

Full Paper

Electrocatalytic Activity of L-Cystine towards the Sensitive and Simultaneous Measurement of Nitrobenzene and 4-Nitrophenol: A Voltammetric Study

Palla Gopal, Tukiakula Madhusudana Reddy,* Pamula Raghu, Kasetty Reddaiah and Palakollu Venkata Narayana

Electrochemical Research Laboratory, Department of Chemistry, S.V.U. College of Sciences, Sri Venkateswara University, Tirupati-517502, Andhra Pradesh, India

* Corresponding Author, Tel.: +91-877-2289303

E-Mail: tmsreddysvu@gmail.com

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Abstract- A new simple, sensitive and selective electrochemical method for the determination of Nitrobenzene (NB) and 4-Nitrophenol (4-NP) at L-Cystine modified glassy carbon electrode was developed with the help of cyclic voltammetry (CV) and differential pulse voltammetry (DPV) techniques. Based on the effect of pH, a detailed electrochemical redox mechanism was proposed and the number of electrons involved in the $R-NO_2 \rightarrow R-NO_2 \cdot$ step was determined. The kinetic parameters such as heterogeneous rate constants (k_s) and charge transfer coefficient (α) values were calculated and was found to be as $0.711 \times 10^{-6} s^{-1}$, $1.486 \times 10^{-6} s^{-1}$ and 0.521, 0.501 for both NB and 4-NP respectively. The NB and 4-NP systems were controlled by diffusion process and the diffusion coefficients values were determined as $3.24 \times 10^{-7} cm^2/s$ and $7.04 \times 10^{-7} cm^2/s$ for NB and 4-NP respectively. The limit of detection (LOD) and limit of quantification (LOQ) values were evaluated as $7.46 \times 10^{-6} M$, $24.9 \times 10^{-6} M$ with linear dynamic range from 30 μM to 105 μM for NB and $0.1049 \times 10^{-6} M$, $0.349 \times 10^{-6} M$ with linear dynamic range from 0.5 μM to 6 μM for 4-NP respectively. The developed method was effectively applied for the simultaneous determination of NB and 4-NP. Moreover the surface nature of the electrode was investigated by the electrochemical impedance spectroscopy. Finally the developed method was successfully applied for the real sample analysis with satisfactory recovery values having low RSD values.

Keywords- Nitrobenzene, 4-Nitrophenol, L-Cystine, Glassy carbon electrode, Electrochemical impedance spectroscopy

1. INTRODUCTION

In recent years, the environmental protection was a main challenge for the researchers. The environment was polluted with many of organic and inorganic compounds. Among the all, nitrobenzene [NB] and 4-nitrophenol [4-NP] are major pollutants in the world, recognized by the U. S. Environmental Protection Agency [1,2] and Chinese Environmental protection Agency [3].

NB (oil of mirbane) is an organic liquid compound, it is used in soaps, floor, leathers, polishes, dressings, paint solvents and also used as precursor in the synthesis of dyes, drugs, pesticides, and explosives [4]. Inhalation of NB vapors may cause the headache, fatigue, dizziness and cyanosis. This will be readily absorbed by the skin and may increases the heart rate. It was considered as a human carcinogen and was classified as group 2B carcinogen by International Agency for Research on Cancer (IARC) [5-7].

4-NP is one of the hazardous waste compounds to the environment. 4-NP was used in the synthesis of many organic materials, such as pharmaceuticals, pesticides and dyestuffs. This is one of the major degradation products of insecticides and used as a leather fungicide. Due to its change of color property from pale yellow to bright yellow this was used as a pH indicator. It irritates skin, eyes and respiratory tract and it also causes cyanosis, confusion and unconsciousness [8-11].

Therefore, due to their wide variety of applications in many fields, NB and 4-NP inevitably releases into the environment. Because of its hazardous characteristics like carcinogenicity, mutagenicity, teratogenicity and high toxicity [10-13], both (NB and 4-NP) of these are treated as major pollutants [14]. Based on the above description, these compounds received much attention by the researchers towards the low level detection and degradation. There was many analytical methods being employed for the quantification of these compounds, they are High performance liquid chromatography (HPLC), Gas chromatography (GC), UV Visible spectrophotometry and Fluorescence quenching [15-18]. However the electrochemical techniques have received much interest, because they are less expensive, less time consuming, more selective, and can be applied potentially.

Cyclic voltammetry (CV) and Differential pulse voltammetry (DPV) methods were extensively used for the determination of pharmaceuticals, dyes, pesticides and environmental pollutants. In electroanalytical chemistry the uses of chemically modified electrodes are of great importance, this is due to its good sensitivity in redox process. Numerous chemicals were immobilized on the electrode surface, such as resembling dyes [19], β -cyclodextrin [20], clay [21], nafion [22], indicator [23] and Enzymes [24]. In our present work we have used L-Cystine as a modifier on the glassy carbon electrode (GCE) towards the construction of poly (L-Cystine)/GCE, which was produced by the electrochemical polymerization. The polymerization process led to the formation of thioalcohol residues on the electrode surface thereby enhancing the sensitivity of the analytes.

There was no literature related to the simultaneous determination of NB and 4-NP by employing electro analytical techniques. The simultaneous resolution of NB and 4-NP is an important task, because the redox potentials of both the compounds are closure. Hence it is a difficult task to predict NB and 4-NP simultaneously, in this point of view, we have focused on simultaneous determination of NB and 4-NP. This work also describes the detailed electrochemical mechanisms of NB and 4-NP at L-cystine modified GCE.

2. EXPERIMENTAL

2.1. Materials

All the chemicals were received from commercial source and used without further purification. Nitrobenzene and 4-Nitrophenol were from Sigma-Aldrich, H_3BO_3 and AcOH was received from Merck specialties Pvt. Ltd, Mumbai. H_3PO_4 was from Thermo Fisher Scientific India Pvt. Ltd, Mumbai and NaOH was collected from SD fine-chem limited Mumbai. $NaH_2PO_4 \cdot 2H_2O$ was from Fisher Scientific India Pvt. Ltd, Mumbai and Na_2HPO_4 was from Merck specialties Pvt. Ltd, Mumbai. Water sample-I was collected from Railway station, Tirupati of Chittoor District, Andhra Pradesh, India, Water sample-II was collected from Mylavaram reservoir near Jammalamadugu of Kadapa District, Andhra Pradesh, India. Water sample-III was collected from Swarnamukhi River near Tirupati of Chittoor District, Andhra Pradesh, India.

2.2. Methods

Cyclic voltammetry (CV), differential pulse voltammetry (DPV) and electrochemical impedance spectroscopy (EIS) techniques were performed through CH – Electrochemical workstation (Model CHI-660D, CH Instruments, USA) with conventional three electrode system made up of saturated calomel electrode (SCE) as reference electrode, platinum (Pt) wire as counter electrode and L-cystine modified GCE as a working electrode. The B-R buffer was prepared by mixing equal amounts of H_3BO_3 , H_3PO_4 and AcOH and was adjusted by adding NaOH to desired pH values and phosphate buffer solution was prepared from $NaH_2PO_4 \cdot 2H_2O$ and Na_2HPO_4 and adjusted to desired pH values by using ELICO pH Meter.

2.3. Preparation of Modified electrode

Commercially available GCE having 3mm diameter was received from CH Instruments, Inc., Part Number: CHI 104 and was polished with 1.0, 0.3, 0.05 micron Al_2O_3 powders respectively. After polishing, the GCE was rinsed with distilled water and used as a bare GCE. The bare GCE was kept in the solution containing 1 mL of 10 mM L-cystine and 9 mL of phosphate buffer solution (PBS)-7.0 and was scanned between the potential ranges from -

0.4 V to +1.6 V for 20 cycles. After the completion of electropolymerization process the poly L-cystine electrode was obtained and thoroughly washed with distilled water to remove any physically adsorbed material and here after the electrode was abbreviated as poly (L-cystien)/GCE.

3. RESULTS AND DISCUSSION

3.1. Voltammetric characterization of L-Cystine

Fig. 1 insert is the CV of 1mL of 10 mM L-cystine solution in 9 mL of PBS-7.0 at GCE and scanned within the potential window from -0.4 V to +1.6 V for 20 cycles. The L-cystine produced only one peak at ≈ 1.4 V and this may be due to the oxidation of '-S-S-' and which is responsible for the formation of thioalcohol group. The formed thioalcohol enhances the rate of the reaction. Fig. 1, clearly exhibits the increase of peak currents for NB in the presence of L-cystine on GCE and the separation of peak potentials (ΔE_p) at poly (L-Cystine)/GCE was greatly decreased from 139 mV (at bare GCE) to 40 mV, this indicates that the L-Cystine modifier enhances the rate of the reaction by decreasing the activation energy and facilitates ease for the formation of the product.

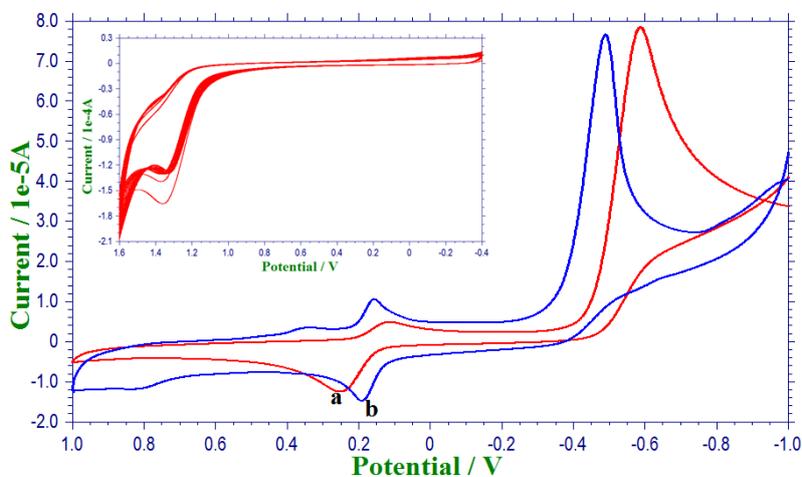


Fig. 1. The CV of 10 mM NB in B-R buffer of pH 4.0 at bare (a) and poly (L-Cystine)/GCE (b). Insert is the CV of 10 mM L-Cystine, 20 cycles at scan rate 0.1 V/s

3.2. EIS and CV characterization of poly (L-Cystine)/GCE

EIS was the most use full technique for the study of interfacial electron transfer properties of chemically modified electrodes. The nyquist plot represents two portions, i.e., semicircular portion at higher frequency region and linear portion at lower frequency region. The semicircular portion explains the charge-transfer resistance (R_{ct}), which is an important

parameter for the characterization of the electrode surface with the help of $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ as a probe. From the data obtained, it is clearly evident that the charge-transfer resistance of ploy (L-Cystine)/GCE ($R_{ct}=357.7 \Omega$) was more in comparison with bare GCE electrode ($R_{ct}=283.8 \Omega$). Fig. 2a and 2b are the Nyquist and bode plots for bare and poly (L-Cystine)/ GCE and the insert in Fig. 2a is the short view of Fig. 2a. From Fig. 2b the phase of ploy (L-Cystine)/GCE shifted to less frequency region indicating the increase in the charge transfer resistance of the electrode. The data was received from Randles circuit fitting and the values were listed in Table 1. From CV results, the bare GCE showed good peak currents for ferri/ferro probe, which in turn after polymerization process peak currents at the same electrode was decreased, conforming the polymerization of L-cystine on GCE [25,26].

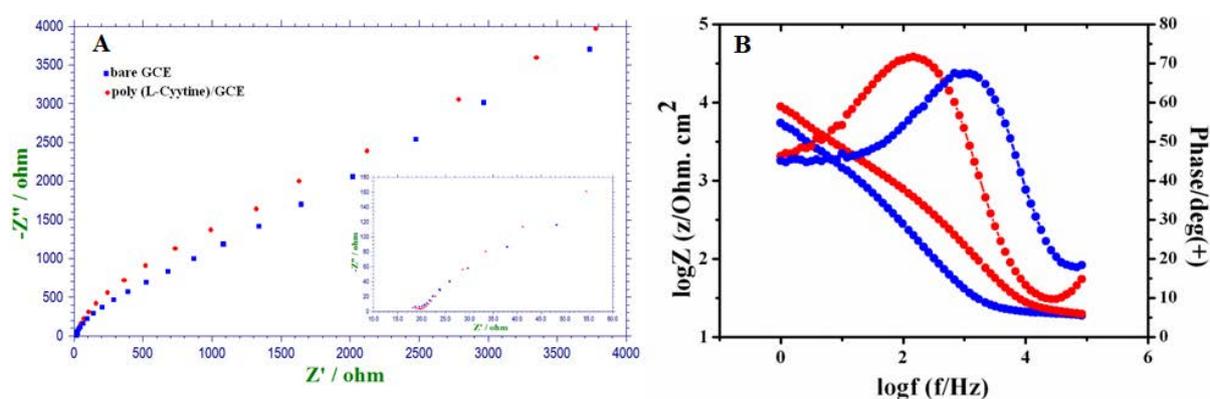


Fig. 2. (A) The Nyquist plot of $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ probe at bare GCE (blue) and poly (L-Cystine)/GCE (red). (B) The Bode plot corresponds to $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ probe at bare GCE (blue) and poly (L-Cystine)/GCE (red) was drawn between logarithm of frequency, logarithm of impedance and phase

Table 1. Comparison of electrochemical impedance results for bare GCE and poly(L-cystine)/GCE

| Electrode | R_{sol}/Ω | $C/\mu\text{F}$ | R_{ct}/Ω | W |
|---------------------|------------------|----------------------|-----------------|----------------------|
| Bare GCE | 20.28 | 9.27E^{-7} | 283.8 | 4.577E^{-5} |
| Ploy(L-Cystine)/GCE | 20.29 | 4.638E^{-6} | 357.7 | 6.744E^{-5} |

3.3. Electrochemistry of NB/4-NP at poly (L-Cystine)/GCE

The electrochemical redox behavior of NB and 4-NP at poly (L-Cystine)/GCE was studied by using CV. The electrochemistry of NB, between the potential window from -1.0 V to +1.0 V was similar to that of 4-NP, hence we have explained the electrochemistry of NB only, but in the basic medium 4-NP produces an oxidation peak ≈ 0.8 V and this may be due

to the oxidation of phenolic alcohol group. From Fig. 3 peak 'II' corresponds to the formation of nitro radical from nitro group i.e. formation of 'II' from 'I' (as shown in Scheme-I) [27,28]. In acidic medium, due to the availability of more number of H^+ ions, the nitro radical receives $3e^-$ and $4H^+$ to give rise to the corresponding hydroxylamine derivative (IV). Whereas in the basic medium another peak was observed, which was due to the formation of nitro radical to nitroso compound (III) and the formed nitroso compound leads to the formation of hydroxylamine (IV). In the basic medium, the formed hydroxylamine (IV) oxidizes reversibly to form nitroso compound (III) [29-32].

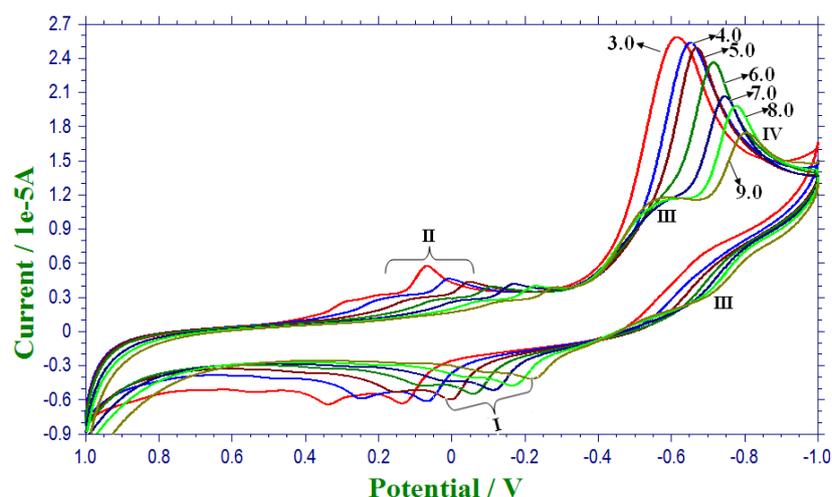
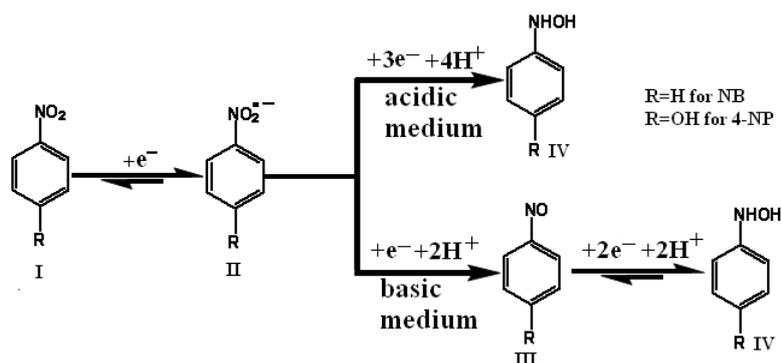


Fig. 3. The CVs of 1mM NB in pH 3.0 (a), 4.0 (b), 5.0 (c), 6.0 (d), 7.0 (e), 8.0 (f) and 9.0 (g) at scan rate 0.1 V/s



Scheme 1. The detailed electrochemical reduction and oxidation mechanism of NB and 4-NP

3.4. Effect of pH

The electrochemical reduction and oxidation behavior of NB and 4-NP was investigated by using B-R buffer between the pH ranges from 3.0 to 9.0. To study the effect of pH, we

have used both CV and DPV, the results depicts that the peak potentials of E_{pa1} , E_{pc1} and E_{pc2} values were shifted to less positive potentials with increase in the pH of the solution. From the DPV results, it was observed that the peak currents were higher at pH 4.0 and hence pH 4.0 was chosen as an optimum pH for all further studies. Fig. 4a and 4b are the 3-Dimensional representations of DPV for NB and 4-NP respectively. The linear regression equations were plotted between the peak potentials and pH values and were found to be as $E_{pa(NB)}(V)=0.274(V)-0.061\text{ pH}$ ($R=0.998$), $E_{pa(4-NP)}(V)=0.48(V)-0.069\text{ pH}$ ($R=0.99$) for NB and 4-NP respectively. The slopes for the two linear equations were closer to the theoretical value (0.059 V) and confirms that the rate determining step proceeds with equal number of protons and electrons. By using the equation (1), we have determined the number of electrons involved in the $R-NO_2 \rightarrow R-NO_2^{\bullet}$ step and it was found to be as 0.92 (≈ 1) and 0.85 (≈ 1) for both NB and 4-NP respectively. Fig. 4c shows the plot drawn between the peak potentials of NB and 4-NP with the corresponding pH values [33].

$$E_p = E_0 - (0.0591/n) \text{ pH} \quad (1)$$

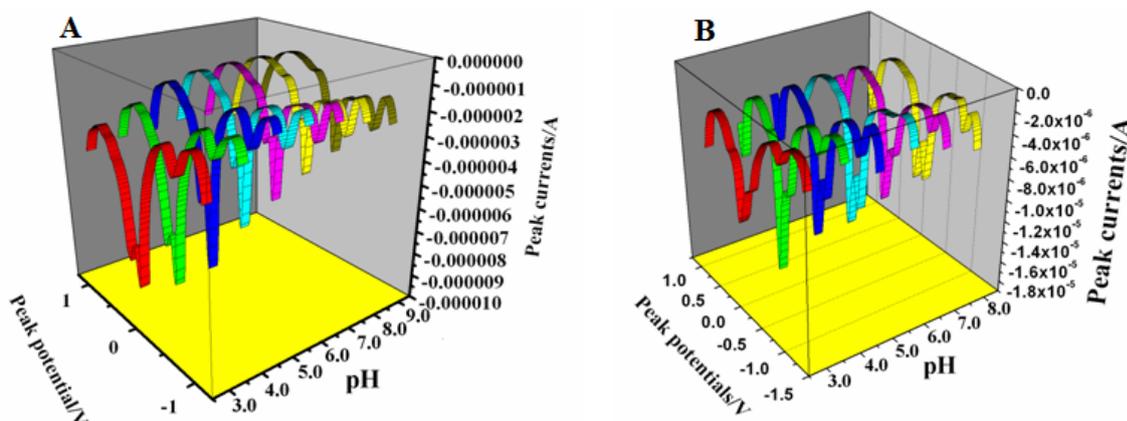


Fig. 4. (A) 3-Dimensional representation of DPV results for 10 mM NB in pH 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, and 9.0; (B) 3-Dimensional representation of DPV results for 10 mM 4-NP in pH-3.0, 4.0, 5.0, 6.0, 7.0, and 8.0

3.5. Effect of Scan rate

In order to find the kinetic parameters, we have studied the effect of scan rate for NB and 4-NP at Poly (L-Cystine/GCE). When the scan rates were varied from 10 mV to 200 mV and the peak currents of NB and 4-NP were increasing linearly with square root of scan rate ($v^{1/2}$) and the linear regression equations were found to be as $I_{pa1(NB)}(\mu A)=0.67(\mu A)-0.3236 v^{1/2}$ ($(V/s)^{1/2}$) ($R=0.9972$), $I_{pa1(4-NP)}(\mu A)=1.043(\mu A)-1.192 v^{1/2}$ ($(V/s)^{1/2}$) ($R=0.994$) for NB and 4-NP respectively. This linearity indicates that the process was controlled by diffusion

process and the diffusion coefficients were found to be as $3.24 \times 10^{-7} \text{ cm}^2/\text{s}$ and $7.04 \times 10^{-7} \text{ cm}^2/\text{s}$ for NB and 4-NP respectively [34]. Fig. 5 was the plot between the peak currents and square roots of scan rates. By using Randles-Secivek equation (2), we have calculated the area of working electrode as 0.123 cm^2 , where 'D' is the diffusion coefficient in cm^2/s , 'n' in number of electrons involved in the reaction, ' α ' is charge transfer coefficient, 'A' is area of electrode in cm^2 , ' ν ' is the scan rate in V/s and 'C' is the concentration of the analyte in mol/cm^3 .

$$I_p = 2.99 \times 10^5 n (n\alpha)^{1/2} A C D^{1/2} \nu^{1/2} \quad (2)$$

Heterogeneous rate constant (k_s) and charge transfer coefficients (α) values were calculated by using equation (3) and (4), the values were found to be as $0.711 \times 10^{-6} \text{ s}^{-1}$, 0.501 for NB and $1.486 \times 10^{-6} \text{ s}^{-1}$, 0.521 for 4-NP respectively. Where 'm' is the slop of the E_p verses $\ln \nu$ values, E^0 is the intercept of the plot between E_p verses scan rate (ν), 'D' is diffusion coefficient, k_s is the heterogeneous rate constant, ' α ' is the charge transfer coefficient, 'n' is number of electrons involved in the rate determining step and 'F' is the faraday constant [35-37].

$$E_p = E^0 - m [0.78 + n(D^{1/2}/k_s) + (m/2)(\ln m)] + m/2 \ln \nu \quad (3)$$

$$m = RT/(1-\alpha)nF \quad (4)$$

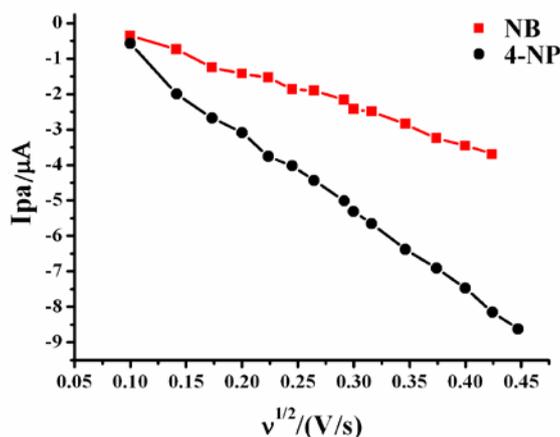


Fig. 5. The plot between the peak currents and square root of scan rate ($\nu^{1/2}$) for NB (black) and 4-NP (red)

3.6. Effect of concentration

The effect of concentration on the peak currents of NB and 4-NP was studied by employing DPV technique between the potentials window from -0.5 V to -1.0 V at Poly (L-

Cystine)/GCE. It was observed that the peak currents of NB and 4-NP were increasing gradually with increase in the concentration of NB and 4-NP. Fig. 6a and 6b exhibits the linear plots for peak currents verses concentrations of NB and 4-NP respectively. The linear regression equations for NB and 4-NP were found to be as $I_{pc} (NB) (\mu A) = 2.289 (\mu A) + 0.0305 C_{NB} (\mu M)$ ($r=0.9949$) and $I_{pc} (4-NP) (\mu A) = 2.164 (\mu A) + 0.406 C_{4-NP} (\mu M)$ ($r=0.988$). Based on the equations (5) and (6), we have calculated the limit of detection (LOD) and limit of quantification (LOQ) values and it was found to be as 7.46 μM and 24.9 μM for NB with linear dynamic range from 30 μM to 105 μM and 0.1049 μM and 0.349 μM for 4-NP with linear dynamic range from 0.5 μM to 6 μM respectively [38-40].

$$\text{LOD} = 3 S/m \quad (5)$$

$$\text{LOQ} = 10 S/m \quad (6)$$

Where 'S' is the standard deviation and 'm' is the slope of the calibration curve.

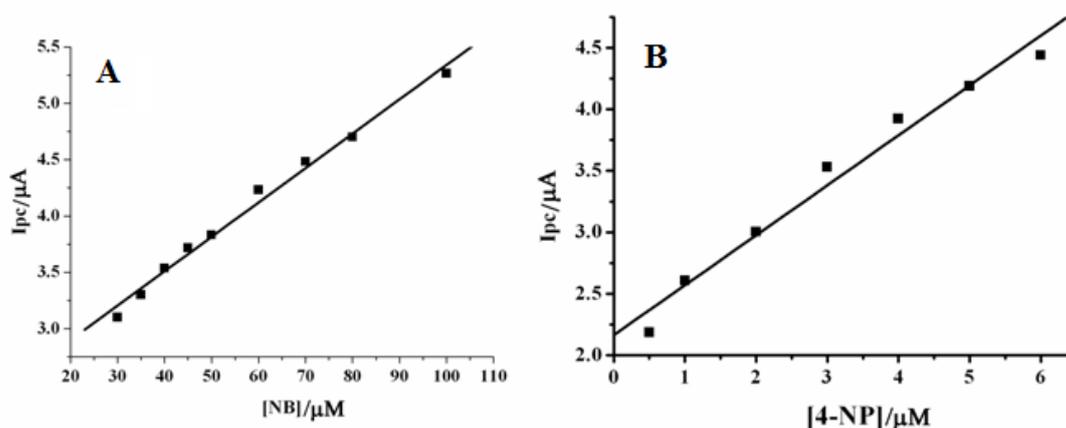


Fig. 6. (A) The plot between the peak currents in μA and concentration of NB; (B) The plot between the peak currents in μA and concentration of 4-NP

3.7. Simultaneous determination of NB and 4-NP

The voltammetric determination of NB in the presence of 4-NP and vice versa was studied by using the CV method. In this method, first we have added 0.5 mL of 1mM solution of 4-NP to the 9.5 mL of B-R buffer and noted CV, and later the concentration of NB was gradually increased from 5 μM to 100 μM and we have observed an redox system of NB around the potential of ≈ 0.01 V. From the Fig. 7a, we can see that, as the concentration of NB was increased the peak currents of the redox system of the NB increases. This confirms the good separation and resolution of NB and 4-NP at poly (Cystine)/GCE. The determination of 4-NP in the presence of NB was carried, we have added 0.8 mL of 1 mM solution of NB to the 9.2 mL of B-R buffer and the CV was recorded. The concentration of 4-NP was increased

from 2 μM to 15 μM , a well resolved redox system was observed at potential ≈ 0.2 V (from Fig 7b) confirming that the developed poly (L-Cystine)/GCE can separate the 4-NP in the presence of NB [41].

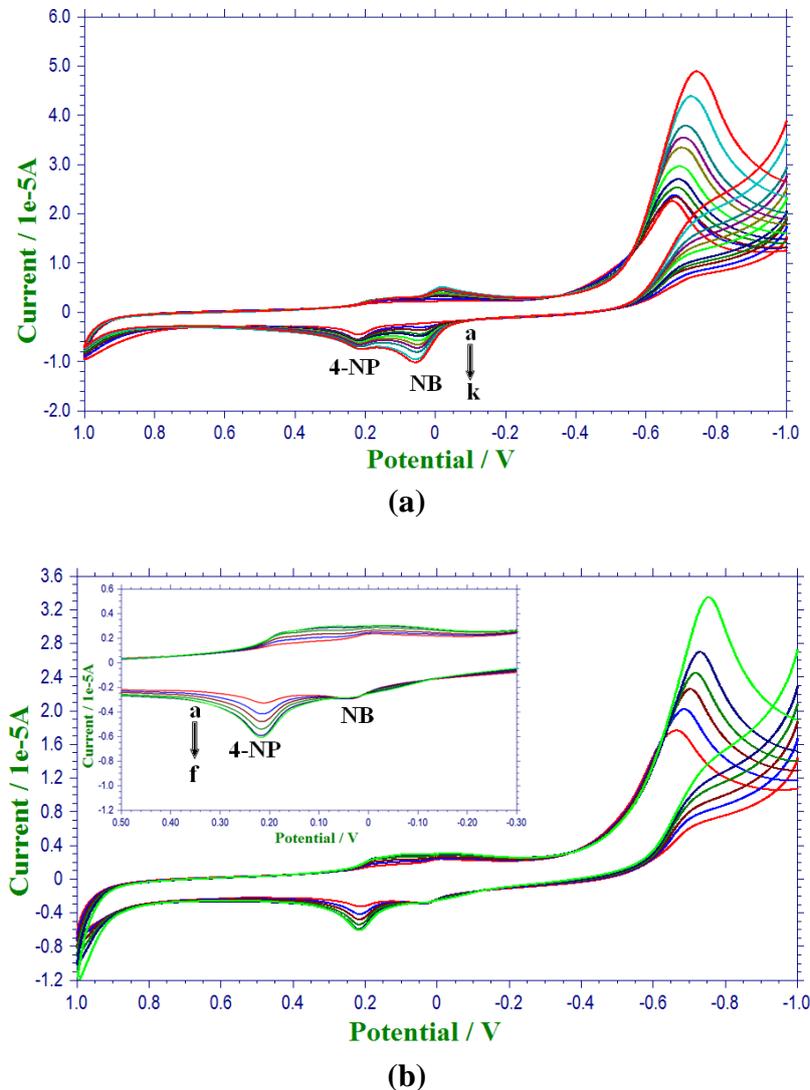


Fig. 7. (a) The CVs for the determination of 4-NP of 50×10^{-6} M (a), in the presence of 5×10^{-6} M (b), 10×10^{-6} M (c), 15×10^{-6} M (d), 20×10^{-6} M (e), 30×10^{-6} M (f), 40×10^{-6} M (g), 50×10^{-6} M (h), 60×10^{-6} M (i), 70×10^{-6} M (j), 80×10^{-6} M (k) of NB at a scan rate of 0.1 V/s; (b) The CVs for the determination of NB of 2×10^{-6} M (a), 4×10^{-6} M (b), 6×10^{-6} M (c), 8×10^{-6} M (d), 10×10^{-6} M (e), 15×10^{-6} M in the presence of 80×10^{-6} M 4-NP (f). Inset is the short view of Fig. 7b

3.8. Analytical applications

The recovery experiments were conducted through the DPV technique. The amounts of added analytes and their recoveries in different water samples were listed in Table 2. From

the results it is clear that the recoveries of the proposed method were within the ranges from 97.27% to 104.85% and the recovery values suggested that the method was effective for the determination of NB and 4-NP. The stability, repeatability and reproducibility of the developed electrode were studied and the results were in satisfactory range [26].

Table 2. Determination of nitrobenzene (NB) and 4-nitrophenol (4-NP) in different water samples at poly(L-Cystine)/GCE

| Sample | Analyte | Added (μM) | Found (μM) | Recovery (%) |
|------------------|---------|-------------------------|-------------------------|--------------|
| Water sample-I | NB | 30 | 29.25 | 97.986 |
| | 4-NP | 30 | 29.89 | 99.63 |
| Water sample-II | NB | 30 | 29.749 | 99.16 |
| | 4-NP | 30 | 30.9 | 103 |
| Water sample-III | NB | 30 | 29.18 | 97.27 |
| | 4-NP | 30 | 31.45 | 104.85 |

4. CONCLUSION

A new simple, sensitive and selective electrochemical sensor was developed for the determination of NB and 4-NP. The redox behavior of NB and 4-NP was investigated in different pH conditions and detailed electrochemical mechanism was proposed. Kinetic parameters such as heterogeneous rate constant, diffusion coefficient, charge transfer coefficient were evaluated for NB and 4-NP. Lower detection limits were achieved for NB and 4-NP, simultaneous determination of NB and 4-NP was successfully carried out. By using EIS, the surface nature of the working electrode was also observed. The applicability of developed method was successfully demonstrated with real water samples and the results were in good agreement with developed method.

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