



Boron doped diamond sensor for sensitive determination of metronidazole: Mechanistic and analytical study by cyclic voltammetry and square wave voltammetry



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ABSTRACT

The performance of boron-doped diamond (BDD) electrode for the detection of metronidazole (MTZ) as the most important drug of the group of 5-nitroimidazole was proven using cyclic voltammetry (CV) and square wave voltammetry (SWV) techniques. A comparison study between BDD, glassy carbon and silver electrodes on the electrochemical response was carried out. The process is pH-dependent. In neutral and alkaline media, one irreversible reduction peak related to the hydroxylamine derivative formation was registered, involving a total of four electrons. In acidic medium, a prepeak appears probably related to the adsorption affinity of hydroxylamine at the electrode surface. The BDD electrode showed higher sensitivity and reproducibility analytical response, compared with the other electrodes. The higher reduction peak current was registered at pH 11. Under optimal conditions, a linear analytical curve was obtained for the MTZ concentration in the range of 0.2–4.2 $\mu\text{mol L}^{-1}$, with a detection limit of 0.065 $\mu\text{mol L}^{-1}$.

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1. Introduction

Metronidazole (2-methyl-5-nitroimidazole-1-ethanol) is an antibiotic and antiparasitic medication that inhibits the synthesis of nucleic acids. It is used for the treatment of diseases related to anaerobic bacteria as well as protozoa infections [1].

Several techniques have been used for the detection and quantification of this drug, including gas chromatography [2,3], fluorescence [4], high performance liquid [5–10], derivative spectrophotometry [11], and spectrophotometry [12–14]. However, most of these methods are deficient in simplicity, cost-effectiveness and easy access. So, there still exists a need for improving an alternative method for metronidazole determination.

Electrochemistry has always provided analytical techniques characterized by instrumental simplicity, moderate cost and portability [15]. Besides, electroanalytical techniques can easily be adopted to solve many problems of pharmaceutical interest with a high degree of accuracy, precision, sensitivity and selectivity, often in spectacularly reproducible way by employing this approach [16–19]. Electroanalytical methods are probably the most versatile of all trace pharmaceutically active compound analyses. Recently, the electrochemical determination of MTZ has attracted considerable attention since it offers a fast, easy, and reliable approach together with good detection limit [20]. MTZ

structure includes a nitro group which is electrochemically known as a reducible functional group, thus enabling the MTZ determination through electrochemical experiments [20–36].

Depending on techniques and electrode materials, the detection limit of metronidazole may vary between 10^{-5} and 10^{-10} mol L^{-1} . However, the reproducibility of the results is not always satisfactory. Indeed, in some cases, different modes of pretreatment lead to different surface states of the electrode which has a significant effect upon the electrode reactions.

Recently, the BDD electrode has received a great attention in electrochemical reactions. Indeed, it has several important characteristics such as an inert surface with low adsorption properties, remarkable corrosion stability even in strong acidic medium, an extremely wide potential window in aqueous solutions (up to 3.5 V) and high reproducibility of electrochemical responses [37–39]. Besides, BDD electrode has been successfully used as an alternative to other conventional electrodes and it is particularly attractive in electroanalytical applications for pharmaceutical compounds [40–44].

The present research work undertakes the study of the performance of a BDD electrode to analyze metronidazole in aqueous medium using cyclic and square wave voltammetry techniques. The effect of parameters such as pH, potential scan rate, initial MTZ concentration and SWV parameters was investigated in order to determine the detection and quantification limits. A comparison study between BDD, glassy carbon and silver electrodes on the electrochemical response was also carried out.

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2. Experimental

2.1. Chemicals

Metronidazole was supplied by Winthrop Pharma Tunisia. The supporting electrolyte was Na_2SO_4 99.5% provided by Prolabo Paris-France. Each solution (50 mL) was prepared in bidistilled water. Sulfuric acid or sodium hydroxide of analytical grade were purchased from Aldrich and were employed for pH adjustment. Before each experiment, the solution was purged with nitrogen for 5 min to remove the dissolved oxygen and kept away from any agitation to achieve a balance between the electrodes and the solution.

2.2. Apparatus

All experiments were performed using a potentiostat-galvanostat (VoltaLab PST050), and a conventional three-electrode cell at 25 °C. A boron-doped diamond, glassy carbon and silver electrodes were used as the working electrode for voltammetric experiments. A Pt electrode (1 cm^2) and a saturated calomel electrode (SCE) were used as auxiliary and reference electrode, respectively.

The BDD electrode ($7 \cdot 10^{-2} \text{ cm}^2$) was provided by CSEM (Centre Suisse d'Electronique et de Microtechnique, Neuchâtel, Switzerland). It was synthesized by the hot filament chemical vapor deposition technique (HF-CVD) on single-crystal p-type Si <100> wafers (1–3 mΩ cm, Siltronix) [45]. The doping level of boron in the diamond layer, expressed as B/C ratio, was about 3500 ppm.

Prior to each experiment, the BDD electrode was subjected to potential cycling conditions, in sulfuric acid (0.5 mol L^{-1}) between -3.0 and $+3.0 \text{ V}$ at a scan rate of 5 V s^{-1} for 120 s, then rinsed with bidistilled water.

The glassy carbon and silver electrodes, $7 \cdot 10^{-2} \text{ cm}^2$ in exposed geometric area, were polished with $0.05 \mu\text{m}$ alumina powder and rinsed copiously with bidistilled water before being transferred to the cell. Next, the glassy carbon electrode was cycled between -2.0 and $+2.0 \text{ V}$ in $0.29 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solution at a scan rate of 5 V s^{-1} for 120 s. The same treatment was carried out for the silver electrode except the potential which was cycled between -2.0 and $+0.2 \text{ V}$. Subjecting the electrode to repeated cycles, the voltammograms performed in a solution containing only the supporting electrolyte reached a steady-state and thus characterized the electrode surface properties.

3. Results and discussion

3.1. Cyclic voltammetry study

The first cyclic voltammograms of $0.29 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solutions containing 5.84 mmol L^{-1} MTZ were recorded at three different electrode materials: boron-doped diamond (BDD), glassy carbon (GC) and silver (Ag) electrodes between 0 and -2 V (vs. SCE) using a scan rate of 0.1 V s^{-1} (Fig. 1). pH 7 was used as a reference for the initial voltammetric tests. All these voltammograms showed only one irreversible cathodic peak at -0.90 , -0.95 and -1.02 V for the Ag, GC and BDD electrodes, respectively. This peak corresponds to the reduction of the nitro group. The maximum peak current was obtained at the BDD electrode, which is related to the electro-catalytic activity, number and nature of the active sites on the BDD surface. For future electroanalytical studies we choose this electrode in order to allow a good compromise between sensitivity and analytical response.

Compared with the first cycle, the second one has the same shape (Fig. 2), which means that the reaction intermediates are not electroactive in the available potential range. Moreover, during the second and successive scans, the current of the peak decreased

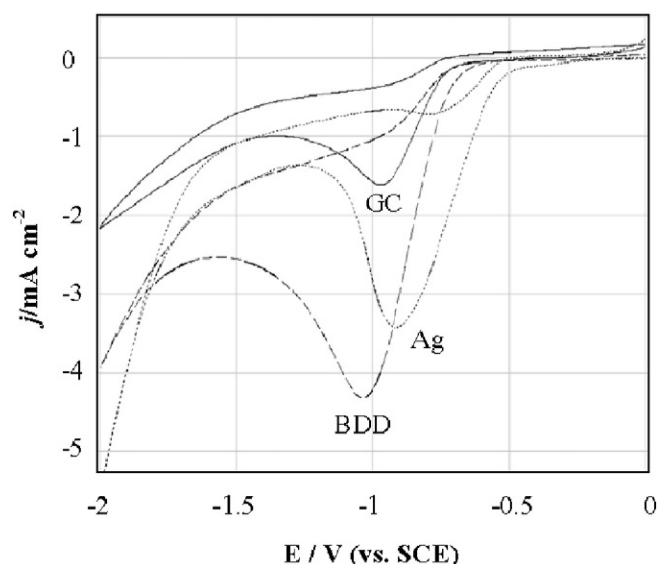


Fig. 1. Cyclic voltammograms of 5.84 mmol L^{-1} MTZ solutions at different electrode materials. $v = 100 \text{ mV s}^{-1}$, $T = 25 \text{ °C}$ and $\text{pH} = 7$.

gradually due to the adsorption of the intermediates at the electrode surface.

The effect of pH on the first cyclic voltammetric response of MTZ solutions was examined at pH between 3 and 11. The reduction of MTZ at BDD has been found to be pH-dependent.

In neutral and alkaline medium (Fig. 3), the voltammogram exhibits one irreversible cathodic peak P_1 . When the pH increased from 7 to 11, the current density of this peak (j_p) increased slightly and its potential (E_{p1}) was shifted to positive values with $E_{p1} = 0.04 \text{ pH} - 1.33$. This observation is a very rare case for organic compounds. The similar case has been also reported for the electrochemical reduction of novobiocin sodium [46].

Moreover, when the scan rate increased from 50 to 300 mV s^{-1} at pH 11, a linear relationship was obtained between the logarithm of the reduction peak current density and the logarithm of the scan rate, with a slope of 0.46 (Fig. 4). This value is close to the theoretical one

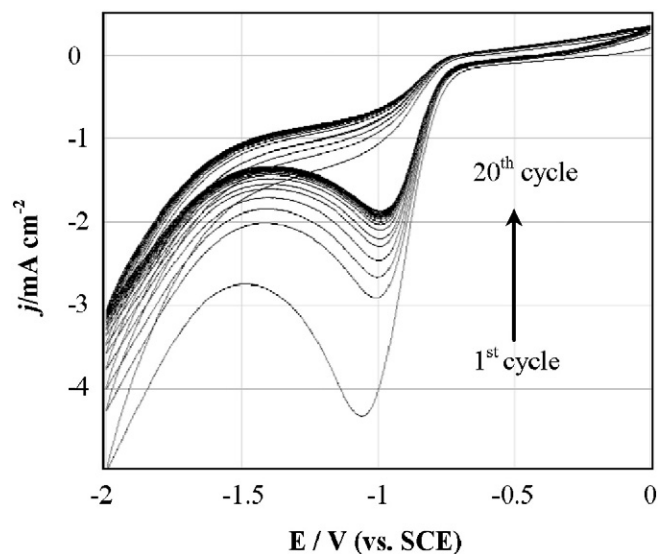


Fig. 2. Cyclic voltammograms of 5.84 mmol L^{-1} MTZ solution at the BDD electrode. $v = 100 \text{ mV s}^{-1}$, $T = 25 \text{ °C}$ and $\text{pH} = 7$.

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