

Cyclic voltammetry study of iohexol behavior in its commercial formulation omnipaque on Ti/Pt electrode

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Received: 20 January 2022 / Received in revised form: 22 March 2022 / Accepted: 15 April 2022

Abstract:

The electro-oxidation of omnipaque was investigated using cyclic voltammetry techniques on platinum electrode prepared by thermal decomposition. The influence of omnipaque concentration, scan rate, temperature and pH were studied. Kinetic parameters such as anodic transfer coefficient, activation energy and Tafel slope were estimated. The scanning electron micrograph of the platinum electrode indicates a smooth and cracked structure. This study revealed that the platinum electrode can be used for a quantitative determination and electrocatalytic degradation of omnipaque. The electro-oxidation of omnipaque on the platinum electrode is an irreversible and diffusion-controlled process followed by a homogeneous chemical reaction. It takes place via direct electron transfer at the platinum/electrolyte interface and indirect oxidation facilitated by hydroxyl radicals generated *in situ*. In the pH range studied, the electro-oxidation of omnipaque involves an exchange of 1 proton and 5 electrons.

The activation energy, anodic transfer coefficient and Tafel slope were 18.456 kJ/mol, 0.34 and 96.4 mV, respectively.

Keywords: Omnipaque; Electro-oxidation; Cyclic voltammetry; Platinum electrode; Iohexol.

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1. Introduction

Humans use a number of pharmaceutical products every day for their health and well-being. After use, the majority of these products are discharged into surface waters at concentrations up to 10 $\mu\text{g/L}$ [1]. Studies have reported that iodinated X-ray contrast media (IXCM) constitute more than 3% of all pharmaceuticals detected in water [2]. IXCMs are a class of pharmaceuticals used in medical imaging to visualize anatomical structures and for the detection of diseases in the body. IXCM molecules are composed of 2,4,6-triiodinated benzoic acid. The presence of iodine in the IXCM structure increases the effective size of the molecule by attenuating the X-rays [3, 4]. The literature shows that IXCMs can be transformed into genotoxic and cytotoxic iodine disinfection by-products [5]. Among the IXCMs, one of the most detected in surface and groundwater at concentrations ranging from ng/L to $\mu\text{g/L}$ is iohexol (IOX). IOX, like other IXCMs, is recalcitrant and very persistent in aquatic environments due to its structure. Thus, the continued release of IOX may pose a potential long-term risk for living organisms [6]. It is therefore necessary to find solutions to this problem. Consequently, work dealing with the degradation of IOX has been carried out [7, 8]. However, fundamental studies using cyclic voltammetry (CV) are very scarce. CV is an electrochemical technique that provides qualitative information such as the kinetic

regime, the anodic transfer coefficient, the activation energy of an electroactive species during an electrochemical process. CV is also used to determine reaction mechanisms, the number of electrons transferred during oxidation or reduction, the theoretical potential, the stoichiometry of a system, heterogeneous rate constants and the diffusion coefficient of electroactive species. CV is a sensitive technique [9]. For the application of this electrochemical technique, the choice of the electrode is one of the important factors that can guarantee a good experimentation. Boron-doped diamond (BDD) is one of the electrodes of choice due to its interesting electrochemical properties [10]. However, the high cost of BDD limits its use. Therefore, other electrodes, such as platinum (Ti/Pt) with very good electrocatalytic properties, are increasingly used for the electrochemical oxidation of pharmaceuticals [11, 12]. In our literature review, no studies on the behavior of IOX on the Ti/Pt electrode have been carried out in Côte d'Ivoire, and in the world, similar studies are very scarce. However, iohexol, known in the pharmaceutical industry as omnipaque (OMP), is one of the products commonly used in medical imaging departments of health establishments in Côte d'Ivoire, a developing country where wastewater treatment systems are non-functional so that the hospital wastewaters are directly discharged in the environment without treatment [13]. It is therefore necessary to investigate the electrochemical behavior of OMP.

The aim of this work is to study the electrochemical behavior of OMP on the Ti/Pt electrode prepared by thermal decomposition at 400 °C. The purpose is to determine some kinetic parameters such as the anodic transfer coefficients, the Tafel slope and the activation energy. For this purpose, the effect of the scan rate, the variation of the OMP concentration, the temperature and the pH on the electro-oxidation of the OMP were studied.

2. Experimental

2.1. Preparation of platinum (Ti/Pt) electrodes

The precursors solution used for the preparation of Ti/Pt electrode was prepared by dissolving the precursor $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in 10 mL of a solvent (isopropanol). The dimension of titanium substrates used are 1.6 cm x 1.6 cm x 0.5 cm. The surface of titanium was sandblasted to ensure the adherence of the precursor. After this step, the titanium substrates were washed in water and in isopropanol to eliminate the eventual sands in its surface. The titanium substrates are dried with the drying oven at 80 °C during 10 min. We thereafter applied the platinum precursor using a brush to the surface of the substrate. The titanium substrates are then put in a drying oven at 80 °C during 10 min for the evaporation of solvent, then with the furnace at 400 °C during 15 min for the decomposition of the precursor. These three stages were repeated about fifteen time. At the end of this

series, the substrates are put at the furnace during 1 h for a last decomposition [14, 15].

2.2. Measurement methods

Cyclic voltammetry (CV) was used in electrochemical measurements carried out in an Autolab Potentiostat of ECHOCHEMIE (PGSTAT 20). A three-electrode electrochemical cell (100 mL) composed of a Ti/Pt as the working electrode, the geometric surface of contact between Ti/Pt and the electrolyte is 1 cm². A saturated calomel electrode (SCE) as a reference electrode (RE) put in a capillary luggin placed at approximately 2 mm of the working electrode in order to overcome the potential ohmic drop. A platinum wire as counter electrode (CE). A thermoregulator MGW LAUDA connected to the electrochemical cell was used for the variation of the temperature. pH of electrolytes was measured using a probe pH-meter HI2211 with glass electrode.

2.3. Chemicals

The pharmaceutical product omnipaque (iohexol) 300 mg I/ml manufactured by GE Healthcare Ireland with the empirical formula $\text{C}_{19}\text{H}_{26}\text{O}_9\text{N}_3\text{I}_3$ (Fig. 1) was purchased from a drugstore in Abidjan (Côte d'Ivoire). The chemicals used in these experiments were used without any further purification. Sulphuric acid (Panreac) was used as the supporting electrolyte. We used sodium hydroxide (Prolabo) to adjust the pH of the electrolyte. The reagents and solids used are stored in the dark and at room

temperature. All solutions were prepared with distilled water.

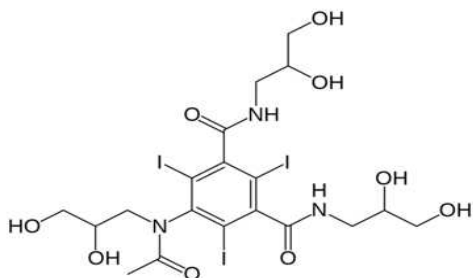


Fig. 1. Chemical formula of omnipaque.

3. Results and discussion

3.1. Physical Characterization of the prepared electrodes

The surface morphology of uncoated sandblasted titanium and Ti/Pt electrode prepared thermally were presented in Fig. 2. For the uncoated sandblasted titanium (Fig. 2.A), the surface is rough and would facilitate the adhesion of the titanium precursor. The surface of the Ti/Pt electrode (Fig. 2.B), is smooth, with a cracked structure. The cracks on Ti/Pt are due to the thermal shock during the withdrawal of the sample from the furnace. The change of morphology observed indicates the presence of a deposit on the titanium surface. The results obtained are quasi-identical to those obtained in the literature [11].

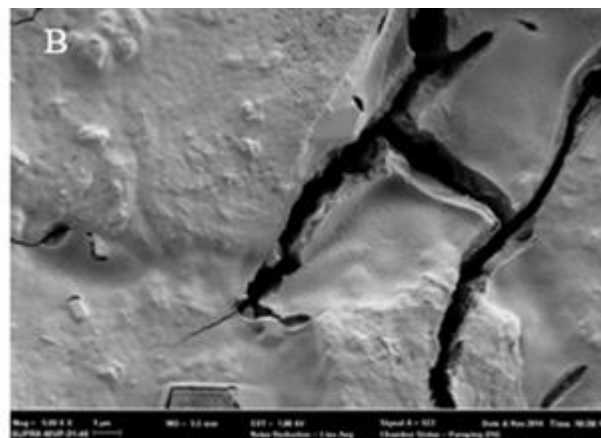
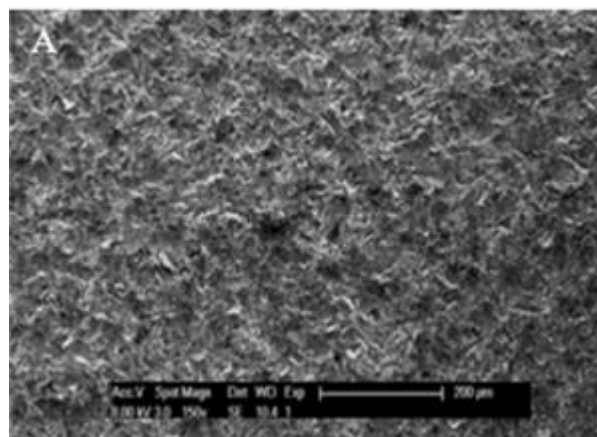


Fig. 2. Scanning electron micrographs of A. sandblasted titanium and B. Ti/Pt electrode.

3.2. Electrochemical characterization of Ti/Pt electrodes

Fig. 3 shows the voltammetric curve of the Ti/Pt electrode prepared by thermal decomposition in H_2SO_4 (0.1 M) under a scan rate of 50 mV/s in the range of -0.4 to 1.4 V vs. SCE. An increase in current density from 1.2 V vs. SCE which is characteristic of oxygen evolution is observed. Higher or lower voltammetric charges are observed on the voltammogram. From 0.8 V vs. SCE to 1.17 V vs. SCE, the curve shows the formation of an oxide layer. In the reverse scan of the voltammogram, the reduction peak of this oxide

layer which corresponds to the desorption of oxygen appears at a potential of 0.39 V vs. SCE. For potential values between -0.27 to -0.08 V vs. SCE, oxidation and reduction peaks which indicate respectively hydrogen adsorption and desorption phenomena are recorded. The shape of the voltammogram obtained are in perfect adequacy with the data of the literature and confirms the presence of platinum on the titanium surface [16].

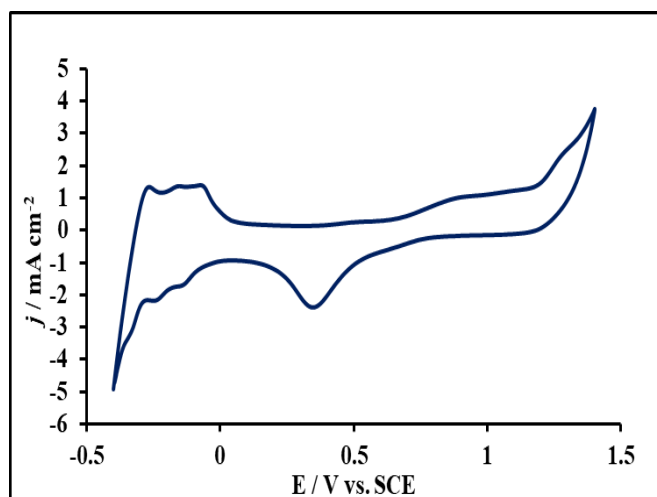


Fig. 3. Cyclic voltammetry curve of Ti/Pt in 0.1 M H_2SO_4 at the potential scan rate: 50 mV/s, CE: platinum wire, RE: SCE, T = 25 °C.

3.3. Influence of OMP in Ti/Pt voltammogram

Fig. 4 shows the voltammetric curves in the presence and absence of OMP in H_2SO_4 (0.1 M). In the absence of OMP, the voltammogram obtained is a regular Ti/Pt curve in H_2SO_4 electrolyte medium as described during the electrochemical characterization. With the addition of OMP, a change in the shape of the voltammogram with the disappearance of the

hydrogen adsorption and desorption peaks is observed. The current density increases in the potential range from 1.1 to 1.3 V vs. SCE with the appearance of a peak around 1.27 V vs. SCE. This peak is characteristic of the electro-oxidation of OMP. The overlap of the OMP oxidation peak and the oxygen release could indicate that the electro-oxidation of OMP on the Ti/Pt surface occurs via two pathways: direct electron transfer at the electrode/electrolyte interface and indirect oxidation of OMP promoted by hydroxyl radicals adsorbed on the Ti/Pt surface. In the reverse scan of the voltammogram, a reduction wave appears between 0.5 and 0.78 V vs. SCE. This reduction wave appears before the reduction peak of the platinum oxide layer (oxygen desorption peak). The presence of this OMP reduction wave could reflect the quasi-reversible character of the OMP oxidation on Ti/Pt.

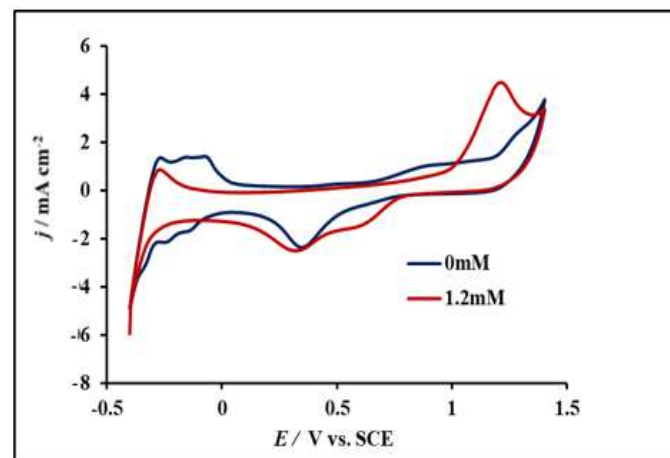


Fig. 4. Cyclic voltammetry curves on the Ti/Pt electrode in 0.1 M H_2SO_4 in presence and absence of OMP at the potential, scan rate: 50 mV/s, CE: platinum wire, RE: SCE, T = 25 °C.

3.4. Influence of varying OMP concentration

The effect of varying the OMP concentration on Ti/Pt electrode in the range -0.4 to 1.4 V vs. SCE was investigated. The results obtained are presented in Fig. 5.A. The current density of the OMP oxidation and reduction peak as well as the current density of the platinum oxide reduction peak increases in absolute value with the OMP concentration. The Fig. 5.B shows the plots of the OMP oxidation and reduction peak currents density as a function of OMP concentration (j vs. C). The curves obtained are straight lines with respective coefficients of determination ($R^2 = 0.9898$, $R^2 = 0.9447$).

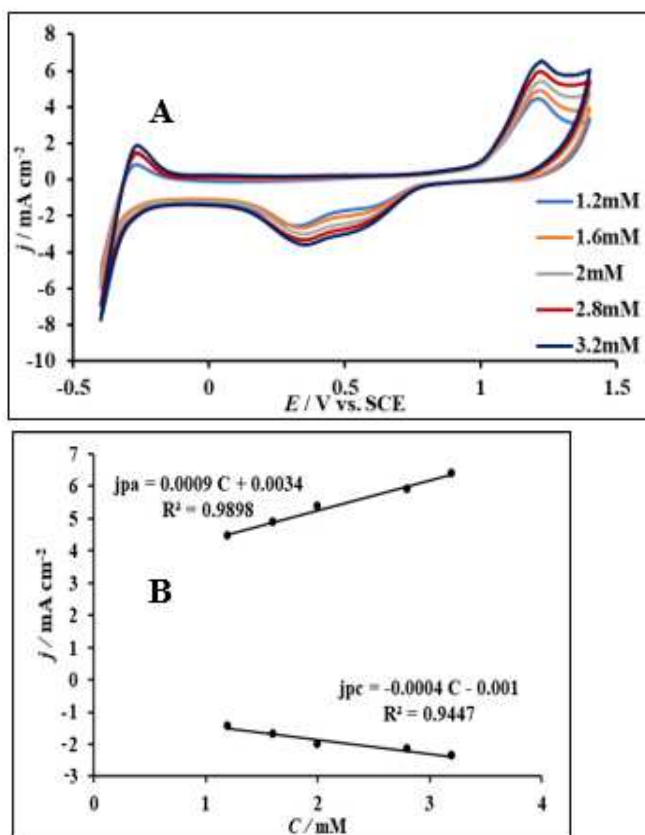


Fig.5. A. Cyclic voltammetry curves recorded on the Ti/Pt in H₂SO₄ (0.1 M) in the presence of different OMP concentrations at 50 mV/s. B. Plots of j vs. C .

The values of the coefficients of determination close to 1 indicate that the increase in the current density of the OMP oxidation peak and the decrease in the current's density of the OMP reduction peak are strongly dependent on the OMP concentration. According to the results obtained, the Ti/Pt electrode can be used for quantitative determination of OMP and OMP can be degraded by a catalytic oxidation mechanism on Ti/Pt.

3.5. Influence of scan rate

The influence of scan rate on the electro-oxidation of OMP studied by cyclic voltammetry is shown in Fig. 6. The oxidation peak current density increases and reduction wave current of OMP decreases with the scan rate. Therefore, the potentials of the oxidation and reduction peaks shift to the positive and negative values of the potential, respectively. For the study of reversibility and kinetic regime (adsorption or diffusion), two approaches are generally used: analyses of peak current density (j_p) as a function of the square root of the scan rate ($v^{1/2}$) and the logarithm of peak current density ($\ln j_p$) as a function of the logarithm of the scan rate ($\ln v$) [17].

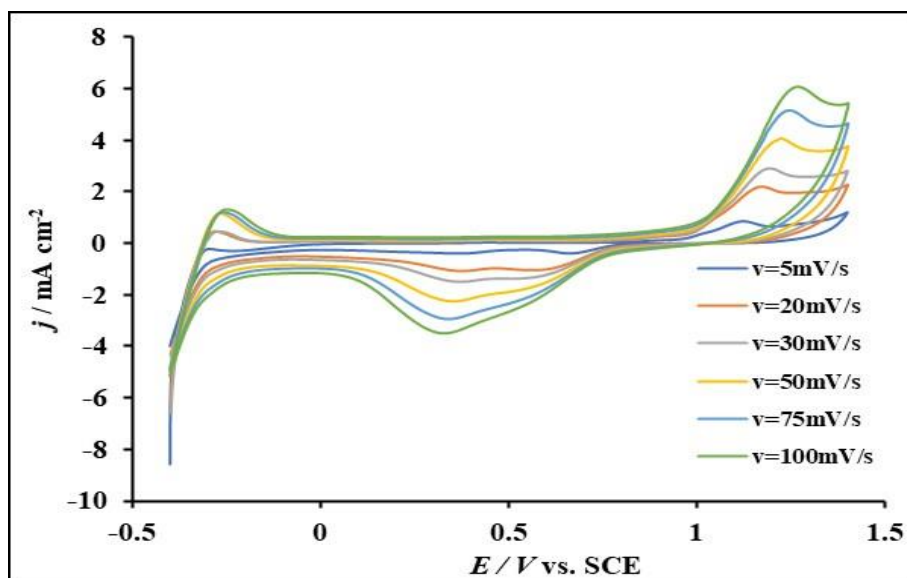


Fig. 6. Cyclic voltammetry curves of Ti/Pt in 0.1 M H₂SO₄ containing 3.2 mM of OMP at different scan rate, CE: platinum wire, RE: SCE, T = 25 °C.

The OMP oxidation peak current density (j_{pa}) and reduction wave (j_{pc}) current density plotted as a function of the square root of the potential scan rates ($v^{1/2}$) are shown in Fig. 7.A. Although the resulting curves are linear ($R^2 = 0.9967$, $R^2 = 0.9945$, respectively), they do not intercept the origin of the axes. This suggests that the reaction at the electrode is diffusion and/or adsorption controlled [16]. Furthermore, the $\ln j_p$ versus $\ln v$ curves shown in Fig. 7.B are straight lines described by the equations:

$$\ln j_{pa} = 0.6626 \ln v - 1.2179 \quad (R^2 = 0.9985) \quad (1)$$

$$\ln j_{pc} = 0.7389 \ln v - 2.1556 \quad (R^2 = 0.9989) \quad (2)$$

The slopes of the curve $\ln j_{pc}$ vs. $\ln v$ is 0.7389 located almost equidistant from 0.5 and 1.

This suggests that the electroreduction process at the electrode surface is controlled by diffusion combined with an adsorption phenomenon. Furthermore, the slope of $\ln j_{pa}$ vs. $\ln v$ is close to 0.5 attesting that the electro-oxidation process of OMP is controlled by adsorption. Indeed, if the slope of the curve $\ln j_p$ vs. $\ln v$ is equal or close to 0.5, the electrochemical process is controlled by diffusion. On the other hand, if it is equal or close to 1.0, then the process is controlled by adsorption [18-20]. According to these two approaches, the electro-oxidation process of OMP on Ti/Pt is controlled by diffusion combined by adsorption and followed by a charge transfer.

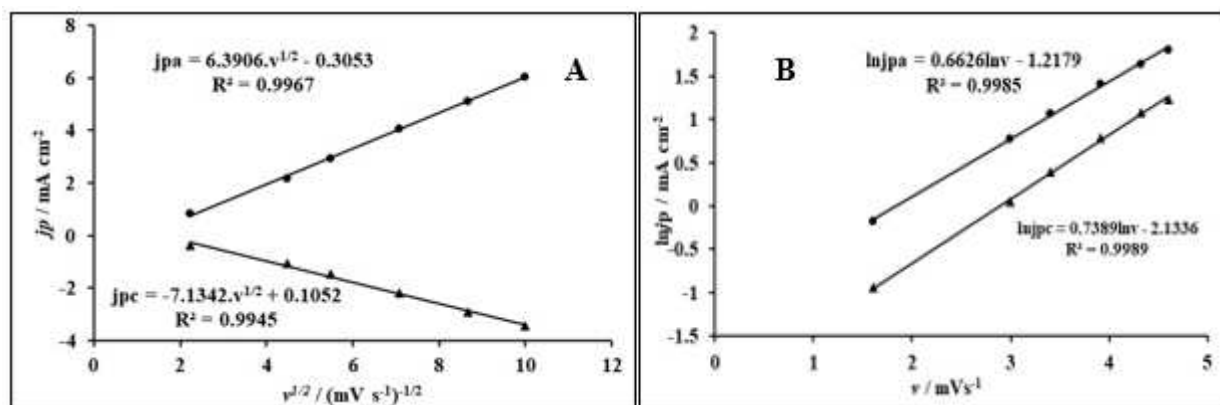


Fig. 7. A. Evolution of the peak of current against the square root of scan rates j_p vs. $v^{1/2}$. B. Curves $\ln j_p$ vs. $\ln v$.

Fig.8.A shows the plots of the oxidation peak (E_{pa}) and reduction wave (E_{pc}) potentials as a function of scan rate (v). E_{pa} and E_{pc} increase and decrease respectively with the scan rate. Thus, the heterogeneous electron transfer during the electro-oxidation of OMP on Ti/Pt is therefore irreversible [12], *i.e.*, the rate of electron transfer is lower than that of mass transport [21]. In other words, there is a homogeneous chemical reaction after each electrochemical reaction on the electrode surface [22].

The value of the anodic electron transfer coefficient ($\alpha \cdot n_\alpha$) for the electro-oxidation of OMP was calculated from the plot of the oxidation (E_{pa}) and reduction (E_{pc}) potentials versus the logarithm of the scan rate

($\ln v$) (Fig. 8.B). The curves obtained show a linear evolution defined as follows:

$$E_{pa} = 0.029 \ln v + 1.2731 \quad (R^2 = 0.898) \quad (3)$$

$$E_{pc} = -0.0165 \ln v + 0.2983 \quad (R^2 = 0.9174) \quad (4)$$

The equalization of the slopes of equation (3) and the Bard and Faulkner expression (equation (5) [23, 24]) for an irreversible, diffusion-controlled process allowed to obtain a value of $\alpha \cdot n_\alpha$ equal to 0.34.

$$E_p = \left(\frac{RT}{2 \cdot \alpha \cdot n_\alpha \cdot F} \right) \ln v + \text{const} \quad (5)$$

Where, E_p represents the peak potential in V, R is the universal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), T is the temperature in Kelvin (298 K), F is Faraday's constant (96487 C mol^{-1}), $\alpha \cdot n_\alpha$ is the anodic transfer coefficient, and v is the potential scan rate (V s^{-1}).

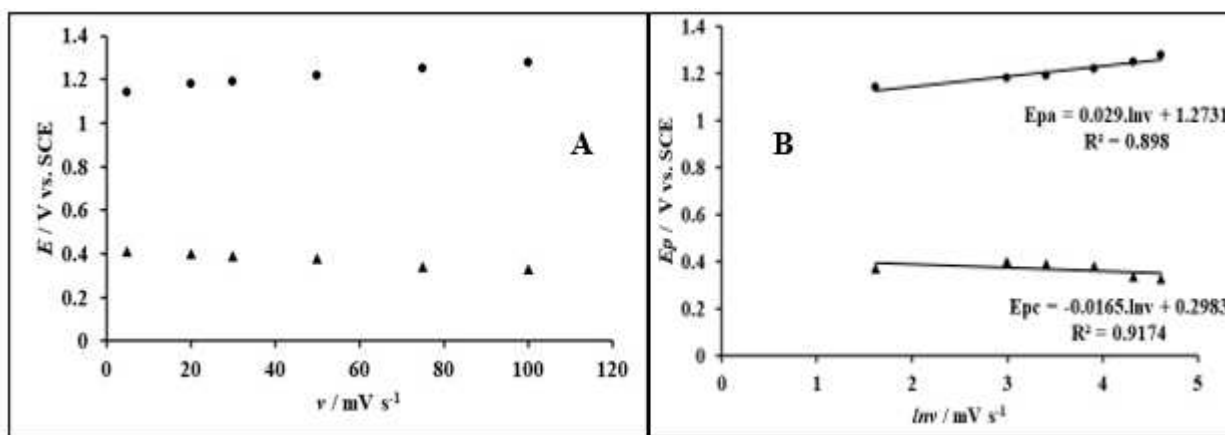


Fig. 8. A. Dependence of peak potential (E_p) versus the potential scan rate (v). B. Dependence of peak potential versus the logarithm of scan rate.

To confirm this value of $\alpha \cdot n_\alpha$, we plotted the curve of the logarithm of anodic peak current density ($\ln j_p$) versus the difference between the peak potential (E_p) and the formal potential (E^0) of the electrode ($E_p - E^0$) presented in Fig. 9.A. The curve obtained is a straight line described by the following equation ($R^2 = 0.9598$):

$$\ln j_p = 13.315 (E_p - E^0) - 1.6668 \quad (6)$$

Thus, $\alpha \cdot n_\alpha$ value was confirmed to be 0.34 using the slope of the equation (6) and the equation (7) [24]:

$$\ln j_p = \ln(0.227FC) - (\alpha \cdot n_\alpha f)(E_p - E^0) \quad (7)$$

Where, C is the OMP concentration (mol/cm^3), and E^0 the formal potential of an electrode (V) obtained from the curve of E_p versus v for $v = 0$ and $f = \frac{F}{RT}$. Moreover, the Tafel slope was determined from the following expression, valid for the processes completely irreversible and diffusion-controlled [24-26]:

$$E_p = b/2 \ln v + \text{const} \quad (8)$$

Where, b is the Tafel slope in mV.

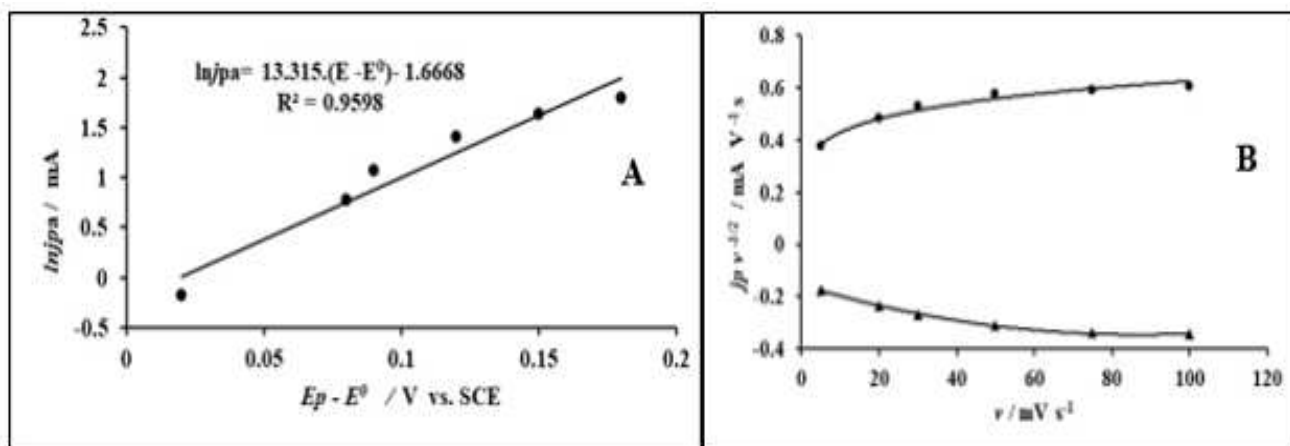


Fig. 9. A. variation of $\ln j_{pa}$ versus ($E_p - E^0$) for the oxidation of OMP at Ti/Pt electrode. B. Curves of $j_p v^{-1/2}$ vs. v .

Equalizing the slopes of equations (3) and (8), b values was estimated to be 96.4 mV in this study. Fig. 9.B shows the plot of the anodic and cathodic peak current density as a function of scan rate during the electro-oxidation of OMP ($j_p/v^{1/2}$ vs. v). The anodic and cathodic peak currents density varies with the scan rate in potential. Indeed, if the process is reversible or irreversible without being preceded or followed by a chemical reaction, the dependence is not observed. Thus, the shape of the curves obtained allows us to conclude that the process is electrochemical and coupled to a chemical reaction.

3.6. Influence of temperature

Voltammetric curves presented in Fig. 10.A are related to the influence of temperature on OMP electro-oxidation. The current density of the OMP oxidation peak increased with the temperature and a decrease in the beginning potential of oxygen release which

passes from 1.56 V vs. SCE for 35 °C to 1.45 V vs. SCE for 82 °C is observed. It thus appears that the oxidation of OMP becomes faster with the increasing in temperature. These results could be explained by the *in-situ* production of hydroxyls radicals by electrochemical decomposition of water and/or more activation of active sites on Ti/Pt surface [11]. Fig. 10.B represents the Arrhenius curve ($\ln j_p$ vs. $1/T$) for the electro-oxidation of OMP on Ti/Pt. The curve shows a linear relationship between $\ln j_p$ and $1/T$ described by equation (9).

$$\ln j_p = -2219.9 \frac{1}{T} + 8.8176 \quad (R^2 = 0.9985) \quad (9)$$

The activation energy value is estimated to be 18.456 kJ/mol and is obtained as follows [24, 25]:

$$E_a = -R \left(\frac{\partial \ln j_p}{\partial (1/T)} \right) \quad (10)$$

This activation energy value lower than 40 kJ mol⁻¹ indicates that the kinetic regime during the electro-oxidation of OMP is diffusion controlled [26, 27].

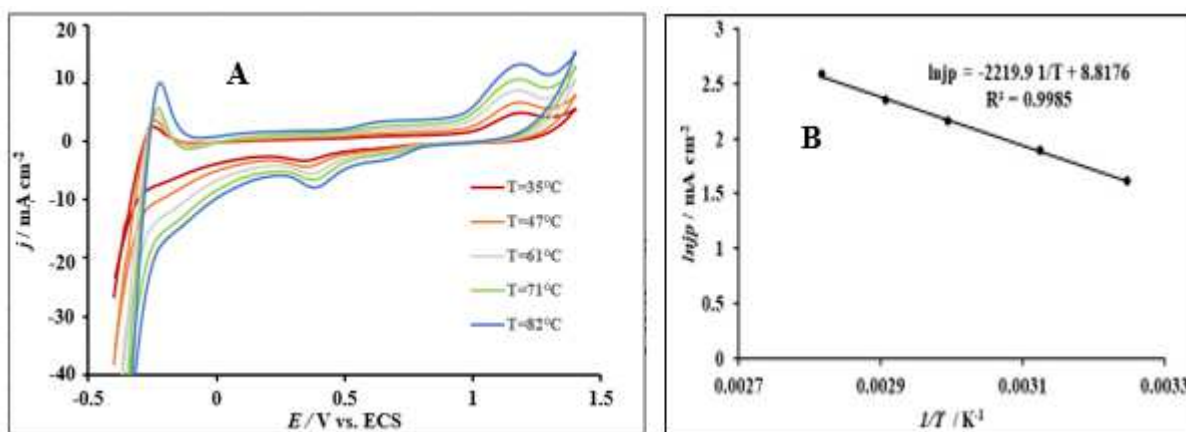


Fig. 10. (A). Cyclic voltammetry curves of Ti/Pt in 0.1 M H₂SO₄ containing 3.2 mM of OMP at several temperatures, CE: platinum wire, RE: SCE, potential scan rate: 50 mV/s. (B). Plot of $\ln j_p$ vs. $1/T$.

3.7. Influence of pH

The pH value is a parameter that influences the protonation or deprotonation of an electrode. Thus, the effect of pH is one of the important factors in the mechanism of electrochemical reactions. Fig. 11 shows the voltammetric curves for pH variations from 0.8 to 12.4. The anodic peak current density of OMP shifts to negative potentials and decreases with increasing pH, indicating that protons are directly involved in the electrochemical oxidation of OMP.

The plot of anodic peak potential (E_p) versus pH (inset of Fig. 11.) is a straight line described by the following equation:

$$E_p = 1.1356 - 0.01 \text{ pH} \quad (R^2 = 0.9936) \quad (11)$$

The m/n ratio representing the number of protons (m) and electrons (n) exchanged during the electro-oxidation of OMP was calculated from equation (12) [12].

$$\frac{dE_p}{dpH} = \frac{2.303 mRT}{nF} \quad (12)$$

Thus, for pH values between 0.8 and 12.4, the m/n ratio is 0.2. This value indicates that 1 proton and 5 electrons were exchanged during the electrochemical oxidation process in the studied pH range.

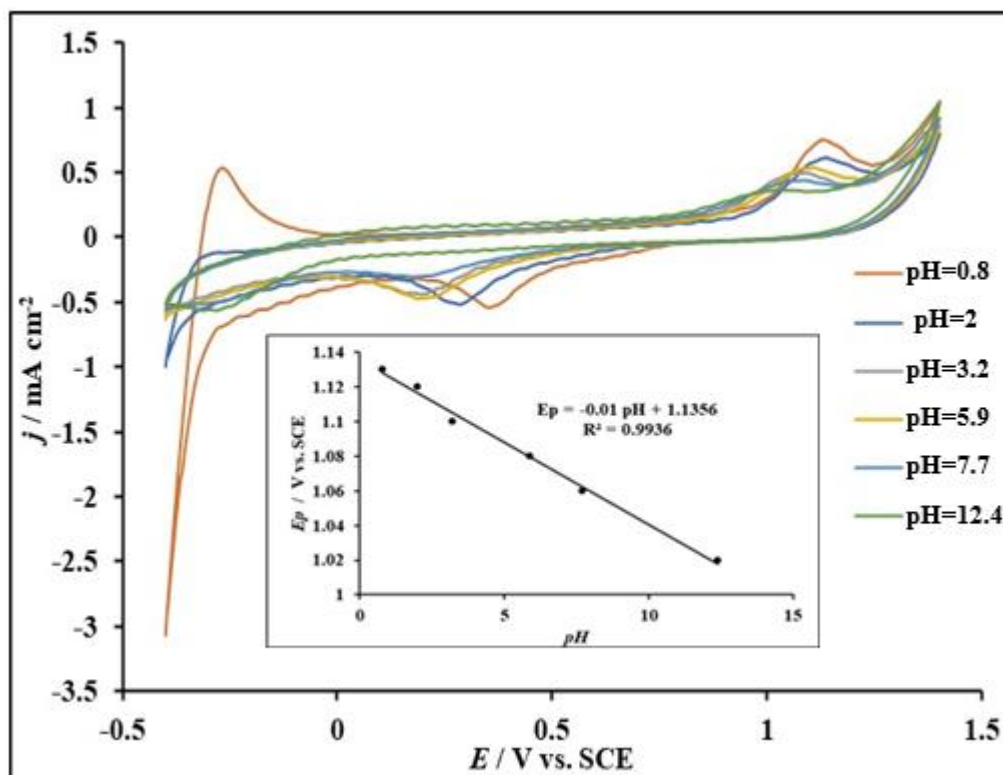


Fig. 11. Cyclic voltammetry curves recorded on Ti/Pt at different pH containing 3.2 mM of OMP in H₂SO₄ (0.1 M) at 50 mV/s; Inset. Peak potential as a function of pH.

4. Conclusion

The surface of the Ti/Pt electrode prepared in this study is smooth with a cracked structure. According to the results, the Ti/Pt electrode can be used for a determination and degradation of wastewater samples containing OMP. The study reveals that the electro-oxidation of OMP on Ti/Pt is an irreversible process, controlled by diffusion followed by a chemical reaction. In the tested pH range, the dependence of the oxidation peak potential on pH is linear and the electro-oxidation process of OMP on the Ti/Pt electrode involves the exchange of one proton and five electrons. The values of activation energy, anodic transfer coefficient and Tafel slope were estimated to be 18.456 kJ/mol, 0.34, 96.4 mV, respectively.

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