https://doi.org/10.30799/jnst.174.18040526 J. Nanosci. Tech. - Volume 4 Issue 5 (2018) 560–563

Share Your Innovations through JACS Directory

Journal of Nanoscience and Technology

Visit Journal at http://www.jacsdirectory.com/jnst

ISSN: 2455-0191

Quantification of 4-Nitrophenol on Nanosize Polyaniline Modified Glassy Carbon Electrode through Electrochemical Method

R. Manikandan[1,2], A. Shoba[3], N. Senthil Kumar[1,4,*]

[1]*Research Scholar, Research and Development Centre, Bharathiar University, Coimbatore – 641 046, Tamilnadu, India.*
[2]*P.R. Engineering College, Thanjavur – 613 403, Tamilnadu, India.*
[3]*Department of Chemistry, Sri Akilandeswari Women's College, Wandiwash – 604 408, Tamilnadu, India.*
[4]*Department of Chemistry, Arignar Anna Government Arts College, Cheyyar – 604 407, Tamilnadu, India.*

ARTICLE DETAILS

Article history:
Received 08 October 2018
Accepted 03 November 2018
Available online 12 December 2018

Keywords:
4-Nitrophenol
Polyaniline
Voltammetry
AFM

ABSTRACT

The electrochemical studies of 4-nitrophenol were carried out in acidic, neutral and basic buffer media at bare glassy carbon (GC) and nanosize polyaniline (PANI) modified GC electrodes. In all pH, 4-nitrophenol exhibits three oxidation peaks in forward scan and three reduction peaks in reverse scan in the CV. The peak current reached its maximum value at pH 7.0. The effect of scan rate was studied between 25 and 500 mVs^{-1} at pH 7. CV results revealed the diffusion-controlled reaction at the electrode surface. The atomic force microscopy used for studies of morphological behavior of nanosize polyaniline and compound adsorbed on PANI surface. Under optimum DPSV experimental conditions, the influence of concentration on the stripping signal was studied A linear relationship between peak current and concentration is obtained in the range 100 to 500 ppb, with lower detection limit of 50 ppb on PANI/GCE. The relative standard deviation of 1.76% for a 250 ppb 4-nitrophenol concentration and relative error of 2.6% were also obtained.

1. Introduction

Phenols are common in industrial effluents; the simple phenols are easily degraded and analysis must be done promptly. 4-Nitrophenol is one of the nitrophenols included in the U.S. Environmental Protection Agency List of Priority Pollutants [1]. Aromatic nitrocompounds are among the most toxic substances and are thus commonly used in the manufacture of explosives, pesticides, dyes, plasticizers and pharmaceuticals [2].

o-Nitrophenol (o-NP) is most significant matter of the nitrophenols isomers which has been exerted significant toxic effects on mankinds, animals, and plants. However, the development of novel method which capable of fast and cost-efficiently method of detecting o-NP in the low concentration is highly desirable and urgently necessary for the atmosphere and health protection. Several instrumental techniques are routinely utilized for the determination of o-NP including high-performance liquid chromatography [3], UV-vis, fluorescence spectroscopies [4], capillaryzone electrophoresis [5] and electrochemical techniques [6]. Among all these techniques mentioned above, electrochemical methods have received considerable attention for o-NP analysis due to their sensitivity, simplicity, low cost, and easy for on-site determination [7]. An electrochemical sensor for the quantification of o-nitrophenol (o-NP) has been developed based on the β-cyclodextrin functionalized graphene nanosheets modified glassy carbon electrode [8].

Now a day's work in this area is centered on the most influence choice of suitable experimental work conditions to prevent fouling and passivation effects of anodes. A variety of electrode materials was used including platinum. A study of the literature indicates that the EC oxidation of phenols is brought with the following challenges: (i) removal of phenols in significantly high concentrations; (ii) prevention of electrode fouling and (iii) reduction in the energy or faradic charge for uttermost removal of phenols. Hence, surfactants can absorb on the electrode surface and influence the fouling. It may also influence oligomerization and coagulation processes initiated by electro generated cation radicals of phenols. The investigation was initiated to evaluate the role of surfactants in addressing the above challenges [9].

Numerous investigations have been made on the reduction of aromatic nitro compounds. The nitro compounds are the best electrophores as regards to both ease of reduction and versatility of derived products. By electro reduction of nitrophenol isomer using stationary and rotating Cu electrodes and $Ti(SO_4)_2$ as additional agents, aminophenols were obtained in good yield. Depending on the electrolysis conditions, a great verity of products can be obtained by electro reduction of p-nitrophenol [10].

The voltammetric characteristics of 4-nitrophenol, 2,4-nitrophenol and 2,4,6-tri nitro phenol in acidic medium was investigated by cyclic voltammetry at glassy carbon electrode. The reduction of the para nitro phenol in the presence of HCl as supporting electrolyte reveals one irreversible peak while the reduction of the 2,4-di nitro phenol shows two irreversible current peaks and the reduction of the 2,4,6- tri nitro phenol gives three irreversible current peaks to produce the derivatives amines as the final products [11]. Screen printed carbon electrode has been modified with single wall carbon nanotube/poly(3,4-ethylenedioxythiophene) composites for the determination of phenol and chlorophenols (phenol, 4-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol). The effect of the modifiers on the electrode characteristics was evaluated and the responses were optimized for the voltammetric determination of phenol and chlorophenols [12].

Developing high selective and excellent sensitive electrochemical sensor for electrochemical active species with dual and multiple electroactive groups is very important in various analytical purposes. Here, on the basis of highly sensitive material of electrochemical reduced graphene oxide films modified glassy carbon electrode, the comparative study on the electrochemical sensing of p-nitrophenol (PNP) based on different current response signals offered by the reduction and oxidation process associated with nitro group and phenol group on PNP molecule was successfully demonstrated [13]. A highly sensitive electrochemical sensor for 4-nitrophenol was facilely constructed based on a Nafion modified glass carbon nano film electrode was reported [14] and simple hydrothermal method used for the synthesis of Cr_2Se_3 hexagons and its application towards electrochemical sensing of 4-nitrophenol were reported [15]. This work is aimed at fabrication of a simple and sensitive electro-analytical method for the determination of 4-nitrophenol on nanosize polyaniline modified electrodes.

*Corresponding Author:nsk.nagai@gmail.com(N. Senthil Kumar)

https://doi.org/10.30799/jnst.174.18040526

Cite this Article as: R. Manikandan, A. Shoba, N. Senthil Kumar, Quantification of 4-nitrophenol on nanosize polyaniline modified glassy carbon electrode through electrochemical method, J. Nanosci. Tech. 4(5) (2018) 560–563.

2. Experimental Methods

2.1 Apparatus and Reagents

All the voltammetric measurements were carried out using a 25 mL capacity single-compartment cell with three electrode cell top. The electrochemical cell contains a three-electrode system, a 0.34 mm glassy carbon electrode (GCE) as the working electrode, Ag/AgCl as the reference electrode, and a platinum wire as the counter electrode. In this work, Differential pulse voltammetry (DPV) and cyclic voltammetry (CV) tests were carried out by using anCH Instruments Electrochemical Workstation (model CH 650C). All potentials with directly respect to the potential of the reference electrode. Aniline and 4-nitrophenol were purchased from e-Merck. The pH values of the buffer solutions were measured by Hanna HI 2211 pH/ORP meter. A 200 ppm stock solution of 4-nitrophenol was made up in aqueous medium. For pH studies in aqueous media, Britton Robinson buffers, 0.1 moldm^{-3} KOH, KCl and 0.1 moldm^{-3} H_2SO_4 were used as the medium for the analysis. 4-nitrophenol was purchased from Merck AR grade. Atomic force microscope (AFM) was used to characterize the polymer and compound adsorbed on surface (Nanosurf Easy Scan 2, Switzerland).

2.2 Modification of the Electrodes

A GCE (3 mm diameter) was polished using 1.0 and 0.05 mm alumina slurry and rinsed thoroughly with Milli- Q water. Ultrasonic agitation for 30 min of 2.0 mg of chemically prepared polyaniline in 2 mL of water gave a homogeneous green solution. 20 micro litre of polyaniline solution was placed on the GCE surface. The electrode was then dried at room temperature to obtain a polymer modified GCE and used as working electrode.

3. Results and Discussion

3.1 Electrode Surface Characterization

AFM image of the nanosize polyaniline and 4-nitrophenol adsorbed on GCE surface and present the Fig. 1. The polymer film is uniformly coated on the electrode surface and forms a nanorod -like porous reticulated morphology. The compound adsorbed surface exhibits granular adsorbed nanosize rod like photographs. This surface morphology accounts for the finding that the active surface area of the composite electrode is 5 times greater than the geometric area. The Fig. 1 shows the surface morphologies of polymer modified electrode, compound adsorbed surface, particle distribution graphs and surface roughness values.

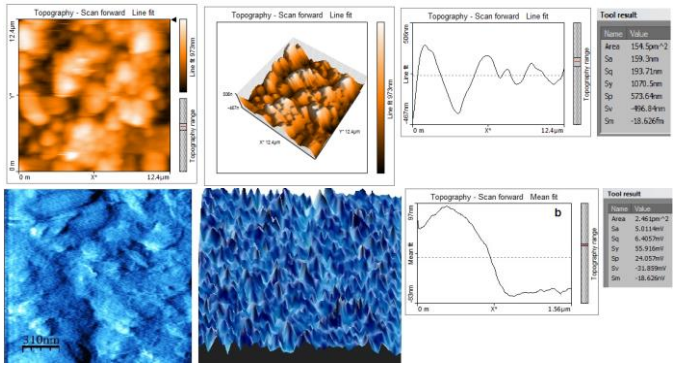


Fig. 1 AFM behavior of a) PANI and b) 4-NP adsorbed on PANI

X-ray diffraction pattern of polyaniline was reported by Mexiang Wan et al [16]. The analysis of XRD pattern of PANI suggests that it exhibits a semi crystalline behaviour. The broad peak between 2θ = 22° and 28° is the characteristic peak of PANI. Same behavior was reported by many researchers [17,18].

3.2 Electrochemical Studies

Cyclic voltammetric studies were carried out at pH ranging between 1.0 and 13.0 on GCE and modified GCE. In all pHs, 4-nitrophenol exhibits three oxidation peaks in forward scan and three reduction peaks in reverse scan in the CV. The peak current reached its maximum value at pH 7.0. The peak current was five folded higher on modified GCE than GCE. The overall redox reaction seems to be same in acidic, neutral and basic conditions. For detailed cyclic voltammograms studies of 4-nitrophenol of concentration 250 ppm and at a sweep rate of 100 mV/s were recorded at various pH media. The detailed study of effect of pH was studied by correlating the peak potential and peak current with pH. Fig. 2 shows the plot between -E_p and pH. The peak potential suffers cathodic shift with increasing the pH, which is a general expectation in electroreduction. Fig. 3 represents the influence of pH on the peak current. It shows that at pH 7.0 maximum peak current is observed.

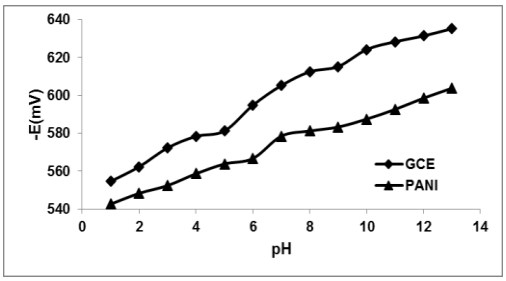


Fig. 2 Curve of potential and pH

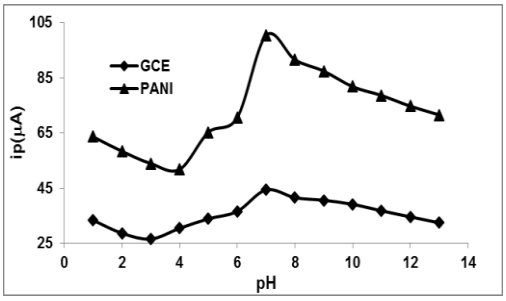


Fig. 3 Curve of peak current and pH

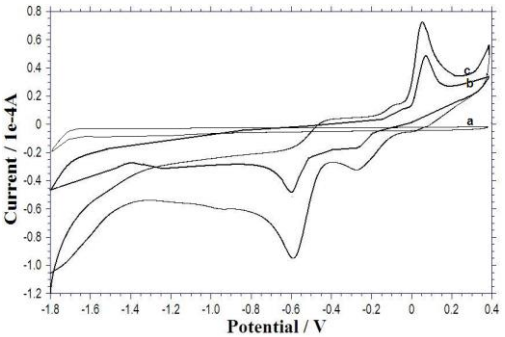


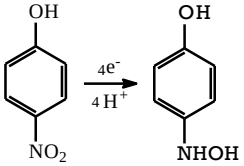
Fig. 4 Cyclic voltammogram behavior of a) Bare GCE b) 250 ppm of 4-nitro phenol on GCE c) 250 ppm of 4-nitro phenol on Nanosize PANI/GCE in pH 7.0 at 100 mV/s

The electrochemical oxidation and reduction of 4-NP were investigated at GCE and nanosize PANI/GCE through cyclic voltammetry and represented in Fig. 4. Redox signals were observed in pH 7.0 without 4-NP at PANI/GCE, suggesting that nanosize PANI is an electrochemically active material in the selected potential range. After 4-NP was added into pH 7.0, an obvious three oxidation and reduction peaks were obtained at both electrodes. It is no doubt that the redox peak should be attributed to the oxidation and reduction of 4-NP. However, corresponding reduction peak was observed in the following reverse scan from -1.8 V to 0.4 V, implying that the reduction of 4-NP is a totally irreversible electrode process under the above experimental conditions.

The effect of scan rate was investigated over the range from 25 to 500 mV/s on the cyclic voltammetric behavior of 4-NP. The peak current vs scan rate plot shows curve line. A plot of peak current vs. the square root of scan was found to be linear for the selective peak. The log of peak current against log of scan rate plot shows a straight line with a slope value of 0.3452. These results indicated that the overall reduction process of 4-NP is diffusion-controlled reaction.

3.3 Reaction Mechanism

Reduction of 4-nitrophenol may be due to transfer of 4e$^-$ and 4H$^+$ in pH 7.0. The nitro group of 4-NP reduced to hydroxyl group (Scheme 1).



Scheme 1 Reduction mechanism of 4-nitrophenol

https://doi.org/10.30799/jnst.174.18040526

Cite this Article as: R. Manikandan, A. Shoba, N. Senthil Kumar, Quantification of 4-nitrophenol on nanosize polyaniline modified glassy carbon electrode through electrochemical method, J. Nanosci. Tech. 4(5) (2018) 560–563.

3.4 Differential Pulse Stripping Voltammetry (DPSV)

Considerable responses of 4-NP in cyclic voltammetry suggested the development of stripping analysis for its analytical determination. Voltammetric studies led to the selection of nanosize PANI/GCE as the most suitable electrode in pH 7.0 as the medium for DPSV studies. A series of experiments were carried out in cathodic direction to optimise the parameters like accumulation potential, initial scanning potential, pulse height, pulse width and scan rate before analytical determination using DPSV.

3.5 Effect of Accumulation Potential

Generally adsorptive stripping voltammetry involves two major steps. The analyte molecules are first accumulated at the electrode surface from the bulk and then the accumulated molecules are stripped out giving specific signals. Hence optimisation of the accumulation potential was done first. For this study, the potential was varied from 400 to -600 mV at an accumulation time of 5 sec. Maximum peak current was observed at -500 mV and it was fixed as the optimum accumulation potential.

3.6Effect of Deposition Time

The effect of accumulation time on the stripping signal was studied by varying it from 0 to 120 sec at optimum accumulation potential. The peak current increased with the accumulation time and reached maximum value at 60 sec.

3.7 Effect of Initial Scanning Potential

The initial scan potential (E_{ini}) is another important parameter as it confirms the non-faradaic nature of the preconcentration step. It also controls both the peak potential and peak current in the stripping voltammogram. The influence of initial potential on the peak current was studied by varying it from 600 to - 200 mV. The peak current is suffered by this initial potential in a different way. Better response i.e. high peak current with better resolution was observed at 400 mV. Hence 400 mV was fixed as initial scanning potential and the reproducibility of the method was determined by making successive measurements.

3.8 Effect of Pulse Amplitude, Pulse Period and Pulse Width

Effect of pulse amplitude was varied between 10 to 100 mV and the optimum value found out was 15 mV. Effect of pulse period was studied by varying from 10 to 75 mSec. Similar to pulse period, pulse width is also examined on peak nature between 15 to 80 mSec. The pulse width of 40 mSec and pulse period 25 mSec were chosen as optimum value where maximum peak current was observed.

3.9 Effect of Scan Rate

After fixing the above parameters, effect of scan rate was also studied. Scan rate was varied from 25 to 125 mV/Sec. Highly resolved higher current stripping response was obtained at the scan rate 75 mV/Sec.

3.10 Concentration Dependence

Experimental results showed that the cylic voltammetric peak current increased with increase in concentration of 4-NP. A representative differential pulse stripping voltammogram is given in Fig. 5. A calibration plot, ip = 0.436 Conc.- 25.8; R^2 = 0.997 showed the linear dependency of peak current with concentration (Fig. 6). The range of determination limit was between 100 and 500 ppb. The LOD is 50 ppb on nanosize PANI/GCE. The reproducibility of the stripping signal was realised in terms of relative standard deviation for 7 measurements carried out at a concentration level of 250 ppb and found to be 1.76% in DPSV.

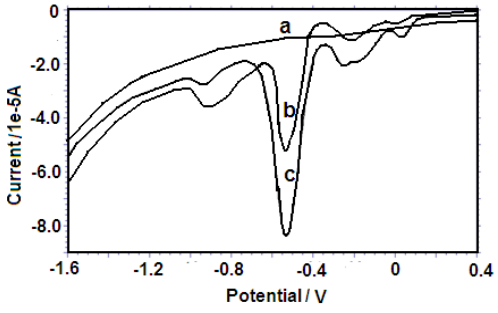


Fig. 5 DPSV of a) Bare GCE b) 250 ppb of 4-nitro phenol on GCE c) 250 ppb of 4-nitro phenol on Nanosize PANI/GCE

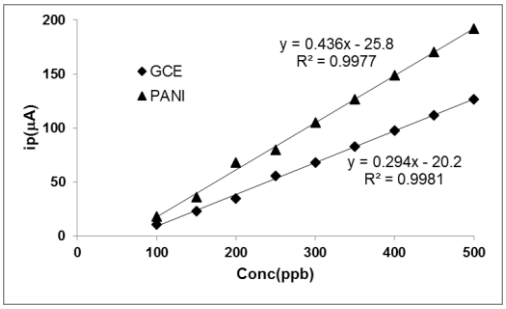


Fig. 6 Calibration plot of DPSV on GCE and Nanosize PANI/GCE

4. Conclusion

The electrochemical oxidation and reduction of 4-nitrophenol was successfully investigated at nanosize PANI modified GCE. The modified electrode was characterized by atomic force microscopy and electrochemically, optimized, and utilized for the determination of 4-nitrophenols. The entire analysis involves a two-step procedure: an accumulation step at open circuit, followed by medium exchange to a pure electrolyte solution for the voltammetric quantification. An electrochemical quantification of 4-nitrophenol has been developed. The AFM behavior of nanosize PANI/GCE and 4-nitrophenol adsorbed on electrode shows nanorod and granular morphology. The DPSV behavior of 4-nitrophenol was studied on nanosize PANI/GCE modified surface and best reproducibility was obtained. The lower limit of detection is 100 ppb on PANI/GCE modified surface whereas 100 ppm on bare GCE electrode. The results indicated that nanosize PANI/GCE showed good electrochemical redox behavior to 4-NP which is attributed to the combination of the excellent properties.

References

[1] M.M. Cordero-Rando, M.B. Zamora, M. Juan, B. Salvador, I.N. Rodroguez, et al., Electro chemical study of 4-nitro phenol at a modified carbon paste electrode, Mikrochimca. Acta. 132 (1999) 7-11.

[2] M.A. El Mhammedi, M. Achak, M. Bakasse, A. Chtaini, Electrochemical determination of para-nitrophenol at apatite-modified carbon paste electrode: Application in river water samples, J. Hazard. Mater. 163 (2009) 323-328.

[3] Galeano-Diaz, Guiberteau-Cabanillas, Mora-Diez, Parrilla-Vazquez, Salinas-Lopez, Rapid and sensitive determination of 4-nitrophenol, 3-methyl-4-nitrophenol, 4,6-dinitro- o-cresol, parathion-methyl, fenitrothion, and parathion-ethyl by liquid chromatography with electrochemical detection, J. Agri. Food Chem. 48 (2000) 4508-4513.

[4] A. Niazi, A. Yazdanipour, Spectrophotometric simultaneous determination of nitrophenol isomers by orthogonal signal correction and partial least squares, J. Hazard. Mater. 146 (2007) 421-427.

[5] X. Guo, Z. Wang, S. Zhou, The separation and determination of nitro phenol isomers by high-performance capillary zone electrophoresis, Talanta 64 (2004) 135-139.

[6] Z. Liu, J. Du, C. Qiu, L. Huang, H. Ma, et al., Electrochemical sensor for detection of p-nitrophenol based on nanoporous gold, Electrochem. Commun. 11 (2009) 1365-1368.

[7] C. Xu, J. Wang, L. Wan, J. Lin, X .Wang, Microwave-assisted covalent modification of graphene nano sheets with hydroxypropyl-β-cyclodextrin and its electrochemical detection of phenolic organic pollutants, J. Mater. Chem. 21 (2011) 10463-10471.

[8] Jinlong Liu, Yihong Chen, Yujing Guo, Fengling Yang, Fangqin Cheng, Electrochemical sensor for o-nitrophenol based on *β*-cyclodextrin functionalized graphene nanosheets, J. Nanomater. 2013 (2013) 632809-1-6.

[9] R. Sripriya, M. Chandrasekaran, K. Subramanian, K. Asokan, M. Noel, Electrochemical destruction of p-chlorophenol and p-nitrophenol - Influence of surfactants and anode materials, Chemosphere 69 (2007) 254-261.

[10] Sangita Gupta, A comparative electrochemical behaviour study of p-nitrophenol using GC and Pt Electrode, IRA Int. J. Appl. Sci. 6 (2017) 94-105

[11] Sulaf Samir Ibrahem, A Study of the Kinetic and mechanism of electrochemical reduction for para nitro phenol, 2,4- di nitro phenol , 2,4,6-tri nitro phenol in HCl (0.5 M) medium, Chem. Mater. Res. 9 (2017) 7-12.

[12] N. Negash, H. Alemu, M. Tessema, A comparative electrochemical behaviour study and analytical detection of the p-nitrophenol using silver solid amalgam, mercury, and silver electrodes, Int. Scholar. Res. Notice 2015 (2015) 459246-1-11.

[13] Honghong Rao, Weiming Guo, Huihui Hou, Hui Wang, Bo Yin, Zhonghua Xue, Guohu Zhao, Electroanalytical investigation of p-nitrophenol with dual electroactive groups on a reduced graphene oxide modified glassy carbon electrode, Int. J. Electrochem. Sci. 12 (2017) 1052-1063.

[14] Ayan Liao, Peng Li, Hui Zhang, Manman Guo, Yue Xia, Zelin Li, Wei Huang, Highly sensitive determination of 4-nitrophenol at a nafion modified glass carbon nano film electrode, J. Electrochem. Soc. 164 (2017) H63-H69.

[15] Sukanya Ramaraj, Sakthivel Mani, Shen-Ming Chen, Selvakumar Palanisamy, Vijayalakshmi Velusamy, et al., Hydrothermal synthesis of Cr_2Se_3 hexagons for

https://doi.org/10.30799/jnst.174.18040526

Cite this Article as: R. Manikandan, A. Shoba, N. Senthil Kumar, Quantification of 4-nitrophenol on nanosize polyaniline modified glassy carbon electrode through electrochemical method, J. Nanosci. Tech. 4(5) (2018) 560–563.

sensitive and low level detection of 4-nitrophenol in water, Sci. Rep. 8 (2018) 4839-4848.
[16] Mexiang Wan, Ming Li, Junchao Li, Zhenxing Liu, Structure and electrical properties of the oriented polyaniline films, J. Appl. Polym. Sci. 53 (1994) 131-138.
[17] C.L. Forryan, R.G. Compton, Studies of the electrochemical reduction of 4-nitrophenol indimethylformamide: evidence for a change in mechanism with temperature, Phys. Chem. Chem. Phys. 5 (2003) 4226-4230.
[18] Bogdan Butoi, Andreea Groza, Paul Dinca, Adriana Balan, Valentin Barna, Morphological and structural analysis of polyaniline and poly(o-anisidine) layers generated in a DC glow discharge plasma by using an oblique angle electrode deposition configuration, Polymers 9 (2017) 732-750.

https://doi.org/10.30799/jnst.174.18040526

Cite this Article as: R. Manikandan, A. Shoba, N. Senthil Kumar, Quantification of 4-nitrophenol on nanosize polyaniline modified glassy carbon electrode through electrochemical method, J. Nanosci. Tech. 4(5) (2018) 560–563.