



Electrochemical Degradation of Amoxicillin on a Ti/Ta₂O₅/Pt-RuO₂-IrO₂ Electrode

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Abstract

This work deals with the degradation of Amoxicillin which is one of the antibiotics commonly used in human and veterinary medicine. For such an investigation, Pt-RuO₂-IrO₂ (PRI) electrode was used as anode and various parameters such as current density (20 - 100 mA/cm²), supporting electrolyte and chloride were monitored. The results showed that the amoxicillin oxidation reaction is diffusion controlled and its degradation rate increases as the applied current increases. The degradation of amoxicillin on the PRI electrode, in the absence of chloride, is very low with less than 10% of the COD abatement rate. But, in the presence of chloride, the degradation of the Amoxicillin on PRI electrode leads to its mineralization. During electrolysis, chloride was oxidized into chlorine under the form HClO at pH < 8 and ClO⁻ at pH > 8 that contribute to a significant degradation of the Amoxicillin. The amoxicillin removal rate goes from 0.83% to 73.8% in the absence and in the presence of Cl⁻, respectively after 10 h of electrolysis. In addition, the degradation kinetic of amoxicillin in HClO₄ is 10 times faster than in KClO₄ and follows pseudo first-order reaction.

Subject Areas

Electrochemical, Environmental Chemistry

Keywords

Amoxicillin, Electrooxidation, Platinum, Ruthenium Oxide, Iridium Oxide

1. Introduction

The pollution of the surface water by hospital wastewaters is a source of major concern in recent years in our country [1] [2]. In fact, the wastewater treatment

system at the Teaching Hospital Center of Treichville in Ivory Coast, built just after his independence, stopped working since 1975 [3]. This, the wastewater of this health center is directly and continuously discharged into the Ebrié lagoon without any treatment [3]. This lagoon is widely used for transportation, fishing activities and also for the development of market gardening. They represent a threat to human health. Indeed, the presence of pharmaceuticals in wastewater not only affects the water quality, but also causes long term potential adverse impacts on the ecosystems and the human health [4] [5] [6] [7]. Among various pharmaceuticals, the occurrence of antibiotics used in both human and veterinary medicine deserves special attention due to their wide, unrestricted use and the emergence of negative effects such as the proliferation of antibiotic-resistant pathogens [8] [9]. Several studies have found widespread antibiotic resistance in major US Rivers, which is attributed to long-term exposure to low concentrations of antibiotics [10]. Amoxicillin is one of the most used drugs worldwide, has been detected in surface waters and showed a resistance to biological treatment [11] [12]. In these conditions, advanced oxidation processes (AOP) appear as an alternative to solve the problem of environmental pollution by biorecalcitrant pharmaceutical compounds [13] [14]. Advanced oxidation processes are characterized by the production of extremely reactive and unselective hydroxyl radicals which are able to oxidize and mineralize almost all organic compounds to CO₂ and water [15] [16] [17]. In this work, advanced electrochemical oxidation processes have been employed because they do not require the addition of toxic chemical reagents and do not induce the production of hazardous compounds [18]. The oxidation of the organic occurs through hydroxyl radicals produced by the decomposition of water on the surface of the anode [19] [20]. The oxidation of large organic compounds in aqueous solution is carried out via these radicals and their production depends on the nature of the anode material used. That needs an overpotential of O₂ evolution which is different from one anode to another. Anodes with high overpotential, such as boron doped diamond (BDD) [21] [22], allow the generation of hydroxyl radicals as intermediate species. In this case, the radicals formed are physisorbed on the surface of the anode (little interaction between the hydroxyl radicals and the electrode), are quasi-free (mobile) and therefore very reactive leading to the mineralization of the organic compound. While for the other electrodes like Pt, IrO₂ and RuO₂ called active anodes, the hydroxyl radical is oxidized to a chemisorbed “superoxide” species with less oxidizing power that only yield the electrochemical conversion of organics into carboxylic acids [23] [24] [25]. Studies conducted on DSAs have shown that the efficiency of these electrodes is improved in the presence of inorganic ions [26]. In this work, the effect of chloride ions on the efficiency of a new DSA electrode, prepared thermally at 400°C, will be investigated in the degradation of amoxicillin. It is an electrode composed of platinum associated with iridium and ruthenium oxides (Pt-RuO₂-IrO₂ or PRI). To our knowledge, such an electrode has never been the subject to a scientific publication.

2. Experimental and Analytical

2.1. Materials

2.1.1. Electrode Ta₂O₅/Pt-RuO₂-IrO₂ Preparation

The Ta₂O₅/Pt-RuO₂-IrO₂ electrode employed as anode was thermally prepared titanium substrate. The substrate titanium used has a dimension of 50 mm × 50 mm × 0.5 mm. It was sanded and then rinsed with distilled water so as to remove the grains of sand remaining on the support. Afterwards, the support was rinsed in pure isopropanol with stirring (800 rpm) for 30 minutes. The precursors were prepared from H₂PtCl₆·6H₂O (Fluka, 38%), RuCl₃·xH₂O (Fluka, 99.98%) and H₂IrCl₆ (Fluka, 99%). These products were each diluted in 10 mL of isopropanol. The mixture of precursors of Pt, RuO₂ and IrO₂ was made in the ratio 2:1:1. Isopropanol (Fluka, 99.5%) was used as the solvent. Procedures for the Titanium and precursor deposition are described in previous work [27] [28]. The final electrode obtained has a surface of 16 cm².

2.1.2. Amoxicillin Solution

Amoxicillin (7-amino-3,3-dimethyl-6-oxo-2-thia-5-azabicycloheptane-4-carboxylic acid) with the empirical formula C₁₆H₁₉N₃O₅S (**Figure 1**) is a bactericidal β-lactam antibiotic of the aminopenicillin family. This product has been used in tablet formulation and purchased from pharmacies in Abidjan. It was dissolved in a 0.1 M solution of KClO₄. Ultra pure distilled water was used to prepare the supporting electrolyte.

2.2. Bulk Electrolysis

For the exhaustive electrolysis, a single compartment in galvanostatic regime and ideally stirred batch reactor was used. The solution flow rate was 2.08 mL·s⁻¹. The other chemicals used in this work are composed of KClO₄ (Fluka), HClO₄ (Fluka) and NaCl (Fluka). All the chemicals have been used as received without any further treatment for the experiment. All the experiences were carried out under magnetic agitation at ambient temperature of 25°C. The mass transfer coefficient determined using the potassium ferri/ferrocyanide redox couple (Fluka) was 2.36 × 10⁻⁷ m·s⁻¹. The anode was Ta₂O₅/Pt-RuO₂-IrO₂ while Zirconium (Zr) plates were used as cathode. During each electrolytic run, samples of 2 mL were taken from the reactor at defined time intervals and analysed in terms of COD and absorbance.

A schematic of experimental mounting is shown in **Figure 2**.

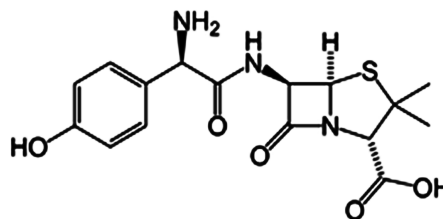


Figure 1. The structure of amoxicillin.



Figure 2. A schematic of experimental mounting.

2.3. Analytical Measurements

Chemical oxygen demand (COD) of the samples was determined using the pre-dosed COD tubes of the HACH product. 2 mL of samples are taken and introduced into a HACH tube and heated in a HACH brand digester at 150 °C for 120 minutes. After cooling, the COD is read directly by means of the spectrophotometer DR/6000 of the HACH product with a wavelength of 620 nm.

For the measurement of the absorbance, 2 mL of the sample taken at predefined intervals of time are introduced into a tube. The wavelength of the sample is also determined using the HACH DR 6000 spectrophotometer.

3. Results and Discussion

3.1. Effect of the Current Density

Current density is a very important parameter in electrooxidation [29]. The effect of current density was investigated during the degradation of an amoxicillin solution (1 g/L) prepared in 0.1M potassium perchlorate (0.1 M KClO_4). The current densities used in this work vary from 20 to 100 mA/cm^2 . To follow the degradation of amoxicillin during its electrolysis, the chemical oxygen demand (COD) was measured. In this work, COD was normalized according to Equation (1).

$$\text{COD}^* = \text{COD}_0 / \text{COD}_t \quad (1)$$

where

COD^* is the normalized value of the COD.

COD_0 is the chemical oxygen demand at the initial time and COD_t , the oxygen demand at any time t .

Figure 3 shows the effect of the current density on the evolution of COD^* at 25 °C as a function of time. COD^* decreases rapidly as the current density increases. Thus, the COD abatement rate (insert **Figure 2**) obtained after 10 h of electrolysis is 0.83%; 10.71% and 40.91% at 20, 50 and 100 mA/cm^2 respectively. Such an observation has also been made in previous work on BDD used as anode for the degradation of amoxicillin (1 g/L) [30]. However, the COD abatement rates obtained on the PRI are very low compared to those obtained on BDD. This could be explained by the fact that on the BDD, the hydroxyl radicals formed by the decomposition of water are free and therefore very reactive. While

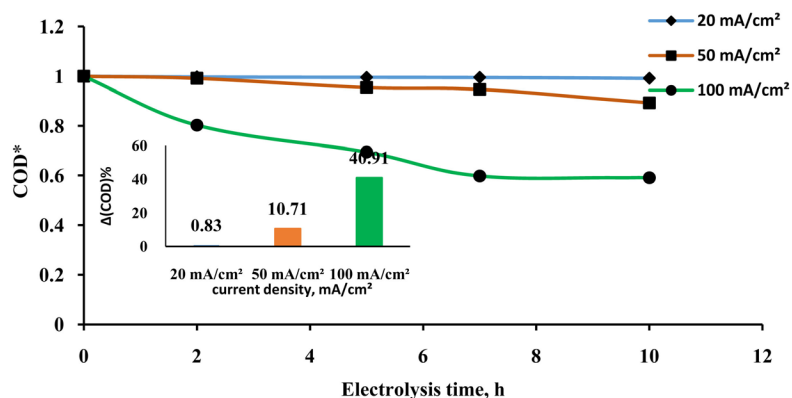
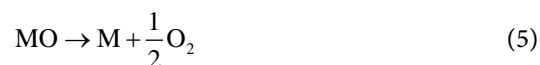
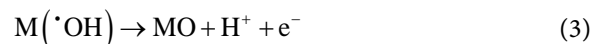
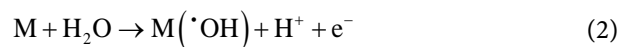


Figure 3. Electrolysis of 1 g·L⁻¹ of amoxicillin on PRI electrode in 0.1 M sodium perchlorate electrolyte under different current densities, Anode: PRI, cathode: Titanium plate, T = 25 °C, inset: plot of ΔCOD % versus current density.

on the PRI, a DSA type electrode, these hydroxyl radicals are chemisorbed and do not contribute effectively to the degradation of the organic compound. Indeed, the initial step in the electrooxidation of amoxicillin on the PRI electrode would be the decomposition or discharge of water leading to the formation of adsorbed hydroxyl radicals (Equation (2)). These hydroxyl radicals have a strong interaction with the surface of the PRI electrode. The next step is the formation of a higher oxide (Equation (3)). This higher oxide is responsible for the degradation of the organic compound (Equation (4)) but that leads to partial and selective oxidation of the organic. However, the oxidation reaction competes with the oxygen evolution reaction (OER) (Equation (5)).



M is the anode material and R is the organic compound.

The initial current density has been calculated using Equation (6).

$$I_{lim} = 4Fk_d A \cdot COD \quad (6)$$

where F is the Faraday constant ($F = 96\,487 \text{ C}\cdot\text{mol}^{-1}$), C , k_d is the mass transfer coefficient ($\text{m}\cdot\text{s}^{-1}$), A is the electrode surface area in contact with the solution (m^2), COD is the chemical oxygen demand ($\text{mol}\cdot\text{m}^{-3}$).

According to literature [31] [32], two main regimes can be reached depending on the applied current compared to the initial limiting current.

If $I < I_{lim}$ a galvanostatic process governs the overall oxidation process *i.e.* limited by charge transfer reaction. Under these conditions, all the applied current is used for the oxidation of the organic compound.

If $I > I_{lim}$ the oxidation process is mass transfer controlled *i.e.* limited by diffusion. Under these conditions, part of the applied current, which is equal to the

limiting current, is used for the electrooxidation of the organic compound and the rest for the side reaction *i.e.* oxygen evolution.

The limiting current density calculated in this work is $7.1 \text{ mA}\cdot\text{cm}^{-2}$. This value of the limiting current density is lower than the applied current density. So the oxidation process of amoxicillin is limited by diffusion. In such a regime, other reactions, such as oxygen evolution reactions, may compete with the oxidation reaction of amoxicillin.

During the electrolysis of 1 g/L of the amoxicillin solution at $20 \text{ mA}/\text{cm}^2$ and $100 \text{ mA}/\text{cm}^2$, the absorbance of the samples withdrawn at different times from the synthetic wastewater tank has been registered. The obtained results are shown in **Figure 4**. For $20 \text{ mA}/\text{cm}^2$ (**Figure 4(a)**), the absorption spectra increase with the electrolysis time. The peak recorded at 350 nm was plotted against the electrolysis time (insert of **Figure 4(a)**). In **Figure 4(a)**, it is observed that the absorbance increases during all the electrolysis duration. This could be due to the production of reaction intermediates that continues to be produced during electrolysis. Indeed, there is a conversion of amoxicillin into

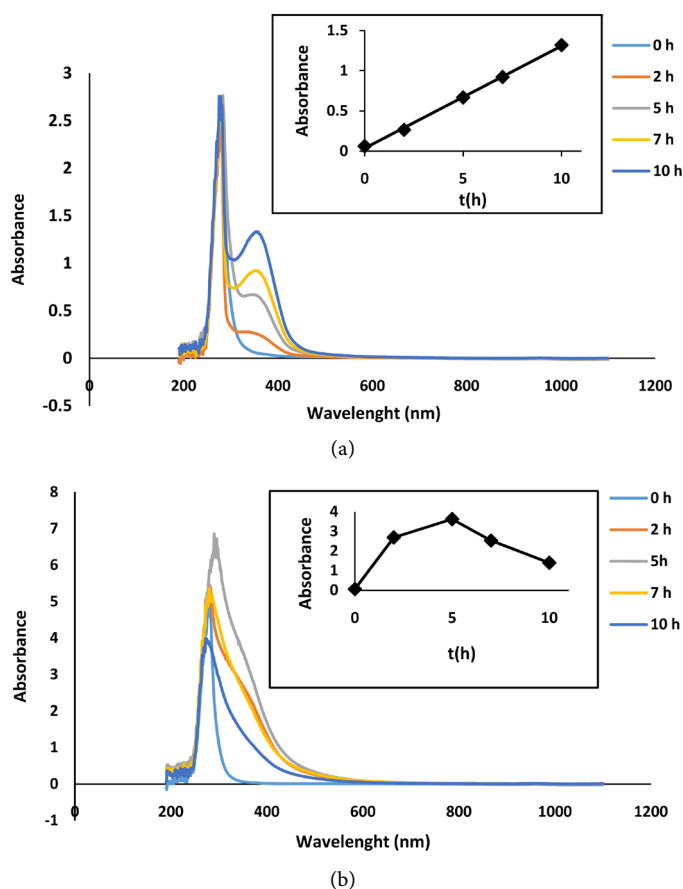


Figure 4. Evolution of amoxicillin absorbance versus wavelength during PRI electrolysis in 0.1 M KClO_4 at different current densities. (a) $20 \text{ mA}/\text{cm}^2$, in insert: Evolution of the absorbance as a function of the electrolysis time (wavelength = 350 nm); (b) $100 \text{ mA}/\text{cm}^2$, in insert: Evolution of the absorbance as a function of the electrolysis time (wavelength = 350 nm).

organic compounds that absorb at the same wavelength as the amoxicillin. The degradation of amoxicillin on the PRI electrode at 20 mA/cm² leads to continuous formation of one or more intermediates that absorbed at the same wavelength. The absorbance of the samples withdrawn from the synthetic wastewater tank was also recorded at 100 mA/cm². The obtained result is shown in **Figure 4(b)**. In the insert of **Figure 4(b)** the peak of the absorbance of the amoxicillin solution was plotted as a function of the electrolysis time for a wavelength of 350 nm. In this figure, the absorbance increases until it reaches a maximum value after 5 hours. After 5 h, there is a decrease of the absorbance up to 10 hours of electrolysis. This shows that the electrolysis of amoxicillin leads to the formation of some reaction intermediates whose concentration increases until 5 h and then decreases. It appears that the degradation of the intermediates produced under this current density occurs during the electrolysis.

These investigations show that the current density plays an important role in the process of the amoxicillin degradation on the PRI electrode. For 20 mA/cm², the electrolysis of amoxicillin leads to the formation of intermediates with an increase in their concentration during electrolysis. This result shows that the oxidation of amoxicillin at 20 mA/cm² favors conversion of the amoxicillin to some reaction intermediates. But under 100 mA/cm², the concentration of the intermediates increases until reaching a maximum value at 5 h (100 mA/cm²) before decreasing in the rest of the electrolysis time.

From these results, it could be noted that increasing the applied current density causes an increase of the adsorbed oxidative species such as hydroxyl radicals at the surface of the anode electrode that contributes to the enhancement of the organic compound degradation [33] [34].

3.2. Effect of the Supporting Electrolyte

The effect of the supporting electrolyte was investigated on the degradation of 1 g/L of amoxicillin at 20 mA/cm² on the PRI electrode used as the anode. The supporting electrolytes used are 0.1 M KClO₄ and 0.1 M HClO₄ at 20 mA/cm². The obtained results are shown in **Figure 5**.

In this figure, the COD * decreases very slowly in HClO₄ whereas it is almost constant (does not change) in KClO₄. After 10 hours of electrolysis, the obtained COD reduction rates are 0.83% for KClO₄ and 8.15% for HClO₄.

The degradation kinetic constant was determined during the degradation of amoxicillin in 0.1 M KClO₄ and 0.1 M HClO₄ (insert of **Figure 5**). In both the solutions, the obtained kinetic constants are 0.0007 h⁻¹ and 0.0089 h⁻¹ in potassium chlorate and perchloric acid, respectively. From these results, it appears that the kinetic of the reaction is pseudo-first order and the degradation seems to occur more easily in HClO₄ than in KClO₄. This finding could probably be due to the participation of protons (H⁺) in the degradation process of amoxicillin. Indeed, it has been shown that in acidic solution, DSA type electrode surface is more active and the oxygen evolution reaction (OER) rate diminishes in favor of amoxicillin degradation [33] [35]. Moreover, it's also reported in some works

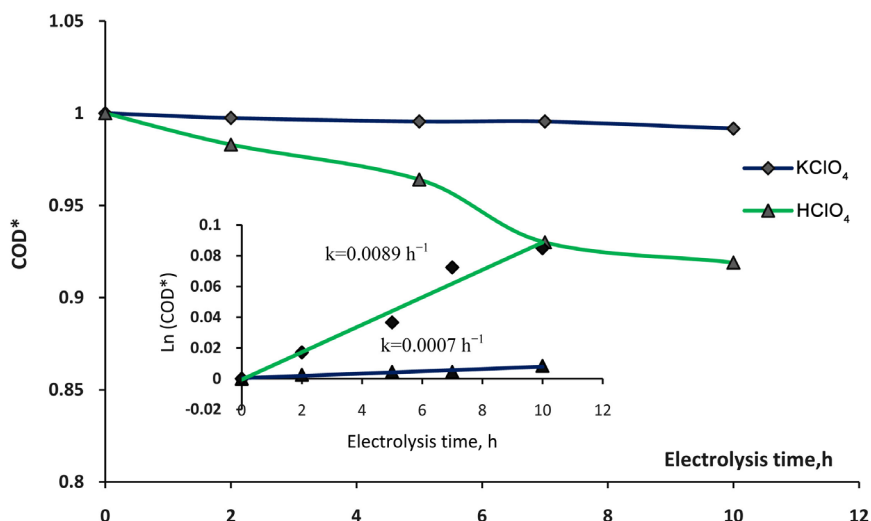


Figure 5. Electrolysis of $1 \text{ g}\cdot\text{L}^{-1}$ of amoxicillin on RuO_2 electrode in KClO_4 0.1 M and HClO_4 0.1 M at $20 \text{ mA}\cdot\text{cm}^{-2}$. Anode: $\text{Pt-RuO}_2\text{-IrO}_2$, cathode: Zr , $T = 25^\circ\text{C}$, in the inset: plot of $\ln(\text{COD}^*)$ versus time.

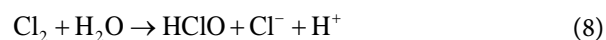
that the oxygen evolution reaction (OER) is kinetically favored in a less acidic medium (neutral or an alkaline medium) [35]. We can conclude that the supporting electrolyte medium influence, significantly the degradation of amoxicillin on the PRI electrode.

3.3. Effect of the Presence of NaCl

In order to be closer to real wastewater which pH should be around neutral to be rejected in the environment, we pursue the work in KClO_4 .

The degradation of a solution of 1 g/L of amoxicillin in 0.1 M KClO_4 was carried out in the absence and in the presence of 400 mM NaCl at $20 \text{ mA}/\text{cm}^2$ on the PRI electrode. The obtained results are shown in Figure 6. In the presence of NaCl , the degradation rate of amoxicillin is faster than that obtained in the absence of NaCl . After 10 hours of electrolysis, the reduction rates of the chemical oxygen demand is 0.83% and 73.8% respectively in the absence and in the presence of NaCl . The oxidation of amoxicillin is rapid in the presence of chloride ions. This observation is in agreement with previous reports on the degradation of organic pollutants using DSA anodes in the presence of chloride ions [36].

From these findings, it can be indicated that the degradation of amoxicillin can undergo direct oxidation on the surface of the electrode and/or through oxidative species such as chlorine. Similar results were obtained on the RuO_2 electrode [19]. In fact, in this experimental condition, specific adsorption Cl^- occurs on the DSA (PRI) surface. Then the adsorbed species react leading to Cl_2 according to Equation (7). Furthermore, Cl_2 passes into solution or is evolved. Moreover, in solution, Cl_2 can be present in various forms depending on the pH of the medium. There can be Cl_2 ($\text{pH} < 3$), HClO ($3 < \text{pH} < 8$) and ClO^- ($\text{pH} > 8$) according to Equations (7) to (9):



During the electrolysis of amoxicillin in the presence of 400 mM NaCl, the pH of the solution was followed (Figure 7). The obtained result showed that Cl_2 is mainly in the form of HClO form predominated during the first 5 hours of the electrolysis. After 5 h of electrolysis, the predominated form is ClO^- .

That means that at the first stage of the degradation of Amoxicillin in that medium, indirect reaction involving HClO happens. After 5 h of electrolysis, ClO^- is responsible for degradation of Amoxicillin or its intermediates.

The color of the amoxicillin solution was followed during the electrolysis in the absence (Figure 8(a)) and in the presence (Figure 8(b)) of NaCl. In the absence of NaCl, the solution goes from colorless to dark yellow. In the presence of NaCl, the solution goes from colorless to a dark yellow for 2 h of electrolysis. After 2 h, it becomes colorless again. These results show that a conversion of the initial amoxicillin is favored on the PRI in the absence of Cl^- . In the presence of Cl^- , mineralization of amoxicillin on the PRI occurs.

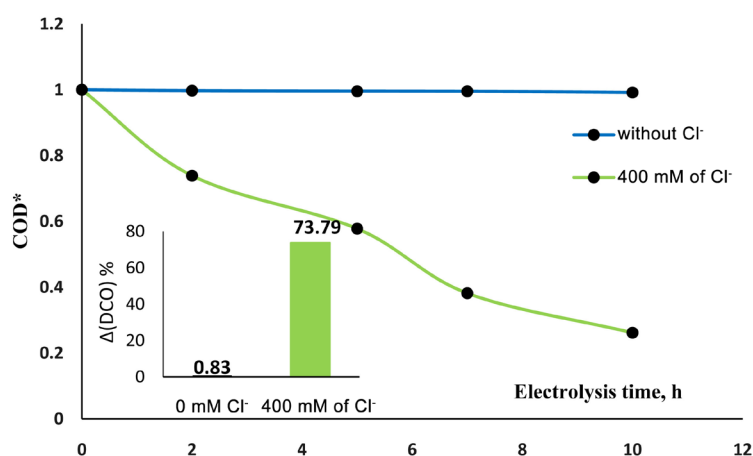


Figure 6. Electrolysis of $1 \text{ g}\cdot\text{L}^{-1}$ Amoxicillin on PRI electrode in KClO_4 0.1 M containing 0 (without) and of NaCl at $20 \text{ mA}\cdot\text{cm}^{-2}$; Anode: PRI; cathode: Titane, $T = 25^\circ\text{C}$; in the inset: (a) plot of $\ln(\text{COD})$ versus time and (b) plot of $\Delta \text{COD} \%$ versus NaCl concentration.

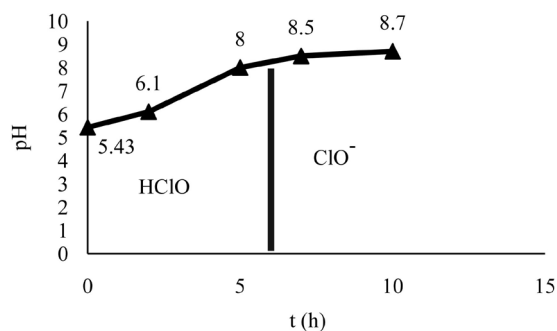


Figure 7. Evolution of the pH during the electrolysis of $1 \text{ g}\cdot\text{L}^{-1}$ amoxicillin.

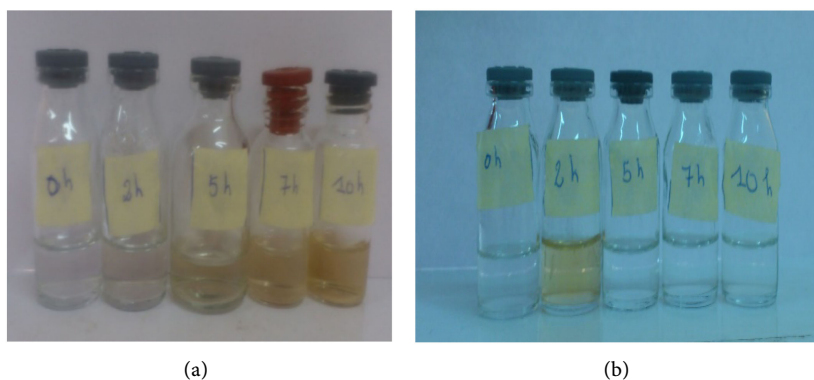


Figure 8. Evolution of the color of amoxicillin in the absence (a) and presence (b) of NaCl.

4. Conclusion

From this work, it appears that amoxicillin oxidation rate increases as the applied current increases. Under the applied current densities of 20, 50 and 100 mA/cm², the amoxicillin oxidation reaction is diffusion controlled. The degradation is more rapid in HClO₄ than in KClO₄ where the surface of the PRI becomes more active. In general, the degradation of amoxicillin on the PRI electrode in the absence of chloride ions is very difficult and leads to the conversion of initial compound. On the other hand, the presence of chloride ions into the solution leads to the mineralization of amoxicillin. The reduction rate of the chemical oxygen demand goes from 0.83% to 73.8% in the absence and in the presence of Cl⁻, respectively. In this work, chloride ions were oxidized into HClO at pH < 8 and ClO⁻ at pH > 8 to degrade amoxicillin.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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