

ELECTROCHEMICAL DETERMINATION OF DICLOFENAC USING BORON-DOPED DIAMOND ELECTRODE

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Abstract. The electrochemical behaviour of sodium diclofenac (DCF) was investigated on boron-doped diamond (BDD) electrode in 0.1 M Na₂SO₄ supporting electrolyte. The oxidation process, kinetics, and useful parameters for DCF detection were studied by cyclic voltammetry (CV) technique. The oxidation peak at about +0.7 V/SCE was selected for amperometric/voltammetric detection of DCF. The linear dependences of the current versus DCF concentrations were reached for the concentration range between 0.31 and 31.1 μM by using CV, chronoamperometry (CA), square-wave voltammetry (SWV) and differential-pulsed voltammetry (DPV). The sensitive, simple and time-saving voltammetric procedure was developed, optimised and tested on spiked tap water sample.

Keywords: water pollutants, electrochemical detection, boron-doped diamond, diclofenac.

AIMS AND BACKGROUND

This study aimed to investigate the electrochemical behaviour of sodium diclofenac (DCF), sodium[*o*-(2,6-dichloroanilino) phenyl] acetate on boron-doped diamond (BDD) electrode and to test the suitability of this electrode for voltammetric/amperometric detection of DCF. The electrochemical oxidation of DCF on BDD electrode, the kinetics aspects and the parameters suitable for detection were studied by cyclic voltammetry (CV) technique. The electroanalytical parameters for voltammetric/amperometric detection of DCF on BDD electrode were established by using chronoamperometry (CA), square-wave voltammetry (SWV) and differential-pulsed voltammetry (DPV). The optimised detection procedure was tested on DCF spiked tap water sample.

DCF, a widely used anti-inflammatory drug, can be found in many wastewater treatment plants effluents^{1–3}. Also, based on water cycle and taking into account that sometimes the wastewater treatment plants are not effective in DCF removal and mineralisation, the rivers, lakes and ground water may be contaminated. DCF

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belongs to a new very important water pollutant class by type of pharmaceuticals because of their potential impact on human health and environment².

These aspects require the development of a simple, sensitive and reliable determination method of DCF in aqueous solution. Several methods for the quantitative determination of DCF have been reported, e.g. spectrophotometric, fluorometric, chromatographic and electrochemical methods⁴⁻⁷.

In the last years, the electrochemical methods have attracted interest as electroanalysis^{8,9}, because of the fast response, large sensitivities, simple operation, and the possibilities of miniaturisation. Because the electrooxidation of DCF proceeds very slowly and almost no current response was observed at the usual electrode, a few studies reported the voltammetric/ampereometric detection of DCF at conventional electrodes. Various voltammetric/ampereometric methods at modified electrodes⁶ and potentiometric techniques⁷ have been reported for the determination of DCF.

Many research studies^{1,10} have been reported about the extraordinary properties of boron-doped diamond (BDD) electrode, e.g. wider potential window for water stability, chemical and mechanical stability, low background currents, resistance to fouling. These properties make this electrode very promising for electroanalysis.

EXPERIMENTAL

Electrochemical measurements were carried out in a Metrohm 3-electrode cell equipped with a BDD electrode (commercial product), a 3-mm diameter stationary disc embedded in a Teflon rod as the working electrode, a platinum foil counter electrode and a saturated calomel (SCE) reference electrode. The BDD electrode supplied by Windsor Scientific Ltd. for electroanalytical use was a mirror polished doped polycrystalline industrial diamond (microcrystalline; doping degree about 0.1% boron). The voltammograms and chronoamperograms were obtained by using an Autolab PGStat 304 EcoChemie system controlled by a PC running GPES Software version 4.9. Prior to the electrochemical measurements, the working electrode was carefully cleaned, degreased and treated by polishing with alumina powder (0.1 mm), and finally washed with doubly distilled water. The interface of the working electrode with the aqueous medium was stabilised by repeated cycling in a supporting electrolyte solution within an extended potential range between -0.5 V and $+1.5$ V versus SCE. Na_2SO_4 was analytical reagent grade from Merck, and DCF was used as received from Amoli Organics Ltd. All solutions were prepared with doubly distilled and deionised water.

RESULTS AND DISCUSSION

Cyclic voltammetric studies. The preliminary study regarding the DCF behaviour on BDD in comparison with DSA electrode was reported in our previous work¹¹.

Some aspects regarding DCF oxidation and determination at BDD were studied by CV. Cyclic voltammograms obtained at BDD electrode in the presence of various DCF concentrations ranged between 3.1 and 31.1 μM in 0.1 M Na_2SO_4 and are shown in Fig. 1. In comparison with the data reported in literature regarding DCF oxidation on BDD electrode¹, a different shape of voltammograms was obtained. Two peaks and two waves starting with the potential value of about +0.4 V versus SCE were noticed, which correspond to direct oxidation of DCF that occurred in several steps. Because the first peak did not increase linearly with DCF concentration, the next peak recorded at low potential value of about +0.7 V/SCE is interesting for the detection applications. The current recorded at the potential value of +0.7 V versus SCE increased linearly with DCF concentrations under the studied concentration range, with the good correlation coefficient (see inset of Fig. 1).

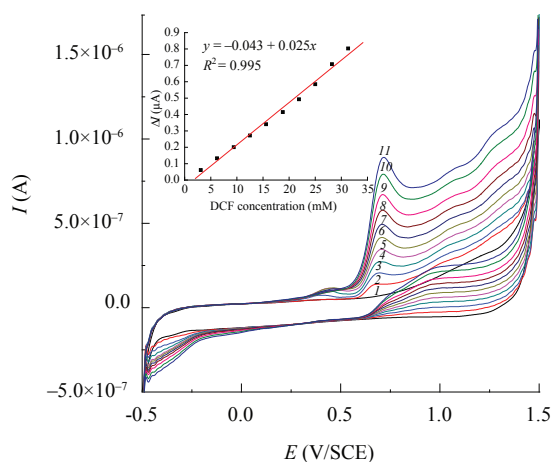


Fig. 1. Cyclic voltammograms of BDD electrode in 0.1 M Na_2SO_4 (*I*) and in the presence of different DCF concentrations: 2 – 3.1; 3 – 6.2; 4 – 9.3; 5 – 12.4; 6 – 15.5; 7 – 18.6; 8 – 21.9; 9 – 25.0; 10 – 28.2, and 11 – 31.1 μM ; potential scan rate 0.05 V s^{-1} ; potential range: -0.5 V to $+1.5 \text{ V/SCE}$; Inset: calibration plot of the currents recorded at $E = +0.70 \text{ V/SCE}$ versus DCF concentration

To elucidate some mechanistic aspects related to the oxidation of DCF on electrode surface, the cyclic voltammograms (CVs) recorded on BDD electrode at various scan rates ($0.01\text{--}0.2 \text{ V s}^{-1}$) in the presence of $6.2 \mu\text{M}$ are shown in Fig. 2. The anodic current recorded at about +0.7 V versus SCE increased linearly with the square root of the scan rate (inset *a* of Fig. 2) suggesting that the oxidation reaction is mass-transfer controlled. Moreover, the starting potential of the peak shifted towards positive potential when the scan rate (ν) increased indicating that the electrooxidation process of DCF is irreversible (inset *b* of Fig. 2), the aspect supported by the lack of any cathodic peak corresponding to anodic ones. However, a small cathodic shoulder direct proportional with DCF concentration was noticed at more negative potential (about -0.3 V versus SCE). This peak could be

attributed to the presence of an oxidation intermediate, which can not be easily reduced on the electrode surface.

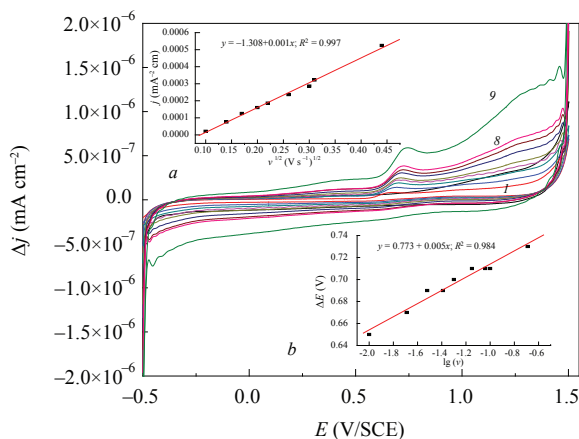


Fig. 2. Cyclic voltammograms at BDD electrode in 0.1 M Na₂SO₄ and in the presence of 6.2 μM (1–9) DCF at different potential scan rates (V s⁻¹): 1 – 0.01; 2 – 0.02; 3 – 0.03; 4 – 0.04; 5 – 0.05; 6 – 0.07; 7 – 0.09; 8 – 0.1; 9 – 0.2; potential range: –0.5 to +1.5 V/SCE; Inset a – the anodic peak current I_p versus $v^{1/2}$; inset b – dependence of the potential of current peak, E_p versus $\lg(v)$

Pulsed voltammetric application. To get better sensitivity, two types of voltammetric techniques, i.e. differential-pulsed voltammetry (DPV) and square-wave voltammetry (SWV) were explored.

DPV is a further improvement of staircase voltammetry, which is a derivative of linear sweep voltammetry, with a series of regular voltage pulses superimposed on the potential linear sweep. Due to the contribution reduction of capacitive charging current the useful current and the detection limits are improved. An example of DPVs recorded on BDD electrode for the concentration range similar with CV application is shown in Fig. 3, and a very good calibration in relation with the correlation coefficient was achieved (inset of Fig. 3). It can be noticed a better sensitivity for DPV application in comparison with CV one. These results were obtained under DPV conditions of 0.1 V modulation amplitude and 0.05 V step potential. Under these conditions DPV technique was applied for the concentration range 10 times lower, and a linear dependence of useful current versus DCF concentration was reached with a lower sensitivity. The same sensitivity was achieved for the concentration range between 0.31–3.11 μM under optimised DPV conditions of 0.1 V modulation amplitude and 0.025 V step potential. The lowest limit of detection (LOD), calculated based on equation (1) was also improved by DPV application (Table 1).

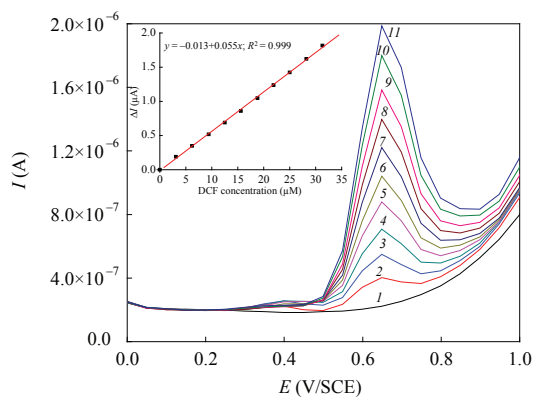


Fig. 3. Differential-pulsed voltammograms (DPVs) recorded on BDD electrode with a potential scan rate 0.05 V s^{-1} between 0 and 1.2 V versus SCE in $0.1 \text{ M Na}_2\text{SO}_4$ (I) and in the presence of different DCF concentrations (μM): 2 – 3.1; 3 – 6.2; 4 – 9.4; 5 – 12.5; 6 – 15.6; 7 – 18.8; 8 – 21.9; 9 – 25.0; 10 – 28.2; 11 – 31.1; Inset: calibration plot recorded at $E = +0.64 \text{ V/SCE}$

Another type of pulsed voltammetry is square-wave voltammetry (SWV), which can be considered a special type of differential-pulsed voltammetry, in which equal time is spent at the potential of the ramped baseline and potential of the superimposed pulse. After the SWV optimisation in relation with the frequency (f), peak height (PH) and scan increment (SI), the best result obtained at $f = 25 \text{ Hz}$, $\text{PH} = 0.01 \text{ V}$, $\text{SI} = 0.002 \text{ V}$ are shown in Fig. 4, and the good signals were achieved for lower DCF concentration. The peak current recorded at $+0.7 \text{ V}$ versus SCE depends linearly on the DCF concentration in the range $0.31\text{--}3.11 \mu\text{M}$, with a correlation coefficient better than 0.989 (the results of the calibration plots are not shown here). Even if the sensitivity was lower compared with DPV application, this technique allowed reaching very good limits of detection (Table 1)

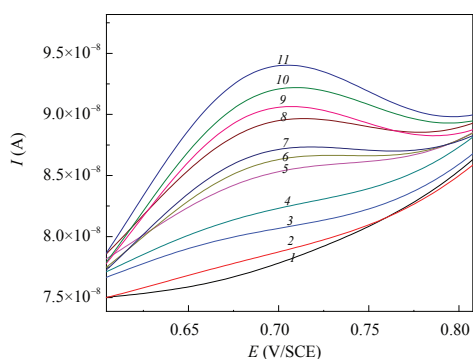


Fig. 4. Square-wave voltammograms (SWVs) recorded on BDD electrode in $0.1 \text{ M Na}_2\text{SO}_4$ (I) and in the presence of different DCF concentrations (μM): 2 – 0.31; 3 – 0.62; 4 – 0.93; 5 – 1.24; 6 – 1.55; 7 – 1.86; 8 – 2.19; 9 – 2.50; 10 – 2.82; 11 – 3.11; frequency of 25 Hz, peak height of 0.01 V and scan increment of 0.002 V

Chronoamperometry. Based on the voltammetric results, the chronoamperometry as the easiest electrochemical technique used for detection was applied for the detection potential value of +0.7 V versus SCE using the standard addition method. Figure 5 shows chronoamperometric measurements of DCF recorded on BDD electrode by applying the potential values of +0.7 V versus SCE. The useful net current signals recorded after about 50 s are linearly dependent on the DCF concentration in the explored concentration range between 3.1 and 31.1 μM , the calibration plot is presented in inset of Fig. 5.

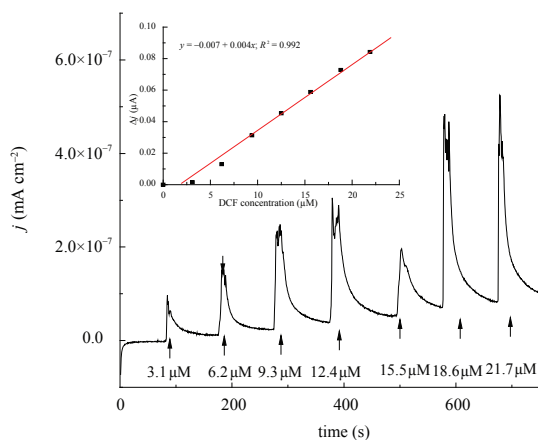


Fig. 5. Amperometric response (CA) of the BDD electrode for the successive and continuous addition of 3.1 μM DCF. Applied potential: +0.7 V versus SCE. Inset: calibration plots of useful signal versus DCF concentration

The lowest limit of detection (LOD) for DCF determination under these experimental conditions was determined based on the following equation:

$$\text{LOD} = 3S_B/b, \quad (1)$$

where S_B is the standard deviation of the mean value for 3 voltammograms of the blank, and b – the slope of the straight line in the analytical curve¹².

All electroanalytical parameters obtained for DCF detection on BDD electrode using CV, DPV, SWV and CA are gathered in Table 1, and the best electroanalytical performance was achieved using pulsed techniques as differential pulsed voltammetry.

Table 1. Analytical parameters of amperometric detection of DCF at BDD electrode using electrochemical techniques

Technique/ parameters	Potential value (V/SCE)	Concentra- tion range (μM)	Sensitivity ($\mu\text{A}/\mu\text{M}$)	Correlation coefficient (R^2)	LOD (μM)
CV	+0.7	3.1–31.1	0.025	0.995	0.6
DPV/MA=0.1 V SP=0.05 V	+0.64	3.1–31.1	0.055	0.998	0.3
DPV/MA=0.1 V SP=0.025 V	+0.64	0.31–3.1	0.055	0.996	0.03
SWV	+0.7	0.31–3.1	0.005	0.996	0.06
CA	+0.7	3.1–21.7	0.004	0.992	1

A recovery test was also performed by analysing the tap water samples spiked with 1 mg dm^{-3} DCF and 14.2 mg dm^{-3} Na_2SO_4 and a recovery of 97% was found with a relative standard deviation of 2.8% by using DPV.

CONCLUSIONS

BDD electrode exhibited useful peculiarities for amperometric/voltammetric detection of DCF in aqueous solution. Based on CV, the potential value for the amperometric detection of DCF was selected (+0.7 V versus SCE). The electroanalytical parameters for DCF detection were determined for each technique studied. DPV allowed a shifting peak maximum at less positive potential, +0.64 V versus SCE instead of +0.7 V versus SCE corresponding to CV, CA and SWV. Based on the lowest limit of detection and sensitivity, DPV technique under operating conditions of 0.1 V modulation amplitude and 0.025 V step potential was selected as the best voltammetric technique in order to use BDD electrode for the detection of DCF at trace level in aqueous environment.

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