Simultaneous detection of sodium diclofenac and tetracycline from aqueous solution

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Abstract
In this paper, the detection protocols for the selective and simultaneous determination of diclofenac (DCF) and tetracycline (TC) in aqueous solutions were developed using a commercial boron-doped diamond electrode modified with graphene oxide and silver, as the Ag/GF/BDD electrode. This electrode presented the possibility to detect only DCF and TC selectively by applying amperometric techniques. However, the pulsed voltammetric techniques operated in optimized working conditions allowed the selective/simultaneous detection of DCF and TC characterized by the improvement of the performance parameters compared to CV. Following the research study related to the electrochemical detection application of the two emerging target pollutants (DCF and TC), the Ag/GF/BDD electrode presented good stability and reproducibility of the results obtained

INTRODUCTION

Due to the detection characteristics of high sensitivity, low detection limit, selectivity, stability, fast response, lifetime, accuracy, repeatability, reproducibility, electrochemical sensors are of great interest for many types of applications in industry everyday life and environmental quality assessment, especially for water quality monitoring [1]. Based on unique and special properties: such as low background current, wide low potential window due to the high overpotential in the release of hydrogen and oxygen, corrosion in very aggressive environments, inert surface with low adsorption properties, stability in aqueous and non-aqueous environments and high resistance against chemicals, boron doped diamond substrates are attractive and of high interest in electroanalytical applications [2-6]. In addition to the advantages above mentioned, sometimes commercial electrodes present some disadvantages and the most important one is related to the slow kinetic rate of the reaction that takes place on the surface of the electrode substrate, which limits their use in the individual/ simultaneous/ selective detection of the target analytes and application in lower leves of concentrations detection, which makes them even less attractive for production use. In order to eliminate this disadvantage, numerous research studies are reported on this sense in

which solutions were presented to improve the kinetics of the electrode surface by modifying them with various carbon-based and metallic nanomaterials. Modification of commercial electrodes with different nanomaterials allows to control their surface properties, focused on improving their selectivity and sensitivity [1,7]. To obtain new sensors used in electrochemical detection, carbon-based nanomaterials (fullerene, carbon nanofibers, carbon nanotubes, graphene, quantum dots, etc.) are widely explored due to their excellent electrical, chemical and physical properties (electrical conductivity high, mechanical strength, chemical stability) [8]. The synergistic effect of carbon-based nanomaterials substantially improves the sensitivity and selectivity of modified surfaces of commercial electrochemical electrodes [9].

Several current studies have been reported the use of graphene oxide in the development of various electrochemical sensors and biosensors due to the high catalytic activity, lower density, mechanical strength, electron transferring and biocompatibility due to the presence of functional oxygen groups, such as carboxylic acids, hydroxyl groups, epoxy, which makes it an excellent and economical nanomaterial for electroanalytical applications [10-14].

Because metal particles possess excellent properties in the modification of electrode substrates such as photocatalytic activity, thermal stability, low cost, extraordinary electrical, optical and molecular advantages, they are suitable for the development of new electrochemical sensors and biosensors that can be used for biological and pharmaceutical applications [15]. The modification of the carbon substrates, especially the diamond substrate doped with boron with metal particles (silver) and graphene oxide shown a much higher electrocatalytic activity reflected by the faster electron transfer rate, which determines an improvement in the performance parameters corresponding to the electrochemical methods of detection, which makes them very useful in the production of electrochemical sensors and biosensors required for individual/simultaneous/selective detection of emerging pollutants [16-19]. Since there are many unknown aspects regarding emerging pollutants, starting even with their identification/detection due to the very large number of substances, more or less known, present in water as a result of human activity, these pollutants constitute a challenge for their quantitative determination, requiring the development of advanced simultaneous electroanalytical detection methods [20]. One of the reasons why the simultaneous detection methods used in the detection of pharmaceutical compounds without any interference are desired is due to the effects of the simultaneous presence of pharmaceutical products on the environment are extensive, complex and very dangerous for fauna and biota. Due to the synergistic effect of the combination of graphene oxide and silver particles deposited electrochemically on the surface of the boron-doped diamond (BDD) substrate used as a support material, in the present paper, the simultaneous and selective detection of two emerging target pollutants that belong to different classes of pharmaceutical products sodium diclofenac DCF from anti-inflammatory class and tetracycline TC from antibiotic class is presented, evaluated and discussed. This study represents continuing the work already published for individual TC detection [21], to explore the possibility to detect simultaneously or selectively TC and DCF.

MATERIALS AND METHODS

An Autolab PGSTAT 302 potentiostat-galvanostat, managed by an electronic computer through GPES 4.9 software and a three-electrode Metrohm cell was used to carry out the electrochemical studies. The cell structure included the electrochemically modified boron-doped diamond (BDD) working sensor, a platinum (Pt) counter-sensor, and a saturated calomel (SCE) sensor used as a reference electrode. Experiments were performed at room temperature without additional temperature control. The surface of the working electrode substrate (BDD) was refreshed after each electrochemical experiment by a circular mechanical movements of the working sensors with Al_2O_3 powder and then washed with purified water. Before each detection experiment the electrochemical stabilization of the electrode was performed by electrochemical technique of cyclic voltammetry (10 repetitive cyclic voltammograms) in the potential domain in relation to the electrochemical behavior of the electrode material. The electrochemical modification of the BDD electrode with graphene oxide (suspension of 4 mg/mL GF spread in water) occurred through

chronoamperometry (CA) technique for graphene deposition at a potential of -1.50 V/SCE for 120s followed by applying potential of -1.3V/SCE for 5s for the deposition of silver. The supporting electrolyte used in the practical research study was 0.1 M Na_2SO_4 prepared with distilled water using analytical grade reagent (Merck, Germany). The stock solutions of diclofenac (DCF) was prepared using distilled water and of tetracycline (TC) was prepared in 0.1 M NaOH. The electrochemical techniques applied for the electrochemical characterization of the modified working electrode and tested for the development of simultaneous/selective detection protocols were: cyclic voltammetry (CV), and advanced voltammetric techniques: differential pulse voltammetry (DPV), square wave voltammetry (SWV), and technique amperometric: chronoamperometry (CA). Also, were used to develop amperometric protocols for silver deposition from 4 mM $AgNO_3$ solution.

RESULTS AND DISCUSSION

Cyclic voltammetry (CV) studies for simultaneous detection of sodium diclofenac (DCF) and tetracycline (TC)

Figures 1 and 2 present the series of cyclic voltammograms recorded on Ag/GF/BDD electrode in the presence of single DCF and respective, single TC, including the calibration curves. In order to develop simultaneous or selective detection method for target pollutants, it is compulsory to study each individual behaviors onto modified Ag/GF/BDD by cyclic voltammetry. The individual CV results obtained for each target pollutant allow getting the detection useful information. Similar sensitivities were achieved for DCF and TC. However, the oxidation and respective, the detection peaks values are different. The detection peak of DCF is +0.340 V/SCE and for TC is +0.800V/SCE. It is obviously that DCF is easier oxidized as TC and the difference between the oxidation potentials are higher than 250 mV, which show the possibility of both target pollutants simultaneous detection. It is important to check is DCF interfere TC detection. Thus, Figure 3 shows CV series obtained for different concentration of DCF followed by different concentrations of TC. It can be seen that DCF does not interfere TC detection related to the detection potential value and the sensitivities (see Table 1). Similar the lowest limits of detections were achieved for simultaneous detection in comparison with individual detection of DCF and TC (about 0.2 µM).
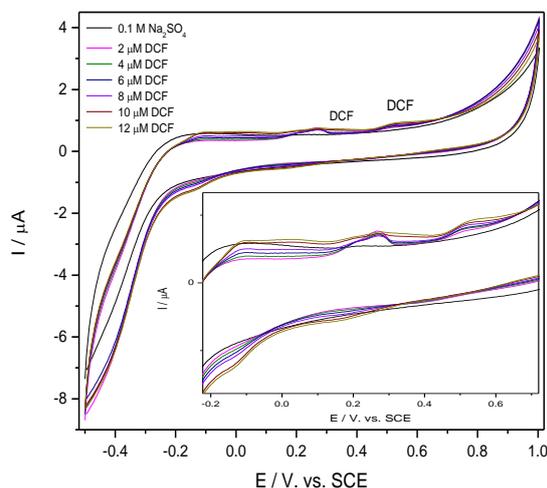
Fig. 1. a). Cyclic voltammograms recorded with the Ag/GF/BDD electrode in the presence of DCF (2-12 µM) concentration and in 0.1 M Na_2SO_4 supporting electrolyte solution; scanning speed 0.05 V·s^{-1}; potential range: -0.500 → 1.00 V/SCE
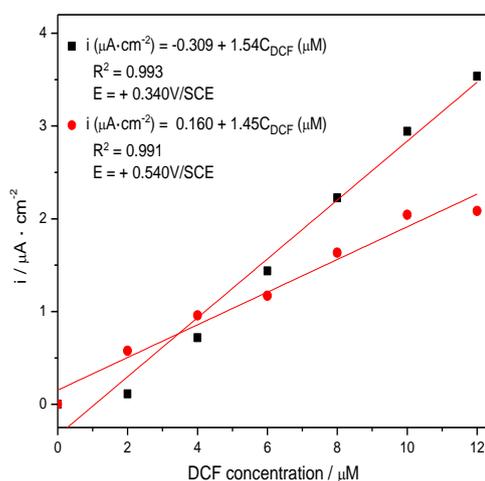
Fig. 1. b). Current density calibration curve corresponding to oxidation peaks at E_1= +0.340V/SCE and E_2 = +0.540 V/SCE vs. diclofenac concentration (µM).
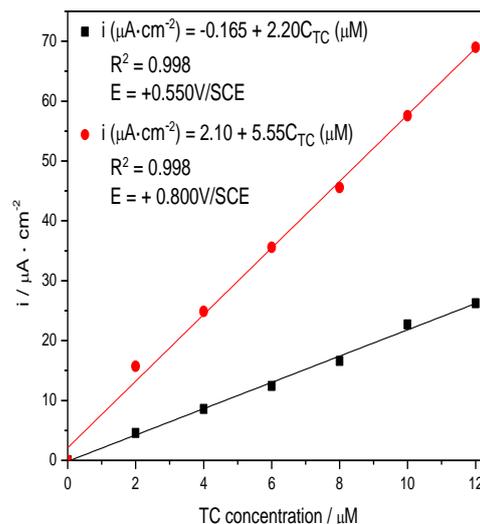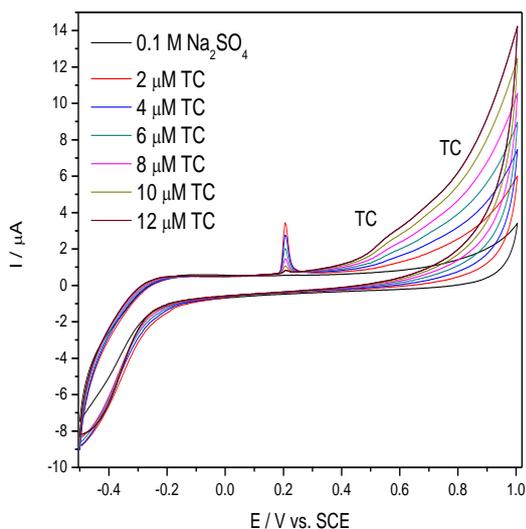
Fig. 2. a). Cyclic voltammograms recorded with the Ag/GF/BDD electrode in the presence of TC (2-12 µM) concentration and in 0.1 M Na$_2$SO$_4$ supporting electrolyte solution; scanning speed 0.05 V·s^{-1}; potential range: -0.500 → 1.00 V/SCE.

Fig. 2. b). Current density calibration curve corresponding to oxidation peaks at E$_1$= +0.550 V/SCE and E$_2$ = +0.800/ SCE vs. tetracycline concentration (µM).
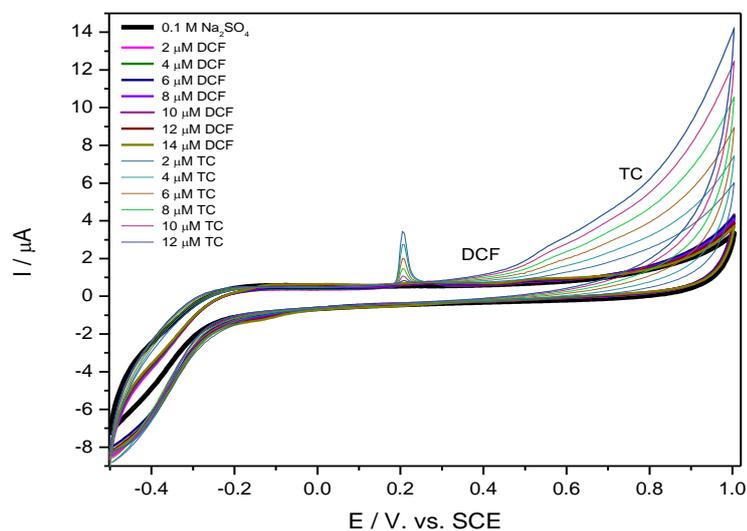
Fig. 3. a) Cyclic voltammograms recorded with the Ag/GF/BDD electrode in the presence of DCF (2-14 µM) and TC (2-12 µM) concentrations and in 0.1 M Na$_2$SO$_4$ supporting electrolyte solution; scanning speed 0.05 V·s^{-1}; potential range: -0.500 → 1.00 V/SCE.
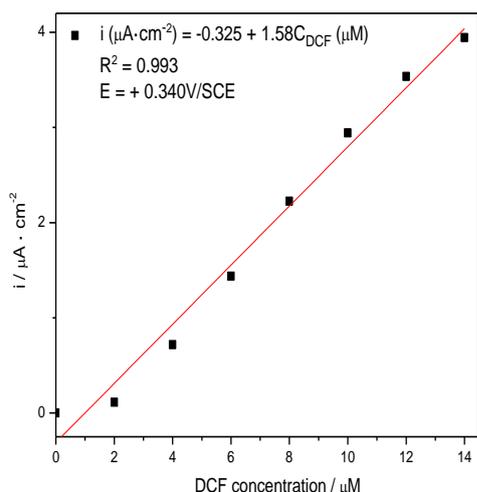
Fig. 3. b). Current density calibration curve corresponding to oxidation peaks at E = +0.340 V/SCE vs. diclofenac concentration (μM).
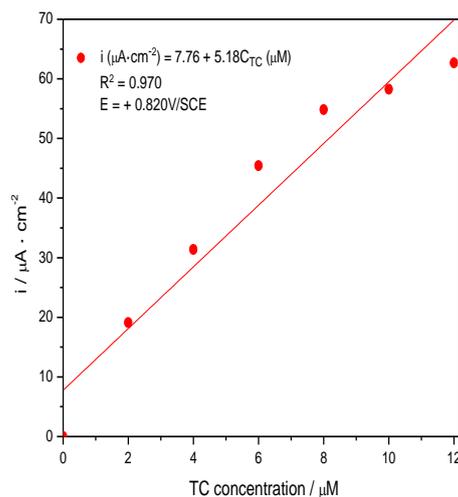
Fig. 3. c). Current density calibration curve corresponding to the oxidation peak at E = +0.820 V/SCE vs. tetracycline concentration (μM).

Table 1. Analytical parameters obtained for the Ag/GF/BDD electrode in the simultaneous detection of diclofenac (DCF) and tetracycline (TC) by applying the cyclic voltammetry (VC) technique

Detection type	Target pollutant	E (V/SCE)	Sensitivity (μA/μM·cm⁻²)	LOD (μM)	LOQ (μM)	RSD (%)	R²
Individual	DCF	+0.340 (ap)*	1.54	0.556	1.85	2.99	0.993
		+0.540 (ap)	1.45	0.238	0.796	3.10	0.991
	TC	+0.550 (ap)	2.20	0.204	0.680	1.37	0.998
		+0.800 (ap)	5.55	0.194	0.647	1.62	0.998
Simultaneous	DCF	+0.340 (ap)	1.58	0.557	1.88	2.99	0.993
	TC	+0.820 (ap)	5.18	0.219	0.731	1.57	0.970

* ap – anodic peak

In order to improve the electroanalytical parameters (sensitivity, limit of detection and respective limit of quantification), and also for the development for simultaneous or selective voltammetric detection protocols, in the following section, the pulsed techniques of differential pulse voltammetry (DPV) and square wave voltammetry (SWV) are tested and optimized by the operating parameters.

Optimization of operating parameters by applying the electrochemical technique of differential pulse voltammetry (DPV)

In order to obtain promising results regarding the development of simultaneous/selective voltammetric detection protocols, the optimization step of operating parameters: modulation amplitude (MA), potential step (SP) and scan rate (v) is required. Thus, for the simultaneous/selective detection of the two target pollutants (DCF and TC), the operating conditions included in certain ranges of values imposed by preliminary tests were tested in a wider range. The amplitude modulation (MA) values were 100 mV and 200 mV, and 5, 25 and 50 mV the step potential (SP). Recording pulsed voltammograms in the presence of diclofenac (DCF) and tetracycline (TC) using the Ag/GF/BDD electrode was performed at a constant scan rate of 0.05 V·s⁻¹ in the potential range -0.500 → +1.00V.

The differential pulse voltammograms recorded using the Ag/GF/BDD electrode for the electrochemical detection of the two compounds for each operating condition are presented in Figures 4-9 including the calibration curves.
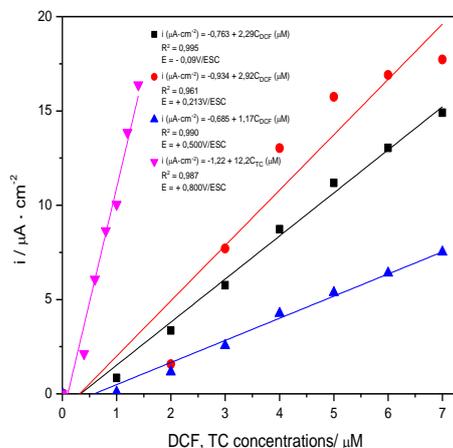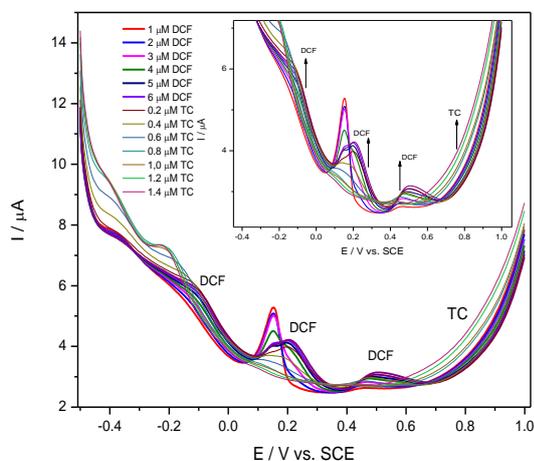
Fig. 4. a). Differential pulse voltammograms (DPV) recorded with the Ag/GF/BDD electrode in 0.1 M Na$_2$SO$_4$ supporting electrolyte solution and in the presence of DCF (1-6 µM) and TC (0.2-1.4 µM); step potential (SP) 5 mV; modulation amplitude (MA) 100 mV; potential range: -0.500 → +1.00 V/SCE.

Fig. 4. b). Current density calibration curve corresponding to oxidation peaks E$_1$ = -0.090 V/SCE, E$_2$ = +0.213 V/SCE and E$_3$ = +0.500 V/ SCE vs. diclofenac concentration respectively at E= +0.800 V/SCE vs. tetracycline concentration.
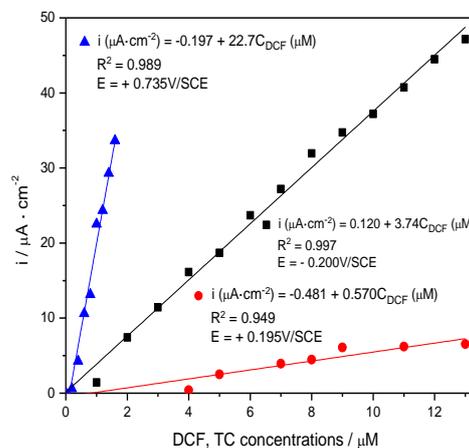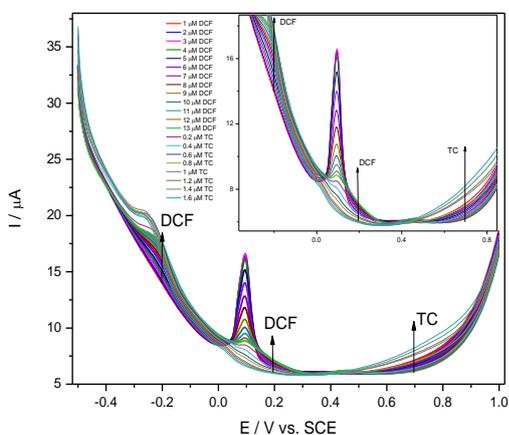
Fig. 5. a). Differential pulse voltammograms (DPV) recorded with the Ag/GF/BDD electrode in 0.1 M Na$_2$SO$_4$ supporting electrolyte solution and in the presence of DCF (1-13 µM) and TC (0.2-1.6 µM); step potential (SP) 5 mV; modulation amplitude (MA) 200 mV; potential range: -0.500 → +1.00 V/SCE.

Fig. 5. b). Current density calibration curve corresponding to oxidation peaks E$_1$ = -0,200 V/SCE, E$_2$ = +0.195 V/SCE vs. diclofenac concentration respectively at E= +0.735 V/SCE vs. tetracycline concentration.
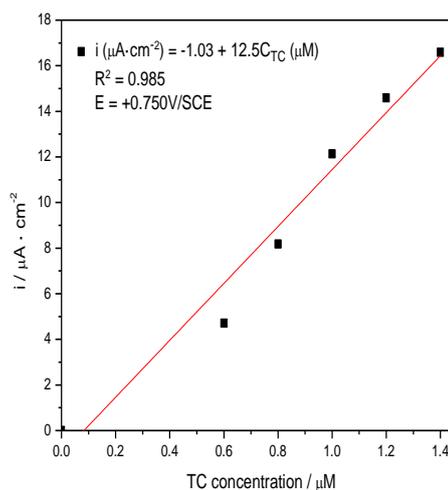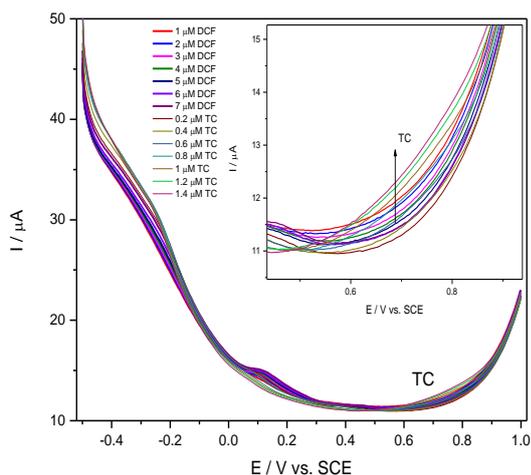
Fig. 6. a). Differential pulse voltammograms (DPV) recorded with the Ag/GF/BDD electrode in 0.1 M Na$_2$SO$_4$ supporting electrolyte solution and in the presence of DCF (1-7 μM) and TC (0.2-1.4 μM); step potential (SP) 25 mV; modulation amplitude (MA) 100 mV; potential range: -0.500 → +1.00 V/SCE.

Fig. 6. b). Current density calibration curve corresponding to oxidation peak at E= +0.750 V/SCE vs. tetracycline concentration.
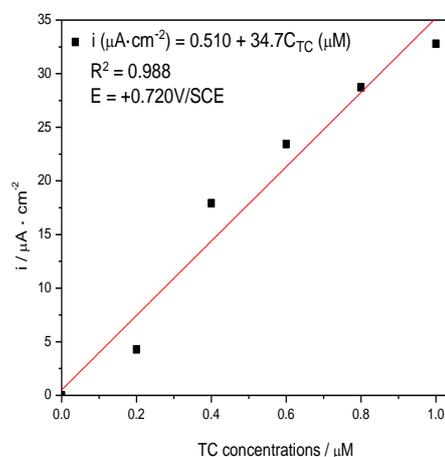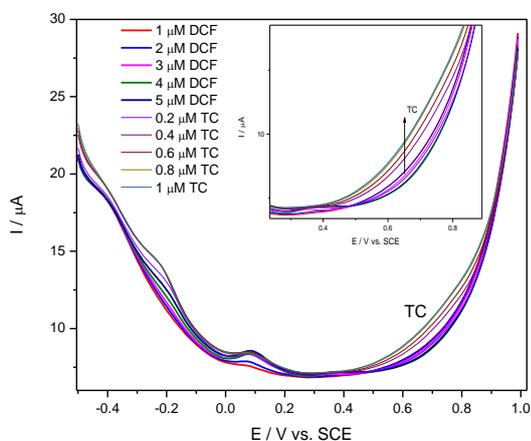
Fig. 7. a). Differential pulse voltammograms (DPV) recorded with the Ag/GF/BDD electrode in 0.1 M Na$_2$SO$_4$ supporting electrolyte solution and in the presence of DCF (1-5 μM) and TC (0.2-1 μM); step potential (SP) 25 mV; modulation amplitude (MA) 200 mV; potential range: -0.500 → +1.00 V/SCE.

Fig. 7. b). Current density calibration curve corresponding to oxidation peak at E= +0.720 V/SCE vs. tetracycline concentration.
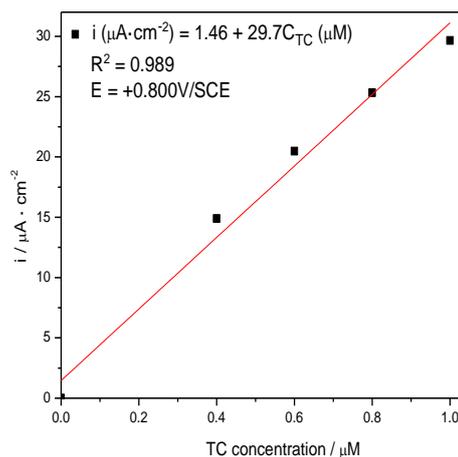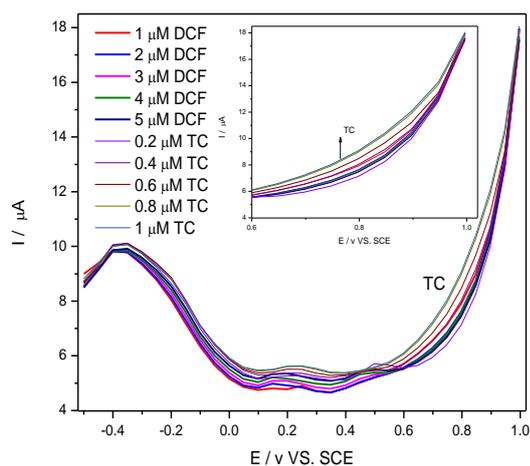
Fig. 8. a). Differential pulse voltammograms (DPV) recorded with the Ag/GF/BDD electrode in 0.1 M Na$_2$SO$_4$ supporting electrolyte solution and in the presence of DCF (1-5 µM) and TC (0.2-1 µM); step potential (SP) 50 mV; modulation amplitude (MA) 100 mV; potential range: -0.500 → +1.00 V/SCE.

Fig. 8. b). Current density calibration curve corresponding to oxidation peak at E= +0.800 V/SCE vs. tetracycline concentration.
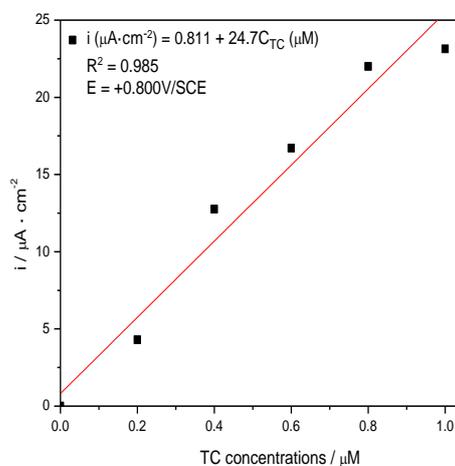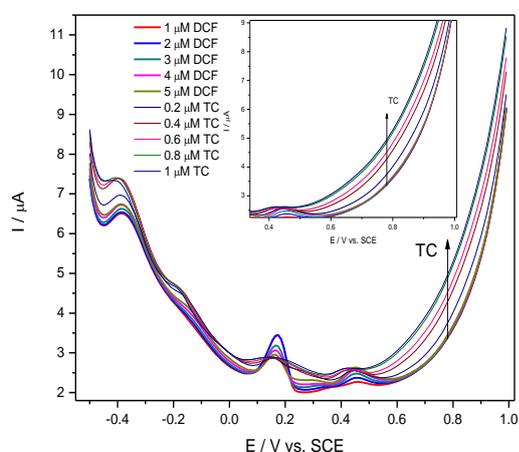
Fig. 9. a). Differential pulse voltammograms (DPV) recorded with the Ag/GF/BDD electrode in 0.1 M Na$_2$SO$_4$ supporting electrolyte solution and in the presence of DCF (1-5 µM) and TC (0.2-1 µM); step potential (SP) 50 mV; modulation amplitude (MA) 200 mV; potential range: -0.500 → +1.00 V/SCE.

Fig. 9. b). Current density calibration curve corresponding to oxidation peak at E= +0.800 V/SCE vs. tetracycline concentration.

It is observed that the application of a potential step higher than ≥25 mV is not suitable for DCF detection but it is suitable for TC detection, which shows that the kinetics of TC oxidation processes is faster than that of DCF. These aspects lead to the possibility of simultaneous determination of DCF and TC or selective TC by simply setting the operating conditions of the advanced DPV

technique. In case of operating conditions with 25 mV SP potential step, only detection of tetracycline (TC) was possible, which implies the possibility of developing selective detection of TC. Considering necessity to separate to separate the oxidation peaks of the two emerging pharmaceutical-pollutant compounds to allow their simultaneous detection, the obtained results were analyzed and it was observed that for all the operating conditions that allowed the detection of the two compounds, a good separation was ensured of their oxidation potential values (detection). Applying a lower potential step also allowed the detection of DCF (5 mV), while SP values of 25 mV and 50 mV, respectively, did not allow the detection of DCF but only TC detection was achieved. The best results regarding the performance of electroanalytical detection parameters (sensitivity, detection limit, quantification limit), were obtained in the case of conditions of SP 5 mV, MA 100 mV, conditions suitable for simultaneous detection (DCF+TC), and the conditions corresponding to the best results obtained in the selective detection of tetracycline were SP 50 mV and MA 100 mV. The results obtained from recording the differential pulse voltammograms in the operating conditions established above were centralized in Table 2.

Table 2. Analytical parameters obtained – the Ag/GF/BDD electrode in the simultaneous/selective detection of diclofenac (DCF) and tetracycline (TC) by applying the pulsed differential pulse voltammetry (DPV) technique

Detection type	Conditions	Target pollutant	E (V/SCE)	Sensitivity ($\mu A/\mu M \cdot cm^{-2}$)	LOD (μM)	LOQ (μM)	RSD (%)	R^2
Simultaneous	SP 5 mV MA 100 mV	DCF	-0.09	2.29	0.076	0.252	0.080	0.995
			+0.213	2.92	0.053	0.178	0.060	0.961
			+0.500	1.17	1.68	5.58	1.73	0.990
		TC	+0.800	12.2	0.048	0.158	0.360	0.987
Simultaneous	SP 5 mV MA 200 mV	DCF	-0.200	3.74	0.319	1.06	0.330	0.997
			+0.195	0.57	11.4	38.0	1.15	0.949
		TC	+0.735	22.7	0.475	1.58	1.97	0.989
Selective	SP 25 mV MA 100 mV	DCF	-	-	-	-	-	-
		TC	+0.750	12.5	0.397	1.32	0.993	0.985
Selective	SP 25 mV MA 200 mV	DCF	-	-	-	-	-	-
		TC	+0.720	34.7	0.132	0.441	1.15	0.988
Selective	SP 50 mV MA 100 mV	DCF	-	-	-	-	-	-
		TC	+0.800	29.7	0.090	0.299	0.820	0.989
Selective	SP 50 mV MA 200 mV	DCF	-	-	-	-	-	-
		TC	+0.800	24.7	0.204	0.680	3.11	0.985

- no anodic peak was observed

By using pulse-differential voltammetry compared to cyclic voltammetry, the improvement of the electroanalytical parameters was obtained regarding both of sensitivity and detection limit.

Optimization of operating parameters by applying the electrochemical technique of square-wave voltammetry (SWV)

Another pulsed technique often used in the simultaneous/selective detection of diclofenac (DCF) and tetracycline (TC) emerging pollutants was square wave voltammetry (SWV). In the case of the application of the SWV technique, in order to improve the electroanalytical performance in the development of simultaneous/selective voltammetric detection protocols, in addition to the optimization of the SP and MA operating parameters, another important parameter, the frequency (f) is considered. Square wave voltammograms were recorded in the potential range of -0.500 → +1.00V for operating conditions shown in Table 3.

Table 3. Optimization conditions of technique-specific operating parameters – square wave voltammetry (SWV)

SP / mV	MA / mV	f / Hz	v / V·s⁻¹
20	100	50	0.100
			1.00
5		25	0.120
20	200	50	1.00
		8	0.160

Figures below (Figures 10 - 14) show the results for each set condition, together with the related calibrations for the simultaneous detection of the two emerging pollutants DCF and TC and for selective detection of TC.
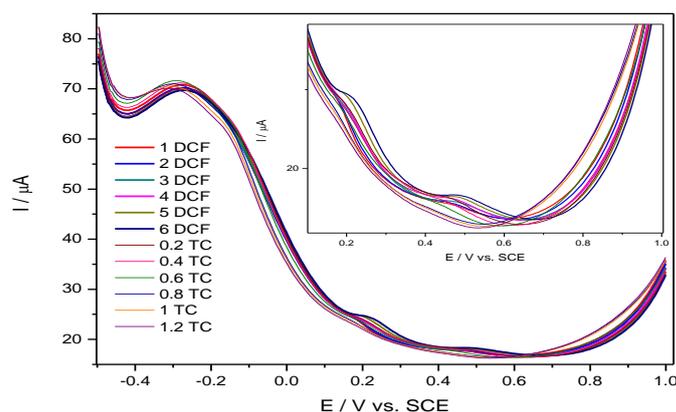
Fig. 10. Square-wave voltammograms (SWV) recorded with the Ag/GF/BDD electrode in 0.1 M Na$_2$SO$_4$ supporting electrolyte and in the presence of DCF (1–6 µM) and TC (0.2–1.2 µM); in optimized conditions: frequency of 25 Hz, potential step (SP) 5 mV, modulation amplitude (MA) 100 mV and scan rate 0.120 V·s⁻¹; potential range -0.500 → +1.00 V/SCE.
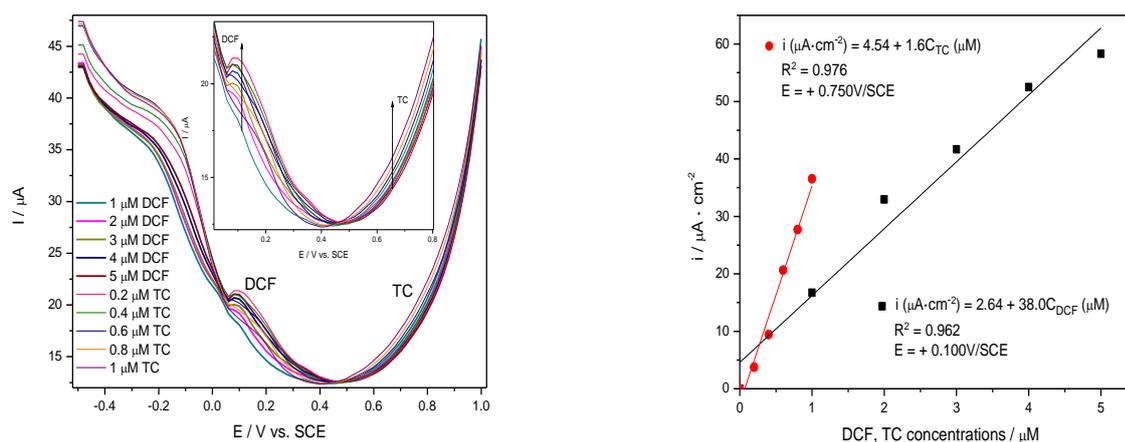
Fig. 11. a). Square-wave voltammograms (SWV) recorded with the Ag/GF/BDD electrode in 0.1 M Na$_2$SO$_4$ supporting electrolyte and in the presence of DCF (1–5 µM) and TC (0.2–1 µM); in optimized conditions: frequency of 8 Hz, potential step (SP) 20 mV, modulation amplitude (MA) 200 mV and scan rate 0.160 V·s⁻¹; potential range -0.500 → +1.00 V/SCE.

Fig. 11. b). Current density calibration curve corresponding to oxidation peaks E = +0.100 vs. diclofenac concentration respectively at E= +0.750 V/SCE vs. tetracycline concentration.
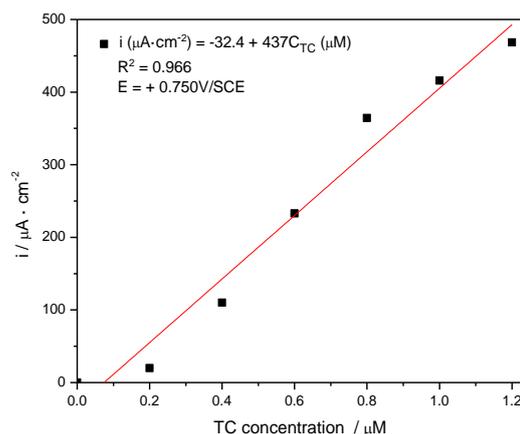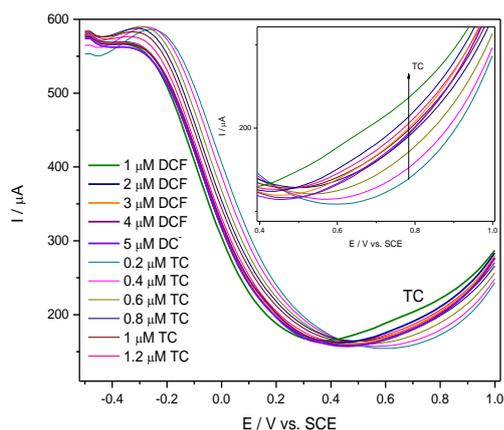
Fig. 12. a). Square-wave voltammograms (SWV) recorded with the Ag/GF/BDD electrode in 0.1 M Na₂SO₄ supporting electrolyte and in the presence of DCF (1–5 μM) and TC (0.2–1.2 μM); in optimized conditions: frequency of 50 Hz, potential step (SP) 20 mV, modulation amplitude (MA) 100 mV and scan rate 1.60 V·s⁻¹; potential range -0.500 → +1.00 V/SCE.

Fig. 12. b). Current density calibration curve corresponding to oxidation peak at E= +0.750 V/SCE vs. tetracycline concentration.
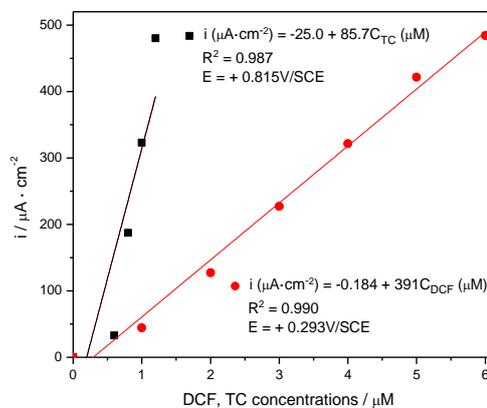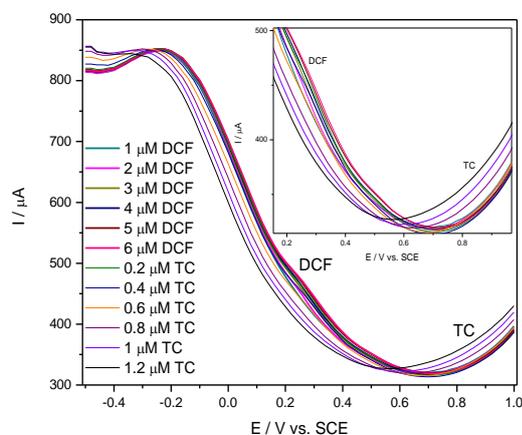
Fig. 13. a). Square-wave voltammograms (SWV) recorded with the Ag/GF/BDD electrode in 0.1 M Na₂SO₄ supporting electrolyte and in the presence of DCF (1–6μM) and TC (0.2–1.2 μM); in optimized conditions: frequency of 50 Hz, potential step (SP) 20 mV, modulation amplitude (MA) 200 mV and scan rate 1.60 V·s⁻¹; potential range -0.500 → +1.00 V/SCE.

Fig. 13. b). Current density calibration curve corresponding to oxidation peaks E = +0.293 vs. diclofenac concentration respectively at E= +0.815 V/SCE vs. tetracycline concentration.
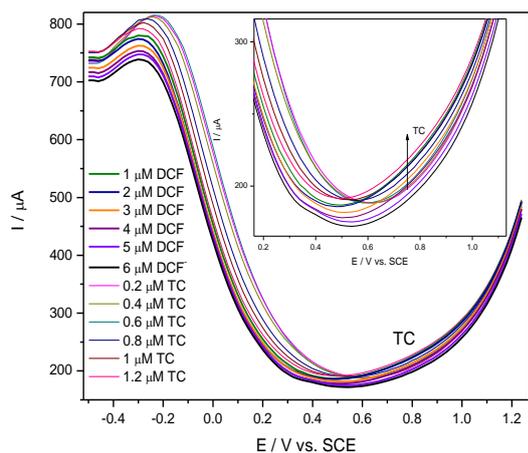
Fig. 14. a). Square-wave voltammograms (SWV) recorded with the Ag/GF/BDD electrode in 0.1 M Na$_2$SO$_4$ supporting electrolyte and in the presence of DCF (1–6 μM) and TC (0.2–1.2 μM); in optimized conditions: frequency of 50 Hz, potential step (SP) 20 mV, modulation amplitude (MA) 100 mV and scan rate 1.60 V·s^{-1}; potential range -0.500 → +1.00 V/SCE.
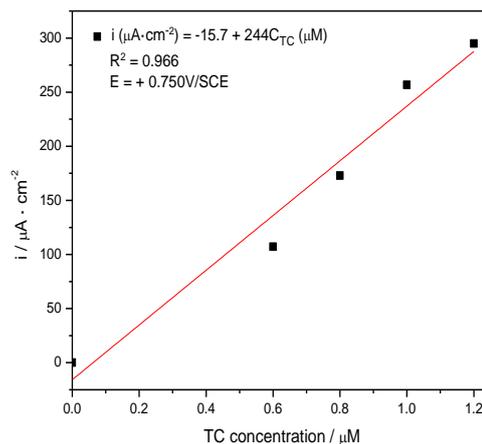
Fig. 14. b). Current density calibration curve corresponding to oxidation peaks at E= +0.815 V/SCE vs. tetracycline concentration.

The results obtained after recording the square wave voltammograms using the Ag/GF/BDD electrode in 0.1 M Na$_2$SO$_4$ supporting electrolyte but also in the simultaneous presence of the two pollutants (DCF and TC) are centralized in Table 4.

Table 4. Analytical parameters obtained using the Ag/GF/BDD electrode in the simultaneous/selective detection of diclofenac (DCF) and tetracycline (TC) by applying the SWV technique

Detection type	Conditions	Target pollutant	E (V/SCE)	Sensitivity (μA/μM·cm^{-2})	LOD (μM)	LOQ (μM)	RSD (%)	R^2
Simulta-neous	SP 20 mV MA 200mV f 8 Hz v 0.160V·s^{-1}	DCF	+0.100	38.0	0.020	0.070	0.230	0.962
		TC	+0.750	11.6	0.030	0.110	0.420	0.976
Selective	SP 20 mV MA 100mV f 50 Hz v 1.00V·s^{-1}	DCF	-	-	-	-	-	-
		TC	+0.750	437	0.017	0.056	0.112	0.966
Simulta-neous	SP 20 mV MA 200mV f 50 Hz v 1.00V·s^{-1}	DCF	+0.293	391	0.013	0.040	0.520	0.990
		TC	+0.815	85.7	0.020	0.094	0.620	0.987
Selective	SP 20 mV MA 100mV f 50 Hz v1.00V·s^{-1} -0.5V→ +1.25V	DCF	-	-	-	-	-	-
		TC	+0.750	244	0.017	0.060	0.140	0.966

- no anodic peak was observed

It can be observed that the optimization of the operating parameters allowed the simultaneous detection of (DCF and TC) but also a favorable selective detection. The application of the SWV technique operating in the conditions of SP 5 mV, MA 100 mV and f 25 Hz did not allow the

detection of the two pollutants, these conditions are not favorable for the selective/simultaneous detection. In the case of simultaneous detection under the operating conditions SP 20 mV, MA 200 mV and f 50 Hz, the lowest detection limits of 0.013 μM DCF and 0.020 μM TC were obtained. The selective detection in the case of TC led to obtaining a detection limit of 0.017 μM TC under the operating conditions of SP 20 mV, MA 100 mV and f 50 Hz in the potential range of -0.500 → +1.00 V. By expanding potential range in the anodic zone, the possibility of detecting only TC was observed, without DCF detection because a displacement of SWV was found, the currents recorded up to the potential value of +0.600 V/SCE being below the background current.

Chronoamperometry technique for the simultaneous detection of TC and DCF
Although the amperometric techniques, due to their simplicity and ease of operation, are very useful in practical applications, in the development of some operating methods they are based on the voltammetric benchmarks for characterizing the electrode material in the presence of the target analyte. The conditions of the amperometric methods were established based on the results obtained by cyclic voltammetry, related to the simultaneous/ selective amperometric detection, and the chronoamperograms were recorded at various detection potentials, results being presented in Figures 15-16.
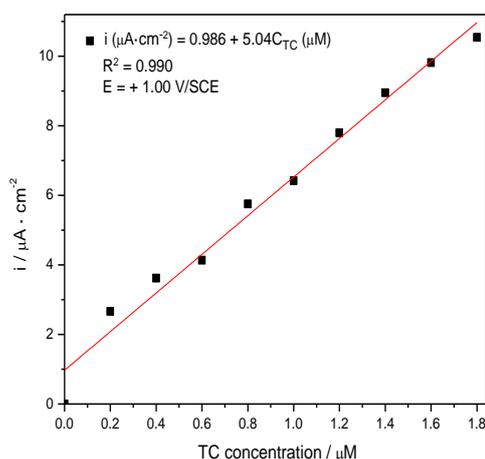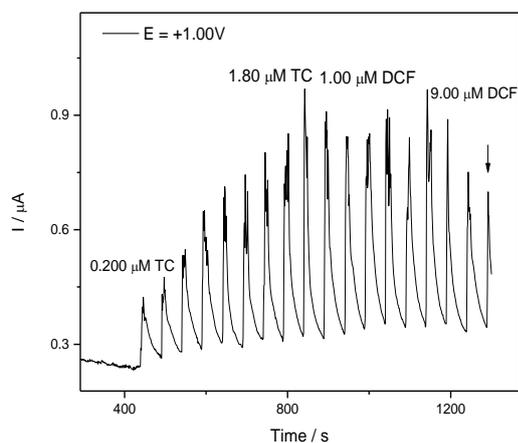
Fig. 15. a) Chronoamperogram (CA) recorded with the Ag/GF/BDD electrode in 0.1 M Na_2SO_4 support electrolyte during the continuous addition of TC (0.2-1.8 μM) and DCF (1-9 μM) concentrations to the value of potential of E =+1.00 V/SCE

Fig. 15. b). Current density calibration curve corresponding to oxidation peaks at E= +1.00 V/SCE vs. tetracycline concentration

The application of the chronoamperometry technique allowed only selective detection either for TC or for DCF. Thus, by multiple setting potential value at +1.00 V/SCE, TC selective detection was achieved and by multiple setting potential value lower than +0.800 V/SCE, the selective detection was achieved higher detection potential value, the better sensitivity is reached. Depending on the electrochemical method applied: cyclic voltammetry, differential pulse voltammetry, square wave voltammetry, and chronoamperometry following the optimization of the operating conditions, the performance of the Ag/GF/BDD electrode compared to the results related to the analytical performance parameters are presented in Table 5.
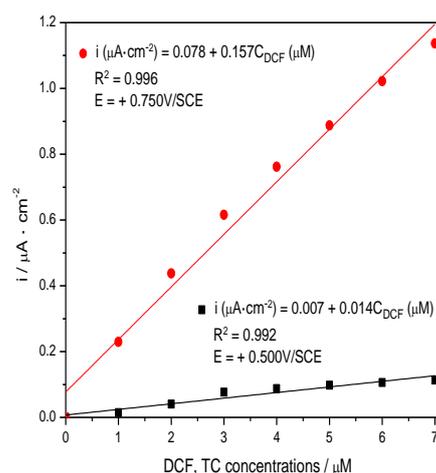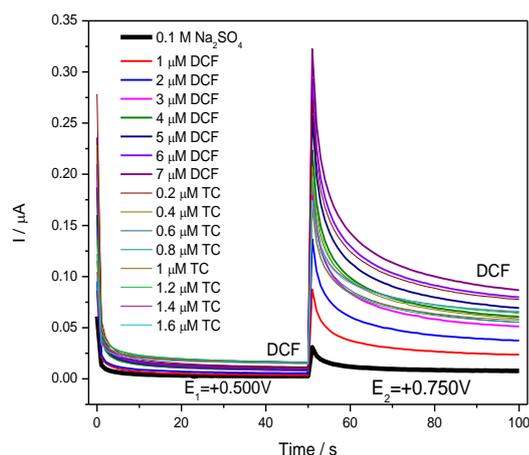
Fig. 16. a). Chronoamperograms recorded with the Ag/GF/BDD electrode in 0.1 M Na$_2$SO$_4$ supporting electrolyte, during the addition of DCF (1-7 µM) and TC (0.2-1.6 µM) concentrations, during 100 s at a potential value of E$_1$ =+1.00 V/SCE and E$_2$ =+0.750 V/SCE.

Fig. 16. b). Current density calibration curve corresponding to oxidation peaks E$_1$ = 0.500 V/SCE and E$_2$ = +0.750 V/SCE vs. diclofenac concentration.

Table 5. The analytical parameters obtained using the Ag/GF/BDD electrode and the CV, DPV, SWV, CA techniques in the simultaneous/selective detection of diclofenac (DCF) and tetracycline (TC)

Detection type	Conditions	Target pollutant	E (V/SCE)	Sensitivity (µA/µM·cm^{-2})	LOD (µM)	LOQ (µM)	RSD (%)	R^2
Simulta-neous	CV	DCF	+0.340 (ap)*	1.58	0.557	1.88	2.99	0.993
		TC	+0.820 (ap)	5.17	0.219	0.731	1.57	0.970
Simulta-neous	DPV SP 5 mV MA 100 mV v0.05V·s^{-1}	DCF	-0.09 (ap)	2.29	0.076	0.252	0.080	0.995
			+0.213 (ap)	2.92	0.053	0.178	0.060	0.961
		TC	+0.500 (ap)	1.17	1.68	5.58	1.73	0.990
			+0.800 (ap)	12.2	0.048	0.158	0.360	0.987
Simulta-neous	SWV SP 20 mV MA 200 mV v 0.1 V·s^{-1} f 50 Hz v 0.1V·s^{-1}	**DCF**	**+0.293 (ap)**	**391**	**0.013**	**0.040**	**0.520**	**0.990**
		TC	**+0.815 (ap)**	**85.7**	**0.020**	**0.094**	**0.620**	**0.987**
Selective	DPV SP 50 mV MA 100 mV v 0.05V·s^{-1}	TC	+0.800 (ap)	29.7	0.090	0.299	0.820	0.989
Selective	1 level	TC	+1.00 (ap)	5.04	0.404	4.08	0.121	0.990
Selective	2 levels	DCF	+0.500 (ap)	0.014	0.763	2.96	0.229	0.992
			+0.750 (ap)	0.157	0.240	3.67	0.072	0.996

* ap – anodic peak

CONCLUSIONS

In this study, the simultaneous or selective detection of two emerging pollutants in water, diclofenac and tetracycline, was pursued by electrochemical voltammetric and amperometric methods. All tested electrochemical voltammetric techniques were suitable for the development of the simultaneous/selective electrochemical procedure for the quantitative detection of DCF and TC in 0.1 M Na$_2$SO$_4$ aqueous solution. The best simultaneous detection results in terms of sensitivity of 391 µA/µM·cm^{-2} and lowest detection limit of 0.013 µM for DCF and sensitivity of 85.7

$\mu A/\mu M \cdot cm^{-2}$ and LOD of 0.020 μM related to the pollutant TC were obtained using SWV under operating conditions: potential step of 2 mV, modulation amplitude of 200 mV and frequency of 50 Hz. Chronoamperometry operated easily by setting one or more potential levels allowed the selective detection of DCF or TC related to the detection potential value. According to the results of this research study, including the reproducibility and repeatability of the suggested methods, it can be said that the BDD electrode modified with electrochemically reduced graphene oxide and decorated with silver is suitable for the simultaneous/ selective electrochemical detection of diclofenac (DCF) and tetracycline (TC) from the water.

ACKNOWLEDGEMENTS

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