

Electrochemical Degradation and Determination of 4-Nitrophenol Using Multiple Pulsed Amperometry at Graphite Based Electrodes

A. Bebeșelea*, F. Manea*, G. Burtica*, L. Nagy**, G. Nagy**

* "Politehnica" University of Timisoara, P-ta Victoriei no.2, 300006 Timisoara, Romania, e-mail: adriana.bebeselea@chim.upt.ro

** Department for General and Physical Chemistry, University of Pecs, Ifjusag u.6, H-7624 Hungary

Abstract: The electrochemical degradation and determination of 4-nitrophenol (4-NP) by multiple pulsed amperometry (MPA) using rotating spectral graphite disc (SG) and expanded graphite-epoxy composite (EG-Epoxy) electrodes is reported. The MPA performance for 4-NP degradation was assessed as function of time for both electrodes, the best results were achieved for SG electrode. The optimal MPA parameters at the both types of graphite based electrodes were established for 4-NP detection, i.e. the detection potential was 1.1 V (versus Ag/AgCl) for 50 ms detection time and 1.4 V (versus Ag/AgCl) oxidation potential as clean potential for 150 ms clean time. The proposed method showed the better analytical performance for EG-Epoxy electrode for the determination 4-NP, with a linear range of 0.2 – 1 mM, detection limits of 0.05 - 0.1 mM and recovery degree of 92.4 – 94.6 %. The application of this method to a drinking water spiked with various quantities of nitrophenol was demonstrated and validated using UV photometric determination method at $\lambda = 398$ nm for 4-NP.

Keywords: multiple pulsed amperometry, graphite-epoxy composite, 4-nitrophenol.

1. Introduction

Priority phenols consists of a number of substituted phenolic compounds included halogenated and nitrated phenols, e.g., nitrophenols (NPs). Priority phenols are used/produced in several industrial processes, being commonly used as preservatives, disinfectants, in pulp processing, in the manufacture of pesticides and intermediars. Many priority phenols are known for their toxicity, carcinogenicity, and persistence in environment [1-3], and are now common pollutants found in water, sediments and soil. Based on the toxicity, stability and bioaccumulation, the European Union has set the „black list” of the dangerous substances that should be monitored in waters [4], which was included later in Water Framework Directive [5]. The severe toxicity of 4-nitrophenol (4-NP) requires the development of simple, sensitive and reliable determination method. Various methods for phenols derivatives are available, e.g., HPLC [6,7], gas chromatography [8,9] biosensors [10]. However, these methods require expensive and complicated instruments, high analytical cost, and are not suitable for in-situ measurements.

Electrochemical methods present a growing interest because of high sensitivity, good selectivity, rapid response, and the instruments are relatively simple with the possibility of miniaturization for in-situ measurement. Some electrochemical methods for the determination of phenol derivatives subjected to the chemically modified electrodes [11-13] and boron-doped diamond electrodes were reported [14-18]. Carbon-based materials such as graphite, carbon fibers, etc. have largely been used in the

last time as the conductive phase in composite materials suitable for electrochemical sensors [19-22]. Although phenols derivatives in general can be oxidized at numerous electrode materials, the oxidation at carbon-based solid electrodes produces phenoxy radicals which couple to form a passivating polymeric film on the surfaces of the electrodes. A simple method to renewing the electrode surface is based on the anodical treatment. Among the electroanalytical techniques presently used, multiple pulsed amperometry (MPA) has proved to be extremely sensitive for the detection of organic molecules because of the advantage of cleaning and reactivating the electrode surface during the electroanalytical detection [23]. This technique can be regarded as an *in-situ* anodical treatment of the working electrode.

The aim of the work is a comparative study subjected to the electrochemical detection of 4-nitrophenol (4-NP) at rotating spectral graphite disc (SG) and expanded graphite-epoxy composite (EG-Epoxy) electrodes using multiple pulsed amperometry (MPA) technique. The development and optimization of a MPA method for the determination of 4-NP in aqueous solution using both graphite based electrodes is described. Finally, the proposed method was applied to determine 4-NP in drinking water using EG-Epoxy electrode.

2. Materials and methods

All measurements were carried out using an Autolab potentiostat/galvanostat PGSTAT 12 (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 spectral graphite and EG-Epoxy composite electrodes were used as working electrodes. The spectral graphite (SG) was an OD 3mm disc electrode (ED), purchased from Electrocarbon Topol'cany (Bratislava, Slovakia).

The EG-Epoxy composite electrode was prepared from two-component epoxy resin (LY5052, Araldite) mixed with conductive expanded graphite (EG) fillers powder (Conductograph, SGL Carbon). To prepare EG-Epoxy composite electrode, the two parts of the epoxy were mixed together and the full amount of the EG was added in steps forming a thick paste. Then the epoxy 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. The prepared carbon-based composites showed good mechanical strength and low electrical resistance [22].

Prior to use, the working electrode with the surface area of 4 cm² was gradually cleaned, first polished with abrasive paper and then on a felt-polishing pad by using 0.6 and 0.3 μm alumina powder (Metrohm, Switzerland) in distilled water for 5 minutes and rinsing with distilled water.

0.1 molL⁻¹ stock solutions of 4-nitrophenol (4-NP) were prepared using distilled water. The supporting electrolyte was phosphate buffer (PBS) with the pH of 7.33, which was prepared by dissolving 1.84 g of NaH₂PO₄, 19.1 g of Na₂HPO₄ and 9 g of NaCl in distilled water and diluting to 1 liter. All reagents were analytical grade. Analytical curves were obtained by the standard addition method.

3. Results and discussion

The multiple pulsed amperometry (MPA) applying for rotating spectral graphite disc (SG) and expanded graphite-epoxy composite (EG-Epoxy) electrodes was testing to improve the detection properties of these electrodes for the quantification of phenols derivatives, i.e., 4-NP in aqueous solution. Based on cyclic voltammograms obtained in PBS supporting electrolyte of pH=7.33 (the data are not shown here), the detection potential (E_{det}) for the phenol derivatives were found to be 1.1 V vs. Ag/AgCl for 4-NP, the potential value at which the oxidation of 4-NP occurred. The previous detection tests using linear scan voltammetry with static electrode and chronoamperometry with rotating disc electrode showed that adsorption processes of phenol derivatives occurred on electrodes with electrode fouling and electrode activity loss, or quite electrode passivation. From this reason, the detection experiments using SG and EG-Epoxy electrodes were carried out using MPA, which offers the advantage of cleaning and reactivating electrode surface without mechanical polishing and during the electrochemical measurements [23].

A typical batch chronoamperometry obtained by MPA and adding 4-NP to PBS supporting electrolyte of pH=7.33 using rotating disc spectral graphite electrode is shown in

Figure 1. The applied potential was set at +1.1 V vs. Ag/AgCl and the response time was about 600 seconds. The calibration plots of current versus 4-NP concentration was linear over the concentration range of 0.1 to 0.7 mM, with the correlation coefficient higher than 0.99. The value of cleaning potential (E_{clean}) was +1.4 V vs. Ag/AgCl for time duration of 0.05 seconds.

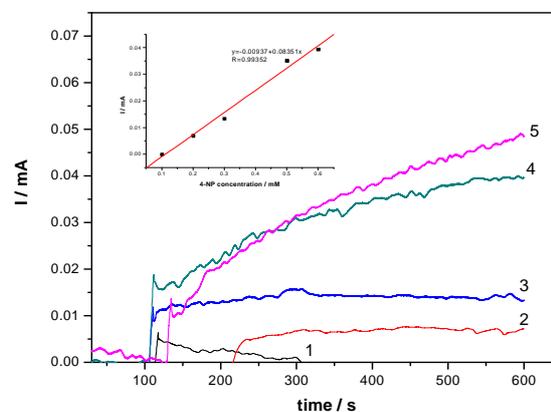


Figure 1. Multiple pulsed amperograms (MPAs) of the rotating SG disc electrode recorded at +1.1 V vs. Ag/AgCl in PBS supporting electrolyte and in the presence of different concentrations of 4-NP: 1-0.1 mM; 2-0.2 mM; 3-0.3 mM; 4-0.6 mM; 5-0.7 mM. Inset: The calibration plots of the currents recorded after 600 seconds vs. 4-NP concentration ($E_{clean}=1.4$ V vs. Ag/AgCl, $t_{clean}=0.05$ s)

A typical multiple pulsed hydrodynamic chronoamperometry (Figure 2) was obtained by successively adding 4-NP to phosphate buffer supporting electrolyte. The detection potential (E_{det}) was set at +1.1 V vs. Ag/AgCl and the response time was about 100 seconds. The cleaning potential (E_{clean}) was +1.4 V vs. Ag/AgCl for the time duration of 0.15 seconds. The calibration plots of current versus 4-NP concentration was linear over the concentration range of 1 to 4 mM, with the correlation coefficient of 0.99893, and the sensitivity of this chronoamperometric assessment was 0.00684 mA·mM⁻¹. The analytical detection performance was lower under these conditions of continuous multiple pulsed amperometry, probably due to the more pregnant adsorption effect on the electrode, which led to the activity loss.

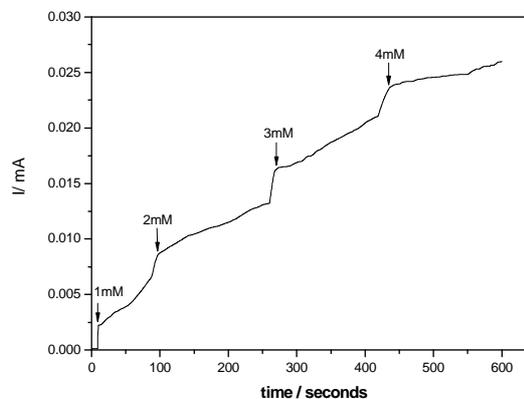


Figure 2. Multiple pulsed hydrodynamic amperogram of the rotating SG disc electrode in PBS supporting electrolyte and in the presence of different 4-NP concentrations; E_{det} was +1.1 V and E_{clean} was +1.4 V vs. Ag/AgCl; t_{det} was 0.05 seconds and t_{clean} was 0.15 seconds

Figure 3 shows the analytical performance of EG-Epoxy electrode for the quantification of 4-NP under the similar conditions of the rotating SG disc electrode application. Under the conditions of EG-Epoxy use for 4-NP determination, the analytical performance subjected to the electrode sensitivity and the correlation coefficient was much better versus rotating SG disc electrode performance. The explanation could be the electrode structure, which influenced the adsorption process of oxidation product.

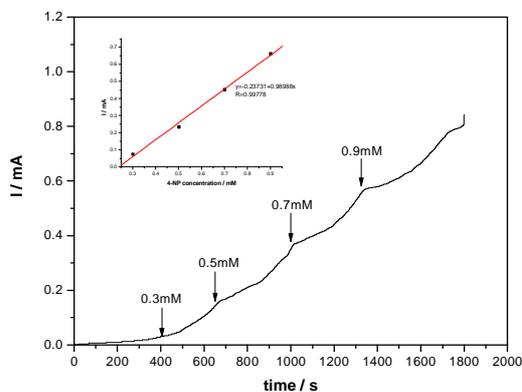


Figure 3. Multiple pulsed hydrodynamic amperogram of EG-Epoxy electrode in PBS supporting electrolyte and in the presence of different 4-NP concentrations; E_{det} was +1.1 V and E_{clean} was +1.4 V vs. Ag/AgCl; t_{det} was 0.05 seconds and t_{clean} was 0.15 seconds; Insert: The calibration plot of the currents recorded at E_{det} +1.1 V vs. Ag/AgCl vs. 4-NP concentration

To receive reproducible and better responses, the electrode should be pulsed adequately at a certain positive potential to remove any adsorbed species. The electrode sensitivity was twice better under the conditions of oxidation potential of +1.4 V vs. Ag/AgCl, by comparison with oxidation potential of +1.2 V vs. Ag/AgCl. The oxidation potential at which the electrode was pulsed to remove the adsorbed species was limited by the electrode stability, because at the more positive potential value the higher oxygen evolution occurred, which influenced the electrode surface peculiarities. Also, it has to be noticed that the t_{clean} =0.05 seconds led to better detection characteristics versus a longer time of oxidation. Based on the above-presented results, the optimal parameters for oxidation step for the MPA method for the 4-NP quantification at SG and EG-Epoxy electrodes was established, such as E_{clean} +1.4 V vs. Ag/AgCl and t_{clean} =0.05 seconds.

The comparative performances of the electrochemical quantifications of 4-NP on rotating SG disc and EG-Epoxy electrodes using batch and continuous MPA technique are gathered in Table 1.

Based on the presented results, taking into account the better sensitivity, the lowest limit of detection and simpler handling, the application of EG-Epoxy electrode for the electrochemical quantification of 4-NP using continuous MPA technique is more suitable.

A recovery test was also performed by analyzing three parallel tap water samples for two spiked levels of 4-NP. This test was run in PBS buffer as supporting electrolyte and the results are summarized in Table 2. Finally, the

results obtained by this method were compared with that obtained by means of a conventional UV spectrometric determination method at a certain wavelengths ($\lambda = 398$ nm for 4-NP). By comparison the results to evaluate the precision of this electrochemical method using EG-Epoxy electrode by continuous application MPA, it can be concluded that the results obtained by the two methods are very closely and the accuracy of the proposed amperometric method is good.

TABLE 1. The electrochemical detection results of 4-NP using MPA technique

| Electrode | MPA type | MPA parameters | Concentration range/mM | Electrode sensitivity/ mA μM^{-1} |
|--------------------|------------|--|------------------------|---|
| SG electrode | Batch | E_{det} +1.1 V E_{clean} +1.4; t_{clean} =0.05 s | 0.1-0.7 | $9.58 \cdot 10^2$ |
| SG electrode | Continuous | E_{det} +1.1 V E_{clean} +1.4; t_{clean} =0.05 s | 1-4 | $7.5 \cdot 10^3$ |
| SG electrode | Continuous | E_{det} +1.1 V E_{clean} +1.4; t_{clean} =0.15 s | 1-4 | $6.84 \cdot 10^3$ |
| EG-Epoxy electrode | Continuous | E_{det} +1.1 V E_{clean} +1.4; t_{clean} =0.15 s | 0.3-0.9 | 0.988 |

TABLE 2. Recoveries of 4-NP in drinking water samples using continuous MPA method at EG-Epoxy electrode

| Spiked/ $\text{mg} \cdot \text{L}^{-1}$ | Recovery, % (n=3) |
|---|-------------------|
| | 4-NP |
| 40 | 94.6 |
| 120 | 92.4 |

Figure 4 shows the oxidation rate of 4-NP during 6h, using MPA method, recorded for both types of electrode. The 4-NP decay corresponds to ca. 31.25% in the case of EG-Epoxy electrode, respective 63.75% for rotating SG disc electrode. Considering the detection results previously obtained, this result can be explained by both that the EG-Epoxy electrode exhibited a higher sensitivity for the phenols derivatives oxidation than rotating SG disc electrode, with stronger electrode fouling effect and the adsorption process was avoided by rotating of SG disc electrode.

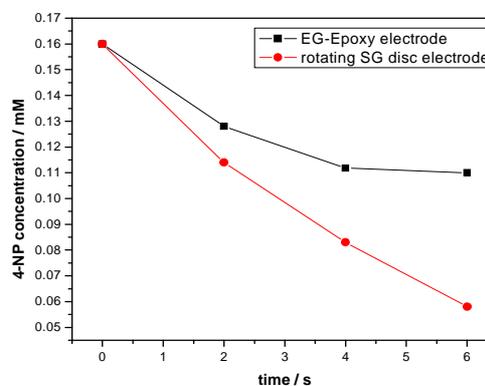


Figure 4. Variation of 4-NP concentration with the oxidation time, using MPA technique, of EG-Epoxy electrode and respective, rotating SG disc electrode, in PBS supporting electrolyte: $C_{4\text{-NPi}} = 22$ mg/L, $E_{\text{ox}} = 1.1$ V; $E_{\text{clean}} = 1.4$ V; $t_{\text{ox}} = 0.05$ s; $t_{\text{clean}} = 0.15$ s

4. Conclusions

The multiple pulsed amperometry detection with rotating spectral graphite disc and expanded graphite-epoxy composite electrodes can be used to determine 4-nitrophenol. The MPA detection method is simple and time saving because the cleaning step occurs simultaneously during the measurement. The optimized conditions were examined by varying the cleaning potentials and times.

Based on the analytical performances subjected to the lowest limit of detection and electrode sensitivity the EG-Epoxy electrode was found to be better versus rotating SG disc electrode. The good recovery degree of both organic pollutants from drinking water demonstrate the possibility of the practical utility of EG-Epoxy electrode using MPA technique for 4-NP detection. Also, both types of electrodes can be applied for the removal of 4-NP from water by electrochemical oxidation, the better results were obtained for rotating SG disc electrode.

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