10], antibiotics resistant bacteria (ARB), and gene resistance to antibiotics in the aquatic environment [11,12].

To prevent environmental pollution from wastewater containing pharmaceuticals, several methods are

used [13]. However, numerous studies have demonstrated that the biological method, effective for treating domestic wastewater [14] is ineffective for hospital wastewater, especially those containing a large number of antibiotics due to the non-biodegradable nature of these pharmaceutical compounds [15]. Consequently, the search for a technique capable of degrading all kinds of organic pollutants is essential.

In this context, electrochemical processes constitute a promising technique for treating wastewater containing biorecalcitrant organic pollutants. Various studies on the treatment of wastewater containing pharmaceutical compounds by the electrochemical method have been carried out [15,17,18]. Degradation of a pollutant by electrooxidation can convert the parent organic compound to other intermediates or their mineralization of the parent compound [19-21]. There are two types of electrochemical oxidation mechanism; these are direct electrochemical oxidation and indirect electrochemical oxidation. In direct electrochemical oxidation, the initial compound can be directly converted or eliminated by an electrochemical reaction. Concerning indirect electrochemical oxidation, the initial compound is oxidized through the intermediary of strong redox oxidative species such as hydroxyl radicals or other oxidizing species formed from water or other species discharging the surface of the anode at a high current. These active species can lead to the conversion or the mineralization of the initial organic compound. In electrochemistry, the type of material used in the anode plays a crucial role in its efficiency. Therefore, the same organic pollutants and their reaction intermediates produced will have different reaction rates with other electrodes [22]. The BDD electrode is commonly used for the degradation of pharmaceutical compounds [23,24]. This electrode has an inert surface with low adsorption properties, high corrosion stability (even in strongly acidic media), and a much higher overpotential for oxygen release than other conventional anodes such as Pt, DSA (Dimensionally Stable Anodes) [25]. However, its use is minimal due to its high cost.
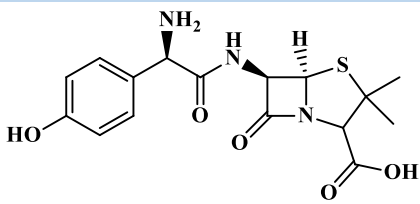
On the other hand, the use of DSA for the degradation of organic pollutants makes it possible to reduce the cost of investment and operation compared to boron-doped diamond (BDD). These electrodes exhibit high electrocatalytic activity, high stability against anodic corrosion, and very high mechanical stability. Among the DSA commonly used in the degradation of organic pollutants, IrO_2 exhibits good electrocatalytic properties to form active chlorine species from chloride ions [26]. Several authors have investigated the degradation of organic contaminants on the IrO_2 electrode alone or combined with other precursors (RuO_2, Pt, etc.) [27-29]. However, there is no study on the effect of various inorganic ions on the degradation of amoxicillin on the IrO_2/Ti electrode to our knowledge. In this work, the iridium oxide (IrO_2) electrode thermally prepared at 400°C will be used to treat simulated wastewater polluting amoxicillin. Several parameters, such as the effect of the current applied density, the support medium, the pH, and the presence of the inorganic ions (SO_4^{2-}, PO_4^{3-}, NO_3^-, Cl^-), are found most often in hospital wastewater, have been investigated. This work was carried out to apply its results to the treatment of real hospital wastewater from the Treichville Hospital and University Center (CHU) in Abidjan.

2. Experimental

2.1. Chemicals

Amoxicillin tablets (Table 1) made by Bailly-Creat laboratory were purchased from a pharmacy in Abidjan and used in its formula commercial. Tablets have been crushed before use. All chemicals used in the study were reagent grade or higher and used as received without further purification. Potassium perchlorate ($KClO_4$), perchloric acid ($HClO_4$), potassium nitrate (KNO_3), sodium chloride (NaCl), potassium sulfate (K_2SO_4), potassium dihydrogen phosphate (K_2HPO_4) were obtained from Fluka. Solutions were prepared with distilled water. $HClO_4$ and NaOH (Fluka) allowed adjusting the pH value.

Table 1. Chemical and physical characteristics of amoxicillin.

Therapeutic class	Bactiricidal β-lactam antibiotic
Brute formula	$C_{16}H_{19}N_3O_5S$
Developed formula	
Molar mass	365.4 g/mol
Melting point	194°C
pKa	2.8
Solubility	3430 mg/L water at 25°C

2.2. Preparation of IrO₂/Ti electrode

The IrO$_2$/Ti electrode was prepared, thermally at 400°C, in our laboratory with an appropriate metallic precursor. The coating precursor was prepared from H$_2$IrCl$_6$,6H$_2$O (Fluka). The precursor was dissolved in pure isopropanol (Fluka) used as a solvent. The preparation procedure is the same as that described in our previous work [30]. The titanium substrate was sandblasted to ensure good adhesion of the deposit on its surface. After sandblasting, the substrate was treated using water and isopropanol to clean its 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 solvent's evaporation fired at 400°C in the furnace for 15 min to allow the decomposition of the precursor. These steps were repeated five times to achieve 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}.

2.3. Cyclic voltammetry

Cyclic voltammetry (CV) was performed in a conventional three-electrode cell using a computer-controlled Autolab potentiostat PGSTAT 20 (ECHOCHEMIE). IrO$_2$/Ti electrode, prepared thermally, was used as the working electrode, saturated calomel electrode Hg/Hg$_2$Cl$_2$/KCl as reference electrode, and Pt wire as the counter electrode. The geometric area of the working electrode that is in contact with the supporting electrolyte is 1 cm². The electrode reference is put in a capillary luggin whose end is placed very close to the working electrode to reduce the ohmic drop. The potential of the electrode was reported relative to the saturated calomel electrode (SCE). The electrolyte was either 0.1M KClO$_4$. Solutions were magnetically stirred during the experiments.

2.4. Electrooxidation experiments

The Electrooxidation experiments were performed in an undivided cylindrical electrochemical cell of 250 mL capacity in a galvanostatic regime and magnatically stirred. The solution flow rate was 2.08 mL s^{-1}. In the reactor, the solution is recirculated using a mini peristaltic pump. All the experiments were done at the ambient temperature of 22-25°C. The anode was IrO$_2$/Ti, and Zirconium (Zr) plates were used as cathode. During each electrolytic run, a sample of 2 mL was drawn from the reactor at defined time intervals and analyzed in COD. Representative runs were performed in triplicate to check for reproducibility, which was found to be quite good.

2.5. Analytical

The COD of the samples was determined during our experiments using HACH brand COD tubes. To determine it, 2 mL of sample is taken and introduced into a COD tube and heated in a digester (HACH) at 150°C for 120 minutes. After cooling, the COD value is read directly using the DR/6000 spectrophotometer (HACH) at a wavelength of 420 nm for the range 10-150 ppm.

COD abatement rate is determined using this formula:

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

Where COD$_0$ and COD$_t$ are respectively the initial COD and the final COD (mg O$_2$/L).

Normalized COD (COD*) is calculated from relation 2

$$COD^* = \frac{\text{COD}_0 - \text{COD}_t}{\text{COD}_0} \qquad (2)$$

3. Results and discussion

3.1. Morphological characterization of prepared electrode

Figure 1 shows the SEM representation of the microphoto of the thermally prepared IrO$_2$ electrode. The pure iridium dioxide (IrO$_2$) electrode's surface shows overlapping layers of iridium dioxide, cracks, and pores. The thermal shock to which the deposits are subjected during their removal from the oven is the cause of the various cracks observed on the surface of the electrodes prepared thermally at 400°C.
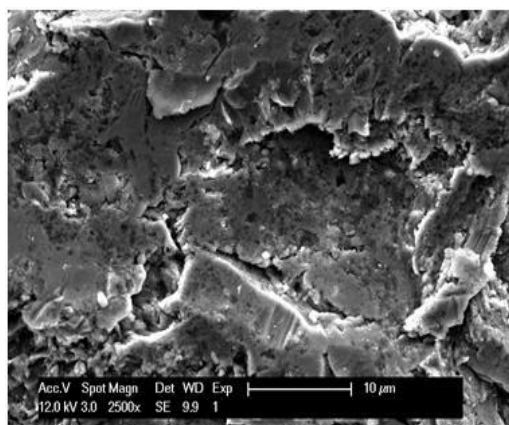

Figure 1. SEM image of IrO$_2$ deposit on Titanium

3.2. Cyclic voltammetry

Cyclic voltammetry is a technique commonly used in electrochemistry for the electrochemical characterization of electrodes. This technique makes it possible to understand the behavior of the electrode. Figure 2 (i) shows the cyclic voltammograms of the IrO_2 electrode in the absence and presence of amoxicillin (1g/L) in the potential range from -0.38 V to 1.24 V. The supporting electrolyte used is 0.1M $KClO_4$.

In the absence of amoxicillin (curve (a)), we note the presence of an anode wave between 0.7 V and 1.1V, which could be attributed to the redox transitions Ir(III)/Ir(IV) and Ir(IV)/Ir(VI) [31,32]. The evolution of oxygen characterized by a rapid increase in oxygen starts from 1.19V. In the presence of amoxicillin (curve (b)), an increase in the voltammetric charge in the anode part is observed from 0.48V, which is before the release of oxygen. That would reflect the start of the oxidation of amoxicillin in the supporting electrolyte's stability domain on IrO_2. This indicates that the oxidation of amoxicillin on the electrode of the IrO_2 electrode occurs by a direct electronic exchange on the electrode's surface.
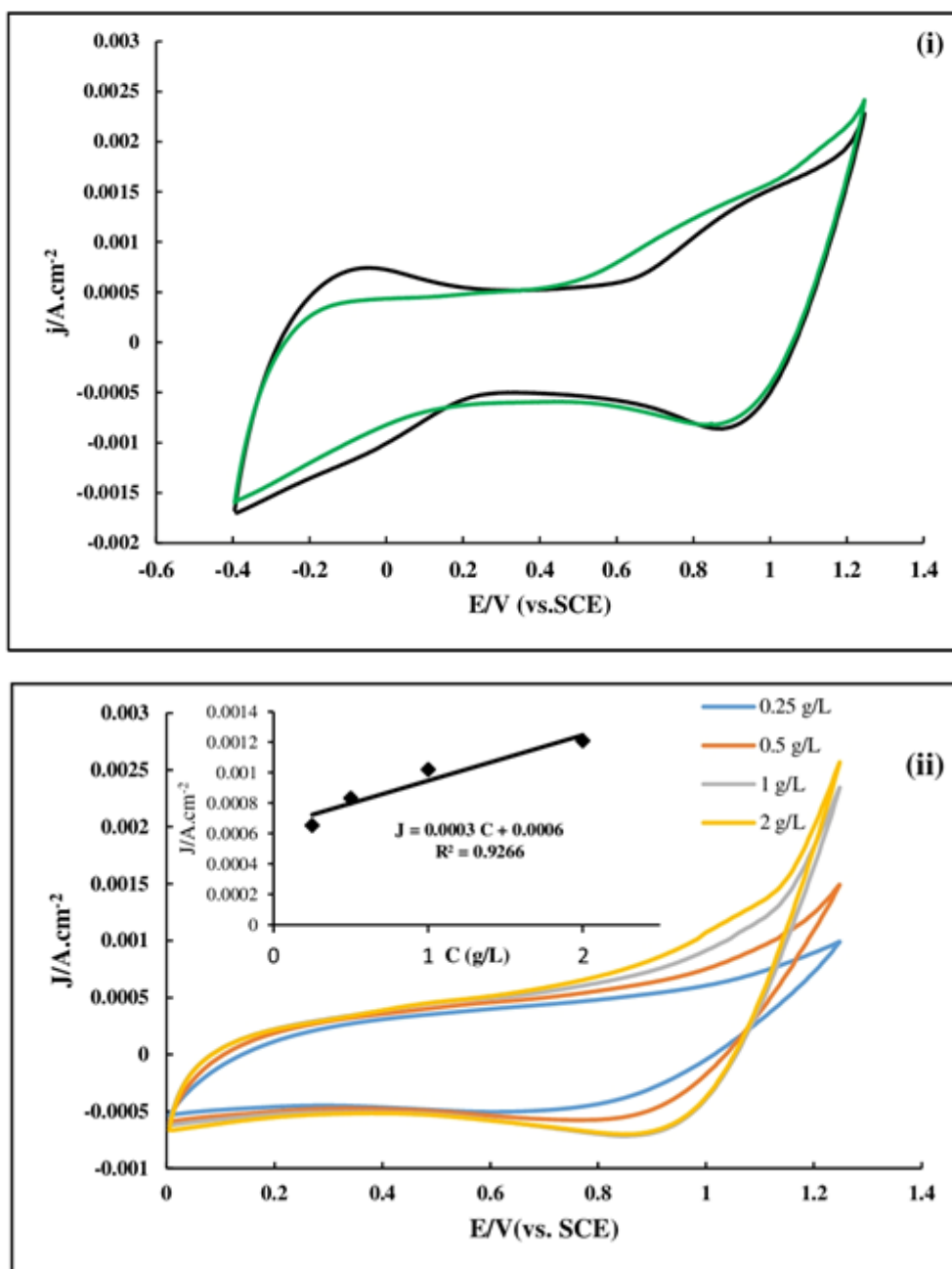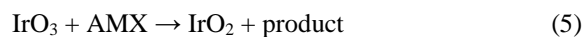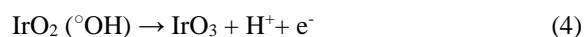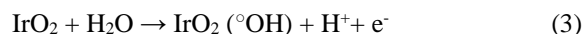

Figure 2. (i): Cyclic voltammograms in the absence (a) and in the presence (b) of amoxicillin on an iridium oxide (IrO_2) electrode in 0.1M $KClO_4$ ER: ECS; CE: platinum wound, T = 25 °C, v = 8mV/s.
(ii): cyclic voltammogram recorded on IrO_2/Ti electrode in 0.1M $KClO_4$ for various concentration of AMX. CE: platinum wound; T=25°C, v=8mV/s.
Insert: Evolution of the current density as a function of the concentration of amoxicillin for E = 1.05V

According to the literature [33,34], the oxidation of the organic compound can result from the higher degree oxide IrO_3 generated on the surface of the IrO_2 from the decomposition of water (Eqs.(3)-(5))

$$IrO_2 + H_2O \rightarrow IrO_2\ (^\circ OH) + H^+ + e^- \qquad (3)$$

$$IrO_2\ (^\circ OH) \rightarrow IrO_3 + H^+ + e^- \qquad (4)$$

$$IrO_3 + AMX \rightarrow IrO_2 + product \qquad (5)$$

The effect of amoxicillin concentration has been investigated in the range 0.25g/L to 2g/L in the positive potential domain. The results are presented in Figure 2 (ii).

In this figure, the current density increases with the concentration. For a potential fixed at 1.05V, the current densities have been recorded and plotted against the concentration (insert of Figure 2 (ii)). A linear relationship of equation J = 0.0003 C + 0.0006 with a correlation coefficient R^2 = 0.9266 was obtained. This attests that these current densities are directly linked to amoxicillin oxidation for the concentration range explored.

Figure 3 shows the consecutive cyclic voltammograms of 1g/L of amoxicillin in 0.1M $KClO_4$ at the potential scan of 8 mV/s between the potentials -0.4V and 1.2V.
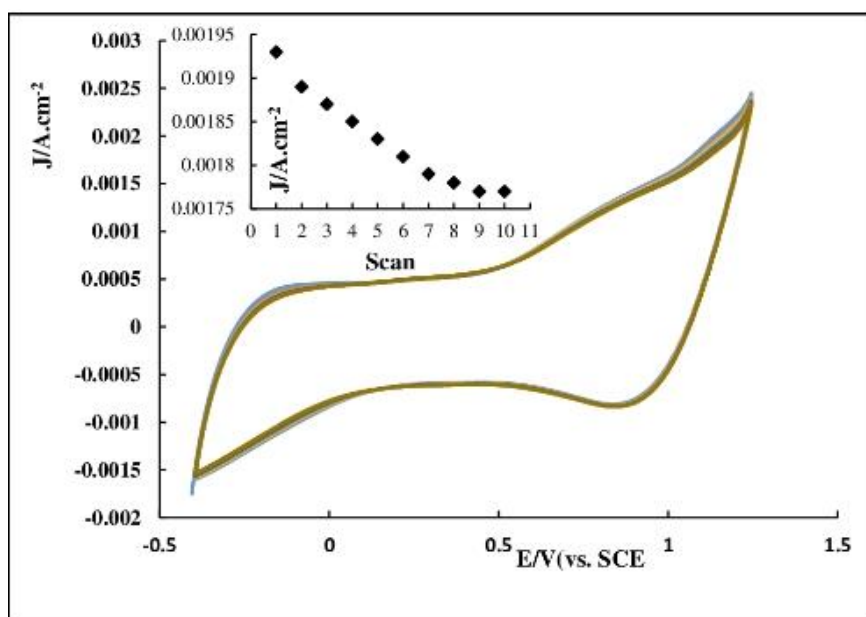

Figure 3. Cyclic voltammogram of amoxicillin (1g/L) on iridium oxide electrode in 0.1M $KClO_4$ at several scans; ER: SCE, CE: platinum, T = 25° C, v = 8 mV / s.
Inset: Evolution of the current density according to the scan for 1g / L of amoxicillin at E = 1.05V

For a potential fixed at 1.12V, the current densities for different scans have been recorded (Insert of Figure 3.
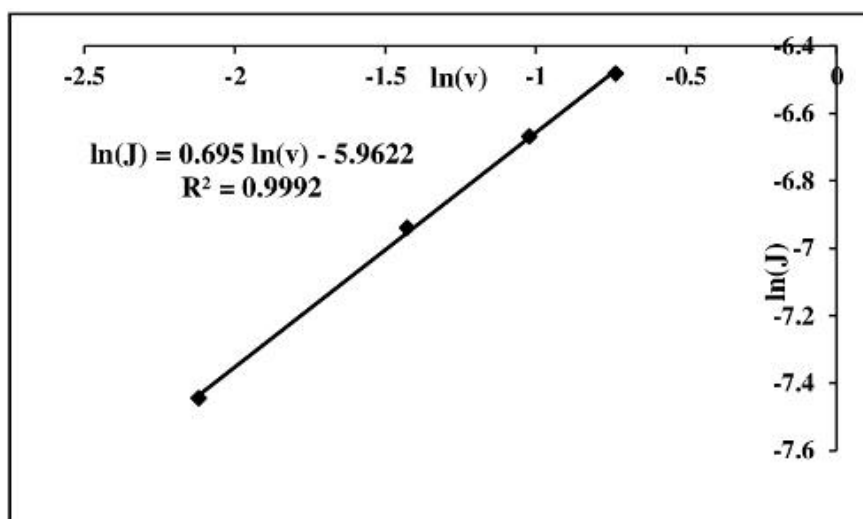

Figure 4. Evolution of the Ln of the oxidation wave of current density at 1V against the Ln of the scan rate of potential

At this potential, the anode current density decrease gradually until the scan 9 and seems to be constant from this scan. The decrease of the current density would reflect the reduction of the

electroactivity of IrO_2 electrode. Other authors have made such observations on the IrO_2 electrode [35,36]. The decrease of the electroactivity of IrO_2 electrode would be mainly linked to the production and adsorption of polymer film on the surface of the electrode [35,36]. The effect of the potential scan rate on the oxidation of amoxicillin has been investigated. Scan rates varying from 2mV/s to 8 mV/s. The current densities were recorded for a potential fixed at 1V. The construction of ln(J) against ln (v) gives a straight line of equation (Figure 4) ln(J) = 0.695 ln (v) -5.9622 with a coefficient of determination R^2 = 0.9992. The slope of the straight line is about 0.695, it is between 0.5 and 1. This indicates that the oxidation process of amoxicillin on the IrO_2 electrode is controlled by diffusion combined with a phenomenon of adsorption[37].

3.3. Electrolysis bulk
3.3.1. Effect of the current density

Current density, the current per unit area of the electrode, is an essential parameter in electrooxidation. A high current density applied leads to a higher generation of reactive oxygen species (ROS) that can increase the efficiency of organic compound degradation.

Figure 5 shows the impact of the current density applied on the degradation of amoxicillin (1g/L) in 0.1M $KClO_4$ medium at 25°C during 10h of electrolysis. The current densities applied are 20 and 100 mA/cm². For this purpose, the pseudo-first-order rate constants were determined using the formula:

$$Ln(COD *) = -k \times t \quad (6)$$

With k the rate constant in h^{-1} and t the electrolysis time in h.

It appears in this figure that the kinetic rate of degradation increases with the applied current density. Indeed, the kinetic constant, after 10h of electrolysis, goes from $0.0024h^{-1}$ for 20mA/cm² to $0.0103h^{-1}$ at 100 mA/cm², respectively. As the current density increases, the rate of degradation of amoxicillin increases.
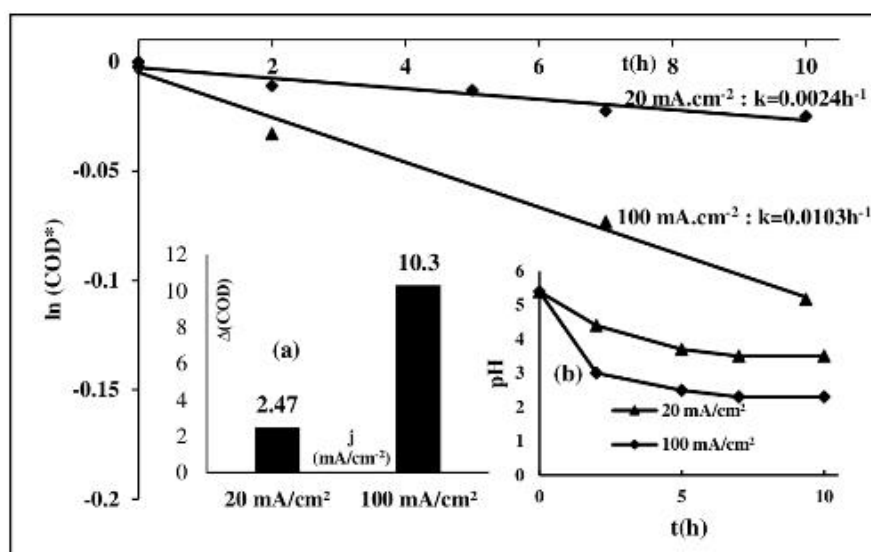

Figure 5. Plot of ln (COD*) versus time
Insert: plot of ΔCOD % versus current density (a) and Evolution of pH during amoxicillin electrolysis at a different current density

The chemical oxygen demand abatement rate (ΔDCO) (Insert (a) in Figure 5), determined after 10 hours of electrolysis, is respectively 2.47% and 10.3% for 20 mA/cm² and 100 mA/cm². The COD abatement rate increases but slightly with current density. In general, the degradation of amoxicillin on the IrO_2 electrode is very low compared to BDD electrode [38]. This weak degradation of amoxicillin could be due to the adsorption of intermediates formed on the electrode's surface. In addition, two mechanisms of organic compound degradation on an IrO_2 electrode are possible: direct and/or mediated oxidation [39]. In direct oxidation, the compound is degraded by the direct electronic exchange at the electrode's surface. In a

mediated oxidation, the organic compound is degraded through oxidative species or by the anode's higher oxide.

During electrolysis, the hydroxyl radicals formed from the decomposition of water interact strongly with the surface of the IrO_2 anode. They, therefore, cannot participate effectively in the degradation of the organic compound. Metal cations in the oxide network can reach higher oxidation states (MOx), participating as a mediator in the oxidation of organic materials, which competes with the side reaction of the evolution of oxygen via chemical decomposition of higher oxide species. Therefore, the hydroxyl

radicals and the higher oxide formed on the surface of the IrO_2 anode promote the electrochemical conversion of organic matter into other intermediate compounds [40].

The pH was monitored during the electrolysis. The results obtained (Insert (b) of Figure 5) show that the pH decreases from 5.4 to 3.5 for 20 mA/cm² and from 5.4 to 2.3 for 100 mA / cm². After 10 hours of electrolysis, the solution's pH is acidic, this would attest that amoxicillin's degradation leads to the formation of intermediate acid compounds.**3.3.2. Effect of supporting electrolyte**
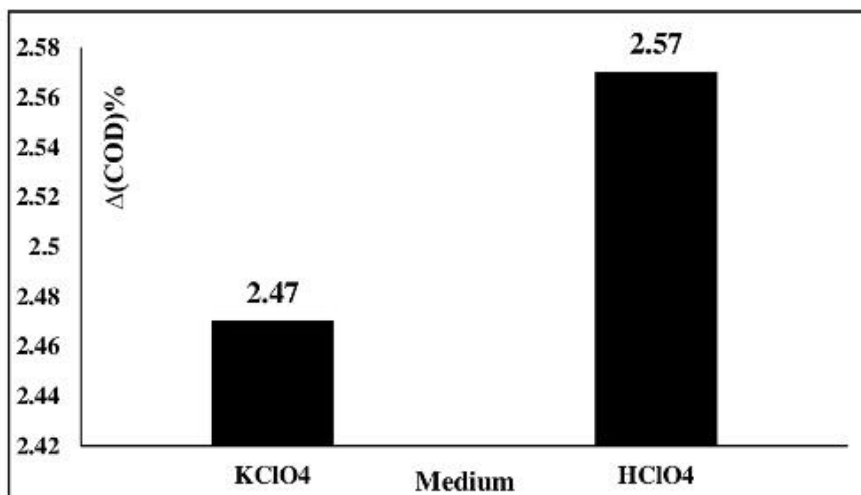
The type of supporting electrolyte is a crucial parameter for the electrochemical process. The supporting electrolyte has many advantages: increase of conductivity, decrease of the medium's resistance, and therefore allow an energy gain. The effect of 0.1M

$KClO_4$ and 0.1M $HClO_4$ on the degradation of amoxicillin (1g/L) was investigated under a current density of 20 mA/cm² at a temperature of 25°C. The results obtained are presented in   Figure 6.

Figure 6. COD Abatement rate of amoxicillin in 0.1M $KClO_4$ and 0.1M $HClO_4$

The COD abatement rate determined after 10 hours of electrolysis is 2.47% and 2.57%, respectively, in 0.1M $KClO_4$ and 0.1M $HClO_4$ medium. 0.1M $KClO_4$ is less efficient for the degradation of amoxicillin (1g/L) than 0.1M $HClO_4$. The presence of the H+ protons can explain these results. Additionally, the cell potential

was monitored during electrolysis (data not shown). The average potential is 4.39 V and 8.24V in 0.1M $HClO_4$ and 0.1M $KClO_4$ medium, respectively. The acidic medium (0.1M $HClO_4$) allows an energy gain by reducing the solution's ohmic resistance.
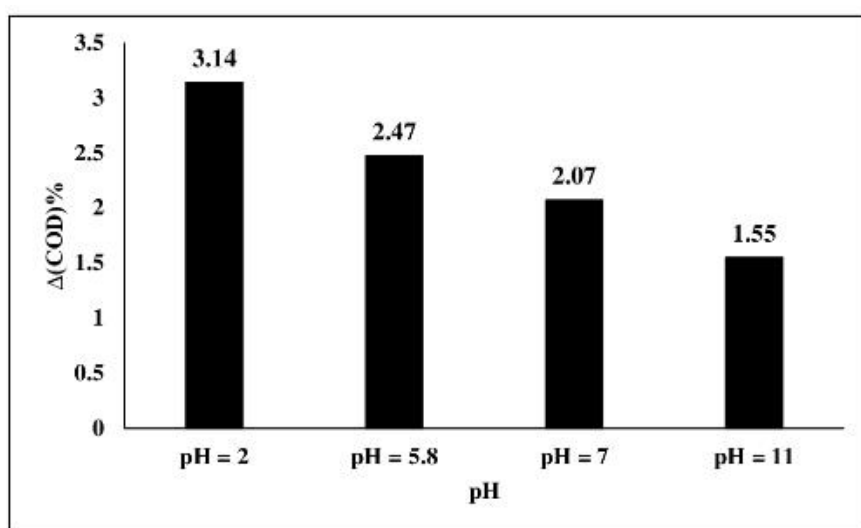

Figure 7. Amoxicillin COD reduction rate for different pH

3.3.3. Effect of initial pH
To improve the degradation rate of amoxicillin on the IrO_2 electrode, investigations into the effect of pH were performed. The pH is a crucial parameter in

electrooxidation because it can strongly influence the organic compound degradation rate and be responsible for generating oxidative species in solution [41]. To determine the effect of the initial pH on

the rate of amoxicillin degradation, the measurements were carried out in a reactor stirred at a current density of 20 mA / cm². The effect of pH has been studied in a pH range of 2 to 11 for a fixed concentration of amoxicillin (1g/L). The results obtained are presented in Figure 7.

It showed that, after 10 hours of electrolysis, the abatement rates of the chemical oxygen demand obtained are 3.14%, 2.47%, 2.07%, and 1.55% for pH 2, 5.8, 7, and 11, respectively. The COD abatement rate is 1.27, 1.52, and 2.03 times greater at pH 2 than at pH 5.8, 7, 11, respectively. The degradation of amoxicillin appears to be better in acidic media than in neutral and alkaline media. Some authors have shown that acidic medium promotes organic compound degradation by inhibiting the oxygen evolution reaction [42,43]. That could explain the enhancement of amoxicillin degradation efficiency at pH 2. It has been demonstrated that the oxidation of organic compounds is more favorable in an acidic medium [42,44]. Moreover, the best elimination of AMX obtained at pH 2 could also be linked to amoxicillin pKa, which is 2.8 close to pH 2. It would be more susceptible to electrophilic attack at this pH than in a weakly acidic or alkaline medium [45,46].

Additionally, we could add the probable formation of oxidative species such as Cl_2 from supporting electrolyte ($KClO_4$) at a very acidic pH (pH <3) (Eq.7) which would contribute to the improvement of the degradation of amoxicillin.

$$2ClO_4^- + 16H^+ + 14e^- \rightarrow Cl_{2(g)} + 8H_2O$$
(7)
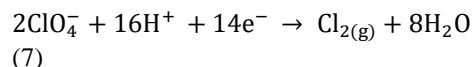
However, the degradation of amoxicillin on the IrO_2 electrode prepared at 400°C is very difficult for all of the pHs explored with COD abatement rates are less than 4%.

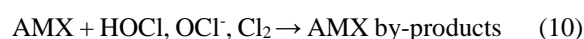### 3.3.4. Effect of SO_4^{2-}, PO_4^{3-}, NO_3^-, Cl^-

The contribution of inorganic ions to the degradation of amoxicillin (1g/L) was investigated in a neutral medium (0.1M $KClO_4$) containing different inorganic ions SO_4^{2-}, PO_4^{3-}, NO_3^-, Cl^-. These ions are commonly found in real wastewater, especially in health centers. The experiments were conducted at a temperature of 25°C under galvanostatic conditions under a current density of 20 mA/cm² for an inorganic ion concentration of 400 mM. Normalized COD was followed. The results obtained are shown in Figure 8. This figure shows that the rate of degradation of amoxicillin is prolonged in the presence of SO_4^{2-}, PO_4^{3-}, NO_3^- ions. However, Cl^- ions' addition has a positive effect on the degradation of amoxicillin on the IrO_2 electrode. The COD abatement rate calculated after 10 hours of electrolysis and presented in Figure 9 gives 2.47%; 2.68%; 7.7%; 16.41% and 71.65% respectively, in the absence of inorganic ions and in the presence of SO_4^{2-}, PO_4^{3-}, NO_3^-, Cl^-. SO_4^{2-} and PO_4^{3-} ions have hardly any effect on amoxicillin. Some authors [34] have shown that the presence of SO_4^{2} ions did not positively impact the degradation of phenol on the IrO_2 electrode. NO_3^- ions have a slightly

positive impact on amoxicillin degradation, while the Cl^- ions have a powerful and very pronounced effect on amoxicillin's degradation kinetics. Gnamba et al. showed that the presence of Cl^- ions allowed to reach 100% of ceftriaxone (1g/L) on the BDD electrode in a neutral medium (pH = 7). In the work of Lic A. Perea et al. [47], in the presence of the Cl^-, 100% of the cephalexin concentration is degraded against only 2 and 5% in the presence of the SO_4^{2-}, PO_4^{3}, respectively. Likewise, Sindy D. Jojoa-Sierra et al. [33] showed that in the presence of Cl^-, 70% of the antibiotic norfloxacin was eliminated on the IrO_2 electrode after 20 min of electrolysis. On the other hand, 9 and 3% of norfloxacin was degraded in the presence of SO_4^{2-} and NO_3^- respectively. According to Sindy D. Jojoa-Sierra et al., in the presence of Cl^-, oxidative species are generated. They effectively contribute to norfloxacin's degradation, which is not the case for the SO_4^{2-} and NO_3^- [47]. Contrariwise, Ana L. Giraldo et al. [34] showed that the NO_3^- provided the best elimination rate (80%) of oxacillin after 1 hour of electrolysis than SO_4^{2-} (less than 25%).
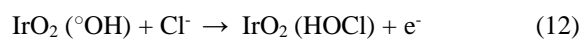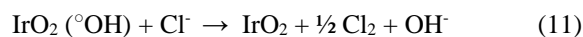
Chloride, through the formation of active chlorine would practically lead to mineralization of the initial compound. Indeed, the oxidation of chloride ions on the surface of IrO_2, on the one hand, leads to the formation of active chlorine which is then hydrolyzed to give HOCl or OCl^- (Eqs (7)-(9)) [26]:
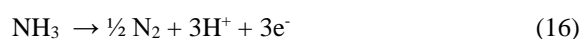
$$2\,Cl^- \rightarrow Cl_2 + 2e^-$$
(7)

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-$$
(8)

$$HOCl \rightleftharpoons OCl^- + H^+$$
(9)
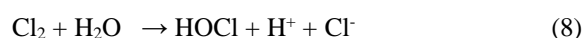
These oxidative species will degrade amoxicillin (Eq.(10))

$$AMX + HOCl, OCl^-, Cl_2 \rightarrow AMX\ by\text{-}products$$
(10)

On the other hand, the oxidation of the chloride with a hydroxyl radical bound on the IrO_2 ($IrO_2(°OH)$) indirectly produces free chlorine [48,49], and the linked hydroxyl radical can lead to the possible formation of bound HOCl on the metal surface which can oxidize an organic substance [50] (Eqs. (11)-(13)) :

$$IrO_2\,(°OH) + Cl^- \rightarrow IrO_2 + ½\,Cl_2 + OH^-$$
(11)

$$IrO_2\,(°OH) + Cl^- \rightarrow IrO_2\,(HOCl) + e^-$$
(12)

$$IrO_2\,(HOCl) + AMX \rightarrow CO_2 + H_2O + Cl^-$$
(13)

In the case NO_3^- ions, it can be reduced at the cathode to nitrite ions and ammonia (NH_3) with the formation of hydroxyl ions leading to an increase of pH to the reaction medium [47]. (Eqs (14) -(15)). NH_3 could compete with amoxicillin's oxidation reaction on the electrode by electronic exchange (Eq.16) [33]. This could explain the slight increase in the rate of elimination of amoxicillin in the presence of NO_3^-

$$NO_3^- + H_2O + 2\,e^- \rightarrow NO_2^- + 2OH^-$$
(14)

$$NO_2^- + 5H_2O + 6e^- \rightarrow NH_3 + 8OH^-$$
(15)

$$NH_3 \rightarrow ½\,N_2 + 3H^+ + 3e^-$$
(16)

SO_4^{2-} and PO_4^{3-} ions can generate $S_2O_8^{2-}$ and $P_2O_8^{4-}$ (Eqs (17)-(18)) [51,52], respectively, which are powerful oxidizing agents that can oxidize organic compounds and thus increase their degradation rate. However, the generation of these oxidants in the reaction medium depends on the electrode material used at the anode. Indeed, their formation is much favored when non-active anodes such as BDD [51,52] are used. The negligible contribution of SO_4^{2-} and PO_4^{3-} ions on the degradation of amoxicillin on the IrO_2 electrode could be explained oxidizing agents $S_2O_8^{2-}$ $P_2O_8^{4-}$ are not formed during electrolysis of amoxicillin on this electrode.

$$2SO_4^{2-} \quad \rightarrow \quad S_2O_8^{2-} + 2e^- \qquad (17)$$

$$2PO_4^{3-} \quad \rightarrow \quad P_2O_8^{4-} + 2e^- \qquad (18)$$

According to the finding below and under our working conditions, the classification of inorganic ions in increasing order of positive impact on the degradation of amoxicillin on the IrO_2 electrode is follows as: $SO_4^{2-} < PO_4^{3-} < NO_3^- < Cl^-$.

During electrolysis, the average current efficiency for COD was determined using the following relation (Eq(19)) [52]

$$ACE = \frac{FV(DCO_0 - DCO_t)}{8I\Delta t} \qquad (19)$$

Where COD_0 and COD_t are the chemical oxygen demand (in g of O_2 dm^{-3}) at times 0 and t (in seconds), respectively, I is the current intensity (A), F is the Faraday constant (96 487 C mol-1), V is the volume of the electrolyte (dm^3), and 8 is a dimensional factor for unit consistency [(32 g of O_2,mol^{-1} of O_2)/(4 mol of e^-,mol^{-1} of O_2)].

After 10 hours of electrolysis of amoxicillin in $KClO_4$ 0.1M as supporting electrolyte, the average current efficiency obtained is 0.94%, 0.97%, 2.85%, 5.29%, and 45.12%, respectively, in the absence and presence of sulfate ions, phosphate ions, nitrate ions, and chloride ions. These results show that part of the current applied was used in the degradation of amoxicillin. The other part of the current could intervene in the production of reactive species that could participate in the oxidation process and/or produce undesirable side reactions like oxygen evolution reaction. ACE strongly depends on the ions present in the solution. These results show that chloride ions seem to better for the degradation of amoxicillin because it leads to the highest degradation rate of amoxicillin and reduces current losses considerably compared to other inorganic ions.

To assess the energy cost linked to amoxicillin's degradation, total energy consumption (TEC) to degrade one kg of COD was determined in the absence and presence of inorganic ion. The results are recorded in Table 2. The TEC was calculated using the following formula [53]:

$$TEC = \frac{t \times U \times I}{V \times \Delta(COD)} \times 1000 \qquad (20)$$

where t is the electrolysis time (h), U the average electrolysis cell voltage (V), I the applied electrolysis current (A), V the wastewater volume (L), and $\Delta(COD)$ the difference in COD (mg L^{-1}).
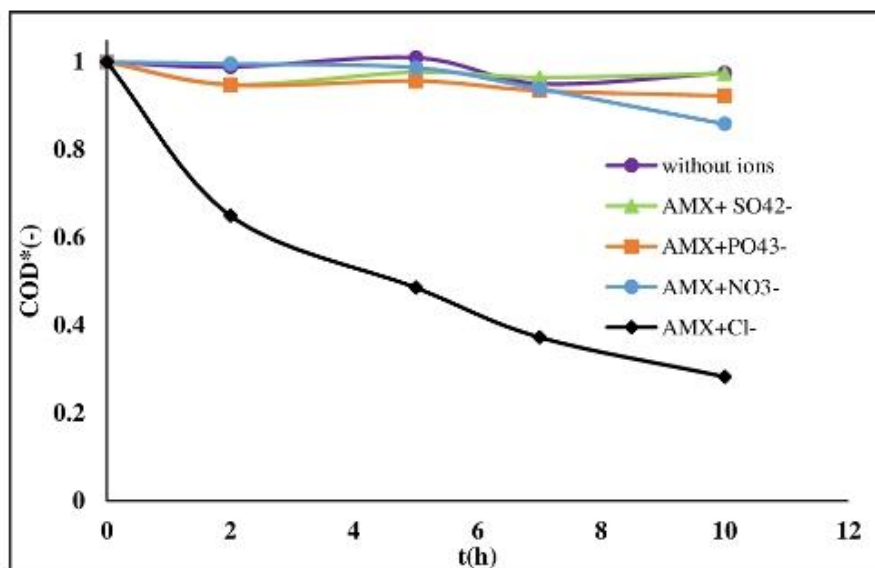

Figure 8. Effect of SO_4^{2-}, PO_4^{3-}, NO_3^-, Cl^- ions on the electrooxidation of 1g /L of amoxicillin on the IrO_2 electrode at current density of 20 mA / cm²
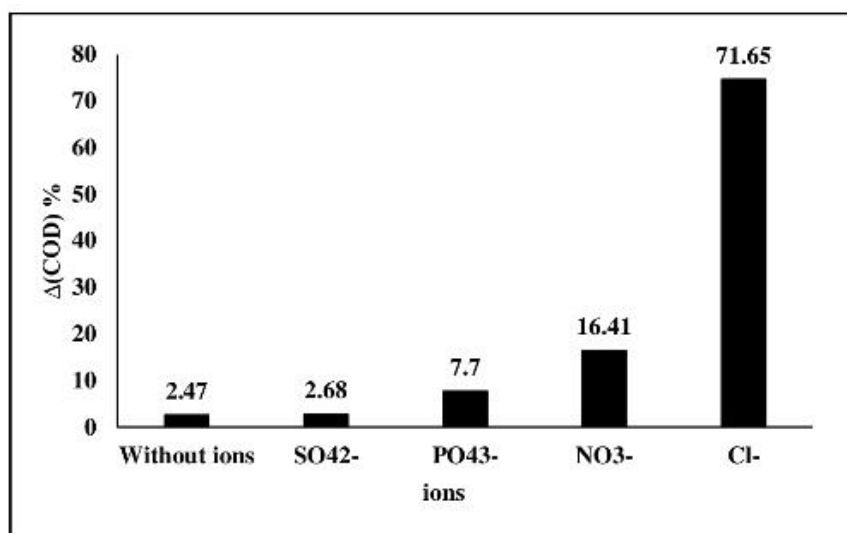
Figure 9. COD abatement rate according to ions SO_4^{2-}, PO_4^{3-}, NO_3^-, Cl^-

According to Table 2, TEC values are 2928.25, 1373.41, 730.42, 287.43, and 33.19 $Kwh.kg^{-1}COD$, respectively, in the absence of inorganic ion and the presence of SO_4^{2-}, PO_4^{3-}, NO_3^-, Cl^-. The degradation of amoxicillin in inorganic ions can significantly reduce energy consumption from 53% to 98%. IrO_2 electrodes can be used to treat real wastewater containing inorganic ions, especially chloride.

Table 2. Total energy consumption.

Ions / 400 mM	TEC / kWh.kg^{-1}COD
Without ions	2928.35
SO_4^{2-}	1373.41
PO_4^{3-}	730.42
NO_3^-	287.43
Cl^-	33.19

4. Conclusion

This work indicates that the IrO_2 electrode prepared at 400°C has a rough surface with pores' presence. The oxidation of amoxicillin causes a deposit on its surface, causing a decrease in its electrocatalytic activity. In addition, the oxidation of amoxicillin can occur directly by the electronic exchange on the surface of IrO_2 or by IrO_3. The current density has a significant effect on the efficiency of this electrode. Amoxicillin degradation kinetic constant increases with current density. The supporting electrolyte and pH also affect the removal of amoxicillin at the IrO_2 electrode. The degradation of this compound is favored in a very acidic medium. However, this degradation remains very low and is less than 11% of the elimination rate, indicating that amoxicillin's degradation leads to converting the parent compound into reaction intermediates.

The effect of some ions commonly found in hospital wastewater was investigated on simulated wastewaters containing 1g/L of amoxicillin. These studies show that these ions' effects are diverse, with COD reduction rates ranging from 2.47%; 2.68%; 7.7%; 16.41%, and 74.65%, respectively in the absence and presence of SO_4^{2-}, PO_4^{3-}, NO_3^-, Cl^-. Sulfate ions have virtually no effect on enhancing the degradation of amoxicillin. Phosphate ions provide a slight improvement in the breakdown of amoxicillin. As for nitrate ions, their effect is 2.31 times that of phosphate ions. In solution, nitrates are reduced at the cathode to nitrites and ammonia. The latter would compete with the degradation of amoxicillin via electron transfer. Chloride ions very significantly improve the performance of the electrooxidation of amoxicillin on IrO_2. The oxidative species resulting from the chloride ions participate effectively in the degradation of the organic compound. The presence of ions, especially chloride ions, makes it possible to go from 2928.35 (absence of inorganic ions) to 33.19 kWh per Kg of COD. This represents an energy gain of over 98%.

This electrode could be used to treat real wastewater containing inorganic ions, especially chloride in large quantities.

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