Voltammetric Quantification of the Pollutants Nitro Compounds Using Glassy Carbon Electrode

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Abstract: ***The voltamatric behavior of some nitro aromatic compound, such as ρ-nitro benzoic acid, ρ-nitrobenzaldhyde and ρ-nitroaniline, was investigated and the method was developed for the simultaneous determination of these compounds. Adsorption of ρ-nitro benzoic acid, ρ-nitrobenzaldhyde and ρ-nitroaniline at glassy carbon electrode has been studied using cyclic voltammetry and linear sweep techniques, it was found that ρ-nitrobenzoic acid in NaH_2PO_4 (0.05M) as a supporting electrolyte (pH=2), ρ-nitrobenzaldhyde in Na_2HPO_4 (pH=10) and ρ-nitroaniline in $NaNO_3$ (0.05M) supporting electrolyte (pH=2), give one defined reduction peak and one oxidation peak. The effect of different parameters on the peaks response as supporting electrolyte, pH, deposition time, accumulation potential and scan rate were examined. A detection limit of $1x^{10-5}$ mol $l^{'}$ was obtained under the optimum conditions for three compounds.***

Keywords: Nitro compounds, Linear sweep Voltammetry, Supporting electrolyte, p-nitrobenzoic, p-nitroaniline, p-nitrobenazldhyde, Glassy carbon electrode.

1. Introduction

The determination of Nitro-aromatic compounds is important. These compounds are stable, persistent and toxic Most of these compounds (i) are considered as poison by ingestion, subcutaneous, intraperitoneal and intramuscular routes, (ii) exhibit human mutagenic and carcinogenic potential, (iii) decompose to emit toxic fumes of NOx, and (iv) are potent uncouplers of oxidative- and photo phosphorylation. While those properties render them valuable feedstock for industry.

The better electrochemical technique to study the reduction of nitro compound is the cyclic voltammetry. In fact, in aqueous medium, in the absence of inhibitor substances, only one irreversible cyclic voltammetric peak. As glassy carbon (GC) electrodes have been widely used for electrochemical measurements, the effects on the electrochemical responses, of various surface states driven by various surface pretreatments have been studied [1]. Besides polishing the surface with alumina powder, a generally known surface preparation method, other procedures such as heating, electrochemical and chemical oxidations, and laser activation have been employed [2-8]. Regarding these pretreatments, explanations of different electron transfer kinetics from different surface states were suggested [9-13]. It was reported that the activity of the electrode degraded with time because of the adsorption of impurities on the surface [3]. Xiao et al [31]studied the adsorption of ρ-nitrobenzoic acid (PNBA) at an Au electrode in 0.1 M HCIO4 solutions has been studied by combining cyclic voltammetry, electrochemical quartz crystal microbalance (EQCM), in situ Fourier transforms infrared spectroscopy (FTIRS) and surface enhanced Raman spectroscopy (SERS). Ji_I Barek et al, [14] studied the possibilities of electrochemical detection of various explosives containing electrochemically active nitro group. Attention is paid both to the use of traditional mercury electrodes and non-traditional, recently developed electrodes based on mercury amalgams, bismuth films, boron-doped diamond films and carbon films in voltammetric and amperometric mode.

2. Experimental

2.1 Preparation of Solutions

1- ρ-nitrobenzoic acid, ρ-nitrobenzalhyde and ρ-nitroaniline solutions:

Stock solution (0.1M) of each (ρ-nitrobenzoic acid, ρ-nitrobenzalhyde and ρ-nitroaniline) was prepared daily, the solutions of lower concentration for experiments were freshly prepared by appropriate dilution from stock solution prior to each run.

The supporting electrolytes and buffers such as disodium hydrogen phosphate, sodium chloride, acetate buffer, and sodium nitrate were prepared using double distilled water Ten ml of the selected buffer solution was studied in absence and presence of the mentioned compounds using cyclic and linear voltammertic technique at glassy carbon electrode.

2.2 Electrochemical Cell and Instrumentation

A three electrode cell was used consisting of the GC working electrode, a Ag/AgCl reference electrode and a Pt wire auxiliary electrode.

A computer-aided electrochemistry system used in the voltametric studies consists of potentiostat model 263(EG&GPARC) Princeton applied corporation (made in USA) and electro analytical software model 270/250 version 4.0 (PARC)

2.3 Parameters for CV and LSV

The parameters of cyclic voltammetric measurements at GC electrode were as follows: start potential +0.1 V, end potential -1.0 V, scan rate of 50 mV/s

3. Results and Discussion

Voltammetric determination of ρ-nitrobenzoic acid, ρ-nitrobenzaldhyde and ρ-nitroaniline was studied using glassy carbon electrode. Different parameters in which affect the peak current and potentials were studied.

Electrochemical Behavior of the Studied Compounds

The cyclic voltammetric measurement of ρ-nitrobenzoic acid showed one reduction peak at -0.312 V and oxidation peak at 0.253 V. The repetitive cyclic voltammograms of $1x10^{-4}$ M of ρ-nitrobenzoic acid in sodium dihydrogenphosphate buffer (pH 2.00) showed that the reduction peak current decreased in the second cycle. (Fig 1) indicating the rapid desorption of the adsorbed form. The same behavior was observed for ρ-nitrobenzalhyde in which the reduction peak was observed at -0.527 V and the oxidation one at 0.125 V. in the case ρ-nitroaniline, the reduction peak was detected at -0.456 and the oxidation one at 0.402V

1. Effect of Supporting, Electrolyte, pH and Scan rate

The influence of different supporting electrolytes was examined (sodium chloride, sodium dihydrogen phosphate, disodium hydrogen phosphate, sodium nitrate and B.R). The results showed that, sodium dihydrogen phosphate buffer gave the best peak also the effect of pH (Fig 1) and the concentration of the supporting or the buffer solution was examined. The collected data for the optimum conditions to determine the mentioned compounds are listed in table 1.

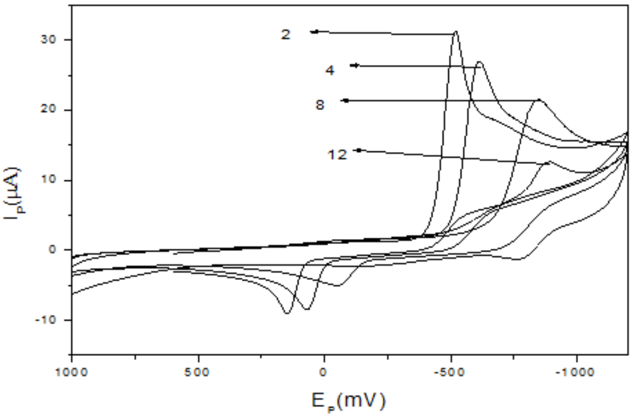

Figure 1: Effect of pH on the peak response of ρ-nitrobenzoic, sodium dihydrogen phosphate, (0.05 M) and scne rate of 50mV/s

2. Effect of Concentration and Calibration Curve

The effect of concentration of ρ-nitrobenzoic acid on the peak current was investigated. The peak current was increased by increasing concentration. Fig. (2) Shows the linear sweep voltammograms for different concentrations ρ-nitrobenzoic acid, 50 mVs-1 scan rates in sodium dihydrogen phosphate buffer (pH 2.00).

On plotting concentration of ρ-nitrobenzoic acid versus the peak current, a linear behavior was observed with standard deviation of 0.53 and correlation coefficient of 0.9887.

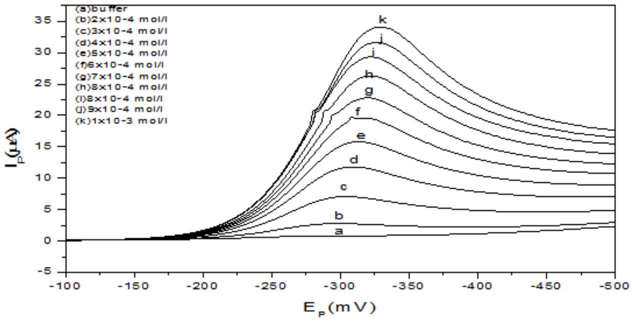

Figure 2: Effect of the concentration on the peak response of ρ-nitrobenzoic, sodium dihydrogen phosphate (0.05 M) and scne rate of 50mV/s

The obtained results for the other compounds are shown in table 2.

2.1 Analytical Applications

By applying the selected conditions for each compounds, the mentioned nitro compounds were determined in industrial waste water and in tap water by spiking

Table 1: The optimum conditions for the determination of the compounds of interest

Compound	ρ-nitrobenzoic acid	ρ-nitrobenzaldhyde	ρ-nitrobenzen
Supporting or buffer	Dihydrogenphosp-hate	Dihydrogenphosp-hate	Nitric acid
pH	2.0	10.0	2.0
Scan rate (mV/s)	50	50	50
Deposition time (s)	80	50	10
Deposition potential (V)	0.0	-0.05	-0.05

Determination of the studied compounds in one run:

The results indicated the possibility of determination both of ρ-nitrobenzaldhyde and ρ-nitroaniline in which two separate peaks were observed. In the presence of ρ-nitrobenzoic, the peak of ρ-nitrobenzaldhyde increased indicating that the first peak corresponds ρ-nitroaniline and the second one corresponds the tow other compounds

4. Conclusion

Linear sweep voltammetry can be applied for the determination of the ρ-nitrobenzoic acid, ρ-nitrobenzaldhyde and ρ-nitroaniline using glassy carbon electrode and the method was applied for the determination of the mentioned pollutants in different water samples

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