Silver/graphene-modified Boron Doped Diamond Electrode for Selective Detection of Carbaryl and Paraquat from Water

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A novel silver/graphene-modified boron doped diamond electrode (BDDGRAg) was obtained to determine selectively carbaryl and paraquat pesticides from aqueous solution, based on the electrochemical oxidation of carbaryl (CR) and the electrochemical reduction of paraquat (PQ). Compared with graphene-modified boron doped diamond electrode (BDDGR), BDDGRAg exhibited excellent electrocatalytic activity towards CR electrooxidation and PQ electroreduction. Simple and fast voltammetric methodology for selective CR and PQ detection was developed based on the selection of potential range corroborated with the optimum operating conditions of the differential pulse voltammetry technique (DPV) at BDDGRAg electrode. The lowest limit of detection of 1.14 nM was determined for the selective detection of PQ within potential range of 0 to -1 V/SCE using DPV under step potential of 5 mV and the modulation amplitude of 200 mV without interference of CR presence. Also, the lowest limit of detection of 1.15 nM was found for the selective detection of CR within the potential range of 0 to +1.5 V/SCE under the step potential of 6 mV and the modulation amplitude of 800 mV. Proof-of-concept is demonstrated by the application in the real surface water sample.

1. INTRODUCTION

Development of reliable, highly sensitive, fast, low-cost, low determination limit, and highly selective sensor devices imply the combination between nanotechnology and modern electrochemical techniques [1]. In the process of electrochemical sensing, involvement of nanotechnology to construct

new electrode or to modify the existing electrode considers the enhancement of the electron transfer rate and implicit, the sensitivity [2].

Carbon class materials exhibit outstanding features as high surface area, high electrical conductivity, electron mobility at room temperature, flexibility and mechanical resistance, making them very attractive in the sensors field [3]. Among these carbon materials, graphene is ideal for electrochemical applications due to its very high electrical conductivity and surface area, and having the advantage to other nanomaterials from its class, the low cost production from graphite and lack of impurities [3,4]. Also, boron-doped diamond (BDD) electrode is recognized for its remarkable properties in electrochemical application, i.e., wide potential window, low background and capacitive current, stability, reproducibility, with very good results in electrochemical detection [5]. However, by electrode interface modifying with nanostructured material, e.g., graphene, carbon nanotubes, carbon nanodots, the electroactive surface area and the electrocatalytic effect is larger [2]. When the electrode is modified with silver particles the electrocatalytic activity is reflected in the superior transfer electron rate and the sensitivity improvement towards the electrochemical detection of the target analytes [2,6-10].

Synergistic effect of the combination of graphene and silver particles onto the BDD electrode as supporting material will be tested in this paper for selective detection of two hazardous pesticides from aqueous solution. Carbaryl and paraquat are included on the priority list of hazardous substances released by Agency for Toxic Substances and Disease Registry (ATSDR) in 2015 [11] due to their toxicity. Carbaryl (1-naftil-methil-carbamate) was the first successful carbamate pesticide, and its indiscriminately application can bioaccumulate in food and water sources, threaten human health with their toxicity exerted on central nervous system [12]. Paraquat (1,1'-dimethil-4,4'-bipyridinium dichloride) is one of the most toxic herbicide used in agriculture, and due to its resistance to biodegradation persist in environment for a very long time [13].

The individual determination of pesticides from waters represent a challenging issue due to two problems, mainly, *i.e.*, their presence in water in traces at concentration ranging from 1 to 100 ngL^{-1}, and the interference with the signal of the other more concentrated compounds present in water. Beside the electrode material, the electrochemical detection control is dependent on the analyzing method performances, requiring a permanent improvement of the analytical parameters as sensitivity, analysis time, limit of detection and selectivity. In this context, the development of fast, sensitive and accessible analysis methods is motivating the researchers to find the optimal solution. Besides the electrode material that represents the core of the electrochemical detection method, the optimized electrochemical techniques allow further enhancement of the electroanalytical performance and should represent the adequate solution for pesticide detection [6,12-21].

In this study, BDD electrode was modified with graphene and silver (BDDCGAg) by electrochemical deposition in two-steps. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were the electrochemical techniques applied for the electrochemical characterization, individual and selective detection of carbaryl and paraquat pesticides from aqueous solution. The selectivity of the method derived by the potential range selection. The operating parameters of DPV technique were optimized in order to achieve very good electroanalytical parameters for each target pesticide detection.

2. MATERIAL AND METHODS

All the electrochemical experiments were performed using a classical three electrode cell, having the saturated calomel electrode (SCE) as reference electrode, platinum as counter electrode and the boron-doped diamond electrode modified with graphene and silver particles (BDDGRAg) as working electrode. The electrodes were connected to an Autolab potentiostat/galvanostat PGSTAT 302 (Eco Chemie, The Netherlands) controlled with GPES 4.9 software. The working electrode support was the commercial boron-doped diamond electrode (Windsor Scientific Ltd, UK), having a disc surface with the 3 mm diameter. The working electrode was modified by electrodeposition. First, the BDDGR electrode was obtained as we previously reported [18]. The comercial BDD electrode was modified first with graphene, by electrodeposition of graphene on the electrode surface at the potential -1.2 V/SCE for 60 seconds from a solution of graphene oxide 4 mg/mL disspersed in water and in the presence of $KClO_4$ 0.1 M, obtaining BDDGR electrode. After the graphene electrodeposition, the silver particles decorated the electrode surface by the electrodeposition at -1.2 V/SCE for 30 seconds from the 10 mM $AgNO_3$ solution. The modified electrode was further stabilized in acetate buffer by cyclic voltammetry through 15 continuous cycles.

The acetate buffer solution with the pH 5.6 was prepared dissolving acetic acid, sodium acetate and acetonitrile in distillated water, as we previously reported [18,19]. To achieve the selective electrochemical detection, the potential range was selected between -1.00 and +1.75 V/SCE, and the applied electrochemical techniques were cyclic voltammetry and differential pulse voltammetry. The limit of detection (LOD) was calculated using equation: LOD=3SD/m and LOQ=10SD/m where SD is the standard deviation of 6 blanks and m is the slope of the analytical plots [24].

The target analytes solution, i.e., carbaryl and paraquat were prepared using PESTANAL analytical standards provided Sigma Aldrich (Germany).

3. RESULTS AND DISCUSSION

3.1. Comparative electrochemical behaviour of Ag/graphene (BDDGRAg) and graphene-modified boron-doped diamond (BDDGR) electrodes

The electrodeposition time for silver deposited on graphene was selected as 30 seconds based on the best voltammetric signal recorded in the presence of 50 μM CR, taking into account that the final aim of the electrode modification is to get the best sensitivity for the electrochemical detection of target analyte. The comparative voltammetric signal was recorded by CV on BDDGRAg and BDDGR electrode in the presence of carbaryl and paraquat and acetate buffer supporting electrolyte solution to achieve the electrode contribution to the detection signal, and the results are presented in Figure 1.

In comparison with our previously reported results related to graphene-modified boron-doped diamond electrode and the boron-doped diamond electrode [18], a different behaviour of BDDGRAg is noticed in relation with the background current and useful voltammetric signal corresponding to Faradayc response. The background current that corresponds to charging current due to the electric double layer decresead while the Faradayc current slightly increased for PQ, which led to improve the

peak current responsible by the electroanalytical signal. These findings show that the new composition of the electrode BDDGRAg exhibits its specific electrochemical peculiarities as new electrode composition electrochemical behaviour that favor the enhancement of the electroanalytical signals for PQ and CR detection. The further experiences were conducted using BDDGRAg electrode to exploit the characteristics of the voltammetric technique to develop the electrochemical detection method for selective detection of PQ and CR. No influence of silver presence on the detection potential values was noticed, thus, the detection potential value for CR detection was +1.48V/SCE and -0.85 V/SCE for PQ detection.
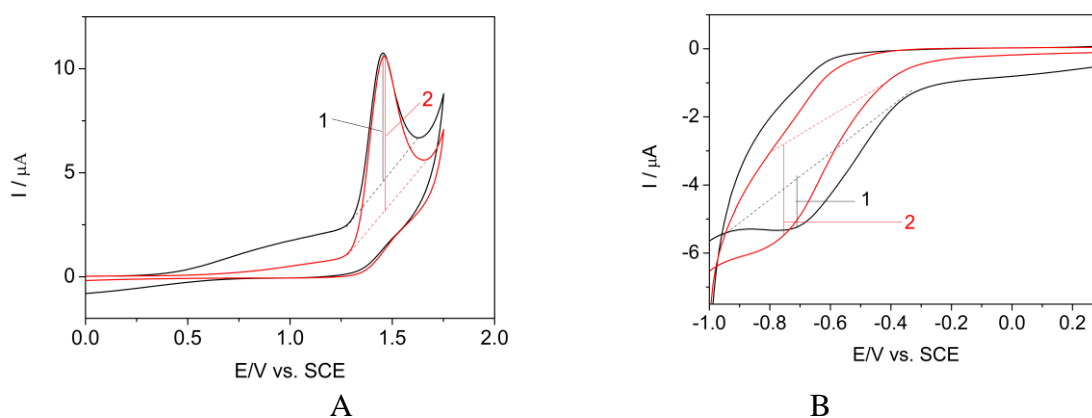

Figure 1. Cyclic voltammograms recorded in acetate buffer supporting electrolyte and in the presence of 50 µM CR (a) and 5 µM PQ (b) on: BDDGR (curve 1) and BDDGRAg (curve 2) electrodes.

3.2. Optimization of differential pulse voltammetry parameters

Two major aspects of sensitivity and the detection potential value must be considered from the analytical point of view, which are in direct relation with the combination of the modified electrode and the electrochemical techniques. Among the existing differential electrochemical techniques, the differential pulse voltammetry (DPV) is extensively used in electroanalysis due to its high sensitivity, good definition of signals and the diminution of background currents [22,23]. The lowering of the detection potential value may be very important if the simultaneous detection is envisaged or the detection potential is near or beyond the supporting electrolyte discharge [23].

The optimization of operating variables of DPV technique was achieved for CR detection due to its detection sensitivity is lower in comparison with PQ and the detection potential is high (+1.48 V/SCE) and near the oxygen evolution. Considering our previous results [18], three different operating conditions were tested: (1) step potential (sp) of 5 mV and modulation amplitude (MA) of 200 mV; (2) sp of 5 mV and the MA of 500 mV; (3) sp of 6 mV and a MA of 800 mV.

Figures 2- 4 present the results obtained at the BDDGRAg electrode in acetate buffer and in the presence of CR for tested DPV operating conditions to assess the responses in terms of signal shape, sensitivity and the detection potential value. For the first condition of sp=5 mV, MA=200 mV, a well-

defined peak and a corresponding very good sensitivity of 35.06 $\mu A \cdot \mu M^{-1} cm^{-2}$ at the detection potential value of +1.35V/SCE were obtained for the CR detection.
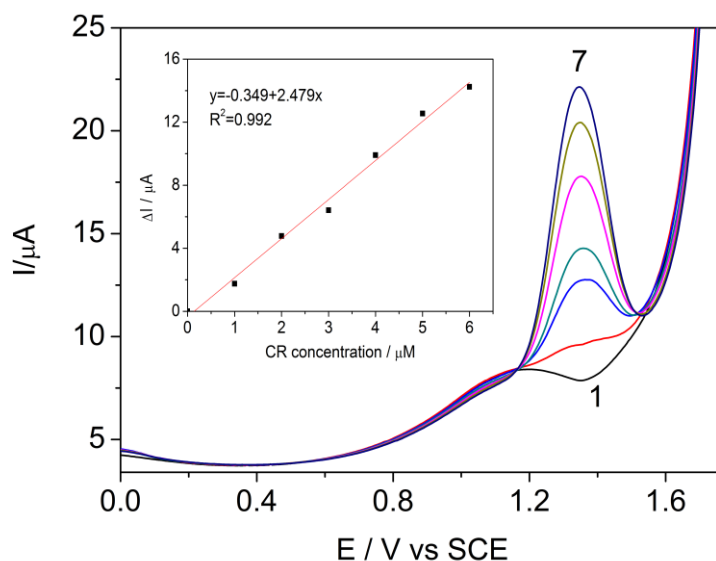

Figure 2. Differential pulse voltammograms recorded on BDDGRAg electrode in acetate buffer supporting electrolyte and in the presence of various CR concentrations: 1- 0 μM, 2- 1 μM, 3- 2 μM, 4- 3 μM, 5- 4 μM, 6- 5 μM, 7- 6μM,; potential scan rate: 0.05 Vs^{-1}, sp of 5 mV and MA of 200 mV. Inset: Calibration plots of the currents recorded at E= +1.35 V/SCE versus CR concentrations.
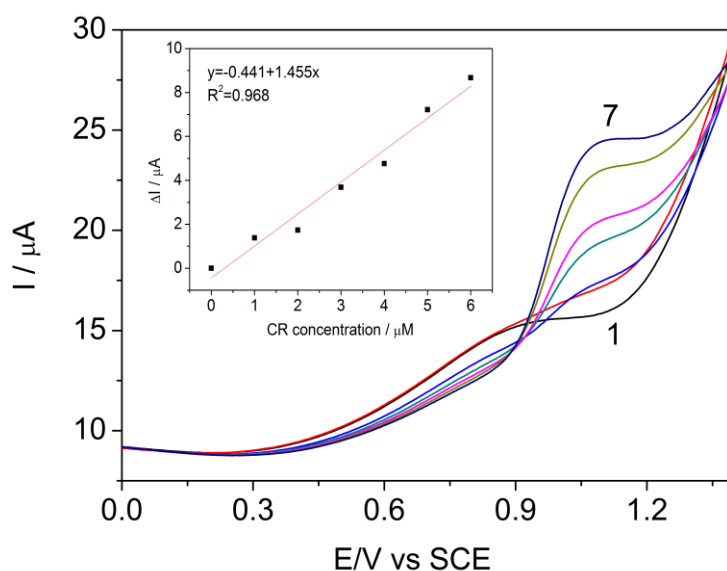

Figure 3. Differential pulse voltammograms recorded on BDDGRAg electrode in acetate buffer supporting electrolyte and in the presence of various CR concentrations: 1- 0 μM, 2- 1 μM, 3- 2 μM, 4- 3 μM, 5- 4 μM, 6- 5 μM, 7- 6μM,; potential scan rate: 0.05 Vs^{-1}, sp of 5 mV and MA of 500 mV. Inset: Calibration plots of the currents recorded at E= +1.11 V/SCE versus CR concentrations.
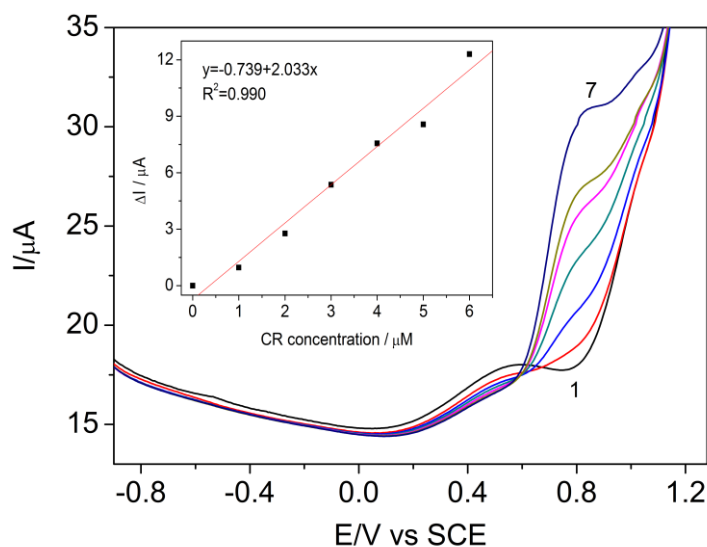
Figure 4. Differential pulse voltammograms recorded on BDDGRAg electrode in acetate buffer supporting electrolyte and in the presence of various CR concentrations: 1- 0 µM, 2- 1 µM, 3- 2 µM, 4- 3 µM, 5- 4 µM, 6- 5 µM, 7- 6µM,; potential scan rate: 0.05 Vs^{-1}, sp of 6 mV and MA of 800 mV. Inset: Calibration plots of the currents recorded at E= +0.84 V/SCE versus CR concentrations.

The second and the third conditions were also tested the shifting of the CR oxidation peak towards smaller overpotentials was noticed by enhancing the modulation amplitude. Hence, at the MA of 500 mV the CR oxidation potential was +1.11 V/SCE, and at a MA of 800 mV, the peak potential was shifted to +0.84 V/SCE but the peaks were not very well-defined, and the corresponding sensitivities decreased. The electroanalytical parameters determined under above-presented DPV operating conditions for CR detection at BDDGRAg are gathered in the Table 1.

3.3. Selective detection of carbaryl and paraquat by DPV technique

Based on our previously reported results for BDDGR [18] and above-presented preliminary CV study, it is obviously that both CR and PQ should be detected simultaneously based on the detection principle and the potential value for each pesticide. The detection response for CR is based on the its electrochemical oxidation at the potential value of about +1V/SCE depending on the electrochemical technique and the operating conditions, and the detection response for PQ is based on its electrochemical reduction at the potential value of about -1 V/SCE on the electrode surface. A very simple voltammetric scanning within a large potential window that includes the detection potentials allows the simple simultaneous detection of both pesticides. To assure the selective detection, the potential window should be narrowed to include only the desired detection potential, which means to apply an anodic potential window (between 0 and +1.5 V/SCE) for the CR detection and cathodic one (between 0 and -1 V/SCE) for PQ detection. The question that arise is if each pesticide interfere with the other detection. The example of the recorded voltammograms under the DPV optimum conditions determined for CR detection of the sp of 5 mV and the MA of 200 mV and applied for PQ detection

within the large potential window presented in Figure 5 showed that quite the response for CR presence decreased during increasing PQ concentration, which denotes a slight interference of each to other pesticide detection. If the potential range is selected for PQ detection, no interference of CR was noticed (see Table 1). The all operating conditions of DPV applied for CR detection were applied for PQ and the optimum in terms of sensitivity was found for sp of 6 mV and the MA of 800 mV. The effect of the potential range scanning was tested and it was found that the selection of the cathodic potential range for PQ detection allowed avoiding the interference of CR presence.
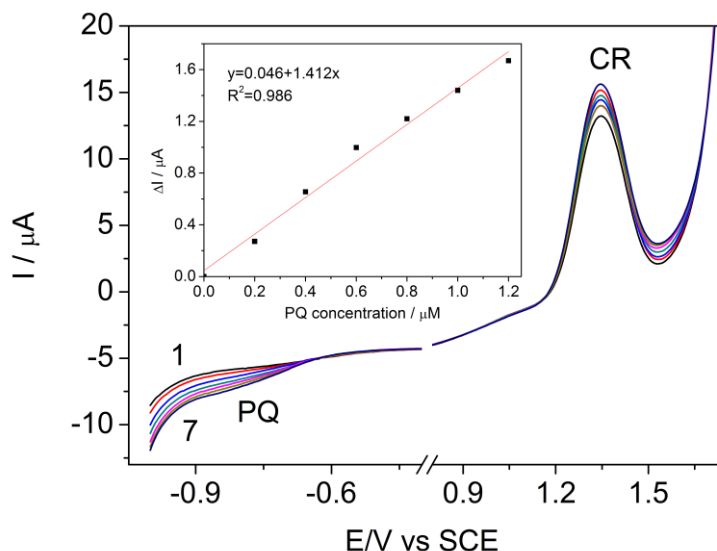

Figure 5. Differential pulse voltammograms recorded on BDDGRAg electrode in acetate buffer supporting electrolyte and in the presence of 6 μM CR and different PQ concentrations: 1- 0 μM, 2- 0.2 μM, 3- 0.4 μM, 4- 0.6 μM, 5- 0.8 μM, 6-1.0 μM, 7- 1.2 μM; at sp=5 mV and MA=200 mV. Inset: Calibration plots of the currents recorded at E= -0.85 V/SCE versus PQ concentrations.

Table 1. Operating DPV parameters and electroanalytical performance recorded on BDDGRAg electrode for voltammetric detection of CR and PQ using DPV

Target analyte	Potential range	Co-existing analyte	Parameters	Potential (V)	Sensitivity ($\mu A \cdot \mu M^{-1} cm^{-2}$)	LOD (M)	LOQ (M)	R^2
CR	-1.0 to +1.5 V/SCE	-	sp=5 mV, MA= 200 mV	+1.35	35.06	$1.18 \cdot 10^{-9}$	$0.39 \cdot 10^{-8}$	0.992
		-	sp=5 mV, MA=500 mV	+1.11	20.58	$3.86 \cdot 10^{-9}$	$1.29 \cdot 10^{-8}$	0.987
		-	sp=6mV, MA=800 mV	+0.84	28.76	$3.68 \cdot 10^{-9}$	$1.23 \cdot 10^{-8}$	0.990
		1.2μM PQ	sp=6mV, MA=800 mV	+0.79	23.62	$4.05 \cdot 10^{-9}$	$1.35 \cdot 10^{-8}$	0.989
	0 to +1.5 V/SCE	1.2μM PQ	sp=5mV, MA=200 mV	+1.35	36.05	$1.14 \cdot 10^{-9}$	$0.38 \cdot 10^{-8}$	0.996
PQ	-1.0 to +1.5 V/SCE	-	sp=6mV, MA=800 mV	-0.89	34.24	$1.21 \cdot 10^{-9}$	$0.40 \cdot 10^{-8}$	0.995
		6μM CR	sp=6mV, MA=800 mV	-0.83	29.31	$1.25 \cdot 10^{-9}$	$0.42 \cdot 10^{-8}$	0.997
	0 to -1.0 V/SCE	6μM CR	sp=6mV, MA=800 mV	-0.85	35.33	$1.15 \cdot 10^{-9}$	$0.30 \cdot 10^{-8}$	0.998

Under the context of the selective detection, all the electroanalytical parameters related to the sensitivity, the lowest limit of detection (LOD), the lowest limit of quantification (LOQ) in relation to the potential range and are gathered in the Table 1, and it was demonstrated that the potential range represents an important operating parameter for the voltammetric detection protocol design.

2.4. Application to real water sample

Each optimized DPV method developed for selective determination of CR in the presence of PQ and reverse was applied for real surface water sample characterized by the turbidity of 7 NTU and Total Organic Carbon of 4 mg C/L. The operating conditions are presented in Table 2.

Table 2. Operating DPV conditions for selective determination of CR and PQ in real water sample

Potential range (V vs. SCE)	Target analyte	Co-existing analyte	Operating conditions
0 to +1.5	**CR**	PQ	sp=5mV, MA=200 mV
0 to -1	**PQ**	CR	sp=6mV, MA=800 mV

The support electrolyte was prepared by addition of acetate buffer to the real surface water sample. The DPV responses were checked for 0.5 and 1 µM PQ in the presence of 4 µM CR under the potential range from 0 to -1 V/SCE, operating conditions of sp=6mV, MA=800 mV, and for 2 and 4 µM CR in the presence of 1 µM PQ under the potential range from 0 to +1.5 V/SCE, operating conditions of sp=5 mV, MA=200 mV. The statistical calculations for the assay results showed suitable precision of the each proposed method for the selective determination of PQ and CR (Table 3).

Table 3. Results obtained for the selective determination of CR and PQ in the real surface water sample

Analyte type	Concentration added (µM)	Concentration found (µM)	Recovery (%)
PQ	0.5	0.45	90.00
PQ	1	1.06	106.00
CR	2	1.90	95.00
CR	4	3.65	91.25

The proposed methodology based on the corroboration between modified electrode characterized by the electrocatalytic activity and the optimum operating conditions of differential-pulse voltammetry has proven to be suitable for the selective detection of carbaryl and paraquat and applicable for the real water sample.

4. CONCLUSIONS

A novel boron-doped diamond modified with graphene and silver particles (BDDGRAg) was developed by the electrodeposition in two-steps. The synergetic electrocatalytic effect of graphene and silver particles onto BDD support was exploited towards carbaryl (CR) electrooxidation and paraquat (PQ) electroreduction to develop the simple and fast methodology for the selective detection of CR and PQ. Compared with graphene-modified boron doped diamond electrode (BDDGR) using cyclic voltammetry technique, BDDGRAg exhibited excellent electrocatalytic activity towards CR electrooxidation and PQ electroreduction, and the voltammetric response was enhanced. A very important parameter to develop the voltammetric methodology for selective CR and PQ detection without each to other interference was the appropriate selection of potential range. The best selective detection signal was achieved by corroborating the potential range with the differential pulse voltammetry technique (DPV) optimum operating conditions and BDDGRAg electrode. The lowest limit of detection of 1.14 nM was determined for the selective detection of PQ within potential range of 0 to -1 V/SCE using DPV under step potential of 5 mV and the modulation amplitude of 200 mV without interference of CR presence. Also, the lowest limit of detection of 1.15 nM was found for the selective detection of CR within the potential range of 0 to +1.5 V/SCE under the step potential of 6 mV and the modulation amplitude of 800 mV. The use of BDDGRAg electrode made the possible the selective detection of CR and PQ in the real surface water without any pretreatment stage, and the recovery percentage higher than 90% is considered very satisfactory for analytical application.

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