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Study of electrodeposition and electrocatalytic properties of palladium for a green degradation of organic pollutants

Research article

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Abstract
Due to their undesirable properties, antibiotics as unavoidable organic pollutants are a major concern in environmental protection issues. Electrochemical oxidation is effectively used to degrade harmful pollutants in water and wastewater. Optimization of these processes is oriented towards the use of electrosynthesis electrode materials with superior electrocatalytic properties. The current investigation evaluates the electrodeposition of palladium and the electromineralization of metronidazole from aqueous solution by homogeneous and heterogeneous electrocatalysis processes. The study involves the use of cyclic voltammetry, chronopotentiometry and galvanostatic methods in combination with UV-Vis spectrophotometry for the analysis of antibiotic solutions. The experimental results fit with maximum probability a zero-order kinetic model for the electrochemical degradation of metronidazole and degradation degrees of 57.3% and 59.3% are obtained following homogeneous and heterogeneous catalytic electrodegradation, respectively.

Keywords: palladium electrodeposition, palladium electrocatalysts, metronidazole electrodegradation, UV-Vis spectrophotometry

1. INTRODUCTION

In recent years, electrosynthesis of materials and research on the properties of these deposits have shown that they exhibit unique physical and chemical properties, different from those of bulk materials. The production of palladium deposits has been directed towards applications such as sensors, catalysts, optical, magnetic and electronic devices, and electrocatalysts due to their superior chemical properties [1-12]. To expand the applicability of working electrodes in electrochemistry, it is necessary to obtain electrodes with superior bioelectronic and biosensor properties. Palladium was electrodeposited onto a different electrodes using potentiostatic or galvanostatic pulse methods in the system containing 1 mM K_2PdCl_4 in 0.1 M H_2SO4 [1], $PdCl_2$ in 1-ethyl-3-methylimidazolium trifluoroacetate ionic liquid [2], ethanol solution of Tetrakis (triphenylphosphine) palladium [3], 2 mM $PdCl_2$ in 0.01 M $HClO_4$ [4], 1 mM $PdCl_2$ and 0.5 M NaCl [5], palladium(II) acetylacetonate [6], 0.5 M H_2SO_4 electrolyte containing 1.0 mM $PdCl_2$ [7], ~0.5–5 mM $PdCl_2$ [9, 10] and deoxygenated alkaline solution containing 50 mM NaOH plus 0.5 mM $K_2Pd(CN)_4$ [11]. The electrodes modified with electrodeposited Pd coatings, compared to uncoated electrodes, exhibited high electrocatalytic activities for the electrooxidation of formic acid, methanol [1, 4], 4-chlorophenol [5], methane [7], glucose [8, 9], aliphatic alcohols [11] and glycerol [12].

The intensive use of antibiotics in human and veterinary medicine has raised concerns about the impact of this type of biologically active compounds on the environment [13-17]. Many studies have shown that residual concentrations of antibiotics have been frequently detected in hospital effluents, wastewater, surface and groundwater, rivers, seas and even oceans. In addition, the occurrence of antibiotics in the environment leads to the development of antibiotic-resistant bacteria, causing the loss of the therapeutic properties of the drug.

For example, a commonly used imidazole antibiotic such as metronidazole is one of the organic pollutants in water and can denature DNA by crossing the cell membrane [13-16]. Considering the above, as well as a high physicochemical stability of this antibiotic, it was necessary to find effective methods to degrade metronidazole in water [18-23].

The objectives of this study were: (i) investigate the electrochemical behavior of the Pt electrode in 10^{-3} M $Pd(ClO_4)_2$ solution by cyclic voltammetry; (ii) investigate the mechanism of palladium electrodeposition by chronoamperometry; (iii) investigate the electrochemical degradation of metronidazole by heterogeneous catalysis using Pt/Pd electrodes; (iv) investigate the electrochemical degradation of metronidazole by homogeneous catalysis from 10^{-3} M $Pd(ClO_4)_2$ solution using Pt electrodes.

2. MATERIALS AND METHODS

2.1. Materials and methods

Palladium perchlorate used as a palladium source and sodium sulfate used as a supporting electrolyte were from Sigma-Aldrich and presented analytical purity. The electrodes were made of high-purity platinum cut into rectangular shapes with a geometric surface of 2 cm^2. The application of electrochemical methods was performed with a VoltaLab 40 potentiostat/galvanostat, VoltaMaster 4 software. UV-Vis spectra were recorded with a Varian Cary 50 spectrophotometer, CaryWin UV software.

2.2. Experimental set-up

The experimental setup consisted of a glass electrochemical cell with an effective volume of 100 mL and two platinum plates (99.99%, Pt) placed face to face. The two platinum electrodes were connected to the DC VoltaLab power supply. The potential and current of the working electrode were recorded relative to the calomel-saturated reference electrode. The platinum electrodes were cleaned in an ultrasonic ethanol bath for 15 minutes before the experiment. The study of the electrode processes was carried out in an electrolyte solution containing both perchlorate as a palladium source and sodium sulfate as a supporting electrolyte. Cyclic voltammograms were recorded with a sweep rate of the working electrode potential of 50 $mV \cdot s^{-1}$. The working solution used in the study of the electrodeposition mechanisms had the same composition. In the chronoamperometric method, potential pulses (-1.0 V, -1.25 V -1.5 V) were applied for a time of 60 s. Pt/Pd electrodes were obtained by galvanostatic electrodeposition at a constant current density of 15 $mA \cdot cm^{-2}$ for a time of 5 min.

The electrochemical degradation of metronidazole was performed under two distinct conditions:

i) heterogeneous catalysis electrodegradation using Pt/Pd electrodes and the working solution contained metronidazole and sodium sulfate;

ii) homogeneous catalysis electrodegradation using Pt electrodes in a working solution contained metronidazole, sodium sulfate and palladium perchlorate.

3. RESULTS AND DISCUSSION

3.1. Study of palladium electrodeposition

Figure 1 shows the cyclic voltammograms corresponding to the platinum electrode in palladium perchlorate solution at different values of the anodic potential. The electrode polarization is initiated at the maximum cathodic overvoltage corresponding to the potential of -1.5 V and is swept in the positive direction.

The initiation of polarization in the cathodic overvoltage range ensures the recording of cathodic current densities corresponding to the electrodeposition of palladium from aqueous solution. In the potential range from -1.5 V to -1.0 V, with the shift of the working electrode potential in the positive direction, the cathodic current densities decrease. These correspond to both the electrodeposition of palladium and the hydrogen evolution reaction.

Independently of the value of the reverse anodic potential, an anodic peak is recorded at the potential of -0.6 V corresponding to the adsorption of hydroxyl on the metal surface as the initial oxidative step of the metal deposit.

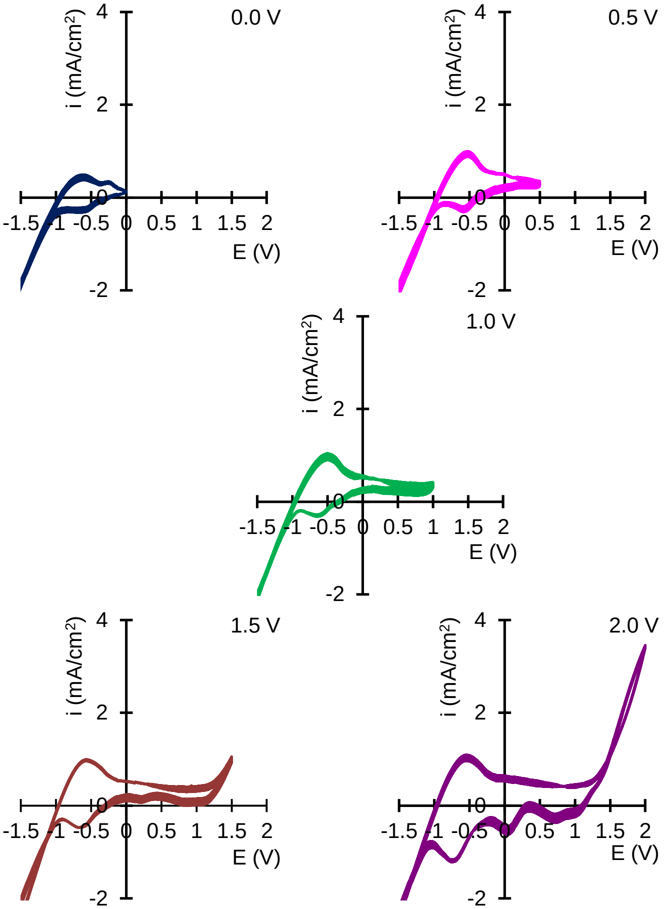

Figure 1. Cyclic voltammograms recorded for Pt electrode in 10^{-3} M $Pd(ClO_4)_2$, 0.1 M Na_2SO_4 solution at different anodic potentials; 0.0, 0.5, 1.0, 1.5 and 2.0 V; v = 50 mV·s^{-1}.

Experimental results show that at anodic potential values higher than 1.0 V, an increase in anodic current densities is recorded, which is due to the formation of palladium oxides in a higher oxidation state and the oxygen evolution reaction.

By reversing the polarization, several cathodic peaks are recorded corresponding to the reduction of surface oxides formed in forward polarization, only when the electrode potential of -1.0 V is reached does the increase in cathodic current densities and palladium electrodeposition occur [2].

The palladium electrodeposition mechanism was also studied by chronopotentiometry. Thus, potential pulses of -1.0 V, -1.25 V and -1.5 V were applied to the working electrode for a period of 50 seconds after 10 seconds of stabilization time. The recorded chronopotentiograms are presented in Figure 2.

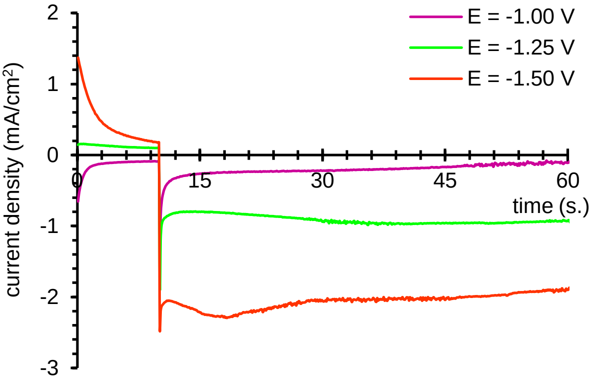

Figure 2. Chronoamperograms of Pt electrode in 10^{-3} M $Pd(ClO_4)_2$, 0.1 M Na_2SO_4 solution at different cathodic potentials; -1.0, -1.25 and -1.5 V.

The values obtained by chronoamperometry were used to determine the type of electrocrystallization mechanism of palladium on the platinum electrode. For this purpose, the current transients corresponding to the 2D and 3D, instantaneous and progressive (2Di, 2Dp, 3Di and 3Dp) electrocrystallization mechanisms were graphically represented.

The current transients corresponding to all four electrocrystallization mechanisms (2Di, 2Dp, 3Di and 3Dp) [1] at three distinct values of the electronucleation potential (-1.00 V, -1.25 V and -1.5 V) are presented in Figure 3.

The data obtained by chronopotentiometry indicate that with the increase of the cathodic overvoltage, at potentials more negative than -1.0 V, a significant deviation of the experimental values from the theoretical ones is observed. This behavior is attributed to the faradic contribution of other processes in this potential range and in particular the hydrogen evolution reaction.

Regardless of the potential at which the current transients are recorded, the suggested mechanism for palladium electrodeposition most closely indicates a progressive mechanism prior to an instantaneous mechanism.

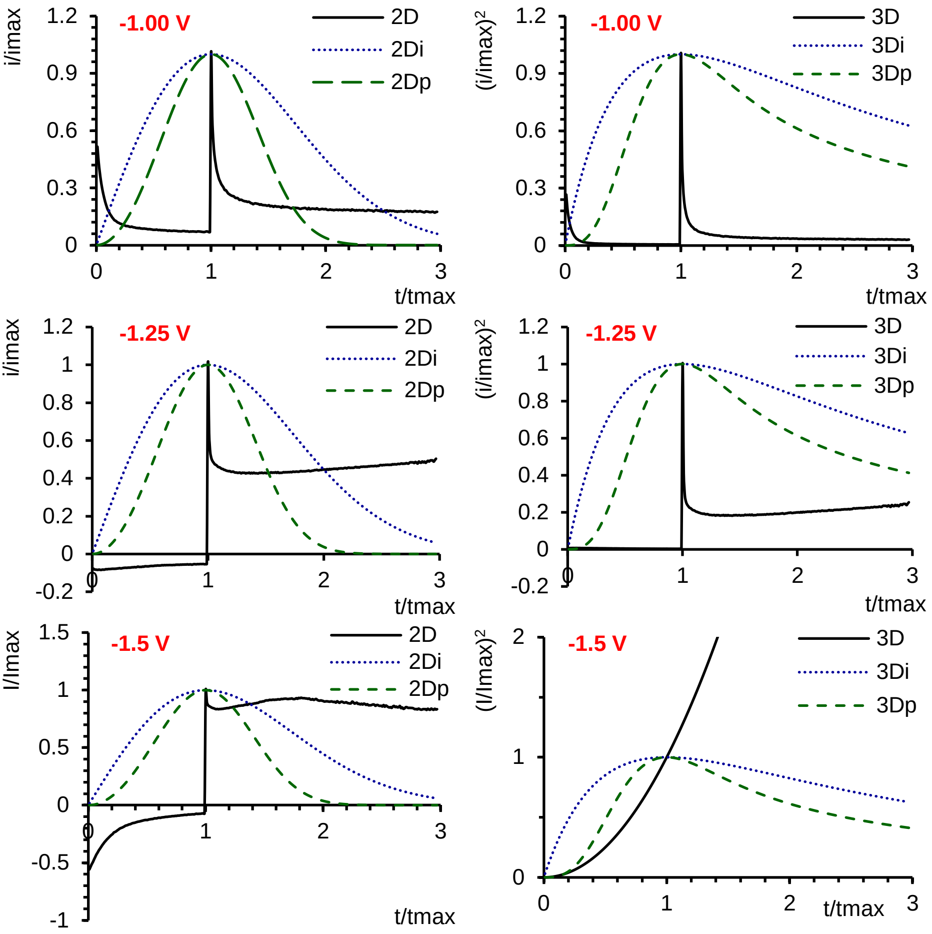

Figure 3. Current transients (2Di, 2Dp, 3Di and 3Dp) corresponding to electrochemical deposition of palladium (10^{-3} M $Pd(ClO_4)_2$, 0.1 M Na_2SO_4 solution), E_{dep} = -1.00 V, -1.25 V and -1.5 V.

As can be seen from Figure 3, the experimental and theoretical current transients at the working electrode potential of -1.0 V suggest a 2Dp electrodeposition mechanism.

To test the electrocatalytic properties of palladium metal deposits, Pt/Pd electrodes were obtained by electrodeposition of palladium from sulfate electrolyte under galvanostatic conditions at a constant current density of 15 $mA \cdot cm^{-2}$ for 5 minutes. The newly obtained electrodes exhibited the surface micrographs shown in Figure 4b and were subsequently washed with distilled water and used as working electrodes in the electrochemical degradation of metronidazole.

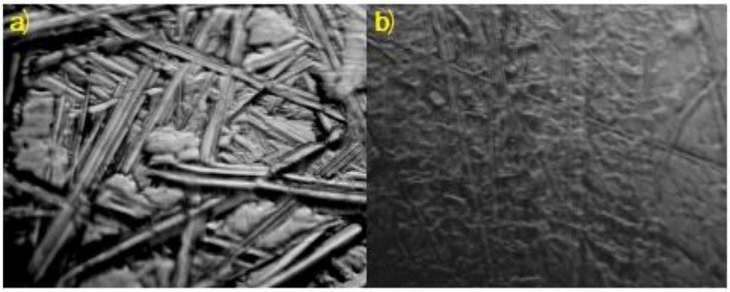

Figure 4. Surface micrographs (×400) of the Pt electrode before (a) and after (b) electrochemical deposition of palladium (Pt/Pd electrode).

The surface micrographs shown in Figure 4b attest to the presence of electrodeposited palladium deposits as a compact and continuous layer with slight traces of scratches due to mechanical processing by grinding the electrodes before the experiments.

3.2. Electromineralization of metronidazole by homogeneous electrocatalysis

Homogeneous electrocatalysis of the electrochemical degradation of metronidazole means in this case that both palladium ions and metronidazole molecules are found in the homogeneous phase, and the electrodes are represented by two identical platinum electrodes.

Figure 5 shows the UV-Vis molecular absorption spectra of the working solution subjected to electrolysis at constant current density, recorded every 5 minutes for one hour.

Knowing that the concentration of metronidazole varies in the same way as the absorbance value [17], it can be stated that, with the passage of time, as electrical charges migrate through the solution, the metronidazole molecules are electrochemically degraded [18] and, consequently, the absorbance values decrease over time, as shown in Figure 5.

Kinetic modeling of spectrophotometric data allowed the evaluation of the kinetics of electrochemical degradation [15, 20], the evaluation of the corresponding rate constant (figure 6) as well as the degree of electrochemical degradation (GD %) [14].

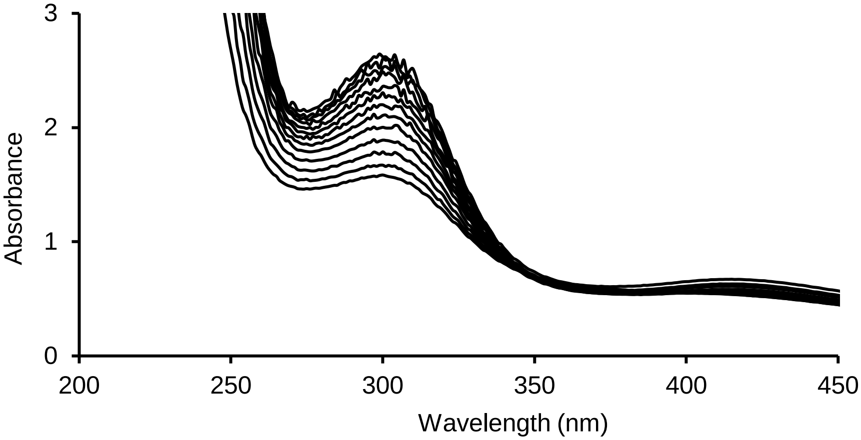

Figure 5. UV-Vis spectra of $2 \cdot 10^{-4}$ M metronidazole, 10^{-3} M $Pd(ClO_4)_2$, 0.1 M Na_2SO_4 solution solution, recorded every 5 minutes, i = 50 $mA \cdot cm^{-2}$, Pt electrode.

According to the data in Figure 6, a linear decrease in the absorbent values is recorded over 60 minutes, corresponding to zero-order kinetics, and the rate constant is 0.0128 $abs \cdot min^{-1}$.

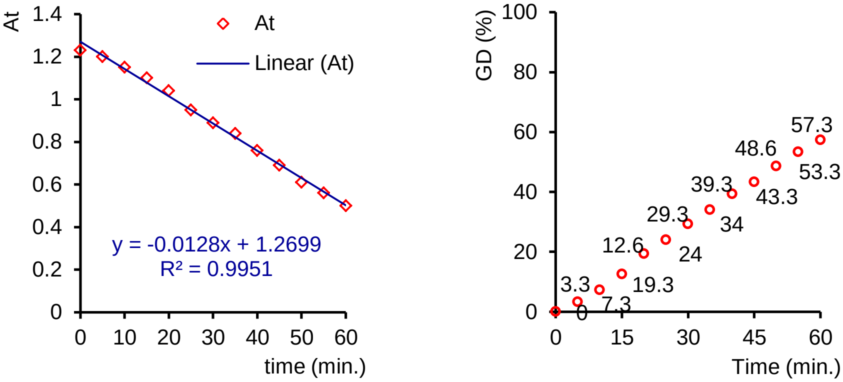

Figure 6. Metronidazole absorbance decay over time (linear fit); variation of degradation degree (DG) over time.

Determining the degree of electrochemical degradation of metronidazole led to a maximum value of 57.3% after one hour of electrolysis.

3.3. *Electromineralization of metronidazole by heterogeneous electrocatalysis*

Heterogeneous electrocatalysis of the electrochemical degradation of metronidazole means in this case that only metronidazole molecules are found in the homogeneous phase alongside the supporting sulfate electrolyte, and the electrodes are represented by two identical newly synthesized Pt/Pd electrodes.

Similar to the previous case, the absorbance values corresponding to the absorption maximum recorded spectrophotometrically at 320 nm decrease with increasing electrolysis time, as can be seen in Figure 7.

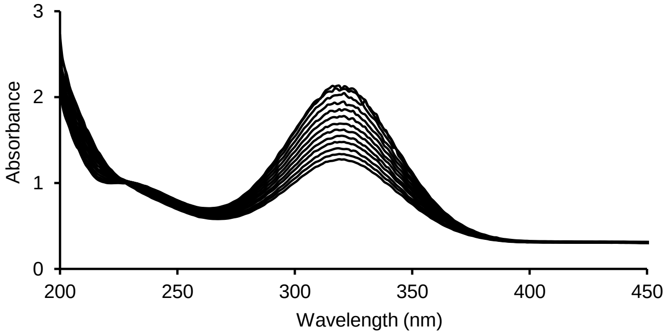

Figure 7. UV-Vis spectra of $2 \cdot 10^{-4}$ M metronidazole, 10^{-1} M Na_2SO_4 solution, recorded every 5 min. (for 60 min.), i = 50 $mA \cdot cm^{-2}$, Pt/Pd electrode.

The decrease in absorbance over time most likely follows a linear decrease, as seen in Figure 8.

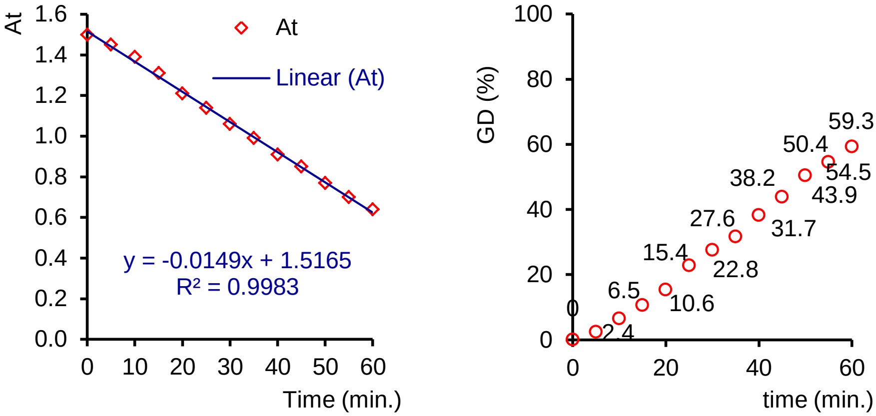

Figure 8. Metronidazole absorbance decay over time (linear fit); variation of degradation degree (DG) over time.

The electrochemical degradation of metronidazole exhibits a rate constant of 0.0149 abs·min^{-1} and a degradation degree of 59.3%.

4. CONCLUSION

This research study investigates the electrodeposition of palladium from a sulfate bath and the potential role of a novel Pt/Pd electrode for the removal of metronidazole antibiotics by electrochemical processes.

Cyclic voltammograms indicate the initiation of palladium electrocrystallization at potentials of -1.0 V, while above potentials of +1.0 V the formation of palladium oxides and the oxygen evolution reaction occur. The current transients corresponding to all four electrocrystallization mechanisms (2Di, 2Dp, 3Di and 3Dp) at three distinct values of the electronucleation potential (-1.00 V, -1.25 V and -1.5 V) indicate a progressive 2Dp-type mechanism prior to any instantaneous mechanism at a nucleation potential of -1.0 V.

Investigation of the electrochemical degradation of metronidazole by heterogeneous and homogeneous catalysis and kinetic modeling of the data showed rate constants of 0.00149 and 0.0128 abs·min^{-1}, respectively.

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