

ENHANCED ELECTROANALYTICAL PERFORMANCE FOR DICLOFENAC DETECTION THROUGH OPTIMIZING VOLTAMMETRIC OPERATING CONDITIONS

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Abstract

In this study, the influence of the operating conditions of the voltammetric techniques, i.e., differential-pulsed voltammetry (DPV) and square-wave voltammetry (SWV) on the electroanalytical performance of fullerene-carbon nanofiber paste electrode (Full-CNF) for diclofenac (DCF) determination is studied. The optimization of the step potential (SP) and the modulation amplitude (MA) were achieved for DPV, which were further applied for SWV technique. The influence of frequency was tested and the SP of 25 mV, an MA of 200 mV, at the scan rate of $0.1 \text{ V} \cdot \text{s}^{-1}$ and frequency of 5 Hz were found as optimized voltammetric operating conditions related to the sensitivity for the determination of DCF in aqueous solution.

Introduction

Pharmaceuticals and personal care products as pollutants (PPCPs) have been identified in the environment for decades. Pharmaceutical compounds can reach detectable concentrations in rivers and lakes if production and use are sufficiently large and the compounds show some mobility and persistence in the aquatic environment [1]. The major concerns with the ecotoxicities of PPCPs come from prescription and over-the-counter medications due to their specific targets on living tissues. Analgesics are pain-relief drugs that include narcotic analgesics, non-narcotic analgesics, and non-steroidal anti-inflammatory drugs (NSAID). They act in various ways on the peripheral and central nervous systems and are widely used to improve the pain present in almost all diseases [2]. NSAIDs include diclofenac (DCF), fenoprofen, ketoprofen, mefenamic acid, indomethacin, naproxen and ibuprofen [3].

Several methods have been developed for the determination of pharmaceuticals such as chromatographic techniques, spectrophotometry and capillary zone electrophoresis [4-6]. However, most of these methods need expensive and sophisticated instruments and are time consuming, and in many cases, due to their relatively low sensitivities, they need a preliminary pre-treatment step, which is laborious and expensive [7]. The electrochemical methods are known to exhibit a great potential for high-performance analytical methods but their performance is in direct relation to the electrode material and the operating techniques [8, 9].

Nanotechnology has become very popular in the sensor fields in the recent times. It is thought that the utilization of such technologies, as well as the use of nanosized materials, could well have beneficial effects for the performance of sensors [7]. Nanosized materials have been

shown to have a number of novel and interesting physical and chemical properties. These can have marked differences from those of the bulk material, offering the possibility of new applications and improved performance [10]. Fullerenes have high melting points and boiling points, like other giant molecular substances. The size, hydrophobicity, three-dimensionality, and electronic configurations make the fullerenes an appealing subject in pharmaceutical chemistry [7]. Carbon nanofibers (CNF) are part of carbon materials class, and they are cheaper in comparison with carbon nanotubes due to the synthesis method, and also have excellent electrical conductivity, and a large surface-to-volume ratio [11].

In this study, a voltammetric method for the diclofenac detection using paste electrode consisted of fullerene (Full) and carbon nanofibers (CNF) in paraffin oil, which was reported previously by our research team for the amperometric detection of DCF [8]. Voltammetric techniques, i.e., cyclic voltammetry (CV), differential pulsed voltammetry (DPV), and square-wave voltammetry (SWV), were applied and optimized operating conditions were found to develop enhanced and fast voltammetric methods for DCF determination in aqueous solutions.

Experimental

The composition of the fullerene–carbon nanofiber paste electrode (Full–CNF) was obtained by manual mixing certain amounts of carbon nanofibers, paraffin oil, and fullerene to reach the ratio of 50 wt. % carbon nanofibers, 25 wt. % fullerene, and 25 wt. % paraffin oil, described detailed in our previously reported work [8].

The electrochemical measurements were performed with a classical three-electrode cell system, consisting of a Full–CNF paste working electrode, a platinum counter electrode, and an Ag/ AgCl as reference electrode using an Autolab potentiostat/ galvanostat PGSTAT 302 (Eco Chemie, The Netherlands) controlled with GPES 4.9 software. The Full–CNF paste electrode with disc geometry was obtained by filling a Teflon mold, resulting in an active surface with a diameter of 3 mm. Prior to use, the electrode was electrochemically stabilized through 10 continuous repetitive cyclic voltammograms within the potential ranging between -0.5 V to +1.5 V/Ag/ AgCl in 0.1 M sodium sulfate supporting electrolyte. Na₂SO₄ used was analytical-grade reagent from Merck, and Diclofenac (DCF), was used as received from Amoli Organics Ltd. All solutions were prepared with doubly distilled and deionised water.

The electrochemical techniques applied for electrochemical characterization and the analytical applications in DCF determination were cyclic voltammetry (CV), differential-pulsed voltammetry (DPV), and square-wave voltammetry (SWV).

Results and discussion

A good distribution of carbon nanofibers and fullerene in oil paraffin was assured and the larger electroactive electrode area was found to be 0.249 cm² versus the value of the electrode geometric area of 0.196 cm² [8].

Figure 1 present the electrochemical behavior of DCF on Full-CNF paste electrode investigated by cyclic voltammetry (CV) in a supporting electrolyte of 0.1 M Na₂SO₄ and in the presence of increasing DCF concentrations ranged from 3.4 to 17 μM, and the anodic peak corresponding to DCF oxidation recorded at the potential value of about +0.7 V vs Ag/AgCl increased linearly with DCF concentration. The calibration plots is presented in the inset of Figure 1, which informed about the diffusion-controlled oxidation process of DCF onto Full-CNF paste electrode. Also, the cathodic peak is noticed at the potential value of about +0.2V vs Ag/ AgCl, which are related to the carbon redox system, confirmed by the results already published [8].

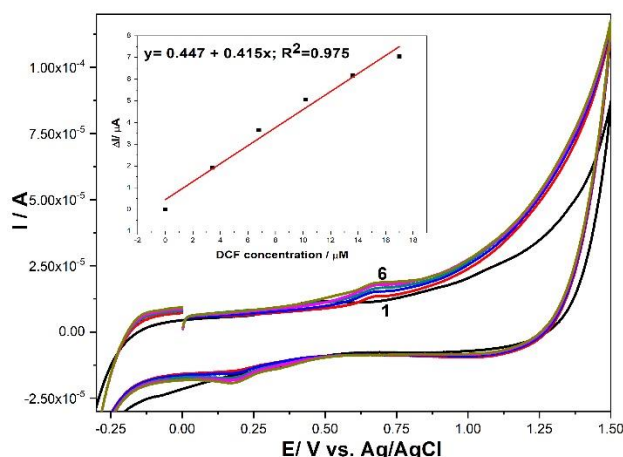


Figure 1. Cyclic voltammogram recorded on Full-CNF electrode in 0.1 M Na₂SO₄ supporting electrolyte (curve 1) and in the presence of various DCF concentrations: curves 2–6: 3.4–17 μM DCF; potential scan rate: 0.05 V·s⁻¹; potential range: -0.5 to +1.5 V/Ag/ AgCl. Inset: Calibration plots of the currents recorded at E = +0.7 V Ag/ AgCl versus DCF concentrations.

Due to the method sensitivity determined by the slope of the calibration plots is low, the advanced voltammetric techniques of DPV and SWV were considered to improve the electroanalytical performance for DCF voltammetric determination. Thus, in order to enhance the sensitivity and the limit of detection (LOD) by voltammetric method, the first voltammetric technique considered in this study is differential-pulsed voltammetry (DPV), and the operating conditions tested are gathered in Table 1.

Figure 2 presents DP voltammograms recorded under the optimized operating parameters (SP of 25 mV, an MA of 200 mV, and at the scan rate of 0.1 V·s⁻¹), and enhanced sensitivity was obtained for DCF determination in comparison with those of cyclic voltammetry (2.465 μA/μM). It can be noticed that the second anodic peak appeared at the potential value of about +1.1. V vs Ag/AgCl, which was not considered for this DCF single component system.

Table 1. Operating conditions for DPV

SP, mV	MA, mV	Scan rate, Vs ⁻¹	Sensitivity, μA/μM
25	100	0.05	0.760
50	100	0.1	2.279
25	200	0.1	2.465
100	200	0.2	Not stable, the scan rate is to high
10	200	0.2	Not stable, the scan rate is to high

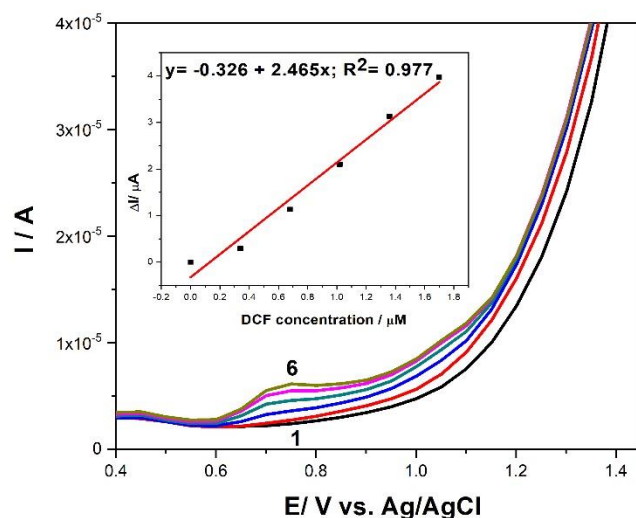


Figure 2. Differential pulse voltammetry recorded on Full-CNF electrode in 0.1 M Na_2SO_4 supporting electrolyte (curve 1) and in the presence of various DCF concentrations: curves 2–6: 0.34–1.7 μM DCF; step potential 0.025V; modulation amplitude 0.2V, potential scan rate: 0.1 $\text{V}\cdot\text{s}^{-1}$; potential range: 0 to +1.5 V vs Ag/ AgCl. Inset: Calibration plots of the currents recorded at $E = +0.7$ V Ag/ AgCl versus DCF concentrations.

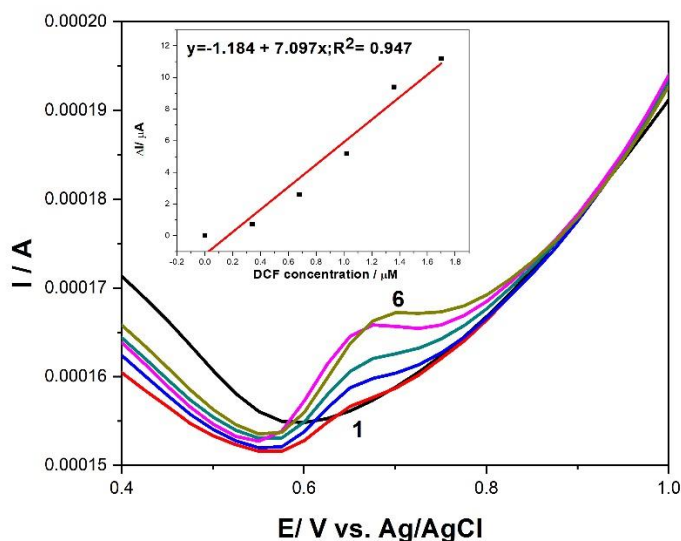


Figure 3. Square-wave voltammetry recorded on Full-CNF electrode in 0.1 M Na_2SO_4 supporting electrolyte (curve 1) and in the presence of various DCF concentrations: curves 2–6: 0.34–1.7 μM DCF step potential 0.025V; modulation amplitude 0.2V, frequency 5 Hz, potential scan rate: 0.1 $\text{V}\cdot\text{s}^{-1}$; potential range: 0 to +1.5 V/Ag/AgCl. Inset: Calibration plots of the currents recorded at $E = +0.65$ V Ag/ AgCl versus DCF concentrations.

Also, the SWV technique was tested under similarly optimized operating conditions as the DPV technique, and the results are presented in Figure 3. Using SWV operated under SP of 25 mV, MA of 200 mV at the scan rate of 0.1 $\text{V}\cdot\text{s}^{-1}$ and frequency of 5 Hz, a good linearity was reached, as can be seen in the inset of Figure 3. About seven times better sensitivity was

reached for optimized operating conditions (7.097 $\mu\text{A}/\mu\text{M}$ vs 1.075 $\mu\text{A}/\mu\text{M}$). All electroanalytical parameters determined for each electrochemical technique were improved under optimized operating conditions using Full-CNF paste electrode and they are summarized in Table 2.

Table 2. Electroanalytical performances of Full-CNF electrode in DCF determination

Technique applied	Detection potential	Sensitivity ($\mu\text{A}/\mu\text{M}$)	LOD (nM)	Reference
DPV	+0.77V	0.689	10.2	[8]
	+0.7V	2.465	1.2	This work
SWV	+0.75	1.076	0.9	[8]
	+0.65V	7.09	7.4	This work

It can be noticed that the optimized operating variables are related to the sensitivity and the lowest limit of detection depending on the practical needs.

Conclusion

The influence of the operating conditions of the voltammetric techniques on the electroanalytical performance are highlighted in this study. The optimized operating conditions depended on the electrode composition through its electrochemical stability and implicit, the electrochemical response signal. The best sensitivity for DCF determination using Full-CNF paste electrode was achieved through SWV under SP of 25 mV, MA of 200 mV at the scan rate of $0.1 \text{ V}\cdot\text{s}^{-1}$ and frequency of 5 Hz (7.097 $\mu\text{A}/\mu\text{M}$) while the lowest limit of detection was achieved for a SP of 2 mV, MA of 10 mV, and frequency of 25 Hz.

Acknowledgements

Funding for this study was provided by a grant of the Romanian Ministry of Research and Innovation, CNCS - UEFISCDI, project number PD 88/2020, project code PN-III-P1-1.1-PD-2019-0676, within PNCDI III.

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