

Comparative testing of Ag/Au/Pt graphene electromodified electrodes in electrochemical detection of tetracycline-emerging pollutant

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Abstract

This study aimed to obtain new electrochemically modified electrodes with graphene and Au, Pt, Ag particles considering graphite (GP) and glassy carbon (GC) substrate by applying the chronoamperometry technique to develop the detection protocol of tetracycline (TC) considered as an emerging pollutant in water, using cyclic voltammetry (CV) technique. The graphite-based substrate used for Ag/ Au/ Pt electrodeposition led to the electrode compositions on which TC oxidation process was not diffusion-controlled and as consequence, TC detection failed. TC detection protocols were developed for all Ag/Au /Pt electrodeposited GC and GC-GP electrodes. Better limits of TC detection was achieved for Ag electrodeposited on GC-GP at the cathodic potential of 0.460 V/SCE.

Keywords: electrochemical modification, graphene, metal particles, tetracycline, cyclic voltammetry

INTRODUCTION

In recent years, the detection and monitoring of emerging pollutants in aquatic ecosystems is a growing concern worldwide. Currently, various micropollutants and emerging pollutants are present in the aquatic environment through in various ways: industrial, hospital, livestock, agricultural, or domestic effluents, due to the non-performance conventional wastewater treatment technology usually applied [1-3]. It is well known that the main characteristic of the emerging pollutants is the lack of maximum allowance concentration setup. Even in low concentrations (ng/L), the presence of antibiotics in wastewater treatment plants (influent and effluent), in environmental matrices (groundwaters, surface waters: lakes, rivers, soils, and sludge) may cause chronic and acute harmful effects on natural flora and fauna and a consequence, to the human health [4, 5]. Tetracycline, aminoglycosides, macrolides, β -lactams, vancomycin, phenols, and fluoroquinolones, are the antibiotics with the widest presence in water matrices [6]. Due to its strong antibacterial activity, easy method of administration, and low cost, tetracycline is one

of the most widely used antibiotics in human and veterinary medicine. Although tetracycline is widely found in a variety of foods, including meat, milk, and honey, the toxicity and accumulation of tetracycline in both the environment and food have become a severe threat due to the negative impact on human health and wildlife. Exposure to very low levels of tetracycline leads to the development of antibiotic-resistant genes, vision problems, tooth discoloration, and allergic symptoms in humans [7]. The reduction of the negative impact of tetracycline on the health of consumers has been achieved by establishing regulations by various food safety authorities. Thus, the European Union has recommended a maximum residue limit of 100 mg kg⁻¹ for tetracycline in milk [8, 9]. Therefore it is necessary to develop fast, analytically accurate methods for the determination of tetracycline in food and environmental samples. Current analytical methods commonly used for the detection and quantification of tetracycline are gas / liquid chromatography spectrometry, inductively coupled plasma mass spectrometry

(ICP-MS), high-performance liquid chromatography (HPLC), molecular and atomic absorption spectrophotometry (AAS), capillary electrophoresis and immunoassays [10]. These analytical techniques are often expensive, require long-term sample preparation activities, are time-consuming techniques, and can only be performed by trained personnel. Regarding the electrochemical methods for the detection of these pollutants, they are some of the most promising alternative methods, with easy adaptability, low costs, short analytical times, and high sensitivity. Due to its wide versatility, low cost, mechanical strength, reproducibility, and high sensitivity, compared to other analytical techniques (gas chromatography, HPLC, or atomic absorption spectroscopy), the use of electroanalytical techniques (voltammetry and amperometry) to quantify important analyzes has increased exponentially. For the development of the electrochemical detection procedure, the electroanalytical techniques and the electrode material should be considered. The key to the electrochemical process performance is the electrode material and its modification should enhance the electroanalytical performance linked to sensitivity, the lowest limit of detection, selectivity [11]. The commercial electrodes, especially carbon-based ones such as glassy carbon (GC) and graphite (GR) electrodes are frequently used in electroanalytical applications, but continued efforts are being made to improve their performance by using them in various modified forms. It is well-known that the use of conventional electrodes there are some serious problems in terms of electrochemical detection, due to their slow surface kinetics, which severely affects the sensitivity and selectivity of the electrodes. Conventional electrodes used in the detection of the target analyte (tetracycline) usually display a low-intensity peak that is generally not visible in the detection of target pollutants at lower concentrations which makes them even less attractive for commercialization. In solving this problem, several research studies have been reported in which researchers have presented solutions to improve the surface kinetics of electrodes by modifying them with various materials [11, 12]. Recently, numerous research studies have been

reported in the literature presenting the modification of conventional electrode surfaces with a large variety of materials intensively explored to improve electrode performance, e.g. graphene (GP) and metal particles: silver (Ag), gold (Au), and platinum (Pt). Graphene is a carbon-based material that has been extensively investigated in recent years following a report by Novoselov et al. on the isolation and measurement of its unique electronic properties [13]. Graphene and graphene oxide are the most promising materials in the field of nanotechnology due to their excellent chemical properties such as high chemical stability, high elasticity, desired catalytic properties, and large specific surface area. A study by Zhang et al described the manufacture of a glassy carbon electrochemical sensor using graphene as a modified nanofiber material stacked in combination with gold nanoparticles. The new sensor obtained presented reproducible results, high long-term stability, and exceptional electrocatalytic properties in terms of electrochemical detection of capecitabine. After testing the electrode, a detection limit of 0.0171 μM was obtained [14]. Electrochemical modification of commercial electrodes is an efficient method for depositing metal particles. The electrochemical deposition in stages of metal particles has the advantage of fine-tuning the amount of metal deposited, the number of metal sites, and their size. The special properties of the carbon materials make them be considered appropriate for use as electrode support to develop the modified electrodes [15]. Silver particles (Ag) are some of the best developed and used to modify the surface of working electrodes, because they are economically cheap compared to other materials, possess good chemical and physical properties, offering excellent rates of electron transfer. Also, due to their optimal conductivity and biological compatibility, in recent decades there has been an emphasis on the use of gold particles (Au-P) in obtaining sensors [12]. Gold nanoparticles (AuPs) have been applied in electrochemical fields to improve sensor performance. AuPs have special properties, such as high conductivity, a large specific surface area, a strong adsorption capacity, biocompatibility, and a high electrochemical catalytic activity [16].

This study aimed to modify two substrates, i.e., graphite (GR) and glassy-carbon (GC) with graphene (GP), Ag, Au, and Pt, and to test them for tetracycline detection. A study was conducted to identify the negative and positive

aspects to select the electrode substrate linked to the sensing application demand (sensitivity, selectivity, the lowest limit of detection, individual simulations detection).

EXPERIMENTAL PART

The electrochemical studies were performed using a potentiostat - galvanostat Autolab PGSTAT 302 (Eco Chemie, The Netherlands), controlled by a computer using GPES 4.9 software and a cell with three electrodes. The cell structure included a working electrode, electrochemically modified, a platinum counter-electrode and a saturated calomel electrode (ESC) used as the reference electrode.

The commercial electrodes used in obtaining new electrodes with improved properties for electroanalytical use were: the glassy carbon (GC) provided by Metrohm and the pencil graphite electrode (GR). The working electrodes were mechanically cleaned using 0.2 μm alumina powder (Al_2O_3), and then washed with distilled water. The electrochemical modification of the commercial electrodes GC and GR with graphene (GP) used graphene oxid, that was electrochemically reduced on the substrate and particles/films of gold (Au), platinum (Pt), and silver (Ag) electrodeposited by applying the chronoamperometry technique at different potentials and as different deposition times. GR deposition on the substrate surface occurred at the potential of -1.5V for 120s. The modification of the

electrodes with Ag particles occurred at the electrodeposition potential of -1.3 V and the electrodeposition time was 5 s. Regarding the modification with gold particles, the potential of -0.3 V and electrodeposition time of 300 s was applied and the deposition of platinum on the surface of the electrodes was assured at the potential of -0.2V and 300s [17]. 3 mM HAuCl_4 concentration solutions + 0.5 M H_2SO_4 , was used for Au electrodeposition, 10mM $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ + 0.5 M HCl for Pt, and 4 mM AgNO_3 for silver deposition. The supporting electrolyte of 0.1 M NaOH solution, was prepared using analytical purity sodium hydroxide (Merck, Germany) and distilled water. The electrode surface was renewed after each experiment by a light mechanical cleaning, washing, and application of an electrochemical treatment by repeating the cyclic scanning voltammetry between -0.5 \rightarrow +1 V/ESC in the 0.1M NaOH support electrolyte. The electrochemical technique applied for electrochemical characterization and analytical applications was cyclic voltammetry. The working conditions for each electrodeposition are gathered in Table 1.

Table 1. Electrodeposition working conditions using chronoamperometry technique

Material Electrodeposition	$E_{\text{deposition}}$, V vs SCE	Deposition time, s	Electrolyte composition	References
Graphene (GR)	-1.5	120	4 mg/mL	[18]
Ag	-1.3	5	4 mM AgNO_3	[19]
Au	-0.3	300	3 mM HAuCl_4 + 0.5 M H_2SO_4	[20]
Pt	-0.2	300	10 mM $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ + 0.5 M HCl	[17]

RESULTS AND DISCUSSION

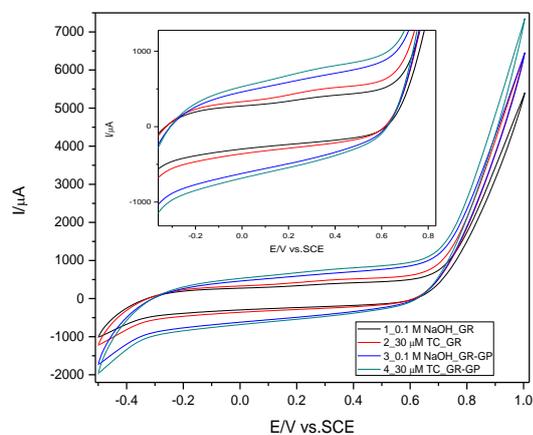
Graphene (GP) was electrodeposited onto graphite (GR) and respective, glassy carbon (GC) substrates using graphene oxide under the conditions reported in the literature [11] to test its effect onto the further electrodeposition of Ag, Au, and Pt, further considering the development of the modified electrode characterized by the superior features for

tetracycline (TC) detection using cyclic voltammetry (CV) technique. Each metal was electrodeposited onto graphite (GR) and glassy carbon (GC)-based substrate according to the reported data, and the resulting electrode compositions were characterized by cyclic voltammetry (CV) in 0.1 M NaOH supporting electrolyte and in the presence of TC.

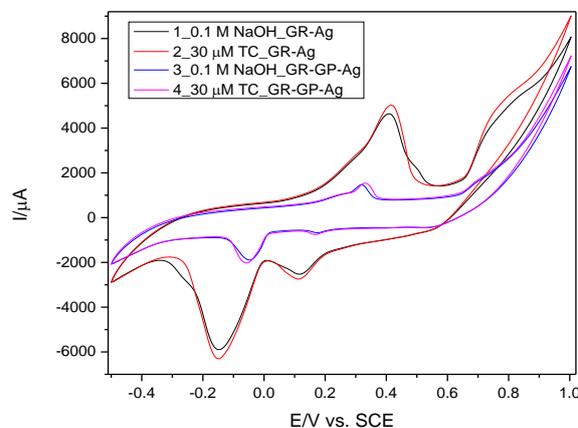
Comparative electrochemical behavior of Ag/Au/Pt electrodeposited onto graphite (GR) and graphene-modified graphite (GR-GP) substrates in alkaline medium and tetracycline (TC) target analyte

The cyclic voltammograms were recorded for each Ag/Au/Pt electrodeposited onto GR and GR-GP substrate in 0.1 M NaOH supporting

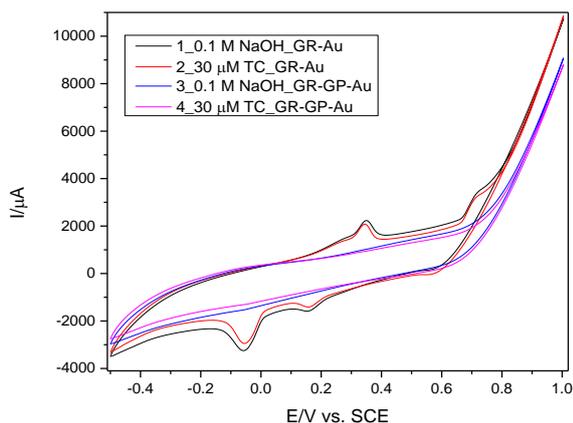
electrolyte and in the presence of 30 μM TC and are presented comparatively for both GR and GR-GP substrates in Figure 1.



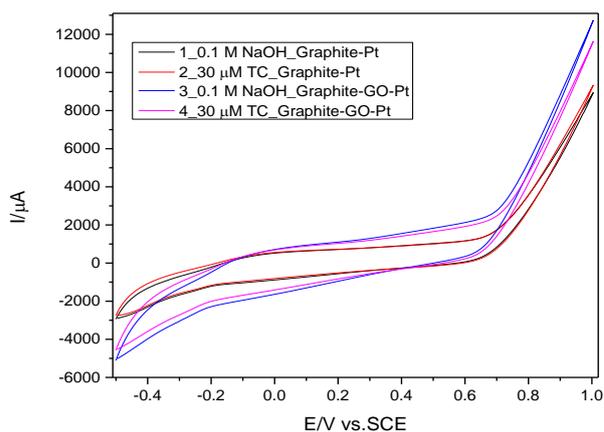
a)



b)



c)



d)

Fig. 1. Comparative cyclic voltammograms recorded in 0.1 M NaOH supporting electrolyte and in the presence of 30 μM TC on: GR and GR-GP (a); GR-Ag and GR-GP-Ag (b); GR-Au and GR-GP-Au (c); GR-Pt and GR-GP-Pt (d)

It can be seen that the graphene presence onto the graphite substrate improved the capacitive component of the current due to the electric double-layer capacitance and depolarization for oxygen evolution is noticed (Fig. 1a). The presence of the graphene within the graphite-based substrate on the metal deposition is can be seen in Fig. 1b-d and it can be noticed that the peaks corresponding to the redox behavior of the metal are smaller, which can be associated with a competition between graphene and metal reduction due to the close potentials

applied for each deposition. For Ag and Au electrodeposited on the graphite substrate the presence of graphene led to the polarization effect towards the oxygen evolution, while for Pt the depolarization is noticed in the presence of graphene. A small change of the voltammogram shape is observed for Pt electrodeposited on the graphite substrate in comparison with GR and GR-GP (Fig. 1a and 1d), which reveal a small presence of platinum within the electrode composition. A similar oxidation and reduction behavior of TC

manifested on the whole potential window between oxygen and hydrogen evolutions was found for GR, GR-GP electrode compositions, which shows a possible electropolymerization process of TC or its oxidation products. For GR-Pt and GR-GP-Pt electrode compositions, the presence of TC reduced both anodic and cathodic currents, the aspect can be associated with a possible electrode fouling effect. Very good signals are found for GR-Ag and GR-GP-

Ag electrode compositions in relation to both detection current and potential. Besides the anodic signal, Ag-based electrode compositions exhibited the cathodic signals, as well as.

The useful current considered as a signal for TC detection obtained after extracting the background current from the peak current values recorded in the presence of 30 μM TC was determined for each composition and are gathered in Table 2.

Table 2. Useful signal and detection potential for TC determination for each graphite-based electrode composition

Electrode	$E_{\text{det}}/\text{V vs.SCE}$	$I_{\text{Background}}/\mu\text{A}$	$I_{\text{TC}(30\mu\text{M})}/\mu\text{A}$	$\Delta I_{\text{useful}}/\mu\text{A}$	$\Delta I_{\text{useful}}/\mu\text{Ac m}^{-2}$	Signal type
Graphite	0.367	405	504	99.0	505	anodic
Graphite- GP	0.367	691	788	97.0	495	anodic
Graphite-Ag	0.283	2465	2550	85.0	433	anodic
	0.415	4614	5017	400	2056	anodic
	-0.150	6310	5903	407	2077	cathodic
	0.771	4562	5089	527	2689	anodic
	0.119	2796	2509	287	1464	cathodic
Graphite-Au	-	-	-	-	-	-
Graphite-Pt	-	-	-	-	-	-
Graphite- GP-Ag	0.242	934	1018	84	429	anodic
	0.348	1119	1340	221	1128	anodic
	-0.056	1860	2022	162	827	cathodic
	0.168	668	753	85	434	cathodic
	0.694	1570	1630	60	306	anodic
Graphite- GP-Au	0.058	185	243	58	296	anodic
Graphite- GP-Pt	-	-	-	-	-	-

- no TC detection signal was found

Comparative electrochemical behavior of Ag/Au/Pt electrodeposited onto glassy carbon (GC) and graphene-modified glassy carbon (GC-GP) substrates in alkaline medium and tetracycline (TC) target analyte

Similar experiments for comparison were carried out for Ag/Au/Pt electrodeposited onto GC and GC-GP substrate in 0.1 M NaOH supporting electrolyte and in the presence of 30 μM in comparison with GC and GC-GP substrates. The cyclic voltammograms are presented in Fig. 2.

In comparison with GR electrode composition, the presence of graphene within GC composition is manifested in special for depolarization effect towards the oxygen

evolution and less for the capacitive component of the current. The current increase in the presence of TC was noticed only within the oxygen evolution potential for GC-GP in comparison with GC, for which a small current increase due to TC oxidation was found within the potential window (Fig. 2a). The effect of the presence of the graphene within the GC based substrate on the metal deposition can be seen in Fig. 2b-d and is similar to metal electrodeposited onto a GR-based substrate.

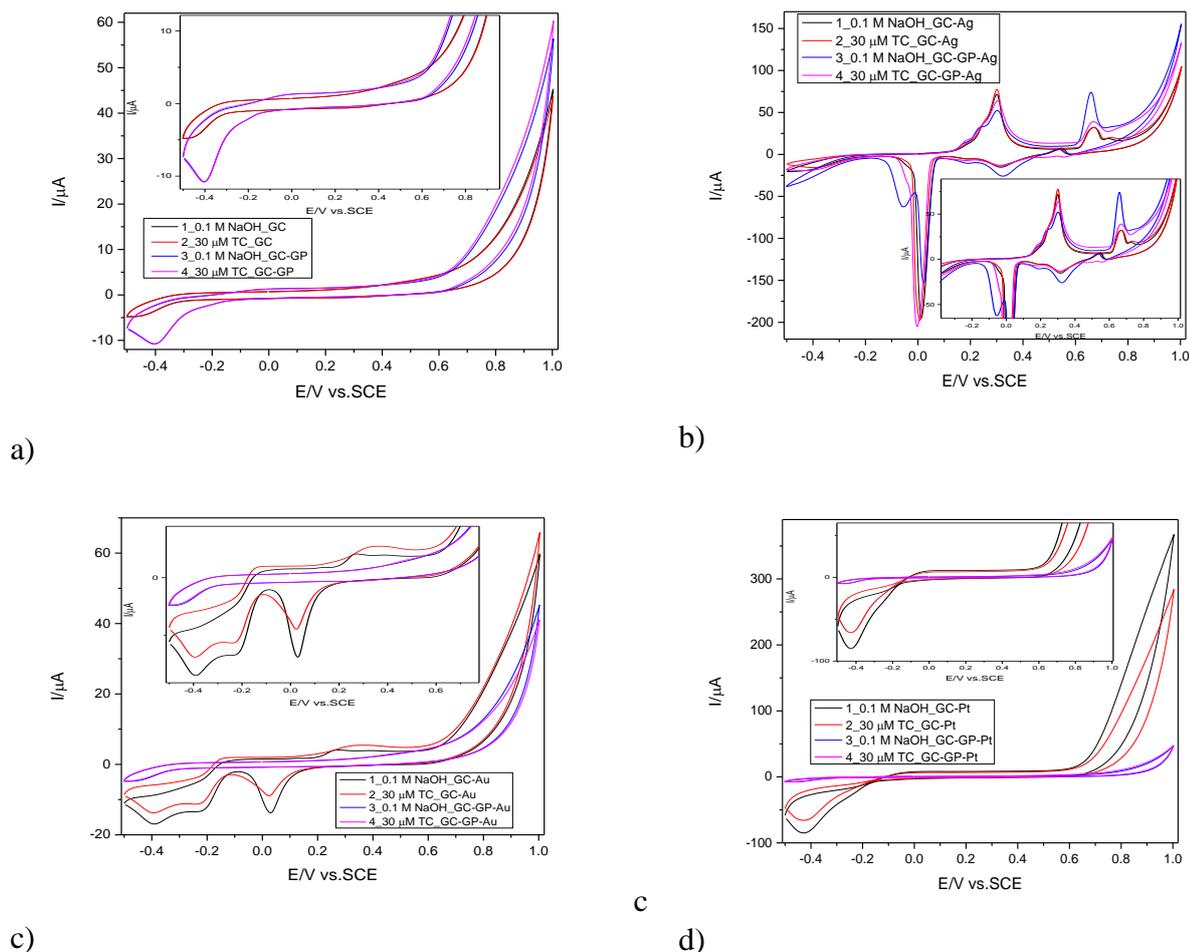


Fig. 2. Comparative cyclic voltammograms recorded in 0.1 M NaOH supporting electrolyte and in the presence of 30 μM TC on: GC and GC-GP (a); GC-Ag and GC-GP-Ag (b); GC-Au and GC-GP-Au (c); GC-Pt and GC-GP-Pt (d)

The useful current reached on GC-based electrode composition is smaller in comparison with those found on the GR-based electrode substrate, which is due to the lower background current that influenced the current domain. However, their behavior is important to consider the detection potential for further

development of the detection protocol using the cyclic voltammetry technique. The detection parameters considered as a reference for the development of the detection protocol related to the detection potentials and the useful current are gathered in Table 3 for glassy-carbon-based electrode compositions.

Table 3. Useful signal and detection potential for TC determination for each glassy-carbon-based electrode composition

Electrode	$E_{\text{det}}/\text{V vs. SCE}$	$I_{\text{Background}}/\mu\text{A}$	$I_{\text{TC}(30\mu\text{M})}/\mu\text{A}$	$\Delta I_{\text{useful}}/\mu\text{A}$	$\Delta I_{\text{useful}}/\mu\text{Acm}^{-2}$	Signal type
GC	0.48	2.90	3.07	0.170	5.41	anodic
GC-GP	0.862	27.9	28.9	1.00	31.8	anodic
GC-Ag	0.185	11.9	13.5	1.60	50.9	anodic
GC-Au	0.370	3.92	5.58	1.66	52.9	anodic
GC-Pt	-	-	-	-	-	-
GC-GP-Ag	0.180	15.4	16.1	0.700	22.3	anodic
	0.460	1.54	3.72	2.18	69.4	cathodic
	0.700	26.3	30.9	4.60	135	anodic
GC-GP-Au	0.400	2.36	2.95	0.590	18.8	anodic
	-0.117	1.37	1.69	0.320	10.2	anodic
GC-GP-Pt	0.55	1.90	2.91	1.01	32.2	anodic

TC detection using CV technique

The study of the influence of TC concentration on the cyclic voltammogram shape allowed selecting the electrode composition that can be used for the development of the TC detection protocol.

Considering GR and GR-GP substrates, Figures

3 and 4 present the cyclic voltammograms recorded in the presence of TC concentrations ranged from 10 to 60 μM and corresponding the calibration plots for the detection potential of 0.370 V/SCE.

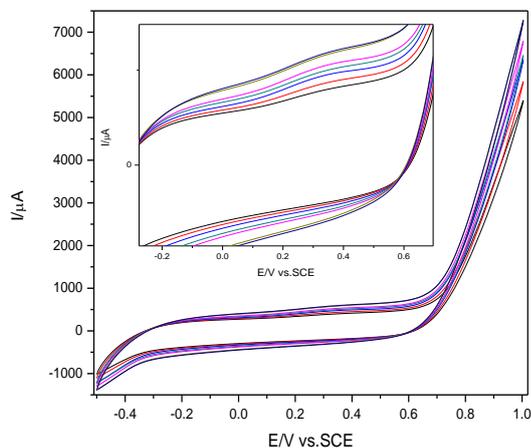


Fig. 3. a) Cyclic voltammograms recorded on GR electrode in electrolyte support 0.1 M NaOH solution and in the presence of 10-60 μM TC; scan rate 0.05 Vs⁻¹; potential range: -0.5 \rightarrow 1V/ SCE.

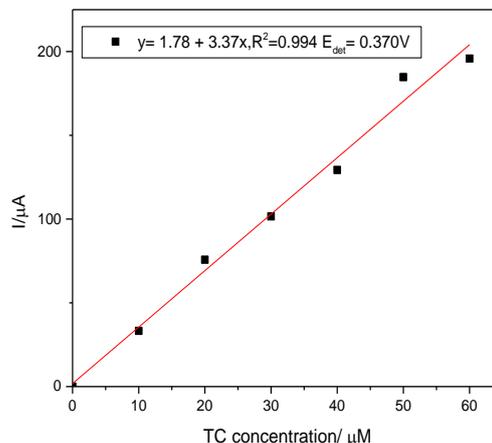


Fig. 3. b) The calibration plots of the currents recorded at $E = +0.370\text{V/SCE}$ versus TC concentrations.

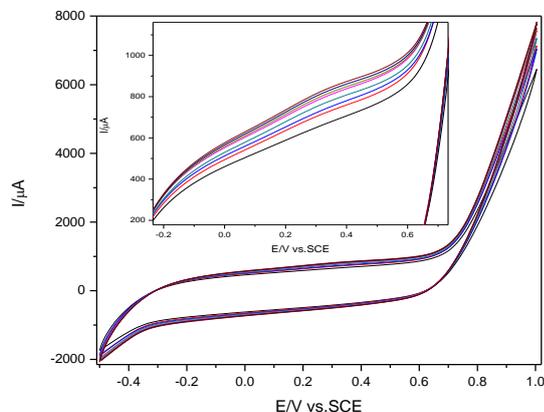


Fig. 4. a) Cyclic voltammograms recorded on GR-GP electrode in electrolyte support 0.1 M NaOH solution and in the presence of 10-70 μM TC; scan rate 0.05 Vs⁻¹; potential range: -0.5 \rightarrow 1V/ SCE

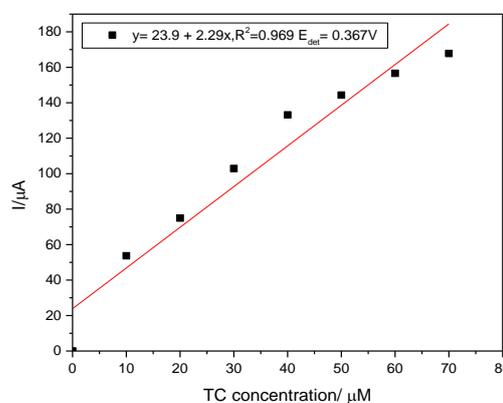


Fig. 4. b) The calibration plots of the currents recorded at $E = +0.370\text{V/SCE}$ versus TC concentrations

Even if Ag/Au/Pt showed the potential for the development of the detection protocol, however, the useful currents prior selected did not increase linearly with TC concentration increasing, which informed that the mechanism of TC oxidation and reduction is not based on the diffusion step and implicit, they are not

suitable for the detection process. Figures 5 and 6 show as examples the cyclic voltammograms recorded on GR-Ag in the presence of TC concentrations ranged from 10 to 60 μM and on GR-GP-Au Ag in the presence of TC concentrations increasing from 10 to 60 μM .

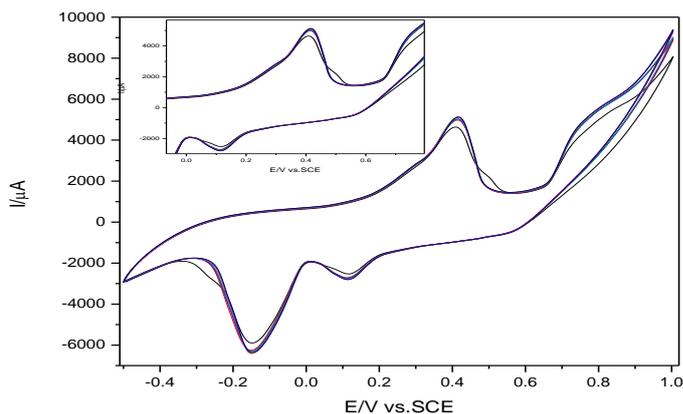


Fig. 5. Cyclic voltammograms recorded on GR-Ag electrode in electrolyte support 0.1 M NaOH solution and in the presence of 10-60 μM TC; scan rate 0.05 Vs-1; potential range: -0.5 \rightarrow 1V/ SCE.

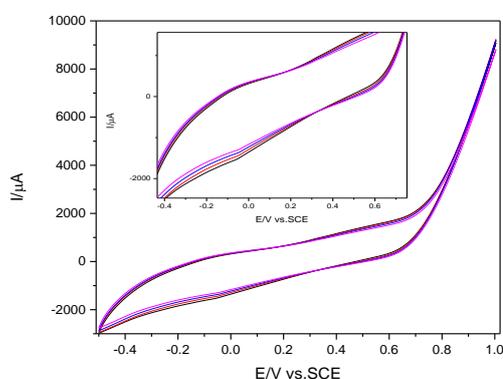


Fig. 6. Cyclic voltammograms recorded on GR-GP-Au electrode in electrolyte support 0.1 M NaOH solution and in the presence of 10-30 μM TC; scan rate 0.05 Vs-1; potential range: -0.5 \rightarrow 1V/ SCE

Even if the useful currents recorded on GC-based substrate are smaller in comparison with GR-based substrate, the diffusion-controlled oxidation and reduction processes of TC are

manifested on the GC-based substrate modified with Ag/Au/Pt, and the results are presented in Figures 7-13.

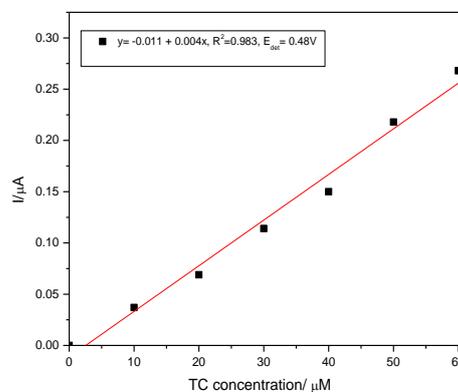
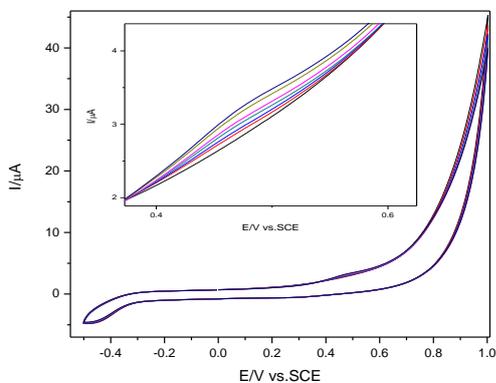


Fig. 7. a) Cyclic voltammograms recorded on GC electrode in electrolyte support 0.1 M NaOH solution and in the presence of 10-50 μM TC; scan rate 0.05 Vs-1; potential range: -0.5 \rightarrow 1V/ SCE.

Fig. 7. b) The calibration plots of the currents recorded at $E = +0.480\text{V/SCE}$ versus TC concentrations.

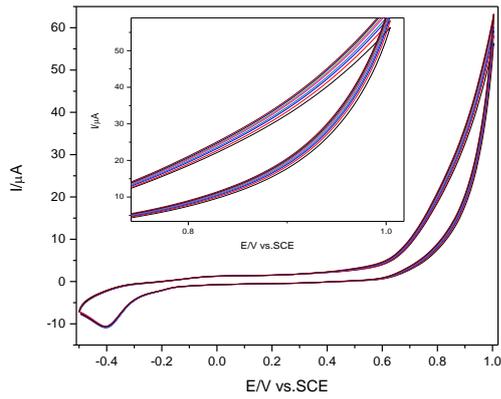


Fig. 8. a) Cyclic voltammograms recorded on GC-GP electrode in electrolyte support 0.1 M NaOH solution and in the presence of 10-70 μM TC; scan rate 0.05 Vs⁻¹; potential range: -0.5 \rightarrow 1V/ SCE.

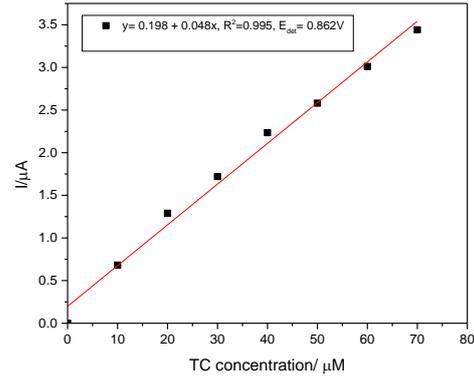


Fig. 8. b) The calibration plots of the currents recorded at $E = +0.862\text{V/SCE}$ versus TC concentrations.

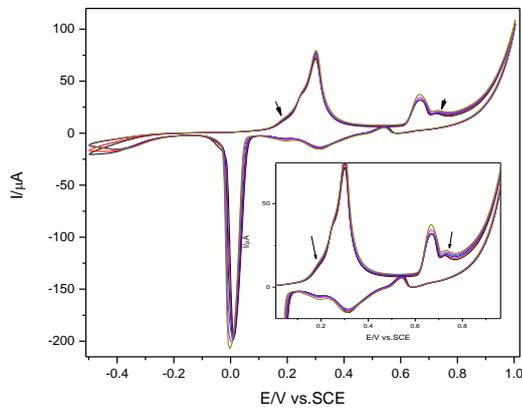


Fig. 9. a) Cyclic voltammograms recorded on GC-Ag electrode in electrolyte support 0.1 M NaOH solution and in the presence of 10-50 μM TC; scan rate 0.05 Vs⁻¹; potential range: -0.5 \rightarrow 1V/ SCE

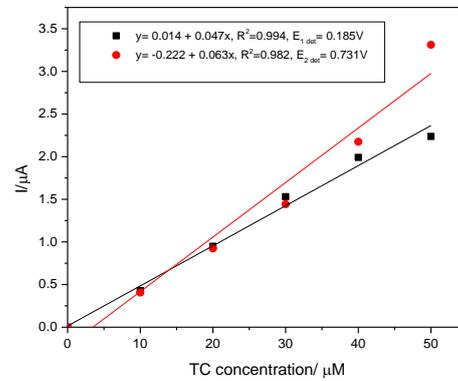


Fig. 9. b) The calibration plots of the currents recorded at $E_1 = +0.185\text{V/SCE}$ and $E_2 = +0.731\text{V/SCE}$ versus TC concentrations

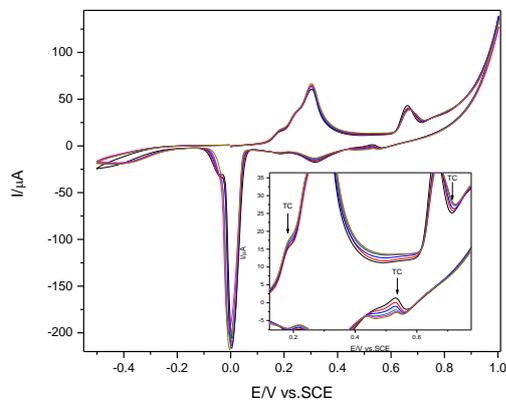


Fig. 10. a) Cyclic voltammograms recorded on GC-GP-Ag electrode in electrolyte support 0.1 M NaOH solution and in the presence of 10-50 μM TC; scan rate 0.05 Vs⁻¹; potential range: -0.5 \rightarrow 1V/ SCE

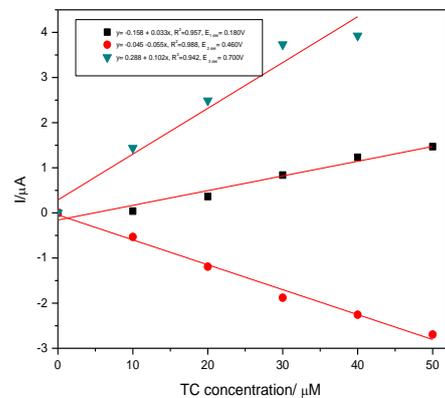


Fig. 10. b) The calibration plots of the currents recorded at $E_1 = +0.180\text{V/SCE}$, $E_2 = +0.460\text{V/SCE}$, and $E_3 = +0.700\text{V/SCE}$ versus TC concentrations

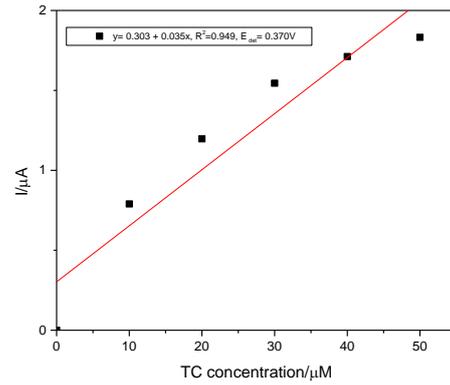
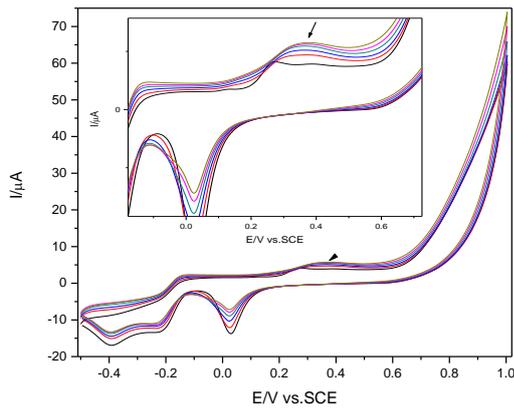


Fig. 11. a) Cyclic voltammograms recorded on GC-Au electrode in electrolyte support 0.1 M NaOH solution and in the presence of 10-50 μM TC; scan rate 0.05 Vs-1; potential range: -0.5 \rightarrow 1V/ SCE

Fig. 11. b) The calibration plots of the currents recorded at $E = +0.370\text{V/SCE}$ versus TC concentrations

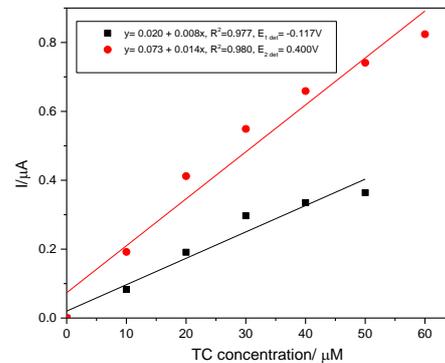
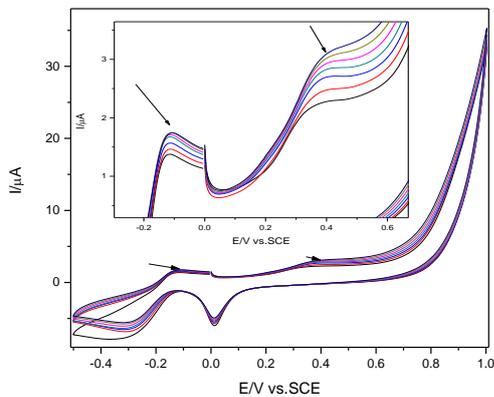


Fig. 12. a) Cyclic voltammograms recorded on GC-GP-Au electrode in electrolyte support 0.1 M NaOH solution and in the presence of 10-60 μM TC; scan rate 0.05 Vs-1; potential range: -0.5 \rightarrow 1V/ SCE

Fig. 12. b) The calibration plots of the currents recorded at $E_1 = -0.117\text{V/SCE}$ and $E_2 = +0.400\text{V/SCE}$ versus TC concentrations

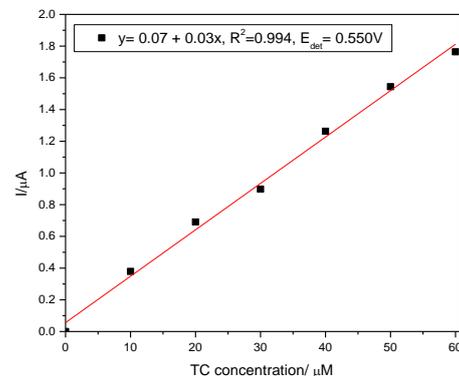
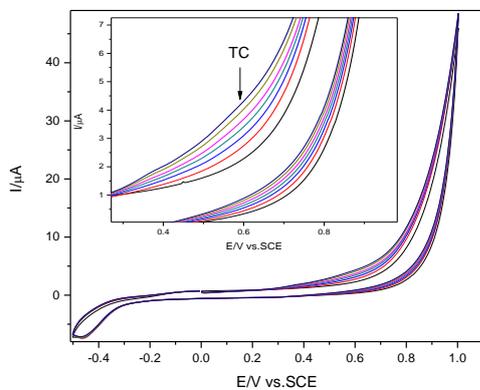


Fig. 13. a) Cyclic voltammograms recorded on GC-GP-Pt electrode in electrolyte support 0.1 M NaOH solution and in the presence of 10-60 μM TC; scan rate 0.05 Vs-1; potential range: -0.5 \rightarrow 1V/ SCE.

Fig. 13. b) The calibration plots of the currents recorded at $E = +0.550\text{V/SCE}$ versus TC concentrations.

All detection characteristics were determined based on the calibration plots for each electrode composition are gathered in Table 4. The relative standard deviation (RSD), the lowest

limit of detection (LOD), and the limit of quantification (LQ) are determined for three replicates based on the following equations [21]:

$$\bar{x} = \frac{\sum_{i=1}^n x_i}{n} \quad (1)$$

$$S = \sqrt{\frac{\sum_{i=1}^n (|x_i - \bar{x}|^2)}{n-1}} \quad (2)$$

$$RSD = \frac{S}{\bar{x}} \quad (3)$$

$$LOD = \frac{3S}{m} \quad (4)$$

$$LOQ = \frac{10S}{m} \quad (5)$$

where x_i is the values current, S is the square average deviation, RSD is the relative standard deviation, LOD is the lowest limit of detection, LOQ is the limit of quantification and m is the value of the obtained sensitivity.

Table 4. Electrode type and the electroanalytical parameters for TC detection

Electrode	$E_{det}(V)$	Sensitivity ($\mu A/\mu M \cdot cm^{-2}$)	R^2	RSD (%)	LOD (μM)	LQ (μM)
GR	0.370	17.2	0.994	3.04	2.09	6.96
GR-GP	0.370	11.7	0.969	1.46	2.54	8.48
GC	0.480	0.127	0.985	3.38	2.27	7.56
GC-GP	0.862	1.53	0.862	1.58	0.826	2.75
GC-Ag	0.185	1.50	0.994	1.09	0.249	0.830
	0.731	2.04	0.982	0.502	0.137	0.457
GC-Au	0.370	1.11	0.949	1.90	0.204	0.680
	0.180	1.05	0.957	1.95	0.821	2.74
	0.460	1.75	0.988	2.33	0.082	0.274
GC-GP-Ag	0.700	3.25	0.942	0.777	0.181	0.604
	0.400	0.446	0.980	4.30	0.629	2.10
	GC-GP-Au	-0.117	0.255	0.977	6.43	0.974
GC-GP-Pt	0.550	0.955	0.994	2.61	0.160	0.534

Based on the above-presented results, it can be noticed that the highest sensitivity for TC detection was achieved for GR and GR-GP electrodes, which was expected to take into account the higher background current of GR in comparison with GC. However, it was not possible to develop the TC detection protocol for Ag/Au/Pt electrodeposited onto the GR and GR-GP substrates.

The results achieved for GC and GC-GP substrates showed that all Ag/Au/Pt electrodeposited GC and GC-GP electrodes exhibited useful properties for the development of TC detection protocol. In comparison with GR, GC electrode exhibited worse electroanalytical parameters. Except for the unmodified GC electrode, all Ag/Au/Pt electrodeposited onto GC and GC-GP substrates

allowed the development of the TC detection procedures using CV characterized by the better limit of detection and lower detection potential (see Table 4). Better limits of detection is the main target for the detection protocol and it can be seen that Ag electrodeposited on GC-CP exhibited the lowest limit of detection for TC determination at the potential detection of 0.460 V/SCE on the cathodic branch of the cyclic voltammogram that represents also, a great advantage for possible selective detection of the TC within the multi-component system, which can be detected through anodic detection procedures. A very interesting behavior was found for GC-GP-Au based on a negative anodic detection potential, which presents also a great potential for simultaneous detection of TC within the multi-component systems.

CONCLUSIONS

Ag/Au/Pt was successfully electrodeposited onto graphite (GR), graphene-modified graphite (GR-GP), glassy carbon (GC), and graphene-modified glassy carbon (GC-GP) substrates and modified electrodes were obtained i.e., GR-Ag, GR-Au, GR-Pt, GR-GP-Ag, GR-GP-Au, GR-GP-Pt, GC-Ag, GC-Au, GC-Pt, GC-GP-Ag, GC-GP-Au, GC-GP-Pt electrodes. All electrodes were characterized and tested for tetracycline (TC) detection using cyclic voltammetry. All electrodes exhibited the useful signal for TC detection based on the TC oxidation and reduction but only GR-GP, GC-Ag, GC-Au, GC-Pt, GC-GP-Ag, GC-GP-Au, GC-GP-Pt electrodes allowed developing TC detection protocol using CV. The highest sensitivity for TC detection was achieved for GR and GR-GP electrodes, which was expected

to take into account the higher background current of graphite in comparison with GC. However, the Ag/Au/Pt electrodeposited onto the GR and GR-GP substrates were not appropriate for TC detection due to the useful signal was not linear dependent by the TC concentration.

TC detection protocols were developed for all Ag/Au/Pt electrodeposited GC and GC-GP electrodes. Better limits of TC detection was achieved for Ag electrodeposited on GC-GP at the cathodic potential of 0.460 V/SCE. GC-GP-Au exhibited an interesting behavior based on a negative anodic detection potential, which presents also a great potential for simultaneous detection of TC within the multi-component systems.

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