FAST SIMULTANEOUS ELECTROCHEMICAL DETECTION OF TETRACYCLINE AND FLUOXETINE IN WATER

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ABSTRACT

The electrochemical methods-based protocol for simultaneous detection of tetracycline (TC) from antibiotics class and fluoxetine (FXT) from anti-depressive pharmaceuticals class, which belongs to emerging pollutants from water, was developed in this study using carbon nanofiber-epoxy composite electrode (CNF). The electrochemical behaviour of each pharmaceutical on CNF was considered the basis for simultaneous detection of both pharmaceuticals from water. TC electrooxidation on CNF occurred in two steps and, consequently, two detection potentials are considered. FXT electrooxidation occurred in one step that is overlaid to the first step of TC detection, this step being considered as cumulative for both pharmaceuticals. Each electrochemical method of cyclic voltammetry (CV) and differential-pulsed voltammetry (DPV) allowed detecting cumulative presence of TC and FXT at the detection potential ranged between 0.65 and 0.815 V vs. SCE and the selective detection of TC at the detection potential ranged between 0.956 and 1.14 V vs. SCE. The electroanalytical parameters related to the lowest limit of detection and sensitivity recommended this electrode to exhibit the potential for practical applications in the electrochemical detection of certain pharmaceuticals as emerging pollutants from water.

Keywords: simultaneous electrochemical detection, tetracycline, fluoxetine, carbon nanofiber composite electrode.

1 INTRODUCTION

In the last years, the persistence of a large variety of pharmaceuticals into natural water resources was evidenced [1]–[3]. The wide use of drugs as tetracycline (TC) and fluoxetine (FXT) made them to be detected as residues in surface water, groundwater and drinking water [4]–[6], sewage treatment plants [7], downstream sewage treatment plants [8], [9], wastewater treatment plant effluent [10]–[12], all over the world.

Tetracycline is an antibiotic broad spectrum with an antibacterial activity and its presence into water as residue represents a major concern as serious risk to humans and to environment [4]. Fluoxetine is a selective serotonin reuptake inhibitor (SSRI) antidepressant and its hydrochloride derivate is commonly known as Prozac [13]. Because this drug does not biodegrade rapidly in wastewater treatment plants, it is recalcitrant to hydrolysis, photolysis and microbial degradation, and it can be adsorbed by sediments. The fate and the effects of fluoxetine over the environment have been intensively studied and this compound is considered one of the most acute toxic human pharmaceutical [14].

The pharmaceutical effects over the environment and human health are wide and very dangerous. This is the reason for which the detection methods which could detect simultaneously pharmaceutical compounds are desired.

Electrochemical methods are powerful and versatile tools that offer high sensitivity, accuracy, precision and a linear dynamic range on a low cost of instrumentation [15], [16] that can be successfully applied to detect pharmaceuticals residues from water.

Taking into consideration our very promising reported results obtained for the FXT detection on boron doped diamond (BDD) electrode [17], in this study, a composite electrode

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based on carbon nanofibers was tested in order to detect individually and simultaneous TC and FXT from aqueous solutions.

2 MATERIAL AND METHODS

Tetracycline was provided by Antibiotice, Iasi, Romania. A stock solution of 1 mM was prepared by using 0.1 M NaOH solution (Merck, Germany). Fluoxetine was provided by Lilly (Pantheon, France). The stock solution was prepared using ethanol (PAM Corporation, Romania) and 0.1 M NaOH solution (Merck, Germany) in a volume ratio of 1:1 to obtain 1 mM FXT solution.

The electrochemical experiments were performed using an Autolab potentiostat/ galvanostat PGSTAT 302 (EcoChemie, The Netherlands), with a standard three electrode cell, using the CNF composite electrode as working electrode, platinum foil as counter electrode and saturated calomel electrode as reference electrode. CNF composite electrode was obtained using two-roll mill procedure, which was previously reported by our research group [18]. The applied electrochemical techniques for electroanalysis of pharmaceutical target analytes were cyclic voltammetry (CV) and differential-pulsed voltammetry (DPV).

3 RESULTS AND DISCUSSION

3.1 Cyclic voltammetry (CV)

3.1.1 Individual detection of tetracycline (TC) by CV

First electrochemical technique applied in our study was cyclic voltammetry. The composite electrode based on carbon nanofiber (CNF) was tested, and the CV shapes of TC on this composite electrode are presented in the Fig. 1.

It can be noticed that the oxidation process started at about +0.4 V/SCE, and two oxidation steps were identified, the second started at +0.95 V/SCE. Also, in according with the paper reported papers by Gan et al. [19], the lack of cathodic peak is noticed, suggesting an irreversible oxidation process. A good linearity anodic current vs. tetracycline concentration was obtained for both regions with correlation coefficient higher than 0.975 (the obtained sensitivities were 0.926 and 3.975 $\mu A \mu M^{-1}$, respectively), which suggest a diffusion-controlled oxidation process.

3.1.2 Individual detection of fluoxetine (FXT) by CV

The electrochemical behaviour of FXT on CNF electrode was studied by CV and the results are presented in Fig. 2. For CNF electrode, FXT oxidation process started at +0.3 V/SCE that

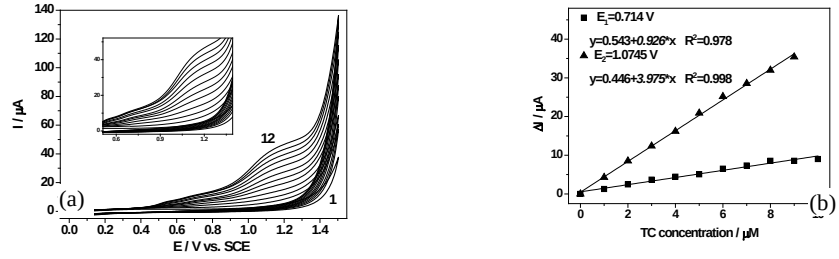

Figure 1: (a) Cyclic voltammograms recorded on CNF electrode in 0.1 M Na_2SO_4 supporting electrolyte (curve 1) in the presence of 50 µL 0.1 M NaOH (curve 2) and 1–10 µM TC (curves 3–12), at a potential scan rate of 0.05 Vs^{-1} in a potential range: 0 to +1.5 V/SCE; (b) Calibration plot of the current vs. TC concentration of the CVs recorded at E_1 = +0.714 V/SCE and E_2 = +1.0745 V/SCE.

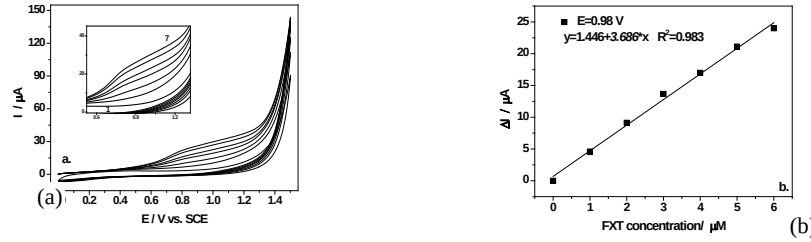

Figure 2: (a) Cyclic voltammograms recorded at CNF electrode in 0.1 M Na_2SO_4 supporting electrolyte (curve 1) and in the presence of 1–6 µM FXT (curves 2–7), at a potential scan rate of 0.05 Vs^{-1} in a potential range: 0 to +1.5 V/SCE; (b) Calibration plot of the current vs. FXT concentration of the CVs recorded at E = +0.98 V vs. SCE.

increased until +0.6 V/SCE, after which a wide plateau is achieved until the potential value of +1.2 V/SCE. Similar behaviour with TC in relation with the irreversibility and diffusion-controlled process is noticed for FXT. Also, the sensitivity of 3.975 µAµM^{-1} was obtained for FXT detection at the potential value of +0.98 V/SCE and the main difference versus TC oxidation is one step oxidation process.

3.1.3 Simultaneous detection of TC and FXT by CV

For the simultaneous detection of TC and FXT the situation is different because the oxidation of tetracycline on CNF electrode occurred in two steps, the first one at a potential value at which fluoxetine is oxidized, and it is expected a cumulative effect between fluoxetine and tetracycline at the potential value of about +0.8 V/SCE. By following the same working protocol used for individual detection, the detection of tetracycline and fluoxetine was studied in the potential range 0→+1.35 V/SCE and the results are presented in Fig. 3.

Table 1 presents the electroanalytical parameters obtained in fluoxetine, respectively tetracycline individually and simultaneous detection on CNF electrode by employing cyclic voltammetry technique.

In the case of fluoxetine, a smaller value of sensitivity was reached in the presence of 2.5 µM TC. A possible cause could be the fouling of the electrode. Still, the peak potential shifted to less positive values. In the case of tetracycline, no significant difference was noticed, as it was expected.

3.2 Differential-pulsed voltammetry (DPV)

For improving the electroanalytical performances regarding target analytes detection on CNF electrode, the versatile differential-pulsed technique was employed. The working parameters applied for DPV technique were: modulation amplitude of 0.2 V, step potential of 0.05 V and a scan rate of 0.025 Vs^{-1}.

3.2.1 Individual detection of tetracycline (TC) by DPV

For the individual detection of TC a sensitivity of 4.812 µAµM at the potential value of +0.671 V (first peak) and 17.286 µAµM at the 0.950 V (second peak) were reached. Also, in the case of detection potential a shifting to less positive values is observed (+0.671 V/SCE vs. +0.714 V/SCE for the first peak, and +0.950 V/SCE vs. +1.075 V/SCE for the second peak). The results are presented in Fig. 4.

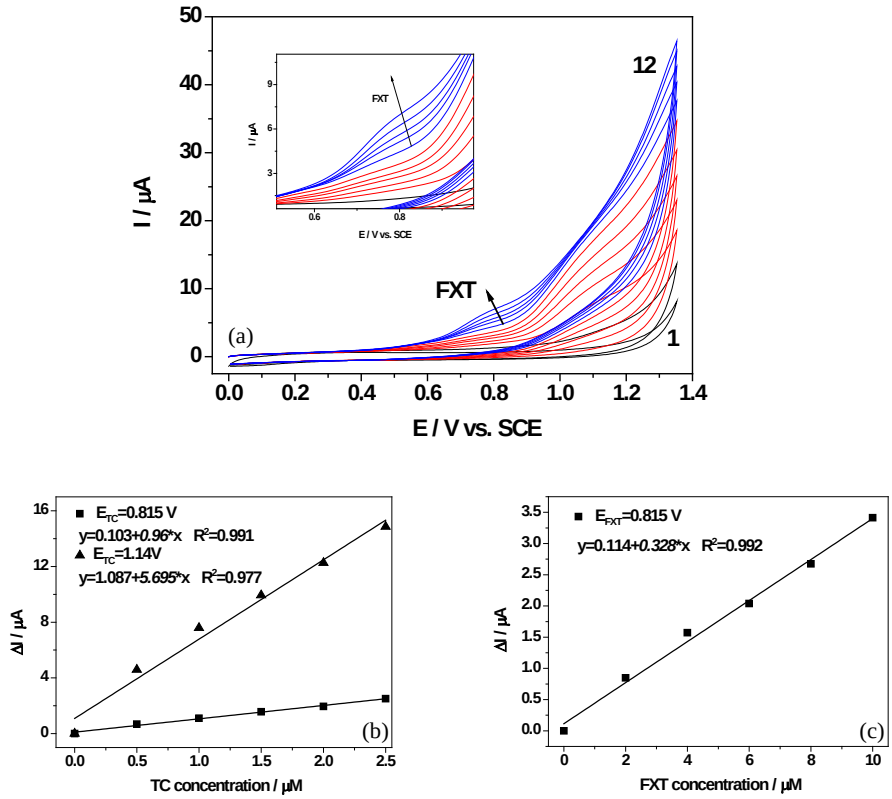

Figure 3: (a) Cyclic voltammograms recorded on CNF electrode in 0.1 M Na_2SO_4 supporting electrolyte (curve 1) in the presence of 50 µL 0.1 M NaOH (curve 2) and 0.5–2.5 µM TC (curves 3–7), and 2–10 µM FXT (curves 8–14) at a potential scan rate of 0.05 Vs^{-1} in a potential range: 0 to +1.35 V/SCE; (b) Calibration plots of the current vs. TC concentration of the CVs recorded at E_1 = +0.815 V/SCE and E_2 = +1.14 V/SCE; (c) Calibration plot of the current vs. FXT concentration of the CVs recorded at E = +0.815 V/SCE.

Table 1: Electroanalytical parameters obtained for individual and simultaneous detection of fluoxetine and tetracycline on CNF electrode using CV technique.

Type	**Analyte**	**E/V vs. SCE**	**Sensitivity (µA/µM)**	**Conc. range (µM)**
Individual	TC	0.714	0.926	0→10
		1.0745	3.975	
	FXT	0.98	3.686	0→10
Simultaneous	TC	0.815	0.96	0→2.5
		1.14	3.695	
	FXT	0.815	0.323	0→10

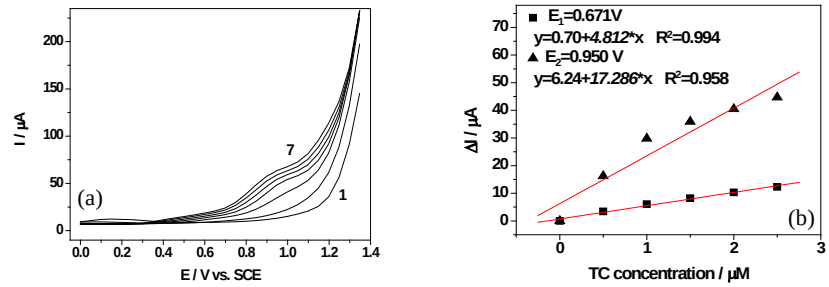

Figure 4: (a) Differential pulse voltammograms recorded on CNF electrode between 0 and +1.25 V/ SCE in 0.1 M Na_2SO_4 supporting electrolyte (curve 1) in the presence of 50 µL 0.1 M NaOH (curve 2) and 0.5–2.5 µM TC (curves 3–10); (b) Calibration plot of the current vs. TC concentration recorded at E_1 = +0.671 V/SCE and E_2 = +0.950 V/SCE.

3.2.2 Individual detection of fluoxetine by DPV

In comparison with cyclic voltammetry, the oxidation peak potential recorded using DPV technique is shifted to the less positive values of oxidation potential (+0.723 V/SCE vs. +0.92 V/SCE), and a better sensitivity was obtained (see Fig. 5).

In Table 2 are gathered the electroanalytical parameters obtained for tetracycline and fluoxetine detection in aqueous media on CNF electrode.

Based on those results, it may be concluded that CNF exhibited the peculiarities for the both pharmaceutical target analytes detection in aqueous media, the oxidation process being controlled by diffusion.

3.2.3 Simultaneous electrochemical detection of TC and FXT by DPV

The operating parameters applied for simultaneous detection by DPV technique were the same as the ones applied in the individual detection, and the corresponding voltammograms are presented in Fig. 6.

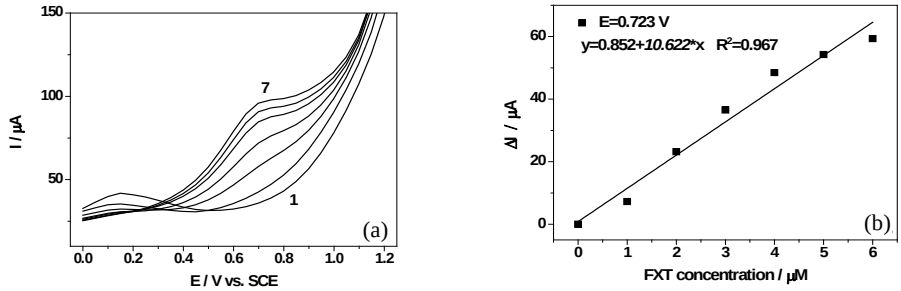

Figure 5: (a) Differential-pulsed voltammograms recorded on CNF electrode with a scan rate of 0.025 Vs^{-1} between 0 and +1.25 V/SCE in 0.1 M Na_2SO_4 supporting electrolyte (curve 1) and in the presence of different FXT concentrations: 0–6 µM (curves 2–7); (b) Calibration plot of the currents recorded at E = + 0.723 V/SCE vs. FXT concentration.

Table 2: Electroanalytical parameters obtained on studied electrodes for individual detection of TC and FXT by DPV.

Analyte	E / V vs. SCE	Sens. (μA/μM)	R^2	RSD (%)	LOD (μM)	LOQ (μM)
TC	0.671	4.812	0.994	0.03	0.161	0.539
	0.950	17.286	0.968	0.01	0.045	0.150
FXT	0.723	10.622	0.967	3.62	0.385	1.285

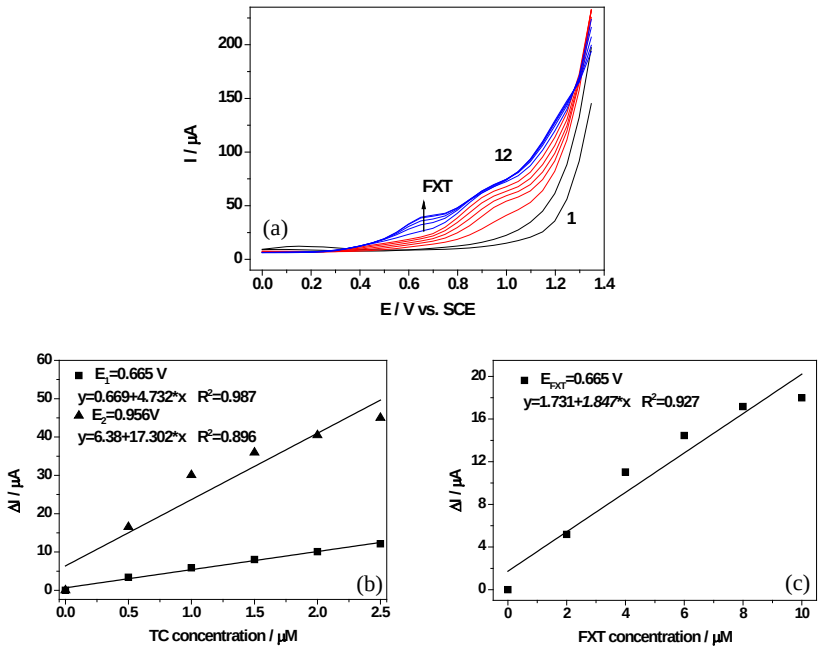

Figure 6: (a) Differential-pulsed voltammograms recorded on CNF electrode at a potential scan rate of 0.025 Vs^{-1} between 0 and +1.35 V/SCE in 0.1 M Na_2SO_4 supporting electrolyte (curve 1 in the presence of 50 μL 0.1 M NaOH (curve 2) and 0.5–2.5 μM TC (curves 3–7), and 2–10 μM FXT (curves 8–12); (b) Calibration plot of the current vs. TC concentration recorded at E_1 = +0.665 V/SCE and E_2 = +0.956 V/SCE; (c) Calibration plot of the current vs. FXT concentration recorded at E = +0.665 V/SCE.

The results obtained on CNF composite electrode for simultaneous detection of fluoxetine and tetracycline are gathered in Table 3. The detection experiments for fluoxetine detection were conducted in the presence of tetracycline, because the signal for fluoxetine detection is lower.

The best performances in relation with the sensitivity and peak potential for both individual and simultaneous detection of TC and FXT pharmaceutical compounds were achieved using differential pulsed voltammetry techniques, in the operating conditions of 0.2 V modulation amplitude, 0.05 V step potential and 0.025 V scan rate.

Table 3: Electroanalytical parameters obtained for simultaneous detection of fluoxetine and tetracycline on CNF electrode by DPV technique.

Technique	Analyte	E /V vs. SCE	Sensitivity (μA/μM)	Conc. range (μM)
DPV	TC	0.500	4.732	0–2.5
		0.956	17.302	
	FXT	0.665	1.847	0–10

4 CONCLUSIONS

Based on the above-presented results it can be concluded that CNF composite electrode is very promising for the detection of tetracycline and fluoxetine in water. The best performances in relation with the limit of detection and limit of quantification for individual detection of TC were obtained by employing cyclic voltammetry on CNF electrode. For FXT detection, good values for limit of detection and limit of quantification were obtained for both cyclic voltammetry and differential pulsed voltammetry techniques. For simultaneous detection of TC and FXT, the best performance in relation with the sensitivity was obtained by employing DPV presented conditions, i.e., modulation amplitude of 0.2 V, step potential of 0.05 V and a scan rate of 0.025 V. By simple selection of the potential range, the selective and simultaneous as cumulative signal corresponding to FXT and TC detection can be achieved. Although, additional research in needed to make the sensor able to analyze more pharmaceutical avoiding any interference, this preliminary study showed its feasibility as potential tool for identification trace quantities of pharmaceutical in water sample.

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