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ELECTROCHEMICAL DETERMINATION OF VETERINARY DRUG DANOFLOXACIN

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The electrochemical oxidation of danofloxacin has been carried out in Britton–Robinson buffer at carbon paste and glassy carbon electrodes. Danofloxacin exhibits a well-defined irreversible oxidation peak over the entire pH range (2-10). Differential pulse voltammetry was used to determine danofloxacin in the pure form. The peak current varied linearly in the following ranges: 8.0×10^{-7}-4.4×10^{-6} mol l^{-1} and 4.0×10^{-7}-4.8×10^{-6} mol l^{-1} in the cases of carbon paste electrode and glassy carbon electrode, respectively. In the case of carbon paste electrode the limits of detection and quantification were 1.194×10^{-7} mol l^{-1} and 3.979×10^{-7} mol l^{-1}, respectively. For glassy carbon electrode, they were 7.465×10^{-8} mol l^{-1} and 2.488×10^{-7} mol l^{-1}, respectively. The percentage recoveries were found in the following ranges: 99.17-101.50 % and 99.38-101.25 % for carbon paste and glassy carbon electrodes, respectively. The relative standard deviations

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were found in the following ranges: 0.564-0.890 % and 0.507-0.884 % in the cases of carbon paste and glassy carbon electrodes, respectively. Differential pulse voltammetry method was successfully applied for the determination of danofloxacin in pharmaceutical form and chicken serum.

Introduction

Danofloxacin, 1-Cyclopropyl-6-fluoro-1,4-dihydro-7-[(1S,4S)-5-methyl-2,5- diazabicyclo [2.2.1] hept-2-yl]-4-oxo-3-quinolinecarboxylic acid is a synthetic antibiotic of the fluoroquinolone class developed specifically for use in veterinary medicine [1]. Danofloxacin has been studied for use in cattle, swine, chickens, and turkeys for the control of respiratory and enteric bacterial infections [2-4]. It is highly effective against many Gram-positive and Gram-negative pathogens [4]. Literature search reveals that very few analytical procedures have been developed for the determination of Danofloxacin (Dano). High performance liquid chromatography (HPLC) with UV spectrophotometric detection [6-7], HPLC with fluorescence detection [8-16], HPLC with photodiode array detection [17], high performance liquid chromatography (HPLC) with fluorescence and mass spectrometery detection [18-20], liquid chromatography - tandem mass spectrometry method [21-24], liquid chromatography with fluorimetric detection [25-26], capillary electrophoresis method [27-31], liquid chromatography - electrospray ionization - tandem mass spectrometry [32-33], liquid chromatography with UV and mass spectrometery detection [34-35], enzyme - linked immunosorbent assay (ELISA) [36], liquid chromatography - coupled electrospray ionization and atmospheric pressure chemical ionization [37], an automated turbidimetric method [38] and time resolved methodology [39].

Electrochemical methods have proved to be fast, accurate, precise, simple and very sensitive for the determination of organic molecules that undergo oxidation or reduction reactions, including drugs and related molecules in pharmaceutical dosage forms and biological fluids [40-46]

Carbon-based electrodes are currently in widespread use in electroanalytical chemistry, because of their broad potential window, low cost, rich surface chemistry, low background current, and chemical inertness. Carbon paste electrode (CPE) has some special characteristics and benefits such as the ease of surface renewal, individual polarizability, and easy to apply modifications. The disadvantage of CPE is the tendency of its organic binder to dissolve in solutions containing an appreciable fraction of organic solvent. Glassy carbon electrode (GCE) is a class of nongraphitizing carbon that is widely used as an electrode material in electrochemistry. It is also known as vitreous carbon. Glassy carbon electrode is used very commonly because of its excellent mechanical and electrical properties, impermeability to gases, and extremely low porosity [5].

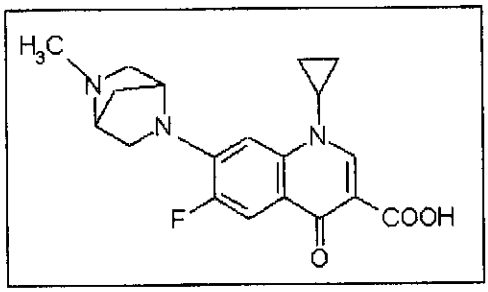

Fig. 1 Molecular structure of danofloxacin

In continuation to our previous work [47-53], the aim of this study is to establish and optimize the experimental conditions for the determination of Dano in the pure form, pharmaceutical form and serum by using cyclic voltammetry and differential pulse voltammetry (DPV) techniques.

Experimental

Apparatus

Voltammetric measurements were carried out using a computer-driven AEW2 analytical electrochemical workstation with ECProg3 electrochemistry software (Sycopel, England) in combination with a C-2 stand with a three-electrode configuration. The working electrode was a glassy carbon disc electrode (BAS model MF-2012) or a carbon paste electrode (BAS model MF-2010), the reference electrode was Ag/AgCl/3 M NaCl (BAS model MF-2063) and the counter electrode was a platinum wire (BAS model MW-1032). Origin 7.0 software was used for the transformation of the initial signal. A cyberscan 500 digital (EUTECH Instruments, USA) pH-meter with a glass combination electrode served to carry out the pH measurement.

Reagents

Danofloxacin (Dano) was supplied from Xinchang Guobang Chemicals Company, China, and its pharmaceutical form Danox powder was manufactured by Marcyrl Company, Egypt. Stock solution of Dano 1.0×10^{-3} mol l^{-1} was prepared by dissolving an appropriate amount of Dano in acetonitrile which was obtained from Labscan Ltd Company, Ireland. The stock solution was stored in a refrigerator. Britton–Robinson (BR) buffer was prepared by using 0.04M phosphoric, acetic

and boric acids. Buffer solutions were adjusted by adding the necessary amount of 2 M NaOH solution in order to obtain the appropriate pH. Graphite powder and Nujol which is a mineral oil were supplied from Aldrich and Sigma, respectively. The serum sample, obtained from healthy Chicken, was collected and stored frozen until assay.

Preparation of the Working Electrodes

The paste was prepared by mixing of 0.5 g graphite powder with 0.3 ml Nujol in a mortar with a pestle. The carbon paste was packed into the hole of the electrode body and smoothed on a filter paper until it had a shiny appearance.

To improve the sensitivity and resolution of the voltammetric peaks, the glassy carbon electrode was polished manually with 0.5 μm alumina powder on a smooth polishing cloth prior to each electrochemical measurement. Then, it was thoroughly rinsed with methanol and double distilled water, and gently dried with a tissue paper.

Assignment of the Optimum Conditions for the Determination of Danofloxacin

To obtain the optimum pH, an appropriate amount of Dano working standard solution 1.0×10^{-3} mol l^{-1} was placed in the electrolytic cell, which contained 5 ml BR buffer solution of pH 2 and the cyclic voltammogram was recorded. The experiment was repeated by using buffer solutions of different pH values (3-10) and the optimum pH was obtained.

To study the effect of scan rate (v) on the peak current (I_p) of Dano, the working electrode was immersed in the optimum buffer solution containing an appropriate amount of Dano standard solution 1.0×10^{-3} M, and the cyclic voltammograms were recorded at different scan rates over the scan range of 10-250 mV s^{-1}. A plot log I_p versus log v was constructed in order to recognize the nature of the process: whether a diffusion-controlled one or an adsorption-controlled one.

The optimum instrumental conditions for the determination of Dano by using DPV method were chosen from a study of the variation of the peak current with pulse amplitude, pulse width and scan rate. During the study, each parameter was varied while the others were kept constant: pulse amplitude over the range of 25-100 mV, pulse width 30-90 ms, and scan rate 10-50 mV s^{-1}.

General Procedure for the Determination of Danofloxacin in the Pure Form

Voltammetric analyses were performed in 5 ml of BR buffer. The solution was continuously stirred at 1200 rpm when accumulation potential (usually open circuit condition) was applied for a certain time to the working electrode. At the end of accumulation period, the stirring was stopped, and 5 sec rest period was allowed for the solution to become quiescent. The used drug was determined by using DPV method. Aliquots of the 1.0×10^{-3} M drug solution were introduced into the electrolytic cell and the procedure was repeated. The voltammograms were recorded. The peak current was evaluated as the difference between each voltammogram and the background electrolyte voltammogram. All measurements were carried out at room temperature.

Determination of Danofloxacin in Danox Powder

The amount of the powder needed to obtain 1×10^{-3} M Dano was accurately weighed and transferred into 100-ml volumetric flask, 80 ml acetonitrile was added; the flask was sonicated for about 15 min and the volume made up with the same solvent. The solution was then filtered to separate out the insoluble excipients, rejecting the first portion of the filtrate. Aliquots of the drug solution were introduced into the electrolytic cell and the general procedure was carried out.

Determination of Danofloxacin in Serum

After gentle thawing, 0.1 ml serum sample was transferred into 10-ml measuring flask, and a suitable volume of the drug solution was added, and the volume was made up to the mark by methanol. After separation of proteins, the supernatant was taken carefully, and appropriate volume of supernatant liquor was transferred to 10 ml volumetric flask and diluted. The obtained solution was used for voltammetric determination by using DPV method as for the pure drug.

Results and Discussion

To elucidate the electrode reaction of Dano, the cyclic voltammograms at carbon paste and glassy carbon electrodes were recorded at different pH values and at different scan rates. As an example, Fig. 2 shows the cyclic voltammograms of 4.0 $\times 10^{-5}$ M Dano solution in BR buffer of pH 5 in the cases of carbon paste and glassy carbon electrodes, at a scan rate of 100 mV s^{-1}. Each voltammogram

exhibits one well-defined anodic peak, with no peak on the reverse scan, suggesting the irreversible nature of the electrode reaction.

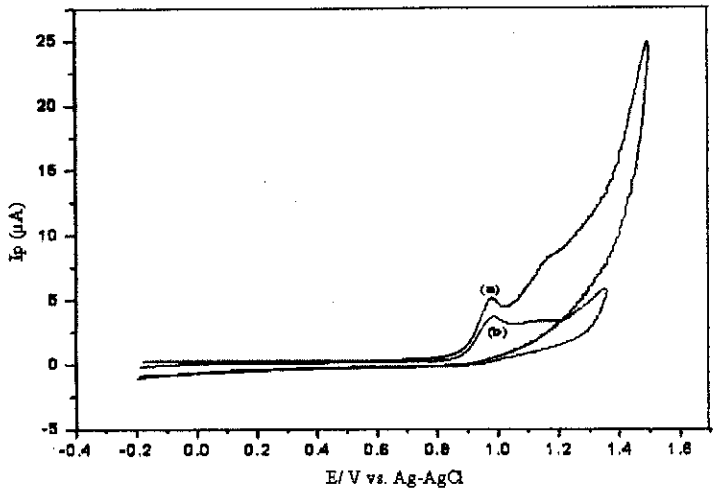

Fig. 2 Cyclic voltammograms of 4.0×10^{-5} M Dano solution in BR buffer of pH 5 in the cases of CPE (a) and GCE (b) at a scan rate of 100 mV s^{-1}

Effect of pH

The influence of pH on Dano at carbon paste and glassy carbon electrodes was studied. Figure 3 shows the plot of peak current (I_p) vs. pH. It is obvious from the figure that the peak current reaches its maximum value at pH 5 in the case of carbon paste and glassy carbon electrodes.

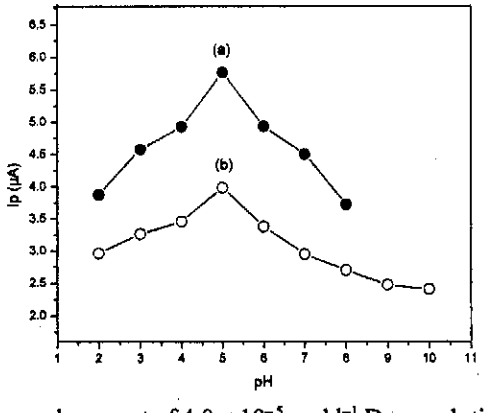

Fig. 3 Effect of pH on peak current of 4.0×10^{-5} mol l^{-1} Dano solution in BR buffer at CPE (a) and GCE (b) at a scan rate of 100 mVs^{-1}

Effect of Scan Rate

The effect of scan rate (v) on the peak current of Dano is shown in Fig. 6. Linear relationships were observed between log I_p and log v over the scan range of 10-250 mV s^{-1} and correspond to the following equations: log I_p = –0.244 + 0.48 log v, and log I_p = –0.306 +0.45 log v in the cases of carbon paste electrode and glassy carbon electrode, respectively. The slope values 0.48 and 0.45 are close to the theoretically expected value of 0.50 for a diffusion controlled process [54].

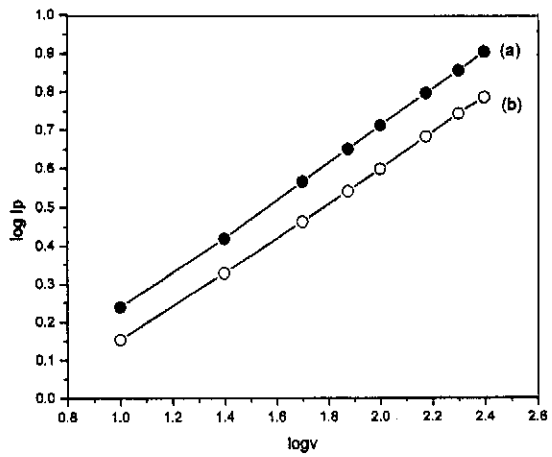

Fig. 4 Anodic peak current response of 4.0×10^{-5} mol l^{-1} Dano solution as a function of scan rate (v) in BR buffer of pH 5 in the case of CPE (a) and GCE (b)

Effect of Instrumental Parameters

It was found that the peak current was increased with increasing pulse amplitude and scan rate, while it decreased with the increasing pulse width. To obtain relatively high and narrow peaks, the values of 50 mV, 30 ms and 20 mV s^{-1} were finally chosen for pulse amplitude, pulse width and scan rate, respectively.

Determination of Danofloxacin in the Pure Form

On the basis of the electrochemical oxidation of Dano at carbon paste and glassy carbon electrodes, analytical method was developed involving differential pulse voltammetry for the determination of the drug under investigation. Linear relations between the peak current (I_p) and Dano concentration (C) were found in the following ranges: 8.0×10^{-7} - 4.4×10^{-6} mol l^{-1} and 4.0×10^{-7} - 4.8×10^{-6} for the carbon paste electrode and glassy carbon electrode, respectively. The calibration

plots were described by the following equations:

1: I_p (μA) = 0.305 C (μM) + 0.788 r = 0.9999 for carbon paste electrode
2: I_p (μA) = 0.263 C (μM) + 0.072 r = 0.9999 for glassy carbon electrode

Three replicate calibration curves were obtained over the concentration ranges 8.0×10^{-7} - 4.4×10^{-6} M in the case of CPE and 4.0×10^{-7}-4.8×10^{-6} M in the case of GCE. The limits of detection (*LOD*) and quantitation (*LOQ*) were calculated by using the following equations: $LOD = 3\ S.D./m$, and $LOQ = 10\ S.D./m$, where "*S.D.*" is the standard deviation of the intercept of the calibration curve and "*m*" is the slope of the calibration curve [55]. The limits of detection (*LOD*) and quantitation (*LOQ*) in the case of CPE were 1.194×10^{-7} mol l^{-1} and 3.979×10^{-7} mol l^{-1}, respectively. They were 7.465×10^{-8} mol l^{-1} and 2.488×10^{-7} mol l^{-1}, respectively, for GCE.

Accuracy and precision of the proposed method were determined by replicate analyses of drug solutions: the results are given in Table I. The recovery (*R*) was in the range of 99.17-101.50 % and the relative standard deviation (*RSD*) was in the range of 0.564-0.890 % in the case of CPE.

For GCE, the recovery was in the range of 99.38-101.25 % and the relative standard deviation was in the range of 0.507-0.884 %. The values of the recovery and the relative standard deviations indicate adequate accuracy and precision of the proposed method.

The proposed method is more sensitive than high performance liquid chromatography (HPLC) method with photodiode array detection [17] and capillary electrophoresis method [30] which have higher detection limits 2.798×10^{-7} mol l^{-1} and 6.321×10^{-6} mol l^{-1}, respectively. Moreover, the proposed method is simple, rapid and inexpensive.

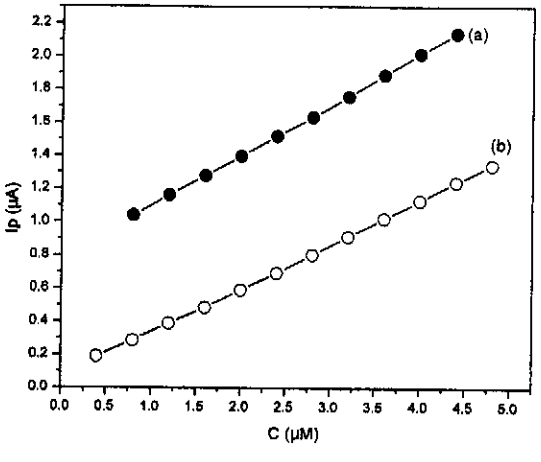

Fig. 5 Calibration curve of Dano at CPE (a), and GCE (b) by using DPV, pulse amplitude 50 mV at a scan rate of 20 mV s^{-1}

The proposed method was successfully applied to the direct determination of Dano in dosage form (Danox powder) without interference from some common excipients used in pharmaceutical preparations. The linearity range was 8.0×10^{-7} - 4.4×10^{-6} mol l^{-1} with mean recovery of 100.24 % and mean relative standard

Table I Analytical parameters of danofloxacin

Parameter	Carbon paste electrode (CPE)	Glasy carbon electrode (GCE)
Linearity range, mol l^{-1}	8.0×10^{-7} - 4.4×10^{-6}	4.0×10^{-7} - 4.8×10^{-6}
Calibration curve equation	I_p (μA) = 0.305C (μM) + 0.788	I_p (μA) = 0.263C (μM) + 0.072
Correlation coefficient (r)	0.9999	0.9999
Limit of detection (LOD), mol l^{-1}	1.194×10^{-7}	7.465×10^{-8}
Limit of quantitation (LOQ), mol l^{-1}	3.979×10^{-7}	2.488×10^{-7}
Relative standard deviation (RSD), %	0.564-0.890	0.507-0.884
Recovery (R), %	99.17 - 101.5	99.38-101.25

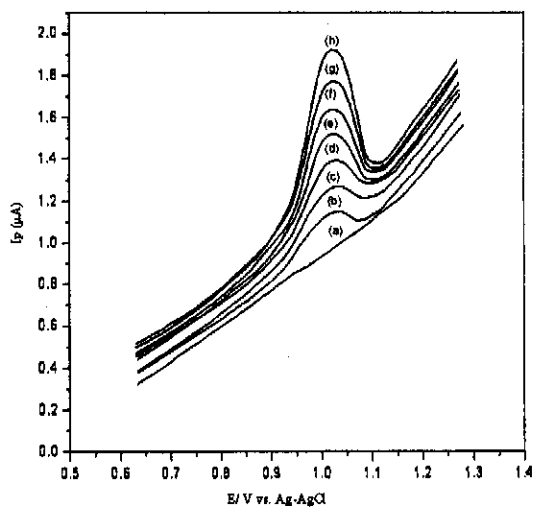

Fig.6. Differential pulse voltammograms for different concentrations of Dano in serum samples at CPE, pulse amplitude 50 mV, and at a scan rate of 20 mV s^{-1}. Blank (a), 1.2 (b), 1.6 (c), 2.0 (d), 2.4 (e), 2.8 (f), 3.2 (g) and 3.6 μM (h)

deviation of 0.696 % in the case of carbon paste electrode. For glassy carbon electrode the linearity range was 4.0×10^{-7}-4.8×10^{-6} mol l^{-1} with the mean recovery of 100.34 % and the mean relative standard deviation of 0.689 %.

Determination of Danofloxacin in Spiked Chicken Serum

The applicability of the proposed DPV method for the determination of Dano in spiked chicken serum was investigated. Figures 8 and 9 illustrate the differential pulse voltammograms for different concentrations of Dano in serum samples. The

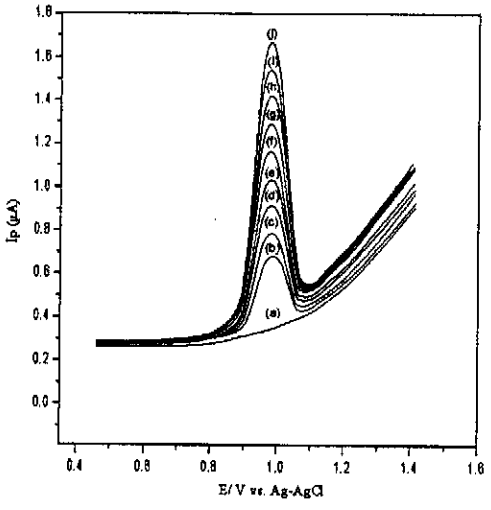

Fig. 7 Differential pulse voltammograms for different concentrations of Dano in serum samples at GCE, pulse amplitude 50 mV and at a scan rate of 20 mV s^{-1}. Blank (a), 0.8 (b), 1.2 (c), 1.6 (d), 2.0 (e) , 2.4 (f), 2.8 (g), 3.2 (h), 3.6 (i) and 4 μM (j)

Table II Determination of danofloxacin in spiked chicken serum

Parameter	Carbon paste electrode (CPE)	Glasy carbon electrode (GCE)
Linearity range, mol l^{-1}	1.2×10^{-6} - 3.6×10^{-6}	8.0×10^{-7} - 4.0×10^{-6}
Limit of detection (*LOD*), mol l^{-1}	3.554×10^{-7}	2.358×10^{-7}
Limit of quantitation (*LOQ*), mol l^{-1}	1.185×10^{-6}	7.862×10^{-7}
Relative standard deviation (*RSD*), %	0.507-0.902	0.555-0.861
Recovery (*R*), %	99.38-101.83	99.44-101.67

linearity range was 1.2×10^{-6} - 3.6×10^{-6} mol l^{-1} with the mean recovery of 100.03 % and the mean relative standard deviation of 0.701 % in the case of carbon paste electrode. For glassy carbon electrode the linearity range was 8.0×10^{-7} - 4×10^{-6} mol l^{-1} with the mean recovery of 100.07 % and the mean relative standard deviation of 0.703 %. The results are given in Table II.

Conclusion

The proposed differential pulse voltammetry method could be used successfully to determine danofloxacin in pure form, pharmaceutical forms and serum. It is a good alternative for the analytical determination of danofloxacin because it is simple, low cost, sensitive, accurate and precise. The proposed procedure showed clear advantages such as short period of real time of drug analysis and no pretreatment or time-consuming extraction steps were required prior to the analysis. Although CPE and GCE give acceptable results in the analysis of danofloxacin, we prefer GCE for biological analysis due to its high sensitivity.

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