ENGINEERING PERSPECTIVE

Research Paper

Electrochemical Behavior and Voltammetric Determination of 2-Nitrophenol on Glassy Carbon Electrode Surface Modified with 1-Amino-2-Naphthol-4-Sulphonic Acid

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Abstract

2NP is among the priority pollutants for the environmental ecosystem and poses a threat to the health of living things by mixing in wastewater. Therefore, the 2NP determination is important. In this study, the glassy carbon (GC) electrode surface was modified with 1-amino-2-naphthol-4-sulfonic acid (ANSA). The electrochemical behavior and voltammetric determination of 2-nitrophenol (2NP) on the modified surface (ANSA-GC) was performed. Firstly, it was decided that the supporting electrolyte medium suitable for 2NP determination was Britton-Robinson (BR) buffer and the effect of pH change on the reduction peak of 2NP in this environment was investigated. The effect of changing scan rate on the reduction peak of 2NP was examined and this study showed that the reduction process of 2NP on the ANSA-GC modified electrode surface was diffusion controlled process. For 2NP determination, two linear working ranges with two different slopes, 1.19×10^{-6}-1.66×10^{-4} M and 1.66×10^{-4}-1.14×10^{-3} M were obtained. LOD and LOQ values were calculated as 0.29 μM and 0.97 μM, respectively. Finally, lake water was used as the real sample, and 2NP was determined in this lake water. The experimental results showed that it can be used with a high accuracy and precision in the determination of 2NP with ANSA-GC modified electrode.

Keywords: Voltammetric determination; modification; electrode; 2-nitrophenol; toxic

1. Introduction

Nitrophenols are widely used as reagents for pesticide, herbicide and explosive production, and as intermediates in dye synthesis [1,2]. These organic compounds are considered by the US Environmental Protection Agency (USEPA) as one of the primary toxic pollutants. 2-nitrophenol (2NP) is among the most toxic and persistent organic pollutants of industrial wastewater. USEPA lists 2NP as "priority pollutant" [3]. 2NP shows high toxicity and/or mutagenicity to many living organisms, directly or through some of its catabolic metabolites [4].

It is important to determine nitrophenols, especially 2NP, with an exact and reliable method due to its negative effects on the ecosystem and living health. In the literature, there are determinations of nitrophenols using methods such as spectrophotometry [5] fluorescence [6] gas chromatography [7] capillary electrophoresis [8] and high-performance liquid chromatography [9]. However, these methods are costly and time consuming, as these methods have many processing steps and require pre-treatment. In addition, the cost of the devices needed for these methods is another disadvantage. On the other hand, electrochemical methods have useful features such as low cost, ease of use, short response time, portable simple devices and high sensitivity and selectivity. For this reason, the determination of 2NP made by electrochemical methods are preferred [10-12].

In this study, an alternative detection method for 2NP determination has been developed. The electrochemical behavior of 2NP was examined with the sensor prepared for this purpose. In order to examine the analytical performance of the sensor for 2NP determination, parameters such as linear working range and detection limit were figured out. Finally, the 2NP determination in lake water was successfully carried out to show the applicability of the sensor in real sample.

2. Experimental Method

2.1 Chemicals

All chemicals were of analytical reagent grade. ANSA, 2NP, phosphoric acid, potassium chloride (KCl) used in the study were purchased from Sigma-Aldrich. Sodium acetate, acetic acid (glacial), sodium phosphate monobasic, sodium phosphate dibasic, boric acid and sodium hydroxide were purchased from Merck.

The stock solution of 2NP was prepared at a concentration of 1×10^{-2} M using ultrapure water. The 1×10^{-4} M ANSA solution in the presence of 0.1 M KCl solution was used for coating the GC electrode.

2.2. Electrochemical Measurements

Electrochemical experiments were carried out using a computer-controlled potentiostat (CHI brand, 660B model) with a three-electrode system. GC electrode (BAS, MF-2012, geometric area 0.071 cm^2) as working electrode, platinum wire as counter electrode (BAS, MW-1032) and Ag/AgCl/KCl(sat.) as reference electrode (BAS, MF-2052) were used. Cyclic voltammery (CV) and differential pulse voltammery (DPV) techniques were used in electrochemical measurements. The ultrasonic bath used in cleaning the electrode surfaces was the Bandelin brand Sonatax super model. The digital pH meter used for pH adjustments of the prepared solutions was Thermo branded Orion 5 Star model.

2.3. Electrochemical Techniques

The CV technique was used for the modification of GC electrode surfaces with ANSA molecule. This process was carried out for 20 cycles between -1.5 V and 2 V and at a scan rate of 100 mVs^{-1} (vs Ag/AgCl(KCl sat.)). DPV technique was used to examine the electrochemical behavior of 2NP on the ANSA-GC modified electrode surface. In this technique, the amplitude was 0.05 V, the pulse width was 0.05 s, and the pulse period was 0.2 s.

3. Results and Discussion

3.1. Preparation of ANSA-GC modified electrode

Before the modification process, the surfaces of the GC electrodes were cleaned. In the cleaning process, GC electrode surfaces were polished with 0.1 and 0.05 micron alumina suspensions and cleaning pad, respectively. Afterwards, these were sonicated in pure water for 15 minutes and rinsed with pure water. The cleaned GC electrodes were immersed in 1×10^{-4} M ANSA solution prepared in 0.1 M KCl. The ANSA film was deposited on the GC electrode surface using the CV technique between -1.5 V and 2 V and at a scan rate of 100 mVs^{-1} (vs. Ag/AgCl(KCl sat.)) for 20 cycles. The multi-cyclic voltammograms (CVs) obtained were shown in Figure 1. Reduction peaks of ANSA were seen at -0.7 V and +0.2 V, and the peak currents increase with the increase in the number of cycles. The current of the oxidation peak obtained in the first cycle at about 0.1 V did not change current value with the increase in the number of cycles. From the tenth cycle, a shoulder-

shaped oxidation peak was observed at approximately +1.4 V with increasing number of cycles.
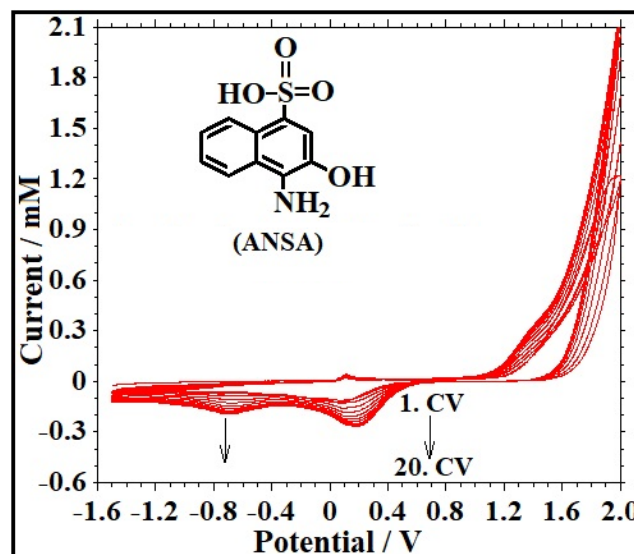

Figure 1. Multiple cyclic voltammogram showing the electrochemical deposition of 1×10^{-4} M ANSA prepared with 0.1 M KCl solution on the GC electrode surface.

3.2. The effect of support electrolyte and its pH on the reduction peak of 2NP

The supporting electrolyte's type and its pH values influence the potential and current of the redox peaks of the analytes [13]. To examine the effect of the supporting electrolyte type on the reduction peak of 2NP, Britton-Robinson buffer (BR) pH 2.0 and pH 6.0, phosphate buffer pH 4.5 and pH 7.0 (PBS), pH 4.5 acetic acid/acetate (HAc/NaAc) buffer and pH 2.0 H$_3$PO$_4$ solution were used. The reduction peaks of 2×10^{-4} M 2NP in these solutions were shown in Figure 2A. The cathodic peak currents of 2NP in these medias were obtained 19.55 μM, 7.99 μM, 14.71 μM, 8.079 μM, 14.30 μM and 17.26 μM, respectively. The cathodic peak current was found to be high in acidic medias, and the highest peak current was obtained in pH 2.0 BR buffer media. Therefore, 2NP determination with ANSA-GC electrode was found appropriate in BR buffer solution.

In order to examine the effect of the change in the pH value of the support electrolyte media on the cathodic peak of 2NP, the reduction peaks of 2×10^{-4} M 2NP in BR buffer solutions prepared with pH values of 1.0, 2.0, 3.0, 4.0, 5.0 and 6.0 were obtained and shown in Figure 2B. Figure 2C showed the peak potential and peak current change with pH value. The highest cathodic peak current of 2NP was obtained in pH 2.0 BR buffer solution. After pH 2.0, it was observed that the peak current decreased as the pH value increased. For this reason, it was decided that the support electrolyte medium suitable for the determination of 2NP with ANSA-GC electrode was pH 2.0 BR buffer. The relationship between pH and potential was obtained by the equation $E(V)= -0.0574pH-0.4840$ ($R^2=0.9990$). This case showed that the reduction of 2NP was directly related to protons. Using the Nernst equation [14] known as dEp/dpH = 2.303mRT/nF, the value of "m/n"

was calculated to be 0.97 (approximately 1). This result showed that the number of electrons and protons were equal in the reduction of 2NP. In Nernst equation, T is the temperature (298.15 K), R is the gas constant (8.314 JK^{-1}mol^{-1}), F is the faraday constant (96485 C mol^{-1}), m and n are the numbers of protons and electrons, respectively.
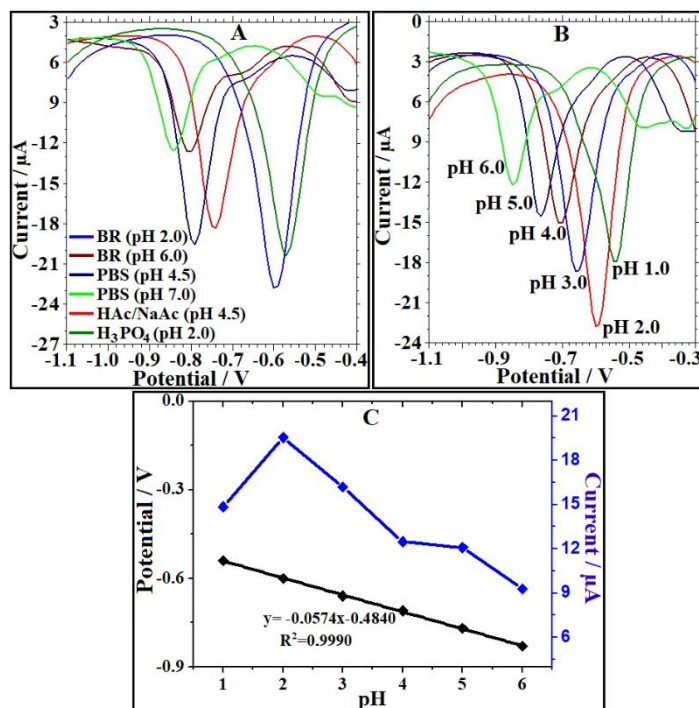

Figure 2. DPVs of 2×10^{-4} M 2NP in different support electrolyte medias (A), DPVs of 2×10^{-4} M 2NP in different pH values of BR buffer (B), Plot of reduction peak current and potential values of 2×10^{-4} M 2NP versus pH values of BR buffer (C).

3.3. The effect of scan rate on the cathodic peak of 2NP

CVs of 2×10^{-4} M 2NP were obtained at scan rates varying between 10-400 mVs^{-1} and were shown in Figure 3A. According to the changing scan rate values, the cathodic peak current values of 2NP were given in Figure 3B and it was seen that the graph was not linear. This case showed that the reduction process of 2NP was diffusion controlled [15]. In Figure 3C, Ipc graph against $v^{1/2}$ was given. The equation of this graph obtained linearly is Ipc (µA) = $25.427v^{1/2}$ (Vs^{-1})$^{1/2}$ +1.367 (R^2=0.9994). The linearity of this graph also showed that the reduction process of 2NP was diffusion controlled [17-19]. In addition, the slope value of the logIpc graph (Figure 3D) drawn with respect to logv was obtained as 0.4085. The fact that this value was close to the theoretical value of 0.5 also confirms that the process was diffusion controlled [15, 16].
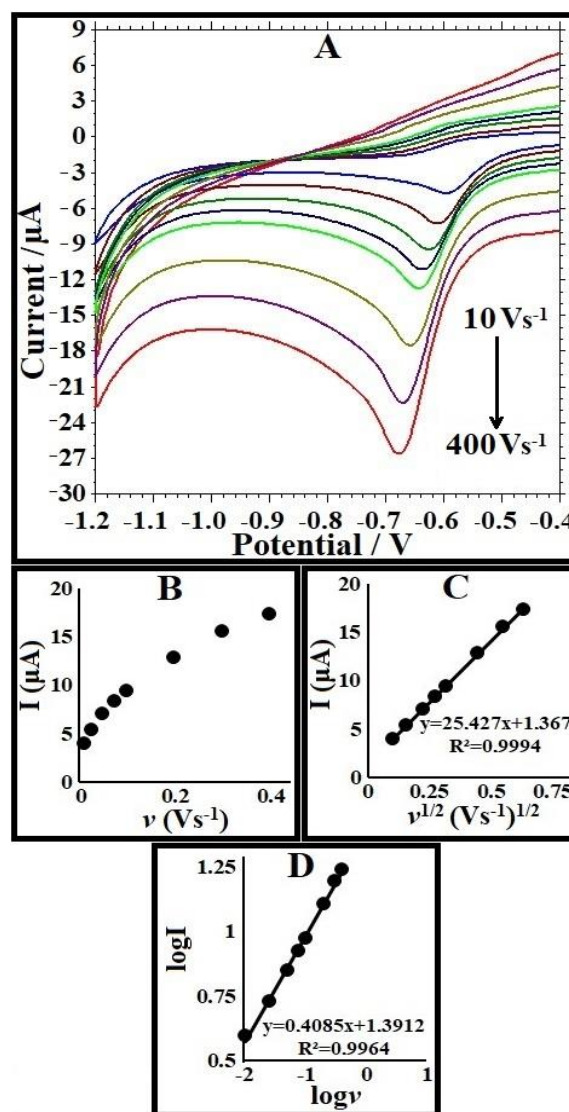

Figure 3. A. CVs of 2×10^{-4} M 2NP taken at 10, 25, 50, 75, 100, 200, 300 and 400 mVs^{-1} scan rate on the ANSA-GC modified electrode surface, B. Ipc versus v, C. Ipc graph against $v^{1/2}$, D. Plot of logIpc versus logv.

3.4. Determination of working range, LOD and LOQ values

2NP additions were made on the support electrolyte to determine the working range of the ANSA-GC modified electrode in the determination of 2NP. Voltammograms and calibration graph were given in Figure 4. A linear working range with two different slopes of 1.19×10^{-6}-1.66×10^{-4} M and 1.66×10^{-4}-1.14×10^{-3} M were obtained. LOD and LOQ values were calculated as 0.29 and 0.97 µM, respectively. LOD and LOQ were calculated using the formulas 3S/m and 10S/m, respectively, with the standard deviation value of S and the slope value of m [16].
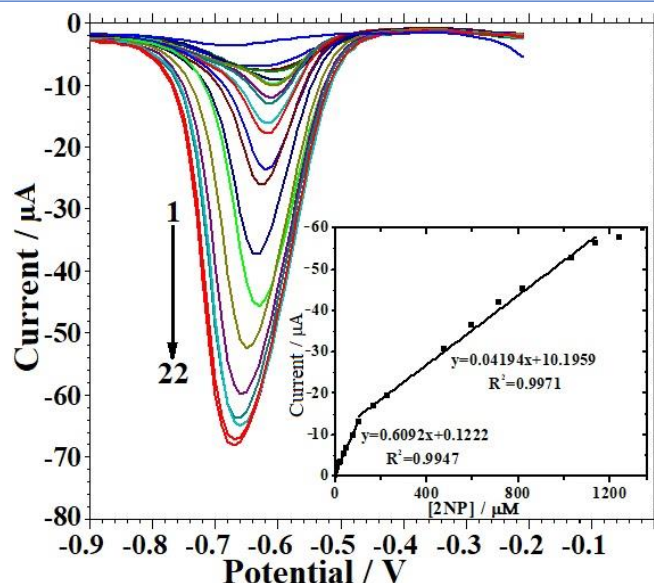
Figure 4. DPVs and calibration graph obtained with ANSA-GC modified electrode by adding 2NP on the support electrolyte. 1 → 22: 0, 1.19, 1.6, 2.64, 3.65, 8.82, 18.67, 24.50, 38.28, 51.67, 77.37, 101.7, 166.6, 230.6, 478.6, 597.9, 714.2, 817.7, 1034.3, 1138.8, 1240.9, 1340.7 μM.

3.5. Repeatability Study

The cathodic peak of 2×10^{-4} M 2NP was obtained with five repeated experiments on the ANSA-GC modified electrode in order to examine the repeatability of the modified electrode. Percent relative standard deviation (RSD%) ($S/X.100$) of the peak currents was calculated as 3.50%. This value showed that the ANSA-GC modified electrode was good repeatability in 2NP determination.

3.6. Determination of 2NP in real sample

Water samples were taken from Mogan Lake in Ankara, Turkey in order to make the actual sample analysis. First, the same volumes of water sample and BR buffer solution were mixed. In order to understand whether there is 2NP in the lake water; DP voltammograms of pH = 2.0 BR buffer and lake water sample mixture were obtained. Obtaining almost the same voltammogram for these two samples showed that 2NP was not found in lake water. For this reason, 2NP was added to the lake water sample at a concentration of 10 μM, and then 2NP additions were continued and the determination was carried out using the standard addition method. The use of the DPV technique in the quantitative determination of 2-NP in real samples by electrochemical methods is quite common [20-23]. Voltammograms obtained are given in Figure 5. In the results of the experiments repeated three times, the % RSD related to the repeatability and the % Bias values related to the accuracy of the method were obtained as 1.51 and 3.8, respectively. These values showed that the reproducibility and accuracy of 2NP determination with the proposed method is good.
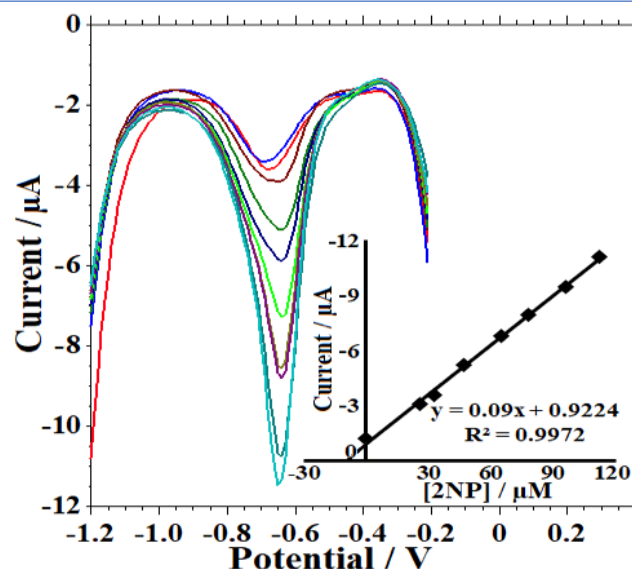

Figure 5. DPVs obtained with 2NP additions in lake water sample and calibration graph (1) pH 2.0 BR buffer (2) Lake water sample, (3) 2NP addition (determined 10 μM 2NP), (4) 26 μM, (5) 33 μM, (6) 47 μM, (7) 65 μM, (8) 78 μM, (9) 96 μM, and (10) 112 μM 2NP.

4. Conclusion

In this study, the GC electrode surface was modified with 1-amino-2-naphthol-4-sulfonic acid molecule. The 2NP determination was successfully performed with the prepared sensor (ANSA-GC). The sensor showed a wide linear working range for 2NP determination. In addition, the modification process of ANSA-GC electrode was extremely simple and fast. With the ANSA-GC electrode, 2NP determination was provided with high sensitivity, short measurement time, repeatability, high accuracy and good analytical performance. In addition, the determination of 2NP in lake water was successfully performed by using ANSA-GC electrode.

This is the extended version of the study presented on 3rd ERASMUS International Academic Research Symposium (March, 2020).

Conflict of Interest Statement

The author declares that there is no conflict of interest

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