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Electrochemical studies and cyclic voltammetry of 3-nitroptalic acid at natural phosphate modified carbon paste electrode

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ABSTRACT

A Cyclic voltammetry (CV) method for the determination of trace amounts of 3-nitroptalic acid (3-NA) at carbon paste electrode modified with Natural Phosphate (NP-CPE) is proposed. The results showed that the NP-CPE exhibited excellent electro catalytic activity to 3-nitroptalic acid. The concentration of 3-NA and measuring solution pH was investigated. This electrochemical sensor shows an excellent performance for detecting 3-NA. The sensor was successfully applied to the determination of 3-NA in tap water with satisfactory results. The results indicate that this electrode is sensitive and effective for the determination of 3-NA. © 2014 Trade Science Inc. - INDIA

KEYWORDS

Modified electrodes;
Cyclic voltammetry;
Natural phosphate;
3-nitroptalic acid.

INTRODUCTION

Phthalic Acid, also called Benzenedicarboxylic Acid with formula $C_6H_4(COOH)_2$, is the name of any of three isomers^[1]. The ortho form (1,2-benzenecarboxylic acid) is called simply phthalic acid. It is a white crystals decomposing at 191°C and slightly soluble in water and ether^[2]. This compound is mainly produced and marketed in the form of its anhydride produced by the oxidation of orthoxylene and naphthalene^[3]. Its wide application is based on the ortho related carboxylic acid groups as their dehydration is highly reactive with broad processing conditions to produce various downstream products^[4]. It is used to make simple esters

widely used as plasticizers. It is used as in making unsaturated polyester resins, alkyd resins, polyester polyols, dyes and pigments, halogenated anhydrides, polyetherimide resins, isatoic anhydride and insect repellents. The meta form is isophthalic acid (1,3-benzenecarboxylic acid)^[5]. It is a white crystals subliming at 345°C slightly soluble in water, alcohol and acetic acid (insoluble in benzene). It is obtained by oxidizing meta-xylene with chromic acid, or by fusing potassium meta-sulphobenzoate, or meta-brombenzoate with potassium formate^[6-8]. IPA has excellent performance characteristics in coatings including excellent hardness, corrosion and stain resistance, hydrolytic stability of coatings and gel coats, excellent thermal stability and low resin

color^[9-11]. It is a key ingredient in FRP markets for such products as marine, automotive, and corrosion resistant pipes and tanks^[12]. Polyesters containing isophthalic acid are also used extensively in industrial coatings applications for home appliances, automobiles, aluminum siding, and metal office furniture^[13]. It used as an intermediate for polyesters, polyurethane resins, plasticizers.

The para form, known as terephthalic acid (1,4-benzenecarboxylic acid) is a combustible white powder insoluble in water, alcohol and ether; (soluble in alkalis), sublimates at 300°C^[14]. It can be produced by oxidizing caraway oil, a mixture of cymene and cuminol or by oxidizing para-derivatives of benzene with chromic acid^[15]. TPA has been used mainly as a raw material of polyester fiber but lately it has been exploited for various uses such as non-fiber field, PET-bottle, PET-film and engineering plastics and as poultry feed additives. Phthalic acid derivatives are also widely used to make dyes, medicine, and synthetic perfumes, pesticides, and other chemical compounds^[16].

The aim of the work reported here was to investigate the electrochemical properties of 3-NA on natural phosphate modified carbon paste electrode as well as the electrochemical characterization of electrodes by cyclic voltammetric technique.

EXPERIMENTAL

Reagent

3-Nitroptalic acid, sodium sulfate, and nitric acid were of analytical grade and from Aldrich.

A natural phosphate (NP) used in this work was obtained in the Khouribga region (Morocco). Stock solutions of 3-NA were prepared by dissolving 3-NA in deionized water. All preparations and dilution of solutions were made with deionized water.

Provisions were made for oxygen removal by bubbling the solution with azotes gas for about 5 min then the solution was blanketed with azotes gas while the experiment was in progress. For reproducible results, a fresh solution was made for each experiment.

Instrumental

Voltammetric experiments were performed using a voltalab potentiostat (model PGSTAT 100, Eco Chemie B.V., Utrecht, The Netherlands) driven by the general purpose electrochemical systems data processing software (votalab master 4 software) run under windows 2007. The three electrode system consisted of a chemically modified carbon paste electrode as the working electrode a saturated calomel electrode (SCE) serving as reference electrode, and platinum as an auxiliary electrode.

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.

Procedure

The initial working procedure consisted of measuring the electrochemical response at NP-CPE at a fixed concentration of 3-NA. Standard solution of 3-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 -1,6 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.

RESULTS AND DISCUSSION

Cyclic voltammetry

Figure 1 shows a cyclic voltammograms (CV) in the potential range -1,6 V to 1 V recorded for natural phosphate modified carbon paste electrode at 100 mV.s⁻¹. No peak is observed in the case of NP-CPE for the absence at 3-NA Figure 1a, contrary to the Figure 1b shows as 3-NA exhibits has

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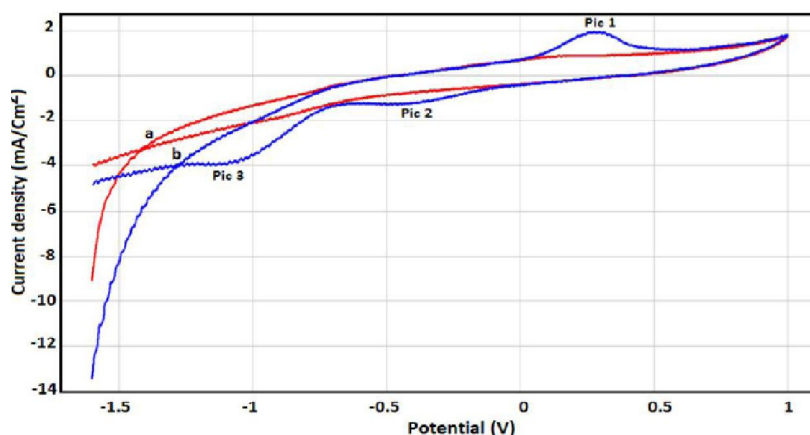
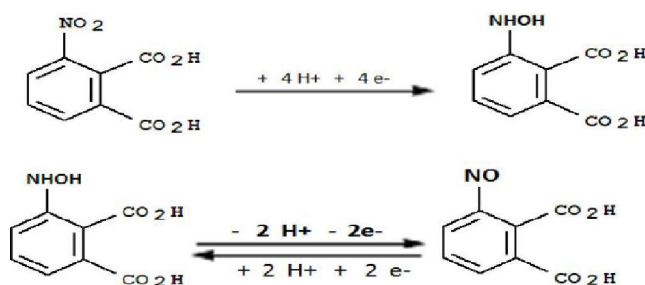


Figure 1 : CV recorded for 0.71 mM 3-NA at pH=5 at bare NP-CPE (a) and NP-CPE/3-NA (b), scan rate 100 mV/s, preconcentration time (tp)= 6min



Scheme 1 : Mechanism of electrochemical redox of 3-NA at NP-CPE

two reduction peaks at $E_{pc}(2) = -0.4\text{V}$ and at $E_{pc}(3) = -1\text{V}$, in addition to oxidation peak at $E_{pa}(1) = 0.28\text{V}$.

The scheme 1 shows the redox of 3-nitroptalic acid.

Influence of accumulation time

The effect of the accumulation time is investigated Figure 2, this significantly affects the oxidation peak (Pic 1) current of 3-NA. The peak current of 0.5 mmol

L^{-1} 3-NA increases greatly within the first 6min. Further increase in accumulation time does not increase the amount of 3-NA at the electrode surface owing to surface saturation, and the peak current remains constant. This phenomenon is due to the cavity structure of NP-CPE that improves the ability of the electrode to adsorb electroactive 3-NA. Maybe this is attributed to the saturated adsorption of 3-NA on the NP-CPE surface. Taking account of sensitivity and efficiency, accumulation time was 6 min in the following experiments.

Effect of scan rate

The influences of scan rate on the redox of 3-NA was examined in 0.1M Na_2SO_4 buffer solution of pH=5 as a supporting electrolyte. The Figure 3 shows both the anodic and the cathodic peak currents linearly increase with the scan rate over the range of 60 to 160 mVs^{-1} . The Figure 4 shows the linear relationship between the scan rate anodic peak and cathodic

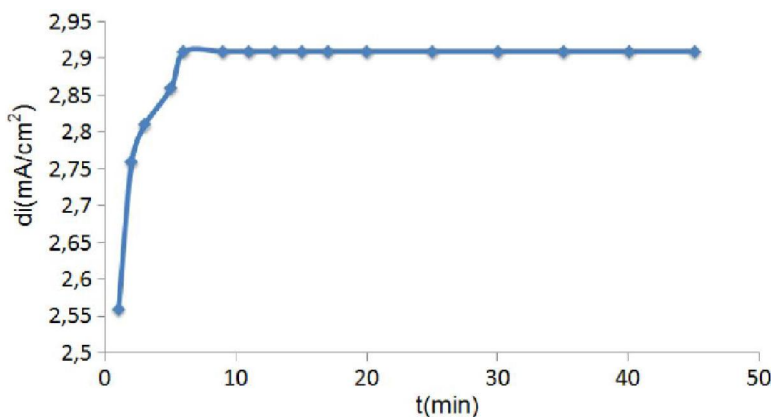


Figure 2 : Effects of accumulation time on oxidation peak currents of 0.5 mmol L^{-1} 3-NA at NP-CPE, supporting electrolyte is Na_2SO_4 0.1M (pH=5)

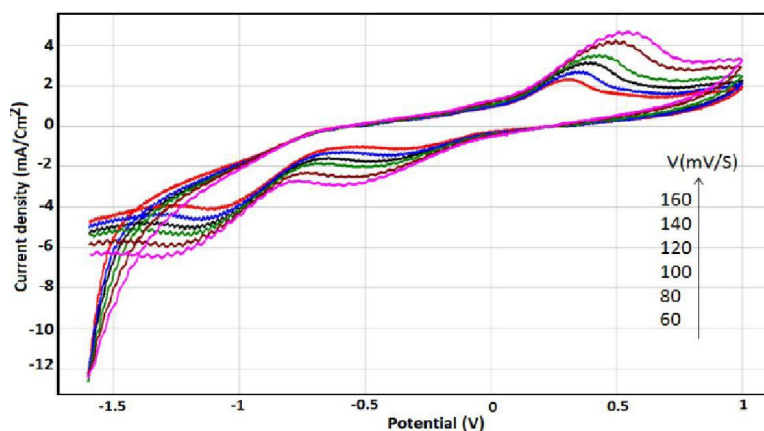


Figure 3 : CV acquired on NP-CPE with 1.2 mM 3-NA in the buffer solution (pH=5) at different scan rates

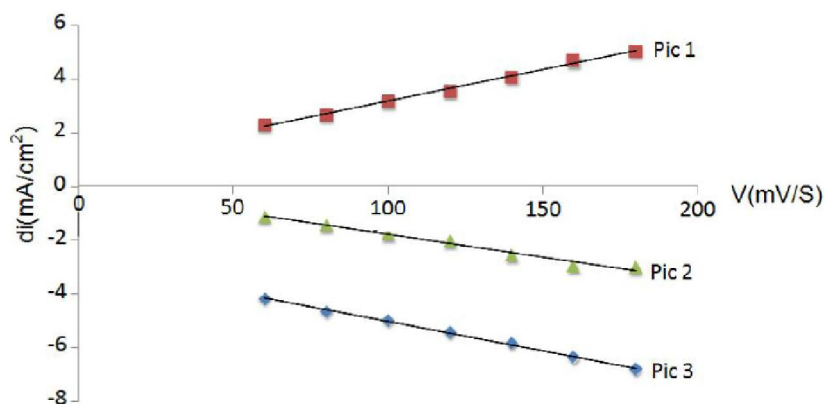


Figure 4 : Plot of peaks area versus scan rate

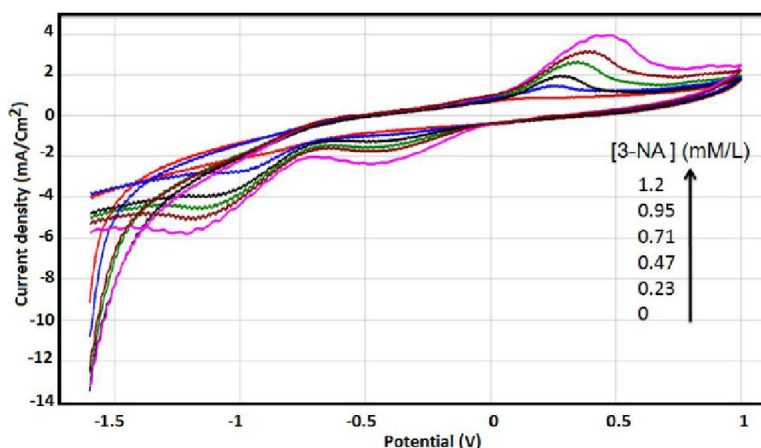


Figure 5 : Cyclic voltammograms of different concentration of 3-NA at NP-CPE in 0.1 M Na₂SO₄ (pH=5), Scan rate 100 mV/s

peak currents of 3-NA at NP-CPE. The linear regression equations:

$$I_{pa} (1) = 0.023V + 0.813 \quad R^2 = 0.995$$

$$I_{pc} (2) = -0.016V - 0.080 \quad R^2 = 0.981$$

$$I_{pc} (3) = -0.022V - 2.815 \quad R^2 = 0.997$$

Calibration graph

Figure 5 show the CV curves of different concentra-

tion of 3-NA at NP-CPE was increased from 0.23 mM to 1.2 mM in 0.1 M Na₂SO₄ buffer solution at pH=5 at a sweep rate of 100 mV s⁻¹. Both the anodic and cathodic peak current increases linearly with the concentration of 3-NA. The Figure 6 shows the linear relationship between the concentration anodic peak and cathodic peak currents of 3-NA at NP-CPE.

The linear regression equations:

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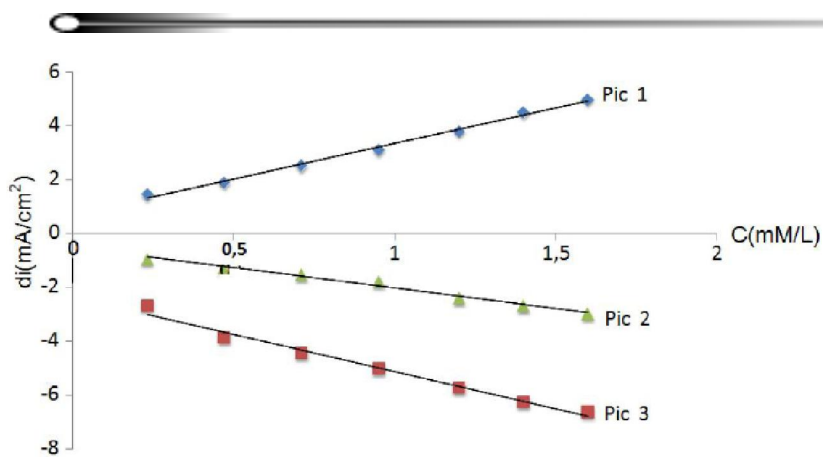


Figure 6 : Plot of peaks area versus added concentration of 3-NA

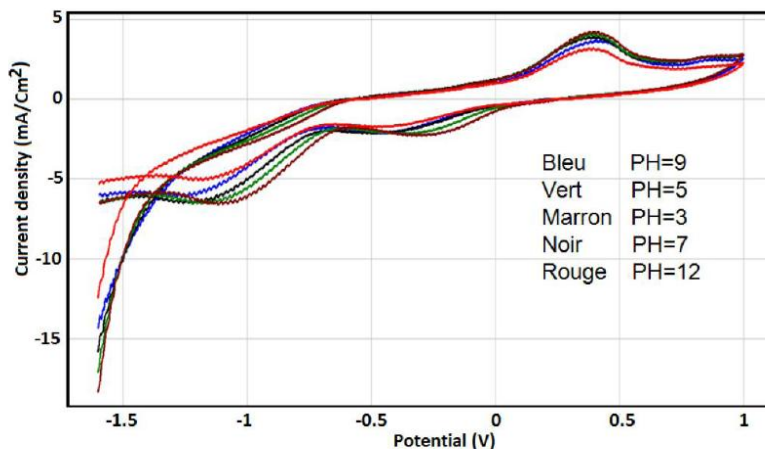


Figure 7 : CV of effect of pH on the redox of 3-NA at the NP-CPE

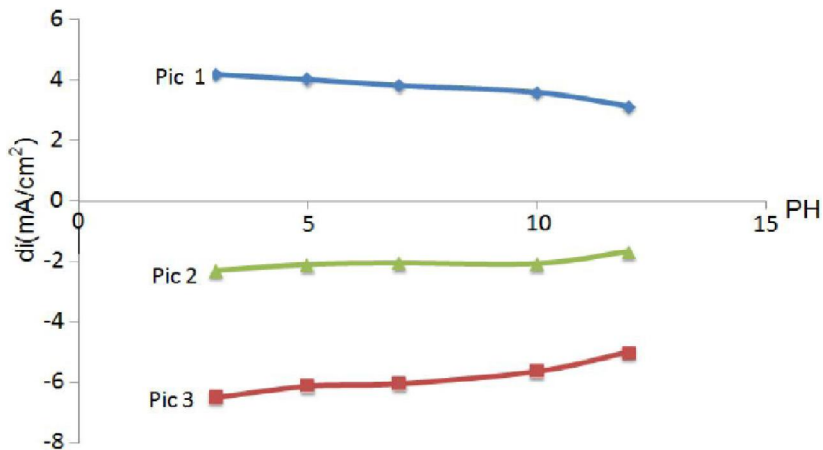


Figure 8 : Plot of the relationship between solution pH and the redox peak Current

$I_{pa} (1) = 2.640 [3-NA] + 0.702$
 $I_{pc} (2) = -1.506 [3-NA] - 0.528$
 $I_{pc} (3) = -2.782 [3-NA] - 2.349$

$R^2 = 0.994$
 $R^2 = 0.984$
 $R^2 = 0.983$

of different pH versus peak current.

ANALYTICAL APPLICATION

Effect of pH

The Figure 7 shows the cyclic voltammograms of the 3-NA at different pH. The current of the peak depend on the solution pH. The Figure 8 shows the graph

In order to evaluate the performance of NP-CPE by practical analytical applications, the determination of 3-NA was carried out in tap water. The analytical curves were obtained by CV experiments in

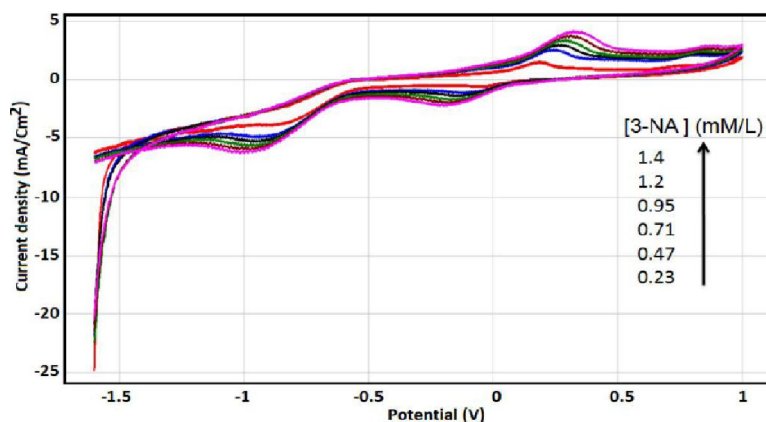


Figure 9 : Cyclic Voltammograms of different concentration of 3-NA at NP-CPE in tap water

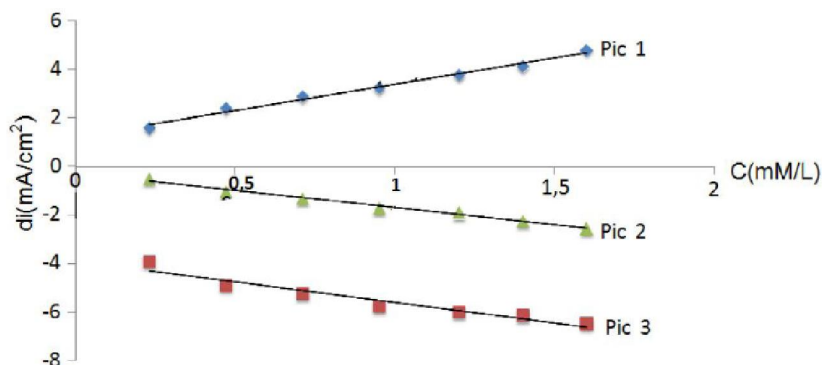


Figure 10 : Plot of peaks area versus added concentration of 3-NA

supporting electrode Figure 9. It was founded that the peaks currents increase linearly versus 3-NA added into the buffer solution Figure 10. The linear regression equations:

$$I_{pa} (1) = 2.167 [3-NA] + 1.224 \quad R^2 = 0.986$$

$$I_{pc} (2) = -1.421 [3-NA] - 0.265 \quad R^2 = 0.988$$

$$I_{pc} (3) = -1.699 [3-NA] - 3.879 \quad R^2 = 0.934$$

CONCLUSION

We have demonstrated the use of natural phosphate modified carbon paste electrode for a greatly CV sensing of 3-NA compounds. The modified electrode increased the amplitude of the current signal of 3-NA and produced good response. The electrode construction was extremely simple and with low cost. No unstable or toxic reagents were used.

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