

# Electrochemical Determination of 2,4-Dinitrophenol from Aqueous Solution at Expanded Graphite – Carbon Nanofiber – Epoxy Composite Electrode

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**Abstract:** An expanded graphite-carbon nanofiber-epoxy composite (EG-CNF-Epoxy) was investigated in order to its use for the electrochemical determination of 2,4-dinitrophenol (2,4-DNP) in aqueous solutions. The electrochemical behavior of the electrode in the presence of target pollutant was investigated using cyclic voltammetry (CV), chronoamperometry (CA), and multiple-pulsed amperometry (MPA). Because of the electrode fouling during the electrochemical oxidation, this electrode can be applied for the electrochemical determination only under certain conditions given by MPA technique.

**Keywords:** 2,4-dinitrophenol, expanded graphite-carbon nanofiber-epoxy composite electrode, electrochemical determination, wastewater.

## 1. Introduction

The intensification of industrial activities, since the latter half of the XIX century and throughout the XX century, has inevitably caused severe environmental pollution with dramatic consequences in atmosphere, waters and soils [1].

Aromatic nitrocompounds, such as: nitrobenzene, nitrotoluenes and nitrophenols are found widely as environmental contaminants in fresh water, in marine environments, and in industrial effluent. They have been used commonly in the manufacture of explosives, pesticides, dyes, plasticizers, and pharmaceuticals [2]. 2,4-dinitrophenol (2,4-DNP) is listed by the U.S. Environmental Protection Agency as priority pollutant, because of its toxicity, which requires the development of a simple and reliable removal process [3,4].

The electrochemical oxidation techniques has been frequently tested in order to quantitative determination of the organic load [5-9].

It has been reported [10-12] that the phenol electrooxidation on carbon based electrodes leads to electrode fouling by electropolymerization that leads to a low rate of oxidation, low permeability, and strong adhesion on the electrode. Among the electrochemical techniques presently used, multiple-pulsed amperometry (MPA) has proved to be extremely efficient for the electrochemical determination of organic molecules because of the advantage of cleaning and reactivating the electrode surface during the electrochemical process [13,14].

Carbon electrodes are widely used in electroanalysis due to their low background current and wide potential window suitable for the investigation of the electrochemical oxidation processes, their chemical inertness, low cost and suitability for various sensing and

detection applications [15].

The aim of this study is to assess the behavior of the expanded graphite – carbon nanofiber – epoxy composite electrode (EG-CNF-Epoxy) for the electrochemical determination of 2,4-dinitrophenol (2,4-DNP) in water. The cyclic voltammetric behavior was investigated first to reveal the basic electrochemical parameters of the electrode. 2,4-dinitrophenol (2,4-DNP) was used as model pollutant representing di-substituted phenol derivatives. The electroanalytical performance of the electrode was determined by chronoamperometry (CA) and multiple-pulsed amperometry (MPA). The multiple-pulsed amperometry technique was applied under different conditions, and the results were compared with those obtained by chronoamperometry technique.

## 2. Experimental

All measurements were carried out using an Autolab potentiostat/galvanostat PGSTAT 302 (Eco Chemie, The Netherlands) controlled with GPES 4.9 software and a three-electrode cell, with a Ag/AgCl reference electrode and a platinum counter electrode. The EG-CNF-Epoxy composite electrode was used as working electrode.

The EG-CNF-Epoxy composite electrode was prepared from two-components epoxy resin (LY5052, Araldite) mixed with two types of conductive carbon fillers: expanded graphite (EG) fillers powder (Conductograph, SGL Carbon) and carbon nanofibers (CNF) (PS-447 BOX). To prepare EG-CNF-Epoxy composite electrode, the two parts of the epoxy were mixed with the conductive carbon fillers in a roll-mill at the room temperature and the obtained paste was cured in a hot press at 80 ° C for 40 minutes. Simultaneously the material was shaped in a plate of 1 mm thickness. The plate was

slowly cooled down (for about 12 h) to the room temperature without removing the applied pressure [16,17].

Plates with a surface area of 4 cm<sup>2</sup> were cut from the composition and put on glass supports. Electrical contacts were made using a silver paint. The electrode was isolated on the sides by epoxy resin. Prior to use, this working electrode was gradually cleaned, first polished with abrasive paper and then on a felt-polishing pad by using 0.03 μm alumina powder (Metrohm, Switzerland) in distilled water for 5 minutes, followed by rinsing with distilled water.

The electrochemical performances of this electrode was studied by cyclic voltammetry (CV), chronoamperometry (CA), and multiple-pulsed amperometry (MPA). Subsequently, an electrochemical pretreatment by three repetitive cyclings between -0.5 V to 1.3 V vs. Ag/AgCl in 0.1 M Na<sub>2</sub>SO<sub>4</sub> supporting electrolyte was performed. Chronoamperometric measurements were performed at +1.25 V vs. Ag/AgCl, while for multiple-pulsed measurements three schemes in relation with the level number, the applied potential and time were carried out.

2,4-dinitrophenol and sodium sulphate were analytical grade from Merck, and the solutions were freshly prepared with double-distilled water.

### 3. Results and Discussion

In Figures 1a and 1b are presented the cyclic voltammograms of the EG-CNF-Epoxy composite electrode behavior in the presence of 0.2 mM 2,4-DNP in relation with the scanning direction. It can be noticed that in the presence of 0.2 mM 2,4-DNP the anodic current increased starting with the potential value of 0.8 V vs. Ag/AgCl, near to the oxygen evolution range. At this 2,4-DNP concentration, even the anodic current increased, no limiting current appeared. It can be noticed that starting with the second CV the peak current decreased substantially, which is due to the electrode fouling. In general, the electrode fouling is due to a complex mechanism of phenols oxidation on carbon based electrodes, which involves both the adsorption of reactant/intermediate or final oxidation products and the formation of a passive, nonconductive layer of oligomer products of oxidation process on its surface [13]. In addition, an increasing of the cathodic current within potential range starting with about -0.3V vs. Ag/AgCl was noticed. The cathodic current could be owed to the presence of the polymer of aminophenol formed cathodically. This polymer resulted from 2,4-DNP is less stable than the polymer resulting from mono-substituted nitrophenol, and can be further oxidized and mineralized [18].

In Table 1 are presented voltammetric anodic and cathodic parameters for the both anodic and cathodic scanning direction. The cathodic current was measured at -0.4 V vs. Ag/AgCl, because at this potential occur the nitrophenol derivatives reduction at aminophenol derivatives [19]. In these conditions of concentration and cycling, the anodic peak current decreased with the increasing of the

number of scans, while the cathodic current remained constantly. Also, it can be seen that the degree of the electrode fouling is influenced by the scanning direction. Cathodic scanning direction favored the oxidation process of 2,4-DNP, and the reducing degree of the anodic peak was diminished.

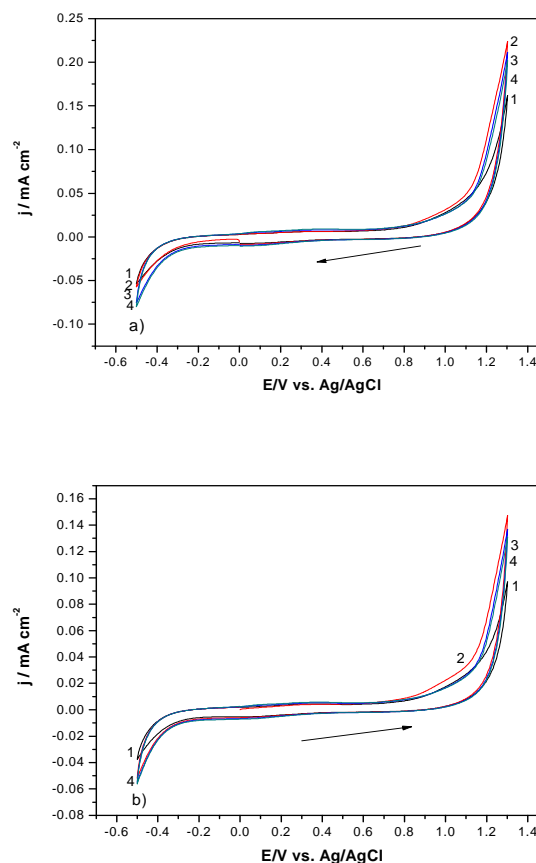


Figure 1. Cyclic voltammograms of EG-CNF-Epoxy electrode in 0.1 M Na<sub>2</sub>SO<sub>4</sub> supporting electrolyte (curve 1) and in the presence of 0.2 mM 2,4-DNP at the scan rate of 0.05 V·s<sup>-1</sup>: curve 2-scan 1; curve 3-scan 2; curve 4-scan 3; start potential: 0 V vs. Ag/AgCl; potential range: -0.5V → +1.3V → -0.5V vs. Ag/AgCl, scanning in cathodic direction (a); -0.5V → +1.3V → -0.5V vs. Ag/AgCl, scanning in anodic direction (b).

TABLE 1. Voltammetric parameters of the electrochemical oxidation of 0.2 mM 2,4-DNP at EG-CNF-Epoxy composite electrode, for the potential range of -0.5V → +1.3V → -0.5V vs. Ag/AgCl

Scanning direction	Scan number	Reducing degree (%)		E(V)	
		Anodic peak	Cathodic current	Anodic	Cathodic
Cathodic	1	-	-	+ 1.23	- 0.5
	2	31.22	-	+ 1.23	- 0.5
	3	49.53	-	+ 1.23	- 0.5
Anodic	1	-	-	+ 1.23	- 0.5
	2	37.60	-	+ 1.23	- 0.5
	3	52.86	-	+ 1.23	- 0.5

In order to elucidate some aspects of the mechanism of the 2,4-DNP oxidation process on EG-CNF-Epoxy composite electrode in 0.1 M Na<sub>2</sub>SO<sub>4</sub> and in the presence of 0.2 mM 2,4-DNP, the effect of the scan rate on the

anodic peak current of the first CV was measured. The linear proportionality of the anodic current recorded at +1.1 V vs. Ag/AgCl with the square root of the scan rate obtained for all tested electrodes indicated control by mass transport [16]. No intercept at 0 suggested that the adsorption steps and specific surface reaction can not be neglected (Figure 2a). The oxidation process of 2,4-DNP is irreversible due to the lack of a cathodic peak corresponding to the anodic oxidation peak. However, the cathodic current increased at the potential value of about -0.4 V Ag/AgCl, which was ascribed to the reduction of  $\text{NO}_2$  [20].

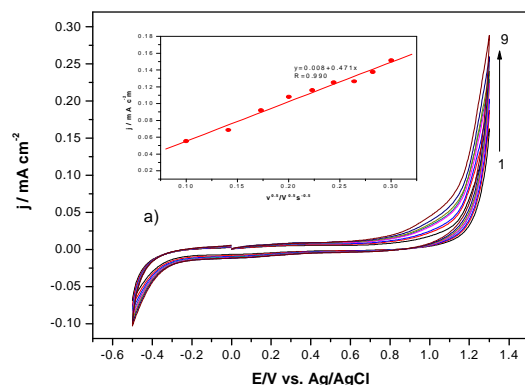


Figure 2. Cyclic voltammograms of the EG-CNF-Epoxy electrode in 0.1 M  $\text{Na}_2\text{SO}_4$  solution and 0.2 mM 2,4-DNP at different scan rates: curve 1-0.01  $\text{V}\cdot\text{s}^{-1}$ ; curve 2-0.02  $\text{V}\cdot\text{s}^{-1}$ ; curve 3-0.03  $\text{V}\cdot\text{s}^{-1}$ ; curve 4-0.04  $\text{V}\cdot\text{s}^{-1}$ ; curve 5-0.05  $\text{V}\cdot\text{s}^{-1}$ ; curve 6-0.06  $\text{V}\cdot\text{s}^{-1}$ ; curve 7-0.07  $\text{V}\cdot\text{s}^{-1}$ ; curve 8-0.08  $\text{V}\cdot\text{s}^{-1}$ ; curve 9-0.09  $\text{V}\cdot\text{s}^{-1}$ ; potential range:  $-0.5\text{V} \rightarrow 1.3\text{V} \rightarrow -0.5\text{V}$  vs. Ag/AgCl. Inset: a) Plots of the anodic peak current recorded at +1.1 V vs. Ag/AgCl versus square root of the scan rate.

Based on above – presented CV results, EG-CNF-Epoxy electrode was tested for the electrochemical detection experiments of 2,4-DNP using CA and MPA techniques. These experiments were carried out by successive adding of 0.2 mM 2,4-DNP. Thus, the multiple-pulse amperometry technique was applied under different conditions gathered in Table 2, and the results were compared with those obtained by chronoamperometry technique.

TABLE 2. The protocol of multiple-pulse amperometry technique application

Scheme	Level number	Potential (V vs. Ag/AgCl)	Time (s)
MPA I	I – oxidation	+ 1.25	0.05
	II - cleaning	+ 1.5	0.15
MPA II	I – oxidation	+ 1.25	0.05
	II - cleaning	- 0.5	0.15
MPA III	I – oxidation	+ 1.25	0.05
	II - cleaning	+ 1.5	0.15
	III - conditioning	- 0.5	0.15

In Figure 3 is presented the chronoamperogram obtained for EG-CNF-Epoxy electrode at  $E=+1.25\text{ V}$  vs. Ag/AgCl. It can be noticed that in the presence of 0.8 mM 2,4-DNP the electrode fouling occurred.

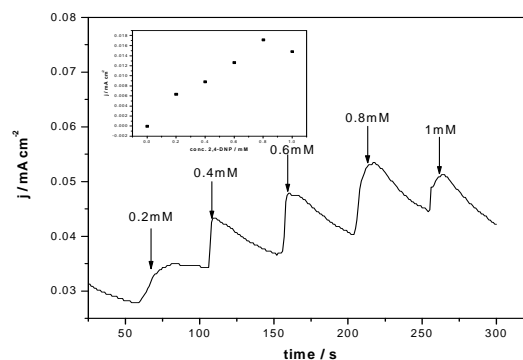


Figure 3. Chronoamperogram of EG-CNF-Epoxy electrode in 0.1 M  $\text{Na}_2\text{SO}_4$  supporting electrolyte and in the presence of different 2,4-DNP concentrations  $E=+1.25\text{ V}$  vs. Ag/AgCl. Inset: the current density variation vs. 2,4-DNP concentration.

Figures 4- 6 show the results of MPA application under the conditions presented in Table 2.

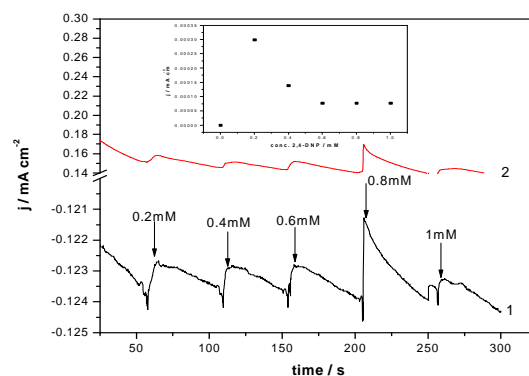


Figure 4. Multiple-pulsed amperograms (MPA) of the EG-CNF-Epoxy electrode in 0.1 M supporting electrolyte and in the presence of different 2,4-DNP concentrations;  $E_{\text{oxidation}}=+1.25\text{ V}$  vs. Ag/AgCl (curve 1) and  $E_{\text{cleaning}}=+1.5\text{ V}$  vs. Ag/AgCl (curve 2);  $t_{\text{oxidation}}=0.05\text{ s}$  and  $t_{\text{cleaning}}=0.15\text{ s}$ . Inset: the current density variation vs. 2,4-DNP concentration.

In Figure 4 is presented the results of MPA applying under the concentration range and the detection potential similar with CA. The difference consists in the application of a higher oxidation potential for the purpose of “in-situ” electrochemical cleaning of the electrode. The application of this cleaning condition did not improve the electrode performance, because at 0.4 mM 2,4-DNP the electrode fouling occurred, without the possibility of reactivate the electrode surface under the operating conditions.

The better results concerning the detection of 2,4-DNP were obtained when it was applied a cathodic potential, about -0.5 V vs. Ag/AgCl as cleaning potential (Figure 5). In these conditions, it was obtained a linear dependence of the current densities recorded at +1.25 V vs. Ag/AgCl vs. 2,4-DNP concentration.

Figure 6 presents multiple-pulsed amperograms obtained in the case of the 3 levels scheme and it can be noticed that the electrode did not fouling and an improvement of the oxidation process rate occurred. The calibration plots presented in Figure 7 showed the better sensitivity for 2,4-DNP determination.

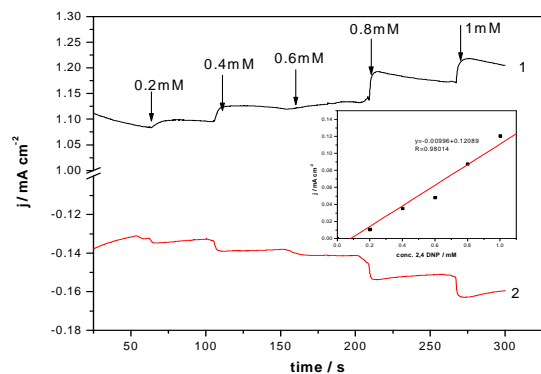


Figure 5. Multiple-pulsed amperograms (MPA) of the EG-CNF-Epoxy electrode in 0.1 M supporting electrolyte and in the presence of different 2,4-DNP concentrations;  $E_{\text{oxidation}} = +1.25$  V vs. Ag/AgCl (curve 1) and  $E_{\text{cleaning}} = -0.5$  V vs. Ag/AgCl (curve 2);  $t_{\text{oxidation}} = 0.05$  s and  $t_{\text{cleaning}} = 0.15$  s.

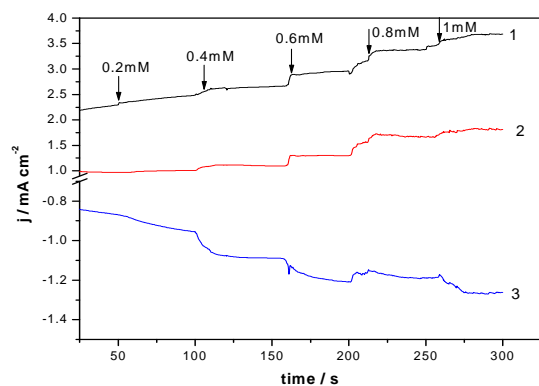


Figure 6. Multiple-pulsed amperograms (MPA) of the EG-CNF-Epoxy electrode in 0.1 M supporting electrolyte and in the presence of different 2,4-DNP concentrations;  $E_{\text{oxidation}} = +1.25$  V vs. Ag/AgCl (curve 1),  $E_{\text{cleaning}} = +1.5$  V (curve 2),  $E_{\text{conditioning}} = -0.5$  V vs. Ag/AgCl (curve 3);  $t_{\text{oxidation}} = 0.05$  s,  $t_{\text{cleaning}} = 0.15$  s,  $t_{\text{conditioning}} = 0.15$  s.

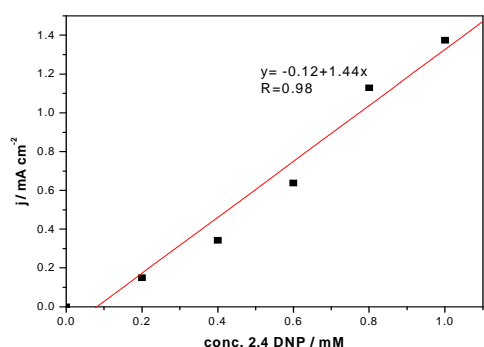


Figure 7. The current densities variation vs. 2,4-DNP concentration:  $E_{\text{oxidation}} = +1.25$  V vs. Ag/AgCl (curve 1),  $E_{\text{cleaning}} = +1.5$  V (curve 2),  $E_{\text{conditioning}} = -0.5$  V vs. Ag/AgCl (curve 3);  $t_{\text{oxidation}} = 0.05$  s,  $t_{\text{cleaning}} = 0.15$  s,  $t_{\text{conditioning}} = 0.15$  s.

TABLE 3. The electroanalytical performance of EG-CNF-Epoxy for 2,4-DNP determination using CA and MPA techniques

Electrochemical technique	The electrode sensitivity ( $\text{mA cm}^{-2} \text{mM}^{-1}$ )
CA	*
MPA I	*
MPA II	0.12
MPA III	1.44

\* no linear dependence of current density with 2,4-DNP concentration increasing

## 4. Conclusions

This study showed the applicability of EG-CNF-Epoxy electrode for the determination of 2,4-dinitrophenol in aqueous solution.

The mechanism of the oxidation process of 2,4-DNP studied by CV indicated that the oxidation process is mass-transfer controlled, and adsorption process can not be neglected.

CV results allowed to propose a detection protocol in relation with the levels number and the potential applied. The potential values were selected based on the CV results, which informed about the occurrence of the reducing process within the cathodic potential range.

Even if CA is the simplest detection technique, it can not be applied for the EG-CNF-Epoxy electrode because of the electrode fouling. Using MPA, which involved the reduction process allowed to detect 2,4-DNP at EG-CNF-Epoxy electrode with good sensitivity. Applying MPA with three levels of detection, including cleaning by oxidation and conditioning led to the enhancement of the electroanalytical performance of EG-CNF-Epoxy electrode for the quantitative determination of 2,4-DNP.

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