



Flow electrochemical determination of 4-nitroaniline transformation in real sample using natural phosphate modified carbon paste electrode

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ABSTRACT

A Cyclic Voltammetry (VC) method for the determination of trace amounts of 4-Nitroaniline (4-NA) at carbon paste electrode modified with natural phosphate (NP-CPE) is proposed.

The optimal potential window of wide range from -1V to 1V was selected. The electron transfer kinetics of the NP-CPE in the detection of analyte was determined by the scan rate effect and concentration variation studies. The scan rate effect showed the electrode process is adsorption controlled. The redox peak currents represented a linear dependence on 4-NA concentration from 0.36 mM to 1.81 mM. The results showed that the NP-CPE exhibited excellent electro catalytic activity to 4-NA. This electrochemical sensor shows an excellent performance for detecting 4-NA. The sensor was successfully applied to the determination of 4-NA in a real sample the tap water. © 2015 Trade Science Inc. - INDIA

KEYWORDS

Modified electrode;
 Cyclic voltammetry;
 Natural phosphate;
 4-Nitroaniline.

INTRODUCTION

4-Nitroaniline ($C_6H_6N_2O_2$, 4-NA), an important nitroaromatic compound, has been widely used as precursor in chemical synthesis of various azo dyes, antioxidants, pesticides, antiseptic agents, poultry medicine, fuel additives as well as an important corrosion inhibitors^[1,2]. However, the chemical stability and toxicity also makes them hazardous^[3,4]. Its treatment and disposal has emerged as an important environmental concern. Furthermore, it shows toxicity, mutagenicity and carcinogenicity towards different experimental model organisms^[5-8]. Consequently, many developed and developing countries have enlisted 4-NA as priority pollutant and imposed

restrictions on its production, usage and disposal etc.^[1]. However, due to extensive applications of 4-NA and its ortho-substituted derivatives e.g. 2,6-dichloro-4-nitroaniline, 2-methoxy-4-nitroaniline in past, several ecological niches have been identified to be severely contaminated with 4-NA and other aromatic amines^[9-12]. A 4-nitroaniline as a particularly prominent member of the family of isomeric nitroanilines has attracted much attention because of the specific effects of an electron withdrawing nitro group and an electron donating amino group being in para position of its aromatic system^[13-14]. In this work, we describe the electrochemical analysis of 4-NA on a natural phosphate modified carbon paste electrode (NP-CPE). The electrochemical charac-

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terization of adsorbed electroactive 4-NA was evaluated using cyclic voltammetric (CV).

EXPERIMENTAL

Instrument

Cyclic voltammetry were carried out with a voltalab potentiostat (model PGSTAT 100, Eco Chemie B.V., Utrecht, The Netherlands) driven by the general purpose electrochemical systems data processing software (voltalab master 4 software). The electrochemical cell was configured to work with three electrodes; using NP-CPE as the working, platinum plate for counter and saturated Calomel (SCE) as reference electrodes. The pH-meter (Radiometer Copenhagen, PHM210, Tacussel and French) was used for adjusting pH values.

Procedure

The initial working procedure consisted of measuring the electrochemical response at NP-CPE at a fixed concentration of 4-NA. Standard solution of 4-NA was added into the electrochemical cell containing 100 mL of supporting electrolyte. The mixture solution was kept for 20 s at open circuit and deoxygenated by bubbling pure nitrogen gas prior to each electrochemical measurement. The cyclic voltammetry was recorded in the range from -1 V to 1 V. Optimum conditions were established by measuring the peak currents in dependence on all parameters. All experiments were carried out under ambient temperature.

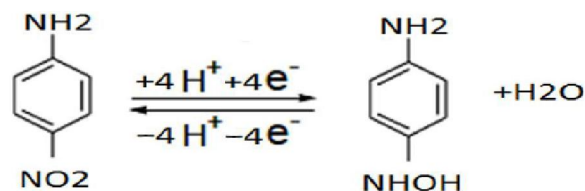
Electrodes

Modified electrodes were prepared by mixing a carbon powder and the desired weight of natural phosphate. The body of the working electrode for voltammetric experiments was a PTFE cylinder that was tightly packed with carbon paste. The geometric area of this electrode was 0.1256cm². Electrical contact was made at the back by means of a bare carbon.

RESULTS AND DISCUSSION

Preliminary voltammetric characterization

Preliminary voltammetric characterization the performance of the newly developed phosphate modified carbon paste electrode is based on the preconcentration of 4-NA from aqueous solution onto the surface of the modified electrode by adsorption onto the modifier surfaces. The probable electrochemical reactions of 4-NA has shown in the scheme.



Scheme : Mechanism of electrochemical redox reaction of 4-NA at NP-CPE

Figure 1 Shows a cyclic voltammograms (CV) in the potential range -1 V to 1 V recorded, respectively, for carbon paste and phosphate modified carbon paste electrode at 100mV.s⁻¹. The voltammograms take different forms. No peak is observed in the case of NP-CPE, it is recognized that carbon surface was effectively modified by natural phosphate.

A CV was used to investigate the electrochemical behavior of 4-NA on a NP-CPE in the buffer solution 0.1M Na₂SO₄ (pH=5) at scan rate of 100 mV.s⁻¹. The figure 2 shows, 4-NA exhibits a pair of redox waves on the NP-CPE with E_{pa} (anodic peak potential)=0.25 V and E_{pc} (cathodic peak potential)=0.15 V.

Influence of accumulation time

The dependence of peak current on the preconcentration time for 0.2 mmol L⁻¹ 4-NA was also investigated (Figure 3). The peak current increases with the increasing in the preconcentration time between 0 and 45 min above which it became nearly constant due to the surface saturation. Hence, a 7 min preconcentration time was used in all subsequent experiments.

Effect of scan rate

The effect of scan rate on the redox of 4-NA was examined in 0.1M Na₂SO₄ buffer solution of pH=5 as a supporting electrolyte. The Figure 4 shows both the anodic and the cathodic peak currents linearly increase with the scan rate over the range of

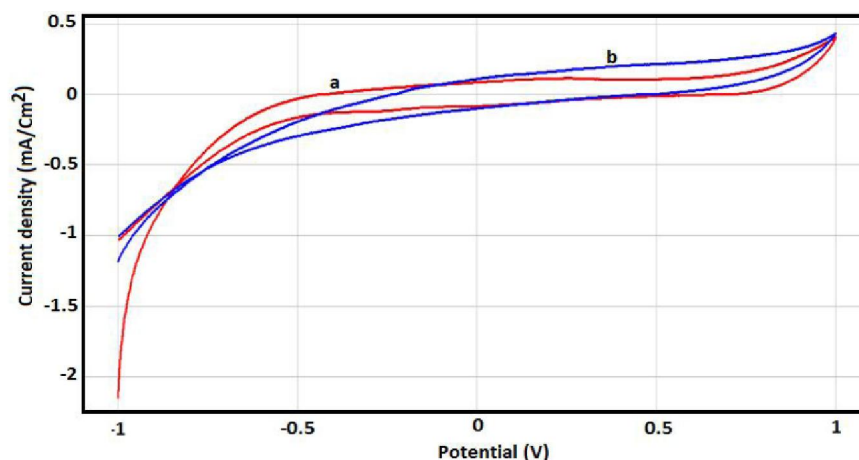


Figure 1 : Cyclic voltammograms recorded for bare CPE (a) and NP-CPE (b), in 0.1 M Na_2SO_4 (PH=5) at 100 mV/s

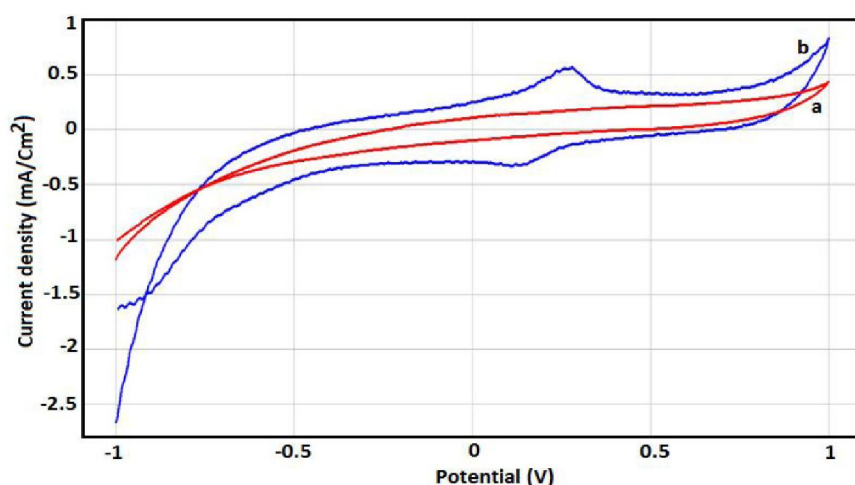


Figure 2 : Cyclic voltammograms recorded for 0.36 mM 4-NA at pH=5 at bare NP-CPE (a) and NP- CPE/4-NA (b), scan rate 100 mV/s

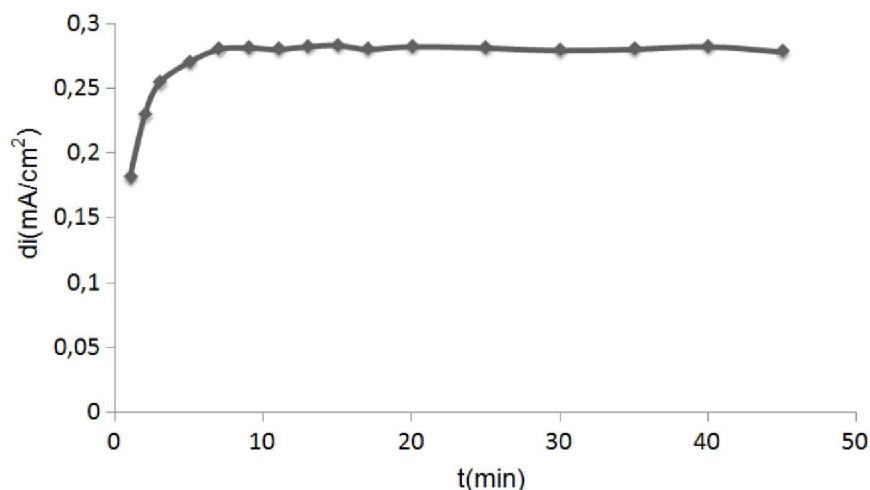


Figure 3 : Effects of accumulation time on 4-NA oxidation peak currents

100 to 200 mVs^{-1} , suggesting that the electron transfers for 4-NA at the phosphate modified CPE is adsorption controlled reaction. The cathodic peak shifted towards negative potential with increased in

scan rate, the anodic peak shifted towards positive potential with increased in scan rate. The Figure 5 shows the linear relationship between the scan rate anodic peak and cathodic peak currents of 4-NA at

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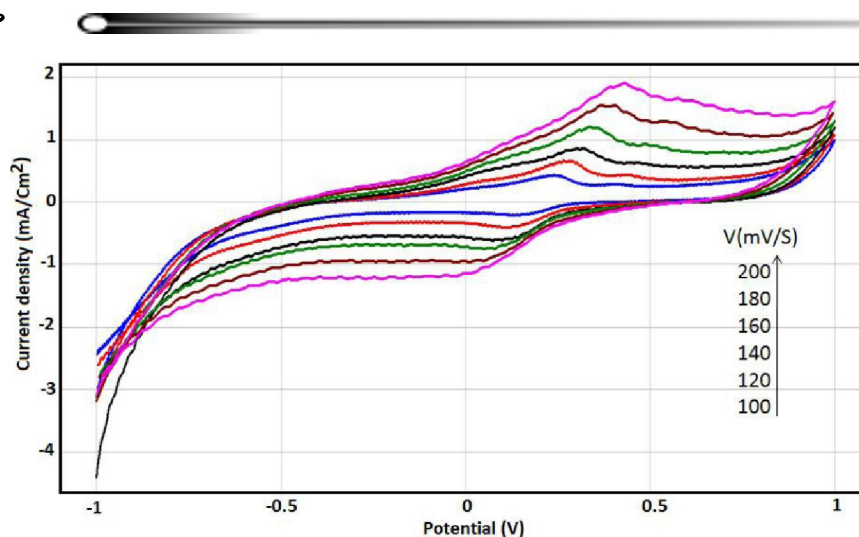


Figure 4 : Cyclic voltammograms acquired on NP-CPE with 1.08 mM 4-NA at different scan rates

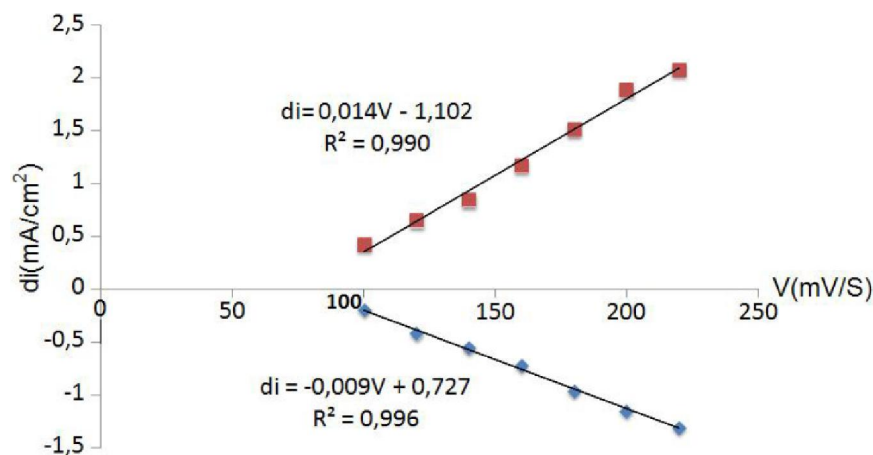


Figure 5 : Plot of peaks area versus scan rate

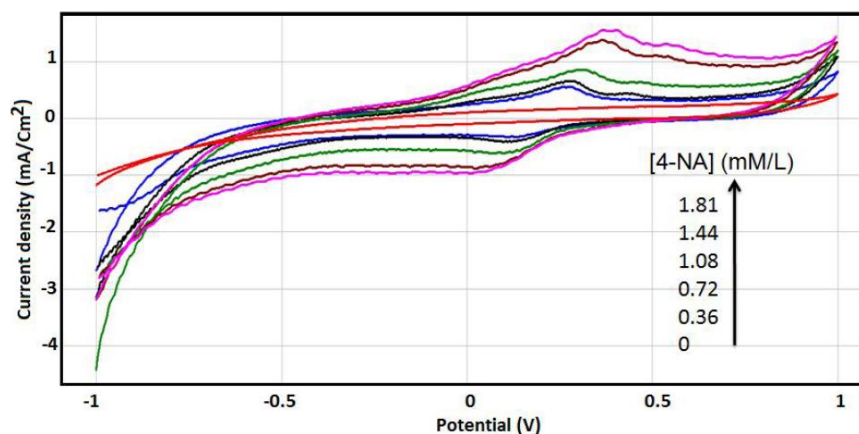


Figure 6 : Cyclic Voltammograms of different concentration of 4-NA at NP-CPE in 0.1 M Na_2SO_4 (PH=5), scan rate 100 mV/s

NP-CPE.

Effect of concentration of 4-nitroaniline

Figure 6 shows the CV curves of different concentration of 4-NA at NP-CPE was increased from 0.36 mM to 1.81 mM in 0.1 M Na_2SO_4 buffer solu-

tion at pH=5 at a sweep rate of 100 mVs^{-1} . Both the anodic and cathodic peak current increases linearly with the concentration of 4-NA and the plot of current versus concentration obeys Randles-Sevcik equation, which implies that the electrode process is adsorption controlled reaction. It was also observed

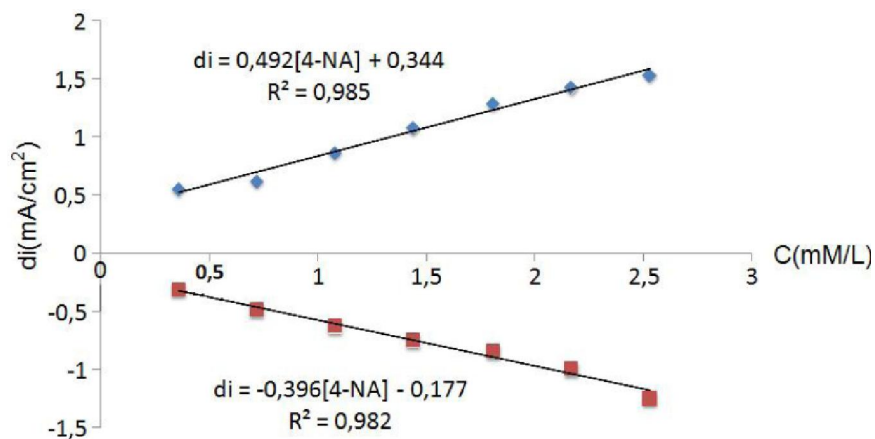


Figure 7 : Plot of peaks area versus added concentration of 4-NA

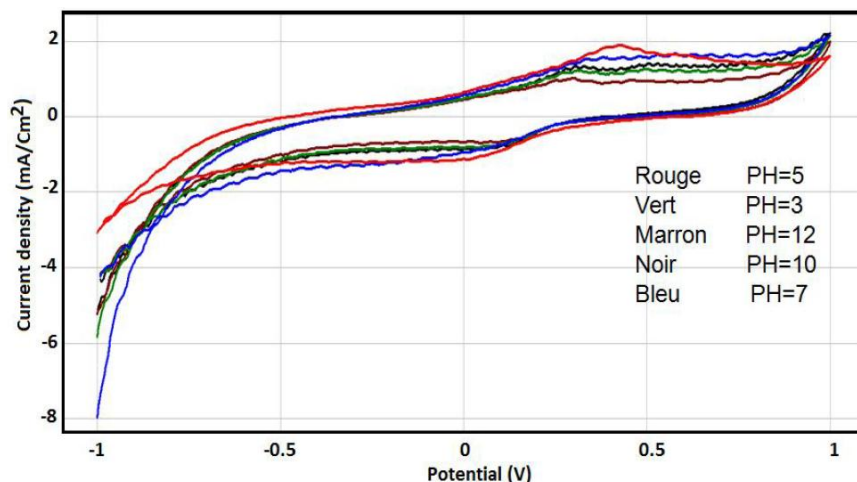


Figure 8 : Effect of pH on the redox of 4-NA at the NP-CPE

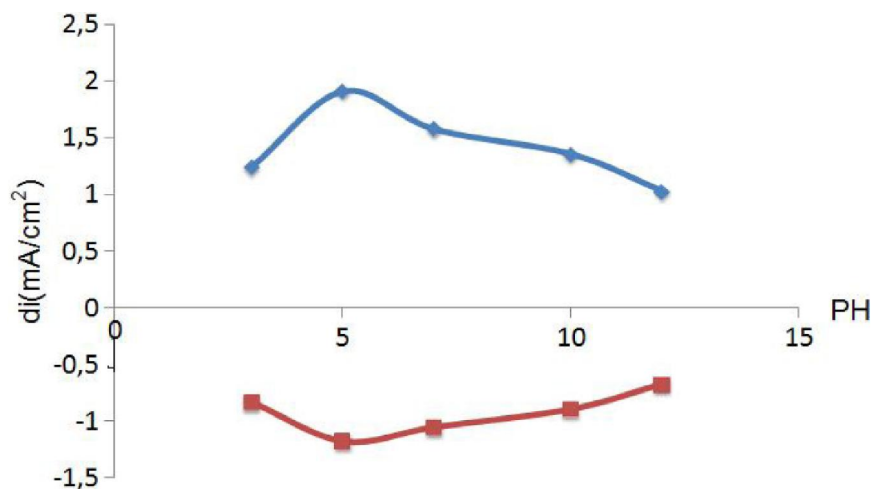


Figure 9 : Plot of the relationship between solution pH and the redox peak current

that the cathodic peak potential shift towards negative values and anodic peak potential shift towards positive side. This kind of shift in E_p in the cathodic and anodic direction with increasing concentration of the 4-NA indicates that the product of 4-NA mol-

ecules are adsorbed over the electrode surface. The Figure 7 shows the linear relationship between the concentration anodic and cathodic peak currents of 4-NA at NP-CPE.

Effect of pH variation of buffer solution

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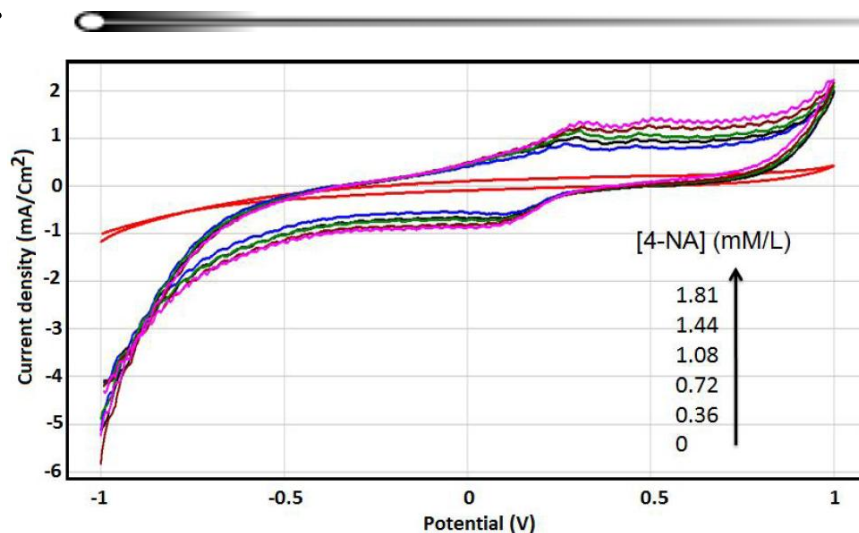


Figure 10 : Cyclic Voltammograms of different concentration of 4-NA at NP-CPE in 100ml tap water, scan rate 100 mV/s

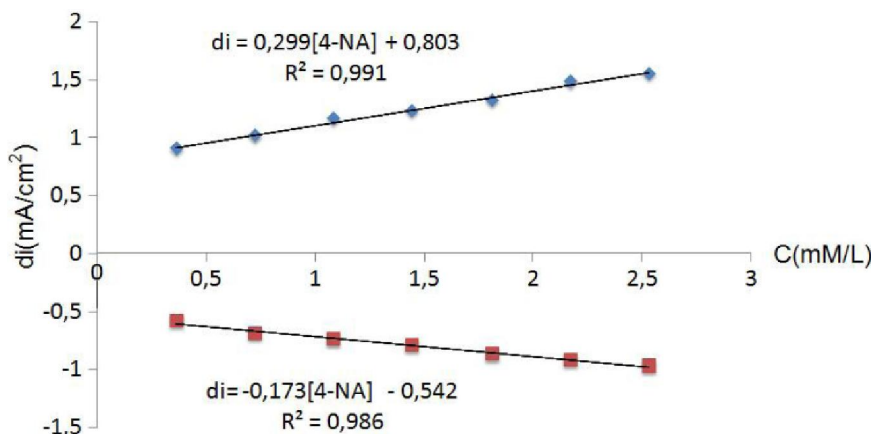


Figure 11 : Plot of peaks area versus added concentration of 4-NA

The effect of varying pH on the current response of NP-CPE at constant 4-NA concentration (2.17mM) is shown in Figs. 8 and 9. As can be seen, the peak current gradually increases with the increase of pH and reach a maximum value when the pH is 5. Further increase in the solution pH yields a gradual decrease in the 4-NA peaks current. The current decreases significantly in higher pH value.

ANALYTICAL APPLICATION

In order to evaluate the performance of the analytical methodology described above, the determination of 4-NA at NP-CPE was carried out in tap water. The analytical curves were obtained by CV experiments in supporting electrode (Figure 10). It was founded that the peaks currents increase linearly versus 4-NA added into the tap water (Fig-

ure 11).

CONCLUSION

We have demonstrated the use of phosphate modified carbon paste electrode for a greatly cyclic voltammetry sensing of 4-NA compounds. The modified electrode increased the amplitude of the current signal of 4-NA and produced good response.

The oxidation of this compound on the modified electrode occurs in an reversible manner. The modified electrode was successfully applied in tap water samples. The method could be improved in a simple way without introducing additional procedures and without increasing the time required for 4-NA quantification. The electrode construction was extremely simple and with low cost. No unstable or toxic reagents were used.

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