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ELECTROCHEMICAL DETECTION OF TETRACYCLINE AS EMERGENT POLLUTANT IN WATER USING CARBON NANOFIBER-$CoAl_2O_4$ ELECTRODE

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Abstract

The aim of this study was to develop an electrochemical procedure for the advanced detection of tetracycline (TC) in water using $CoAl_2O_4$ dispersed onto carbon nanofiber-epoxy composite electrode substrate, which was selected from a series of tested carbon-based electrode substrates, *i.e.*, commercial glassy-carbon and boron-doped diamond electrodes and home-made carbon nanotube-epoxy and carbon nanofiber-epoxy composites. Carbon nanofiber-epoxy composite electrode was found the best host for $CoAl_2O_4$ modifier based on the electrocatalytic effect towards TC oxidation and detection using cyclic voltammetry (CV) technique. The electrochemical techniques applied for electrochemical detection applications were CV, differential-pulse voltammetry (DPV), square-wave voltammetry (SWV) and chronoamperometry (CA). All the tested electrochemical techniques allowed TC determination and the electroanalytical parameters varied related to the technique type. DPV operated at the step potential of 50 mV and the modulation amplitude of 200 mV allowed the lowest limit of detection of 9 nM for TC determination. The recovery test applied for real surface water spiked with known TC concentrations among the reproducibility and the repeatability showed the great potential for the advanced quantitative determination of TC in real water or in pharmaceutical formulations.

Keywords: carbon nanofiber-epoxy electrode, substrate modification, tetracycline voltammetric/amperometric detection

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1. Introduction

Both world society and many researchers' increasing interest in the subject of emerging pollutants (EPs) is linked to their potential negative environmental impact and human health risk (Taheran et al., 2018). Also, even by the definition of this category of pollutants provided by Environmental Protection Agency (EPA), a series of questions and problems related to their presence in environment arise (Vargas-Berrones et al., 2020). Due to the fact that a main category of EPs is represented by the organic compounds in very low concentrations, their analysis is challenging and involves continuous updates related to new compounds to be detected and improvements for the sensitivity and the lowest limit of detection (Teodosiu et al., 2018).

The antibiotics class is considered representatively for the pharmaceutical category of emerging pollutants due to their potential adverse effects on the ecosystem and human health. Although antibiotics are biodegradable, they have been frequently detected in a variety of environments due to a continous discharge into waterways (Peng et al.,

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2000). Also, many research studies have reported that in natural environments, the concentrations of antibiotics can vary from a few nanograms to hundreds of micrograms per liter. The largest amounts are found in areas with strong anthropogenic pressures, such as hospital effluents. Residual environmental concentrations of antibiotics are due not only to the continuous release into the environment, but also to their high intrinsic persistence.

Antibiotics, such as tetracyclines, are considered to be much more persistent in the environment, spreading more widely and accumulating in higher concentrations. Considered as an organic contaminant in water, tetracycline is difficult to degrade and remains an active form in environmental water, leading to a negative effect on ecosystems and human health (Zhou et al., 2018).

Therefore, in order to avoid its negative impact on the ecosystem, it is necessary to control the amount of tetracyclines that can significantly affect the environment (Zhang et al., 2019). Residues of tetracycline and its metabolites have been widely detected in surface water, groundwater, and soil. Given the importance to be given to water quality and public health, it is desirable to develop rapid, effective and accurate analytical methods for determining tetracycline in environmental samples. Several analytical methods for the determination of EP including tetracycline have been reported *e.g.*, high performance liquid chromatography (HPLC), nuclear magnetic resonance spectroscopy, solid phase extraction coupled to LC-MS, hydrophilic interaction liquid chromatography (HILIC), liquid chromatography in tandem with mass spectrometry (LC/MS), molecular and atomic absorption spectrophotometry, capillary electrophoresis, immunoassays, fluorescence, UV-Vis spectroscopy, spectrofluorimetric (Calixto et al., 2012; Richardson and Ternes, 2018; Sultana et al., 2018). These techniques exhibit high sensitivity and accuracy, but are expensive, and time consuming, complicated equipment, thus limiting their application in routine analysis.

Electrochemical methods are powerful and versatile tools that provide high sensitivity, excellent selectivity, fast response, time saving and simple operation. Good accuracy and a linear dynamic range at a low cost of instrumentation can be achieved by the electrochemical methods to detect emerging pollutants in water (Achargui et al., 2016; Ardelean et al., 2017). Several electrochemical methods have been developed to provide rapid, simple and low-cost determination of tetracycline. Several methods for the voltammetric determination of tetracycline have been reported using different types of electrodes, including multiwalled carbon nanotubes-ionic (Zhou et al., 2012), glassy carbon (Guo et al., 2009) and boron-doped diamond (Vasilie et al., 2018) thin film electrodes. The performance of electrochemical sensors depends on the composition of the working electrode (Calixto et al., 2012; Calixto et al., 2015; Taghdisi et al., 2016; Zhou et al., 2018). The electrode surface is usually modified with suitable functional materials to improve its sensitivity (Palisoc et al., 2019).

Due to the development of nanotechnology and materials science, many types of carbon-based materials have been created within the range from zero-dimensional (0D) to three-dimensional (3D) for sensor applications. Carbon nanotubes (CNTs) are one-dimensional (1D) nanomaterials widely used in the manufacture of various high performance sensors and biosensors characterized by high sensitivity and selectivity due to their unique mechanical, electrical and magnetic properties (Zhoua et al., 2020). Also, carbon nanofibers (CNFs) have also been extensively studied due to their chemical and physical properties (Wang et al., 2019). Unlike CNTs that have diameters usually smaller than 100 nm, the CNF diameter is between 10 and 500 nm and the length can reach 10 μm, but CNFs have exclusively basal graphite planes and edges, which have a high potential for surface modification or functionalization. Several functional hybrid nanomaterials based on CNF have been applied in the fields of biomedicine, tissue engineering, nanodevices, sensors, energy and environmental science (Hahm et al., 2019; Li et al., 2011; Magana et al., 2016; Ning et al., 2016).

Electrochemical sensors based on carbon nanofibers (CNF) have been attracting increasing attention due to their high mechanical strength, superior stiffness, excellent electrical and thermal conductivities (Zhao et al., 2015), which make them interesting for usage as substrate to develop modified electrode characterized by enhanced electrocatalytic properties. For example, a carbon paste electrode modified with carbon nanofibers for the detection of bisphenol A (BPA) was reported by Achargui et al. (2016). Also, our research group have reported a good sensitivity of CNF-epoxy composite electrode for TC detection (Ardelean et al., 2017). The main advantages of CNF in comparison with carbon nanotubes are refferd to its low cost and chemical inertness, non-toxicity and acceptable biocompatibility, which make them extremely attractive for development of novel sensor surfaces (Eksin and Erdem, 2016).

The aim of this paper is to select the best carbon-based electrode substrates to develop a new $CoAl_2O_4$-modified carbon-based electrode characterized by enhanced electroanalytical performance for TC detection. Cobalt aluminate ($CoAl_2O_4$) known as Thenard's blue has received significant attention due to its unique properties such as high refractive index, chemical reactivity, good thermal stability and can be used as catalyst/photocatalyst in sensing applications (Mindru et al. 2019) and our previously reported results related to the electrocatalytic activity towards TC oxidation (Dumitru et al., 2017) justified to develop an electrochemical detection procedure for TC detection in water and pharmaceutical formulation.

The carbon nanofiber-epoxy composite electrode was selected from a series of commercial glassy-carbon, boron-doped diamond electrodes and

home-made carbon nanotubes-epoxy, carbon nanofibers-epoxy composite electrodes, which was modified by simple imersion with cobalt aluminate (CNF-$CoAl_2O_4$) suitable for the electrochemical detection of tetracyline as emergent pollutant in water. The optimum operating parameters was established considering cyclic voltammetry (CV), differential-pulse voltammetry (DPV), square-wave voltammetry (SWV) and chronoamperometry (CA). The proposed electrochemical method was tested for the detection of TC in the real surface water.

2. Experimental

The electrochemical experiments were performed using an Autolab Pontentiostat / Galvanostat PGStat 302 (EcoChimie, The Netherlands) controlled with GPES 4.9 software and three-electrode cell consisted of working electrode, saturated calomel electrode as reference (SCE) and platinum electrode as counter-electrode. The carbon-based substrates used in the research study as host for $CoAl_2O_4$ modifier were commercial glassy carbon (GC) provided by Metrohm Ltd (Switzerland), commercial boron-doped diamond (BDD) provided by Windsor Ltd (UK), and home-made carbon nanotube-epoxy (CNT) and carbon nanofiber-epoxy (CNF) composites, for which the morphostructural and electrochemical characteristics have been reported previously by our research groups (Ardelean et al., 2017; Remes et al., 2012).

The commercial and composite electrodes tested for tetracycline detection were modified by simple immersion within an aqueous suspension (10 mg mL^{-1}) of cobalt aluminate ($CoAl_2O_4$). Cobalt aluminate ($CoAl_2O_4$) was obtained through thermal conversion of oxalate coordination compound at 700°C and detailed morphostructural characterized, which was previously reported by our group (Dumitru et al., 2017).

The first step of the experiment was the electrochemical stabilization of the working electrodes through 10 continuous repetitive cyclic voltammograms within the potential ranging between 0 and +1.25 V/SCE 0.1 M sodium sulfate (Na_2SO_4) solution prepared using analytical-grade reagent from Merck was used as suporting electrolyte. Tetracycline (TC) was provided by Antibiotics Iasi, Romania and the stock solution of TC was prepared using 0.1 M NaOH solution (Merck, Germany). All the solutions used in the experiments were prepared with doubly distilled and deionised water.

For electrochemical characterization and analytical applications, the electrochemical techniques were used: cyclic voltammetry (CV), differential pulsed voltammetry (DPV), square-wave voltammetry (SWV) and chronoamperometry (CA). All electrochemical experiments were performed at room temperature.

3. Results and discussion

3.1. Cyclic voltammetric measurements

The electrocatalyst effect of $CoAl_2O_4$ on the TC oxidation and detection has been reported by our research group (Dumitru et al., 2017), which shown that the sensitivity of the TC detection by cyclic voltammetry was four times higher for $CoAl_2O_4$-modified BDD electrode in comparison with unmodified commercial BDD electrode. However, a major effect onto the electroanalytical performace of the modified electrode is given by the electrode substrate that acts as host for the electrocatalyst ($CoAl_2O_4$). In order to get a significant enhancement of the electroanalytical performace for TC detection related to the sensitivity, the lowest limit of detection and the detection potential, it is essential to find the better substrate characterized by high conductivity, chemical stability and the surface area (Cheng et al., 2020).

In Figs. 1 (a-d) are presented cyclic voltammograms (CVs) recorded on each $CoAl_2O_4$-modified commercial and home-made carbon-based substrates in comparison with the CVs recorded on the unmodified carbon-based electrodes (insets) in the presence of 10 μM TC and 0.1 M Na_2SO_4 supporting electrolyte. It can be noticed that the shape of voltammogram in the presence of 10 μM TC is specific to each carbon-based electrode that exhibited own capacitive behaviour in direct relation to the morphostructural and the electroactive specific area. Thus, commercial GC and CNF composite electrode allowed the TC electrooxidation in two steps, the first step at about +0.4 V/SCE for GC and about +0.3 V/SCE for CNF, and the second step at about +1V/SCE.

TC electrooxidation onto commercial BDD electrode occurred only in a step starting with the potential value of +0.8 V/SCE. No any clear anodic peak characteristic to TC electrooxidation was noticed for CNT composite electrode, and a current increasing for the whole potential range can be seen, which should be attributed to the electrode surface modification in the presence of TC, aspect that will obstruct TC detection. It is obviously that presence of $CoAl_2O_4$ onto the electrode substrate improves significantly the intensities of the anodic peaks and the best sensitivities were achieved for CNF composite used as substrate for $CoAl_2O_4$ distribution (Table 1).

A very interesting aspect that should be noticed is that for this modified CNF-$CoAl_2O_4$ a cathodic current appeared starting with +0.8 V/SCE within backward scanning that informed about a possible cvasi-reversible cathodic process, which can be attributed to the reduction of the TC anodic oxidation by-products generated during forward scanning of cyclic voltammogram. Table 1 presents the detection parameters related to the detection potential value and the sensitivities determined based on the CVs series

recorded on each $CoAl_2O_4$ dispersed onto carbon-based electrode substrate within the TC concentration ranged from 1 to 10 µM (the results are shown Supplementary information file). Except CNT composite electrode, CVs results showed a linear increase of the anodic peaks with TC concentration, which shows the potential for the voltammetric detection of TC. Based on these preliminary results obtained by CV that is well-known as the first experiment for the electrochemical characterization of the electrode in the presence of various analytes considering the electrochemical detection, the CNF-epoxy composite was selected as the most appropriate substrate for $CoAl_2O_4$ distribution by simple immersion and the modified electrode named CNF-$CoAl_2O_4$ was used for further development of the detection procedure for the advanced quantitative determination of TC in the aqueous solution.

3.2. Detection measurements

The voltammetric and the amperometric techniques were applied for the development of voltammetric and amperometric procedure for TC detection. Differential-pulsed voltammetry (DPV) and square-wave voltammetry (SWV) were applied to determine the optimum conditions for the voltammetric detection and chronoamperometry (CA) for the simple amperometric detection.

3.2.1. Differential-pulsed voltammetry operating parameters for TC detection

It is well-known that differential pulsed voltammetry (DPV) is an extremely useful and sensitive technique for trace levels detection applications because the capacitive current of corresponding background contribution is decayed.

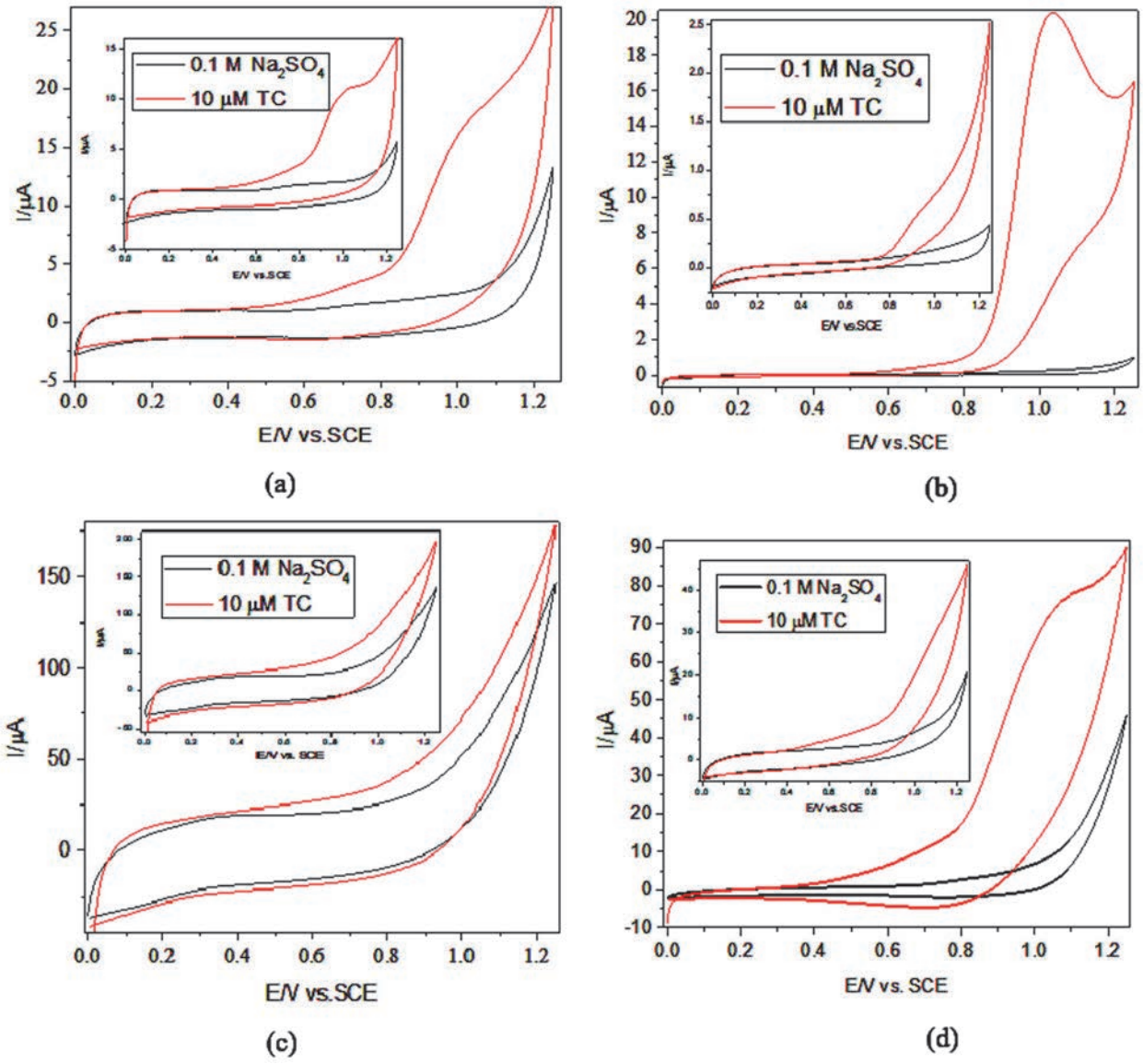

Fig. 1. Cyclic voltammograms recorded in 0.1 M Na_2SO_4 supporting electrolyte and in the presence of a10 µM TC at potential scan rate of: 0.05 Vs^{-1}, within the potential range between 0 to +1.25 V/SCE at the electrodes: (a) GC-$CoAl_2O_4$ (Inset: GC); (b) BDD- $CoAl_2O_4$ (Inset: BDD); (c) CNT- $CoAl_2O_4$ (Inset: CNT); (d) CNF- $CoAl_2O_4$ (Inset: CNF)

Table 1. The electroanalytical parameters obtained from testing commercial/composites unmodified electrodes and commercial/composites modified with cobalt aluminate

Electrode	***E_{det} (V/SCE)***	***Sensitivity (μA/μM)***	***Correlation coefficient, R^2***	***RSD (%)***
GC	0.65	0.096	0.981	6.04
	1	0.924	0.987	3.03
$CoAl_2O_4$ / GC	0.65	0.133	0.887	2.58
	1.00	1.610	0.977	2.41
BDD	1.00	0.533	0.941	3.32
$CoAl_2O_4$ / BDD	0.65	0.025	0.990	4.90
	1.00	2.175	0.998	6.38
CNT	-*	-	-	-
$CoAl_2O_4$ / CNT	-	-	-	-
CNF	0.65	0.230	0.971	5.03
	1.1	2.2	0.980	4.62
$CoAl_2O_4$ / CNF	0.65	0.83	0.990	6.68
	1.1	6.98	0.990	4.83

**-no anodic peak was noticed*

The selection of the operating parameters related to the modulation amplitude (MA), the step potential (SP) and the scan rate requires tarde-off among sensitivity, resolution and the speed (Wang, 2000) considering the aim of the DPV application either in mechanism elucidation or in detection application. It is obviously that for the development of the detection procedure the priority is considered the sensitivity and the lowest limit of the detection. In this context, is important to study the effect of the MA and SP to find the optimum conditions for the detection measurements. The MA values were ranged from 50 to 200 mV and the SP from 5 to 50 mV and the best results related to signal recordings are presented in Figs. 2a and 2b and respective, Figs. 3a and 3b. It can be noticed that the shapes of DPVs are different related to the step potential for this system CNF-$CoAl_2O_4$ modified electrode and TC oxidation.

Applying MA of 200 MV, the SP of 50 mV allowed to obtain more well-defined and broader anodic peak in comparison with SP of 5 mV that led to larger peaks. A more defined shoulder is noticed, also at the SP of 50 mV, allowing the calibration plots at two detection potential value, of +0.64 and +1 V/SCE.

For both presented operating conditions, a linear anodic current increasing with TC concentration until the 7 μM, for the higher concentration a plateau appeared probably due to a "concentration saturation"or the electrode fouling. Based on the calibration plots the sensitivities were calculated and the optimum operating parameters for DPV-based voltammetric procedure for TC determination are considered to be MA of 200 mV and SP of 50 mV at the scan rate of 50 mVs^{-1}(Table 2).

3.2.2. Square-wave voltammetry operating parametrs optimization for TC detection

SWV is a large-amplitude differential technique that imposed the pulse amplitude (MA) of 200 mV based on the previous results regarding DPV optimization. Also, the major advantage of SWV is given by its speed (Wang, 2000), which is controlled by product of frequency (f) and step potential (SP).

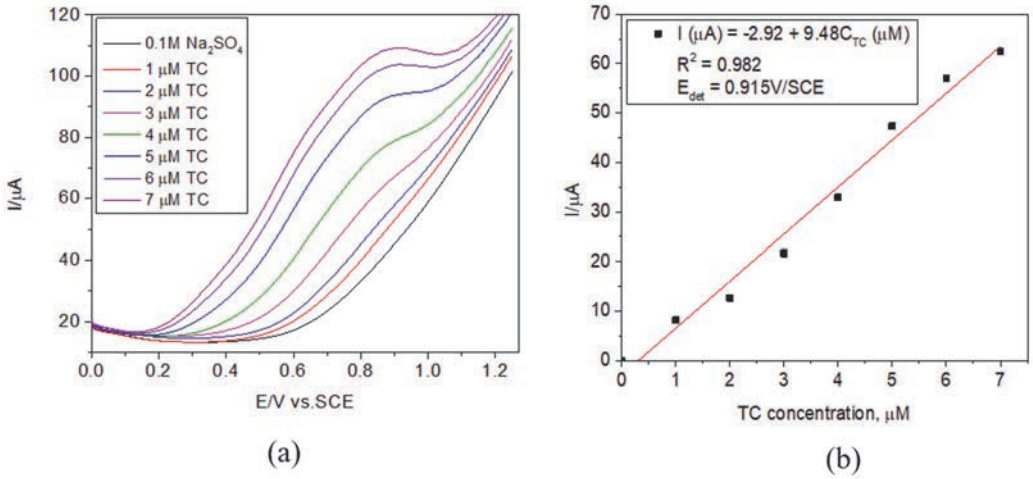

Fig. 2. (a) Differential pulsed voltammograms recorded at the CNF-$CoAl_2O_4$ in 0.1 M Na_2SO_4 supporting electrolyte in 0.1 M Na_2SO_4 supporting electrolyte and in the presence of various TC concentrations: 1-7 μM TC; step potential (SP) 5 mV; modulation amplitude (MA) 200 mV; potential range: 0 to +1.25 V/SCE; (b) Calibration plots of the currents recorded at E = +0.915V/SCE versus TC concentrations

Table 2. The electroanalytical parameters obtained using differential-pulsed voltammetry

Operating parameters		*Electroanalytical parameters*		
MA/mV	***SP/mV***	***E_{det} (V/SCE)***	***Sensitivity (μA/μM)***	***Lowest limit of detection, LOD (μM)***
200	5	0.910	9.48	0.067
200	50	0.640	9.20	0.009
		1	10.6	0.018

The frequency value ranged from to 10 to of 50 Hz and the SP from 5 to 50 mV and the best results obtained for SP of 50 mV, f of 10 Hz and SP of 1 mV, f of 20 Hz are presented in Figs. 4 and 5. In contrast to DPV, SWV considers the reverse pulse that causes the reverse reaction of the byproduct obtained through forward pulse. Even if the scan rate is similar, the different SPs and frequencies led to different shapes of SWV, the higher SP and lower frequency allowed a separation of the two peaks that corresponded to the two steps of TC oxidation on the electrode surface, which is in according with CV and DPV results. An important advantage of SP of 50 mV and f of 10 Hz referred to the lower detection potential of 0.83 V/SCE at which the sensitivity is the best.

The electroanalytical parameters determined based on the calibration plots presented in Figs 4b and 5b are gathered in Table 3, and it can be seen that the best sensitivity is achieved for SP of 50 mV and f of 10 Hz but the lowest of detection (LOD) for SP lower (1 mV) and higher f of 20 Hz.

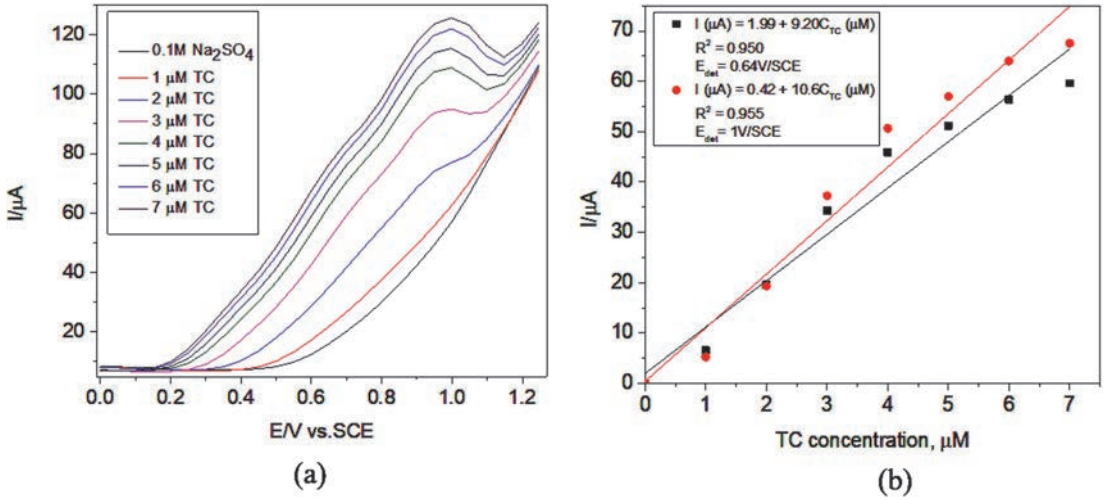

Fig. 3. (a) Differential pulsed voltammograms recorded at the CNF-$CoAl_2O_4$ in 0.1 M Na_2SO_4 supporting electrolyte in 0.1 M Na_2SO_4 supporting electrolyte and in the presence of various TC concentrations: 1-7 μM TC; step potential (SP) 50 mV; modulation amplitude (MA) 200 Mv; potential range: 0 to +1.25 V/SCE; (b) Calibration plots of the currents recorded at E_1 = +0.64 V/SCE and E_2 = +1V/SCE versus TC concentrations

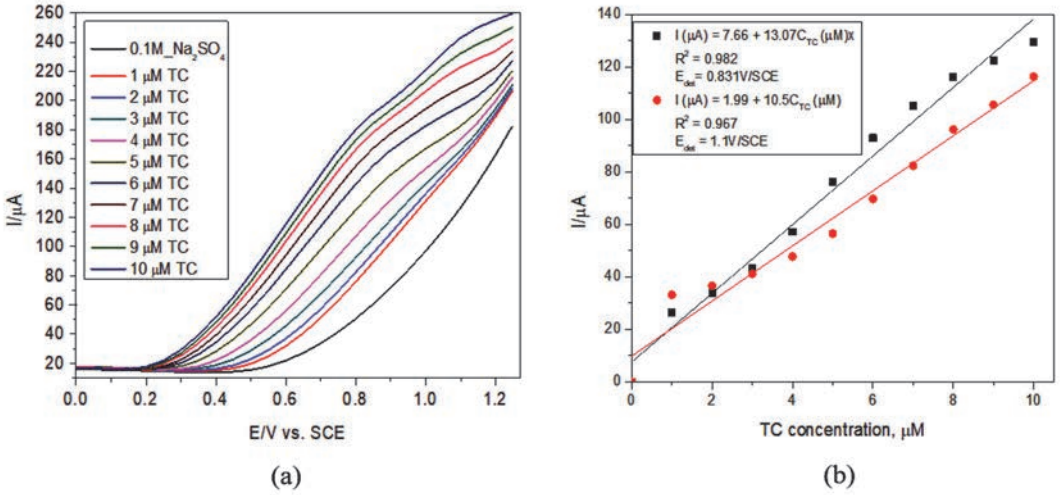

Fig. 4. (a) Square-wave voltammograms recorded on a CNF-$CoAl_2O_4$ in 0.1 M Na_2SO_4 supporting electrolyte under optimized conditions at a frequency of 10 Hz, step potential (SP) 5 mV and modulation amplitude (MA) 200 mV in the potential range of 0 to +1.25 V vs. SCE in the presence of a 1-10 μM TC concentration; (b) The calibration plots of the currents recorded at recorded at E_1 = +0.831V/SCE and E_2 = +1.10V/SCE versus TC concentrations

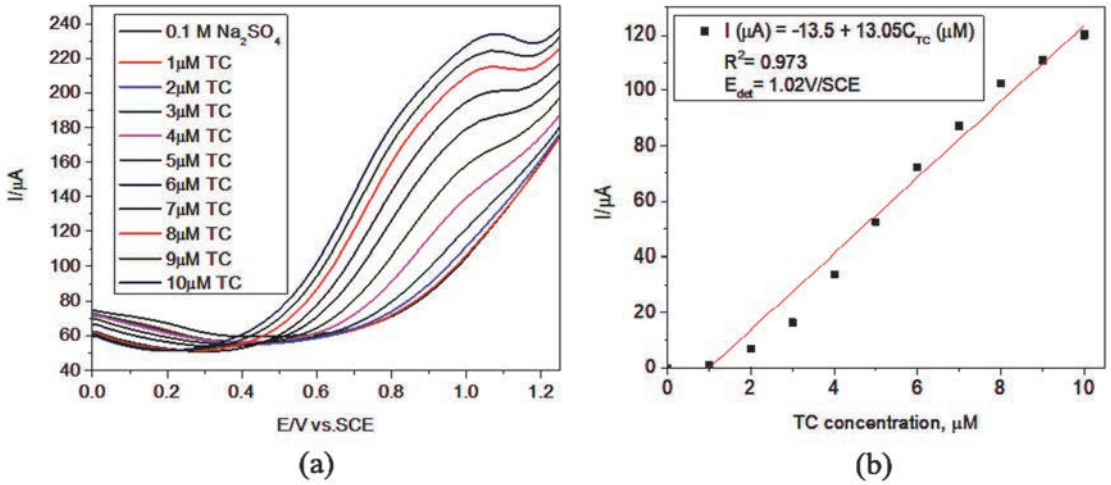

Fig. 5. (a) Square-wave voltammograms recorded on a CNF-$CoAl_2O_4$ in 0.1 M Na_2SO_4 supporting electrolyte under optimized conditions at a frequency of 20 Hz, step potential (SP) 1 mV and modulation amplitude (MA) 200 mV in the potential range of 0 to +1.25 V vs. SCE in the presence of 1-10 μM TC concentration; (b) The calibration plots of the currents recorded at E 1.02 V/ SCE vs. tetracycline concentration

Table 3. The analytical parameters obtained using square wave voltammetry

Operating parameters			***Electroanalytical parameters***		
MA/mV	***SP/mV***	***f/Hz***	***E_{det} (V/SCE)***	***Sensitivity (μA/μM)***	***Limit of detection, LOD (μM)***
200	50	10	0.83	13.07	0.860
			1.10	10.50	1.143
200	1	20	1.02	13.05	0.022

3.3.3. Application of chronoamperometry for tetracycline detection

Because is considered one of the easiest electrochemical techniques for practical detection applications, chronoamperometry (CA) was applied based on the references determined through voltammetric techniques, especial CV. Based on the previous voltammetric results, two constant potential levels - CA was selected in according with the two steps of TC oxidation found after applying the voltammetric techniques. Fig. 6 presents the chronoamperograms recorded on CNF-$CoAl_2O_4$ electrode and it can be noticed that the liniar dependence between the current and TC concentration is achieved only at +1.1 V/SCE not at +0.7 V/SCE, at which not a current increase with TC concentration was found, rather a randomized behavior was noticed. This aspect should be explained by the probability as a surface-controlled mechanism to govern the first step of TC concentration, which is significantly manifested under the constant potential based technique at the lower potential value. Also, this phenomena is responsible also, for the lower sensitivity achieved by CA in comparison with other voltammetric techniques operated at the same potential value (CV and SWV). Thus, a sensitivity of 0.620 μA/μM was achieved that is at least ten times lower than one get by voltammetry techniques.

The electroanalytical performances for TC detection obtained by all studied electrochemical voltammetric and amperometric techniques are gathered in Table 4. The SWV technique achieved the best sensitivity at a high potential value (+0.83 V vs. SCE), while by using DPV, the best LOD and LQ were achieved at a lower potential value (+0.64 V vs. SCE).

The comparison of the lowest limit of detection obtained with this modified CNF-$CoAl_2O_4$ electrode by DPV with previous work is presented in Table 5, and it can be seen the superiority of the voltammetric detection procedure proposed in this work.

Table 4. Electroanalytical parameters obtained for tetracycline detection in an aqueous solution at a CNF-$CoAl_2O_4$ electrode by applying electrochemical techniques

Technique	***Conditions***	***E_{det} (V)***	***Sensitivity (μA/μM)***	***R^2***	***RSD (%)***	***LOD (μM)***	***LQ (μM)***
CV	v= 0.05 Vs^{-1}	1.10	6.98	0.990	4.83	0.529	1.764
DPV	SP 50 mV, MA 200mV	0.64	6.89	0.949	0.413	0.009	0.030
		1.00	8.36	0.961	0.777	0.159	0.532
SWV	SP 5mV, MA 200mV, f 10 Hz	0.83	13.20	0.991	4.87	0.858	2.862
		1.10	10.40	0.986	2.58	1.142	3.809
CA	E=+1.1V	1.10	0.620	0.992	0.523	0.211	0.705

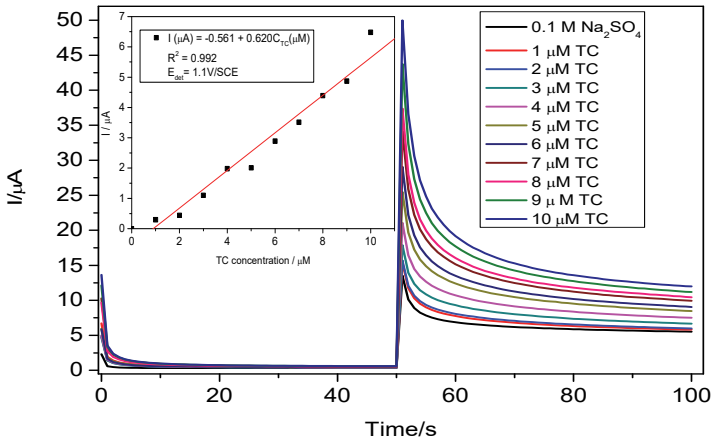

Fig. 6. Chronoamperograms recorded on CNF-$CoAl_2O_4$ electrode at the potential value of E_1 = 1.1 V/SCE in 0.1M Na_2SO_4 supporting electrolyte and in the presence of 1 to 10 μM TC. Inset: the calibration plots of the currents recorded at E = 1.1 V/SCE vs. TC concentrations

Table 5. Comparison of the LOD obtained in this study with other reported works

Modified electrode	*LOD (μM)*	*Reference*
Graphite-polyurethane composite electrode	2.80	Calixto et al. (2012)
Carbon nanofiber-epoxy composite electrode	0.045	Ardelean et al. (2017)
Modified carbon paste electrode with graphene oxide/functionalized carbon nanotubes (CPE GO/MWCNT-COOH)	0.810	Vega et al. (2007)
Reduced graphene oxide and magnetite nanoparticles	0.585	Taghdisi et al. (2016)
Electrodeposited carbon nanotubes on gold coated glassy carbon electrode	0.0945	Palisoc et al. (2019)
Boron-doped diamond electrode modified with $CoAl_2O_4$	0.500	Dumitru et al. (2017)
CNF- $CoAl_2O_4$	0.009	This work

A recovery test was performed by analyzing three parallel surface water samples, which were spiked with 50 and 100 μgL^{-1} TC. The recoveries test was running in the same 0.1 M Na_2SO_4 supporting electrolite using DPV operated at the optimum operating conditions. The recovery values higher than 96 % and the RSD values smaller than 5 % for both concentrations indicated good recovery and reproducibility of the results and the great potential of the CNF-$CoAl_2O_4$ for water quality monitoring related to the quantitative determination of the tectracycline. Repetability of the proposed detection procedure was evaluated by comparing the results of the determination of a solution containing 100 μgL^{-1}TC during the three days. The relative standard deviation less than 5 % demonstrated a good repetability of the proposed CNF-$CoAl_2O_4$ based voltammetric procedure.

4. Conclusions

In this study the importance of the electrode substrate as host for a $CoAl_2O_4$ modifier within a modified electrode characterized by the electrocatalytic effect towards tetracycline oxidation and implicit, its detection was proved. Cyclic voltammetry results allowed to select carbon nanofiber -epoxy composite electrode as the most suitable among a series of carbon-based electrode substrates, *i.e.*, commercial glassy-carbon and boron-doped diamond and home-made carbon nanotube-epoxy and carbon nanofiber-epoxy composite electrodes.

All electrochemical voltammetric and amperometric techniques tested were appropriate for the development of the electrochemical detection procedure for the quantitative determine of tetracycline in aqueous solution. The best results regarding the sensitivity (13.20 μA/μM) was achieved using square-wave voltammetry operated at the step potential of 5 mV, modulation amplitude of 200 mV and the frequency of 10 Hz, while the lowest limit of detection for TC (9 nM) was reached using the differential-pulse voltammetry operated at the step potential of 50 mV and the modulation amplitude of 200 mV. The best electroanalytical results related to the sensitivity were achieved under optimized working conditions for SWV and related to the detection limit for DPV.

Chronoamperometry allowed reaching better results related to the lowest limits of detection in comparison with CVand CA allowed good results for the TC lowest limit of detection and this simple electrochemical technique should be selected for higher TC concentrations in water or in pharamaceutical formulations. Based on the results of this study including the reproducibility and the repeatability of the proposed method, it can be

concluded that $CoAl_2O_4$ modified carbon nanofiber-epoxy composite electrode is appropriate for the electrochemical detection of tetracycline in water and the future work will consider the development of the procedure for the detection of other antibiotics in real water.

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