VOLTAMMETRIC DETECTION OF TETRACYCLINE IN WATER AT BORON-DOPED DIAMOND ELECTRODE

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Abstract

In this work a voltammetric based protocol for detection of tetracycline (TC), considered as emergent pollutant in water, was developed. The electrochemical behavior of TC studied by cyclic voltammetry was considered to optimize operating conditions of advanced voltammetric tehniques, e.g., differential-pulsed voltammetry (DPV) and square-wave voltammetry (SWV). The best electroanalytical parameters for TC detection of 2,29 μA/μM sensitivity and limit of detection (LOD) were achieved using SWV under SP of 0.05V, MA of 0.1V and frequency of 10 Hz.

Introduction

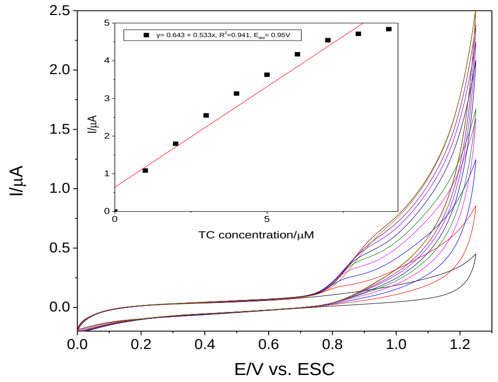
According to the Norman Network (2016), over 1000 substances combined in 16 classes (pharmaceuticals, personal care products, pesticides, perfumes) are part of the category of emerging pollutants present in the environment due to the combined effects of both natural processes and human activities [1-3].The presence of emerging pollutants in the environment is due to excessive results of chemicals and/or biological substances used in everyday life, whose toxicity and / or persistence is able to alter the metabolism of a living being. Among the various antibiotics frequently used, more attention is paid to tetracycline, as it presents serious environmental problems, including environmental risks and damage to the human health. Tetracycline (TC) belongs to the main groups of antibiotics used for veterinary purposes, for human therapy and for agricultural purposes. Due to their widespread use, most of the real evidence suggests that tetracycline based antibiotics are ubiquitous compounds found in various ecological compartments [4]. The antibiotic quantification procedure usually involves solid phase extraction (SPE), followed by instrumental analysis usually using liquid chromatography coupled with mass spectrometry (LC-MS / MS), which provides sensitivity, selectivity and reliability of results [5,6]. The disadvantages of conventional methods of detecting emerging pollutants are well known and include increased labor, operating time and high costs in terms of purchasing equipment and reagents needed to carry out the detection method. To complete the list of instruments for the detection of these emerging pollutants, efforts have been made to develop electrochemical methods for the electrochemical detection of TC [7]. Electrochemical methods are powerful and versatile tools that offer high sensitivity, excellent selectivity, fast response, time saving, simple operation and high accuracy in detecting emerging pollutants in water [8]. In this context, it is necessary to develop simple, reliable and fast methods to allow a fast and selective detection of emerging pollutants without high costs. Due to their high sensitivity, ease of use, short operating time (provides analyte detection in just a few seconds) and the ability to analyze complex samples, the enhancement of electrochemical sensors has attracted great attention in recent decades. The use of electrochemical sensors has become a powerful tool in various fields, such as environmental monitoring, biotechnology and industrial control processes [9]. Also, the electrode material is the key to the performance of electrochemical methods in the detection of emerging pollutants. Due to its remarkable potential window, low background currents and long-term stability, the boron-doped diamond electrode (BDD) is recognized as one of the most versatile electrode materials used in electroanalytical applications [10,11]. The aim of the research study was to develop a detection protocol based on certain voltammetric techniques for the detection of TC in aqueous solution using the boron diamond electrode (BDD). Detection based on the direct oxidation of tetracycline were investigated by cyclic voltammetry (CV), differential pulsed voltammetry and square-wave voltammetry (SWV) techniques.

Experimental

Electrochemical studies were performed using a potentiostat - galvanostat Autolab PGSTAT 302 (Eco Chemie, The Netherlands), controlled by a computer using GPES 4.9 software and a cell with three electrodes. The cell structure includes a boron-doped diamond electrode (BDD) as the working electrode with a diameter of 3 mm, a platinum counter-electrode and a saturated calomel electrode (SCE) as the reference electrode. The BDD electrode was produced by Windsor Scientific Ltd. for electroanalytical use, being a doped polycrystalline industrial diamond polished like a mirror (with a boron content of about 0.1%). All measurements were performed at room temperature without its control. The working electrode was mechanically cleaned using 0.2 µm alumina powder (Al_2O_3) and then washed with distilled water. The support electrolyte of 0.1 M Na_2SO_4 solution was prepared using analytical purity Na_2SO_4 (Merck, Germany) and distilled water. The electrode surface was renewed after each experiment by a light mechanical cleaning, washing and application of an electrochemical treatment by repeating the cyclic scanning voltammetry between 0 and +1.25 V/SCE in the 0.1M Na_2SO_4 support electrolyte. Standard tetracycline solution was prepared using distilled water and 0.1 M NaOH solution (Merck, Germany) in a 1: 1 volume ratio to get a 1 mM TC solution.

Results and discussion

For the elaboration of the tectracycline detection protocol (TC), the electrochemical characterization of the BDD electrode in the present TC using the cyclic voltammetry (CV) technique is studied in a first stage. The electrochemical behavior of the BDD electrode in the presence of TC was studied using CV technique in 0.1 M Na_2SO_4 as support electrolyte to simulate closely the real water composition. Figure 1 shows the cyclic voltammograms recorded for the BDD electrode in the presence of different TC concentrations at the scan rate of 0.05 Vs^{-1}.



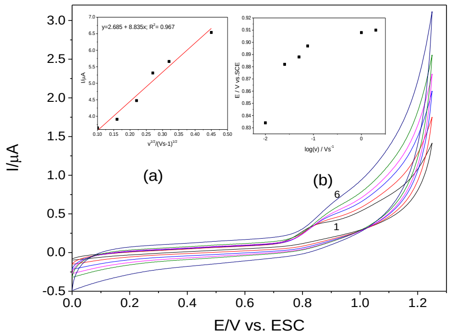
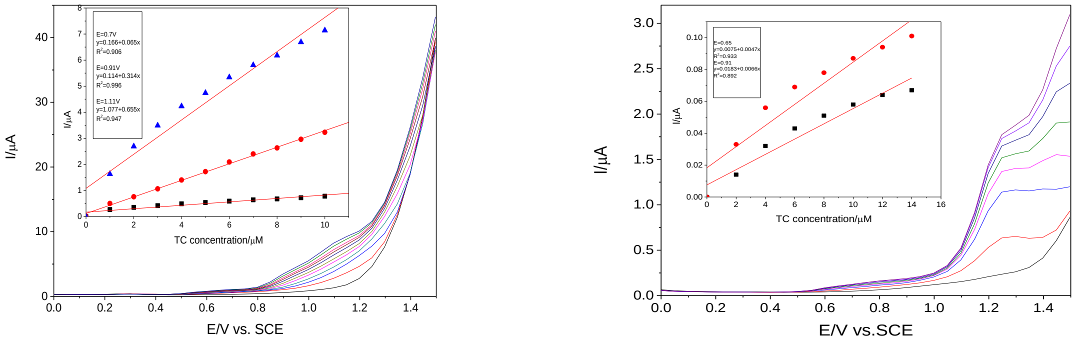


Figure 1. Cyclic voltammograms recorded at the BDD electrode in the 0.1 M Na_2SO_4 solution electrolyte and in the presence of 10-90 μM TC; potential range: 0-1.25 V / SCE. Inset: the calibration plots of the currents recorded at E = +0.95V/SCE vs. TC concentrations

Figure 2. Cyclic voltamograms recorded at the BDD electrode in 0.1 M Na_2SO_4 solution support electrolyte at different scan rates (curves 1-6). Inset: (a) The liniar current dependance vs. the square root of the scan rate; (b) The potential variation vs. scan rate logarithm

It is observed that the oxidation process starts at the potential value of about +0.8 V / SCE at low concentrations, and as the concentration increasing the oxidation potential shifts to more positive values. The oxidation peak current increases with increasing TC concentration, and a linear dependence between the oxidation peak current and the TC concentration was achieved. For concentrations higher than 70 μM clogging the electrode appeared and the oxidation peak current reached a plateau. The cathodic branch of the cyclic voltamogram does not show any peak, which would lead to the hypothesis of the irreversibility of the oxidation process of TC on the BDD electrode. In order to elucidate some aspects related to the mechanism of the TC oxidation process, the influence of the scanning rate on the profile of cyclic voltamograms recorded on the BDD commercial electrode in the presence of 50 μM TC is studied. The evolution of cyclic voltamograms recorded on the BDD electrode at different scan rates (0.01; 0.025; 0.05; 0.075; 0.1; 0.2 Vs^{-1}) is presented in Figure 2. The linear dependence of the anodic peak current recorded in the presence of TC as a function of the square root of the scanning rate suggests that the reaction is controlled by mass transfer, which is promising for electrochemical detection protocol development. Moreover, the shift of the peak potential to a positive potential as the scanning rate increases indicates that the process of electro-oxidation of TC is irreversible (Inset of Figure 2).

Pulsed voltammetric techniques are very suitable for the development of enhanced detection methods, due to their specific characteristics related to the minimization of the background current and the improvement of the faraday component and implicit, the electrochemical response. The use of differential-pulsed voltammetry (DPV) requires to set up the optimal operating parameters, the potential step (SP) which represents the increase of the potential between two consecutive values and the value of the modulation amplitude (MA). Two operating conditions of the DPV technique were tested, MA of 0.1V and 0.2 V, respectively, for the potential step SP = 0.05V.The series of differential pulse voltammograms obtained at different TC concentrations are presented in Figure 3 a and Figure 3 b.



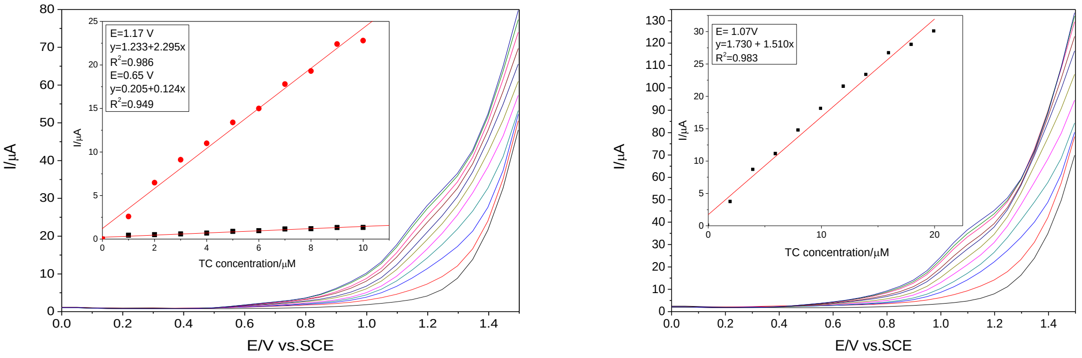
(a) (b)

Figure 3. Differential-pulsed voltamograms recorded under the conditions: SP = 0.05V, v = $0.05 Vs^{-1}$ at the BDD electrode in electrolyte support 0.1 M Na_2SO_4 solution in the potential range: 0 -1.5 V / SCE: (a) MA = 0.1V and in the presence of 1-10 μM TC; (b) MA = 0.2V and in the presence of 1-10 μM TC, Inset: The calibration plots of the currents vs. TC concentrations.

It is noticed that the different operating conditions of DPV lead to modified shapes of the voltamograms. Although voltamograms appear to be better defined and differentiated for MA of 0.2V, however, the best sensitivity is obtained for MA = 0.1 (Figure 3a). Based on the results obtained for these operating conditions, the best results were obtained at the potential step of 0.05 V and the modulation amplitude of 0.1 V, which are better in comparition with CV related to the electroanalytical parameters involving the detection potentials.

Square wave voltammetry (SWV) technique was tested at the both above presented DPV conditions regarding SP and MA for the frequency of 10 Hz. The results are presented in Figure 4 a and Figure 4 b.

For the detection potential value of 1.17 V/SCE the best sensitivity was obtained compared to the previously presented techniques.



(a) (b)

Figure 4. Square wave voltamograms recorded at the frequency f = 10Hz, having MA = 0.1V, SP = 0.05V, v = $0.5 Vs^{-1}$ at the electrode BDD in the electrolyte support 0.1 M Na_2SO_4 solution in the potential range: 0 -1.5 V / SCE: (a) MA = 0.1V and in the presence of 1-10 μM TC; (b) MA = 0.2V and in the presence of 2-20 μM TC, Inset: The calibration plots of the currents vs. TC concentrations.

The comparative results regarding the electroanalytical parameters (sensitivity, detection limit, quantification limit) obtained for the application of the BDD electrode in the detection of tetracycline using the techniques presented above, are presented in Table 1.

Table 1. Analytical parameters obtained at the BDD electrode using various electroanalytical techniques

Tehnique	***Conditions operating***	**E_{det} (V/SCE)**	***Sensitivity (µA/µM)***	***R^2***	**RSD (%)**	**LOD (µM)**	**LQ (µM)**
CV	v 0.05Vs^{-1} v	1	0.034	0.933	4.47	0.841	2.81
DPV	0.05V SP 0.1V MA	0.7	0.065	0.906	11.4	1.87	6.22
		0.91	0.317	0.996	9.07	0.580	1.94
		1.11	0.655	0.947	11.7	0.849	2.83
	0.05V SP 0.2V MA	0.65	0.004	0.933	5.75	1.69	5.63
		0.91	0.006	0.892	3.83	1.72	5.72
SWV	0.05V SP 0.2V MA, 10Hz f	1.07	1.510	0.983	3.59	0.315	1.05
	0.05V SP 0.1V MA, 10Hz f	0.65	0.124	0.949	5.94	1.30	4.33
		1.17	2.29	0.986	6.43	0.320	1.07

Conclusion

The protocol based on the advanced voltammetric techniques using commercial BDD electrode was proposed for the detection of TC, as emergent pollutant in water. The mechanistic aspects regarding TC oxidation onto BDD were determined using CV technique, which were considered as references for optimizing the detection protocol. The optimization of the operating conditions for DPV, allowed to propose a SWV based protocol which assure a great sensitivity of 2.29 µA/µM and LOD of 0.32 µM TC.

Acknowledgements

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