iJRASET
International Journal For Research in Applied Science and Engineering Technology



# INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

**Volume:** 6 **Issue:** II **Month of publication:** February 2018

**DOI:** http://doi.org/10.22214/ijraset.2018.2036

www.ijraset.com

Call: 08813907089 | E-mail ID: ijraset@gmail.com

International Journal for Research in Applied Science & Engineering Technology (IJRASET)
*ISSN: 2321-9653; IC Value: 45.98; SJ Impact Factor :6.887*
*Volume 6 Issue II, February 2018- Available at www.ijraset.com*

# Electrooxidation and Kinetic Study of p-Nitroaniline in Acidic Solution

Richa Paliwal[1], Rajdeep Malik[2], Ravi Kant[3]
[1, 2, 3]*Department of Chemistry, Gurukula Kangri Vishwavidyalaya, Haridwar, Uttarakhand 249404*

***Abstract:*** ***In this study, electro-oxidation of p-nitroaniline (p-NA) was carried out in an acidic solution (acetone and sulphuric acid (0.5M) mixture) on a platinum electrode (PE) by employing an eco-friendly electrochemical technique, cyclic voltammetry. Variations in anodic peak current with the scan rates and p-NA concentrations are taken into account to find out the control of the reaction, kinetic and analytical parameters of the reaction. The anodic reaction is found to be as diffusion-controlled nature with a one-electron transfer in the rate-determining step. Kinetic parameters such as standard heterogeneous rate constant ($k^0$, $1.761 \times 10^3$ $s^{-1}$), anodic electron transfer rate constant ($k_{ox}$, $2.136 \times 10^3$ $s^{-1}$), electron transfer coefficient of reaction (α, 1.271) and formal potential ($E^0$, 1.171 V) were evaluated under the influence of scan rates. The result showed fast electrode-kinetics of p-NA electro-oxidation on a PE.***

***Keywords: p-nitroaniline, Electrooxidation, Kinetic parameters, Cyclic voltammetry, Platinum electrode***

## I. INTRODUCTION

Aromatic amine includes aniline and substituted anilines [1]. p-nitroaniline(p-NA) is a nitro-substituted aniline. p-NA has been used as a precursor in various industrial products such as drugs, pesticides, dyes, plastic, explosives, rubber, and epoxy polymers and combustion products [5,6]. It has harmful effects such as genotoxic, allergenic, mutagenic, and carcinogenic on human health [2-4]. Various manufacturers of herbicides, pesticides, dyes, and pharmaceuticals industries release toxic effluents consisting of p-NA in it [6]. US Environmental Protection Agency (EPA) listed nitroaniline isomers as priority pollutants [7]. It is an environmental concern that carcinogenic effluents and toxics released as the end products of the degradation of herbicides and azo dyes etc. in water from different industries are the main cause of enhancing toxicity in water. As water has a direct impact on human health, so water should be treated necessarily.

p-NA, due to having specific effect of an electron withdrawing nitro group at para position to an electron-donating amino group, has attracted much scientific attention [9]. p-NA has been detected by many techniques and methods such as spectro photometry, chromatography, Fenton oxidation process [5], surface-enhanced Raman scattering [10], flow electrochemical determination [11-12], transient photolysis, steady-state photo degradation [13] and electrochemical techniques. But electrochemical technique is the most proficient technique since it provides a very consistent outcome, simple to operate, highly sensitive, accurate, rapidly analyzed [14]. Voltammetry is an eco-friendly technique to investigate pollutants and other compounds [15]. p-NA has also been investigated using different electrodes with the help of this technique [16-17]. Ryan developed cyclic staircase voltammetry in the late seventies [18]. It is widely used to determine the mechanism and kinetic parameters of reactions [19-20]. Jeff Bacon showed the anodic oxidation of p-NA [21]. Polarographic oxidation and reduction of p-nitroaniline [22] have also studied. Rudolf Holze [23] showed the p-NA adsorption on gold and silver electrode in neutral and acidic perchlorate solutions [24]. In electrochemical studies, chemically-modified electrodes and nanoparticle-modified electrodes are used to enhance the activity of electrode for redox reaction and electro-deposition. It is now in trend for many years [25-26]. Chemically-modified electrodes are being used to detect samples in different analytical application [27]. A chemical sensor electrode was also used to detect p-NA [28].

The aim of this study is to find out: (1) the control of electrochemical reaction: diffusion-controlled or adsorption-controlled (2) the electro-oxidation parameters of p-NA: (a) kinetic parameters (standard rate constant: ko; electron transfer rate for anodic reaction: kox and transfer coefficient: α) (b) analytical parameters (linearity, limit of quantification: LOQ and limit of detection: LOD),

## II. MATERIAL AND METHODS

### *A. Chemicals and solutions*

All the chemicals such as ethanol, acetone (as solvent), sulphuric acid ($H_2SO_4$) (as supporting electrolytes) were of analytical grade and were used without further purification. An aqueous solution of $H_2SO_4$ (0.500 mol $L^{-1}$) and dilute solution of a 0.100 mol $L^{-1}$ $H_2SO_4$ were prepared using double distilled water (DDW). Recrystallization methods were used to purify p-NA (Molychem)

©IJRASET (UGC Approved Journal): All Rights are Reserved

respectively in ethanol. After purification,the stock solutions were prepared in acetone. All experiments were carried out at room temperature (24-26°C).

*B. Voltammetric Apparatus*

An Autolab model PGSTAT 101 potentiostat/galvanostat 663 VA Stand (Metrohm AG, Netherlands) was used to conduct cyclic voltammetry. Three electrode system consisted of a Pt disc electrode (PE) (0.031 $cm^2$) as the working electrode, Ag/AgCl/3M KCl electrode as the reference and a Pt wire as the counter electrode. All potentials mentioned in this work were as referred to a reference electrode. All electrodes were rinsed with DDW. The working electrode was polished with alumina powder ($Al_2O_3$) before each cyclic voltammetric experiments.

*C. p-NA electro-oxidation*

The cyclic voltammetric experiment was conducted within the scan potential window range from +0.5 V to +1.3 V at the 50 $mVs^{-1}$-250 $mVs^{-1}$ different scan rates in a voltammetric cell with the p-NA solution (1 mmol $L^{-1}$) in an acidic solution [acetone and sulphuric acid (0.5M) mixture (A/SA mixture)] using the aforementioned voltammetric setup.

*D. Electrochemical kinetics*

Evaluation of the kinetic parameters by the analysis of the anodic peak current under the influence of different scan rates was studied. A linear relationship was established between anodic peak currents and concentrations (within the range from 1 to 15 mmol $L^{-1}$), between anodic peak currents and scan rates, and between peak potential and scan rates to find out the kinetic parameters of p-NA electro-oxidation.

## III. RESULT AND DISCUSSIONS

In the present work, the cyclic voltammetric technique was employed for p-NA electro-oxidation and to find out the control of the reaction, transfer of electron in the reaction, kinetic and analytical parameters.

*A. Cyclic Voltammetric study for PE*

Cyclic voltammogram (CV) of p-NA electro-oxidation showed only one anodic peak at the scan rate 50$mVs^{-1}$ in A/SA mixture when scanning towards positive potential [figure (1a)]. Any corresponding cathodic peak was not observed on the reverse scan indicating the reaction was irreversible.

Consecutive CVs in a solution containing 1mM of p-NA in A/SA mixture at the scan rate 50$Vs^{-1}$ were performed to find out the activity of bare PE (figure 1b). With the increasing number of cycles in CVs, the peak current descended and the peak potential shifted towards the more positive potential indicating the slow rate of the transferred electrons. After performing the number of cycles, the slow oxidation process occurred due to adsorption of p-NA on PE surface. A further increase in the number of cycles may block electrode surface by forming a layer on it. So, the first anodic peak of p-NA electro-oxidation has considered for further analytical experiments in this study.

FIGURE 1 (a) and (b)

1) *Influence of concentration:* The CV of different concentrations of p-NA ranging from 1 to 15mM in A/SA mixture at the scan rate of 50$mVs^{-1}$ has shown in Figure 2 (a). The peak potential is proportional to the concentration of p-NA for the reactionwhen scanning towards positive potential. It shifts towards negative potential while concentration increases. It indicates the expertise of electro-oxidation of p-NA at the high concentration of p-NA. The CVs of all concentrations produce the same shape. The anodic peak current is also proportional to the concentration. It indicates that no remarkable adsorption has shown on the electrode surface for the first anodic peak. The value of the limit of detection and the limit of quantification (LoD = 3δ/m, LoQ = 10δ/m; where δ=the standard deviation of the intercept of the y-coordinates from the line of best fit, and m the slope of the same line) is found to be 0.989mM and 3.290mM respectively From the plot of Ip versus concentration [figure 2 (b)].

FIGURE 2 (a) and (b)

2) *Influence of Scan Rate:* The influence of different scan rates on p-NA electro-oxidation investigated by using cyclic voltammetry with the different scan rates ranging from 0.05 to 0.25$Vs^{-1}$ (figure 3). The peak currents and peak potentials were ascertained for the first scan of p-NA electro-oxidation at different scan rates. There was no cathodic peak has examined while scanning reverse direction.

Figure 3

©IJRASET (UGC Approved Journal): All Rights are Reserved

The reversibility of electrochemical reaction rate, controls by diffusion or adsorption, has investigated by two ways: dependence of Ip on $\nu^{1/2}$ and of log Ip on log ν [29] [figure 4 (a), (b)]. Figure 4 shows these plots for the first anodic peak of p-NA in A/SA mixture. If Ip changes linearly with $\nu^{1/2}$, intercepting the origin of the coordinates, then the process is considered as without kinetic interferences. However, for the linear coefficient, if Ip has a value of intercept which is not zero, then the process is considered as preceded or pursued by a homogeneous chemical reaction. [30]. At various scan rates ranging from 0.05 to 0.25$Vs^{-1}$, the anodic peak current depends linearly on the sqare root of scan rate and is described by the following equation:

$$Ip(\mu A) = 63.041\, V^{1/2}\left(Vs^{1/2}\right)^{1/2} - 0.532\,\mu A\ (R = 0.999)$$

The origin of the coordinates is not intercepted by this linear fit, [figure 4 (a)], the electrode process is diffusion-control in nature and is proceeded by a chemical reaction. Alternatively, the dependence of log Ip on log ν is linear. The slope of this linear fit is 0.505. Therefore according to Bard, Faulkner, and others [19], this process is only controlled by diffusion and is described by the following equation:

$$\log\ Ip = 0.505 \log v\ (Vs^{-1})\mu A + 1.794\ (R = 0.999)$$

While when the value of a slope is close to 1.0, the process is expected to be an adsorption-controlled process [19, 32, 33].Further, the Tafel slope, b, has determined by using the following equation for an irreversible diffusion-controlled reaction [34].

$$Ep = b/2 \ln\ \upsilon + constant$$

FIGURE 4 (a) and (b)

A linear relationship and a slope (b⁄2)= ∂Ep⁄∂(logν) ) of 0.034V has determined from the plot of Ep versus logν in the range from 0.05 to 0.25$Vs^{-1}$ applied potential (figure 5). From the plot, Tafel value (b) is obtained 68.580mV for p-NA electro-oxidation. This value exhibits no remarkable adsorption for the first anodic peak. The Tafel value indicates adsorption or the participation of reaction intermediates on the electrode surface for a one-electron process in the rate determining step if it is more than 118 mV [32]. With the increase in scan rate, the peak potential shifted towards a more positive value. It confirms that the oxidation process is irreversible (figure 5). The relationship can be expressed as

$$Ep\ (V) = 0.034\ logv\ (Vs^{-1}) + 1.220\ (R = 0.979)$$

Figure 5

As for an irreversible electrode process, according to Laviron [35], Ep is defined as

$$Ep = E^0 + (2.303RT/\alpha nF)log(RTk^0/\alpha nF) + (2.303RT/\alpha nF)logv$$

where α is the transfer coefficient, $k^0$ is the standard heterogeneous rate constant of the reaction, n is the number of electron transferred, ν is the scan rate, and $E^0$ is the formal potential. Other symbols should be considered as conventional. Consequently, from the slope of a plot of Ep versus logν (figure 5), the value of αn can be determined as 1.724. According to Bard and Faulkner [19], α can be expressed as

$$\alpha = 47.7/E_p - E_{p/2}\ mV$$

Where $E_{p/2}$ is the potential at half-peak current.

So, the average value of α is calculated as 1.270.

Further, the number of the transferred electron (n) was calculated from the αn value as 1.35-1 in the p-NA electro-oxidation. We can calculate the standard heterogeneous rate constant ($k^0$) by knowing the value of the formal potential ($E^0$) (from the intercept of the plot Ep versus ν by extrapolating to the vertical axis at ν=0) [36-37]. The formal potential ($E^0$) and the standard heterogeneous rate constant ($k^0$) for the reaction were obtained as 1.171 and 1.761 × $10^3$ $s^{-1}$ respectively. The electron transfer rate constant ($k_{ox}$) is a function of the applied potential thus can be calculated from the equation [38].

$$K_{ox} = K_0 \times exp\{-(1-\alpha)nF(E-E^0)/(RT)\}$$

So, the $k_{ox}$ was obtained as 2.136 × $10^3$ $s^{-1}$.

©IJRASET (UGC Approved Journal): All Rights are Reserved

Accordingly, the p-NA anodic oxidation is found to be a one-electron process. Scheme A [39] shows the Suggested-mechanism of p-NA electro-oxidation.

## IV. CONCLUSIONS

This study suggests that the electro-oxidation of p-NA in an acidic solution is a one-electron irreversible oxidation to form cation radical at the high rate constant on a bare electrode with the product name 4-nitrocyclohexa-2, 5-dienimine. Kinetic parameters were evaluated for the reaction.

## REFERENCES

[1] T. Kahl, K. W. Schröder, F. R. Lawrence, W. J. Marshall, H. Höke, R. Jäckh, "Aniline" in Ullmann's Encyclopedia of Industrial Chemistry, John Wiley & Sons: New York (2007).
[2] H. M. Pinheiro, E. Touraud, O. Thomas, Aromatic Amines from Azo Dye Reduction: Status Review with Emphasis on Direct UV Spectrophotometric Detection in Textile Industry Wastewaters. Dyes Pigm. 62 (2) (2004) 121-139.
[3] WHO/IARC. Monographs on the evaluation of carcinogenic risks to humans: some aromatic amines, organic dyes and related exposures. Lyon (France): IARC/WHO. (2010) 99.
[4] R. S. Nair, C. S. Auletta, R. E. Schroeder, F. R. Johannsen, Chronic toxicity, oncogenic potential, and reproductive toxicity of p-nitroaniline in rats, Apppl. Toxicol, 15 (3) (1990) 607-621.
[5] Jian-HuiSun,Sheng-Peng Sun, Mao-Hong Fan, Hui-Qin Guo, Li-Ping Qiao, Rui-Xia Sun, A kinetic study on the degradation of p-nitroaniline by Fenton oxidation process,J. Hazard Mater., 148 (2007) 172-177.
[6] A. Khalid, M. Arshad, D. E. Crowley, Water Res, 4 (4), (2009) 1110-1116.
[7] EPA, Method 1625, Washington, DC: Fed. Reg. U.S. Government Print Office, September (1994).
[8] B. Jurado-Sanchez, E. Ballesteros, M. Gallego, Occurrence of aromatic amines and N-nitrosamines in the different steps of a drinking water treatment plant. Water Res. 46 (14) (2012) 4543-4555.
[9] A. Qureshi, V. Verma, A. Kapley, H. J. Purohit, Degradation of 4-nitroaniline by Stenotrophomonas strain HPC 135, IntBiodeterior Biodegradation, 60 (2007) 215-218.
[10] T. Tanakaa, A. Nakajimab, A. Watanabeb, T. Ohnoa, Y. Ozakib, Surface-enhanced Raman scattering spectroscopy and density functional theory calculation studies on adsorption of o-, m-, and p-nitroaniline on silver and gold colloid, J. Mol. Struct., 661-662 (2003) 437-449.
[11] W. Ma, Y. Fang, Experimental (SERS) and theoretical (DFT) studies on the adsorption of p-, m-, and o-nitroaniline on gold nanoparticles, Journal of Colloid and Interface Science, 303 (2006) 1-8.
[12] T. E. L. Ouafy, A. Chtaini, H. Oulfajrite, R. Najih, H. E. L. Ouafy, Flow electrochemical determination of 4-nitroaniline transformation in real sample using natural phosphate modified carbon paste electrode, Org ChemInd J., 11 ( 8) (2015) 293-299.
[13] H. Ma, M. Wang, C. Pu, J. Zhang, S. Zhao, S. Yao, J. Xiong, Transient and steady-state photolysis of p-nitroaniline in aqueous solution, J. Hazard Mater. 165 (1-3) (2009) 867-873.
[14] A. Carlos. Martı´nez-Huitle, S. Ferro, Electrochemical oxidation of organic pollutants for the wastewater treatment: direct and indirect processes, Chem. Soc. Rev., 35 (2006) 1324-1340.
[15] R. S. Nicholson, I. Shain, Theory of stationary electrode polarography single scan and cyclic methods applied to reversible, irreversible, and kinetic Systems, Adv. Anal. Chem. 36 (4) (1964) 706-723.
[16] F. Zhao, L. Liu, F. Xiao, J. Li., R. Yan, S. Fan, and B. Zeng, Sensitive voltammetric response of p-nitroaniline on single-wall carbon nanotube-ionic liquid gel modified glassy carbon electrodes, Electroanalysis, 19 (2007) 1387-1393.
[17] V. N. Maistrenko, S. V. Sapel'nikova, F. Kh. Kudasheva, F. A. Amirkhanova, Isomer-selective carbon-paste electrodes for the determination of nitrophenol, nitroaniline, and nitrobenzoic acid by adsorption-stripping voltammetry, J anal. Chem. 55 (2000) 586-589.
[18] M. D. Ryan, Cyclic staircase voltammetry, J. Electroanal. Chem. 79 (1977) 105-119.
[19] A. J. Bard, L. R. Faulkner, Electrochemical Methods: Fundamentals and Applications, second edition, John Wiley and Sons, New York, (2001).
[20] R. G. Compton and C. E. Banks, Understanding Voltammetry, second edition, Imperial College Press, (2011).
[21] J. Bacon, R. N. Adams, Anodic oxidation of aromatic amines III substituted anilines in aqueous media, J. Am. Chem. Soc. 90 (24) (1968) 6596-6599.
[22] C. Oslon, H. Y. Lee, R. N. Adams, Polarographic oxidation and reduction of p-nitroaniline at carbon paste electrodes. J. Electroanal. Chem. 2 (1961) 396-399.
[23] R. Holze, The adsorption of p-nitroaniline on silver and gold electrodes as studied with surface enhanced Raman spectroscopy (SERS), Electrochim. Acta, 35 (6) (1990) 1037-1044.
[24] A. A. Jbarah, R. Holze, A comparative spectroelectrochemical study of the redox electrochemistry of nitroanilines, J. Solid State Electrochem 10 (2006) 360-372.
[25] M. H. A. Zavar, S. Heydari, G. H. Rounaghi, H. Eshghi, H.A. Toupkanloo, Electrochemical behavior of para-nitroaniline at a new synthetic crown ether-silver nanoparticle modified carbon paste electrode, Anal. Methods 4 (4) (2012) 953-958.
[26] H. Li, J. Li, Q. Xu and X. Hu, Poly(3-hexylthiophene)/TiO2 nanoparticle-functionalized electrodes for visible light and low potential photoelectrochemical sensing of organophosphorus pesticide chlopyrifos, Anal Chem., 83 (2011) 9681-9686.
[27] R. W. Murray, Chemically modified electrodes, Technical Report No. 12, Acc. Chem. Res, (1980).
[28] R. Ahmad, N. Tripathy, M. S. Ahn, Y. B. Hahn, Development of highly-stable binder-free chemical sensor electrodes for p-nitroaniline detection, J. Colloid Interface Sci. 494 (2017) 300-306.
[29] R. S. Nicholson, Theory and application of cyclic voltammetry for measurement of electrode reaction kinetics. Adv. Anal. Chem. 37 (11) (1965) 1351-1355.

©IJRASET (UGC Approved Journal): All Rights are Reserved

[30] E. Wudarska, E. Chrzescijanska, E. Kusmierek, J. Rynkowski, Voltammetric studies of acetylsalicylic acid electro-oxidation at platinum electrode, Electrochim. Acta 93 (2013) 189-194.
[31] G. Arslan, B. Yazici, M. Erbil, The effect of pH, temperature and concentration on electro-oxidation of phenol, J. Hazard. Mater. 124 (2005) 37-43.
[32] C. M. A. Brett, A. M. O. Brett, Electrochemistry: Principles, Methods and Applications, Oxford University Press, New York, (1994).
[33] P. T. Kissinger, W. H. Heineman, Laboratory Techniques in Electroanalytical Chemistry, second ed., Marcel Dekker, New York, (1996).
[34] J. A. Harrison, Z. A. Khan, The oxidation of hydrazine on platinum in acid solution, J. Electroanal. Chem. and Interface Electrochem., 28 (1970) 131-138.
[35] E. Laviron, General expression of the linear potential sweep voltammogram in the case of diffusionlesselectrochemical systems, J. Electroanal. Chem., 101(1979) 19-28.
[36] L. Fotouhi, M. Fatollahzadeh, M. M. Heravi, Electrochemical behavior and Voltammetric determination of sulfaguanidine at a glassy carbon electrode modified with a multi-walled carbon nanotube, Int. J. Electrochem. Sci., 7 (2012) 3919-3928.
[37] W. Yunhua, J. Xiaobo, H. Shengshui, Studies on electrochemical oxidation of azithromycin and its interaction with bovine serum albumin. Bioelectrochemistry. 64 (2004) 91-97.
[38] J. J. Van Benschoten, Y. T. Lewis, W. R. Heineman, D. A. Roston, P. T. Kissinger, Cyclic voltammetry experiments, J. Chem. Educ. 60 (1983) 772-776.
[39] X. Lin, Y. Ni, S. Kokot, Voltammetric analysis with the use of a novel electro-polymerised graphene-nafion film modified glassy carbon electrode: Simultaneous analysis of noxious nitroaniline isomers, J. Hazard. Mater. 243 (2012) 232-241.

©IJRASET (UGC Approved Journal): All Rights are Reserved

Figures

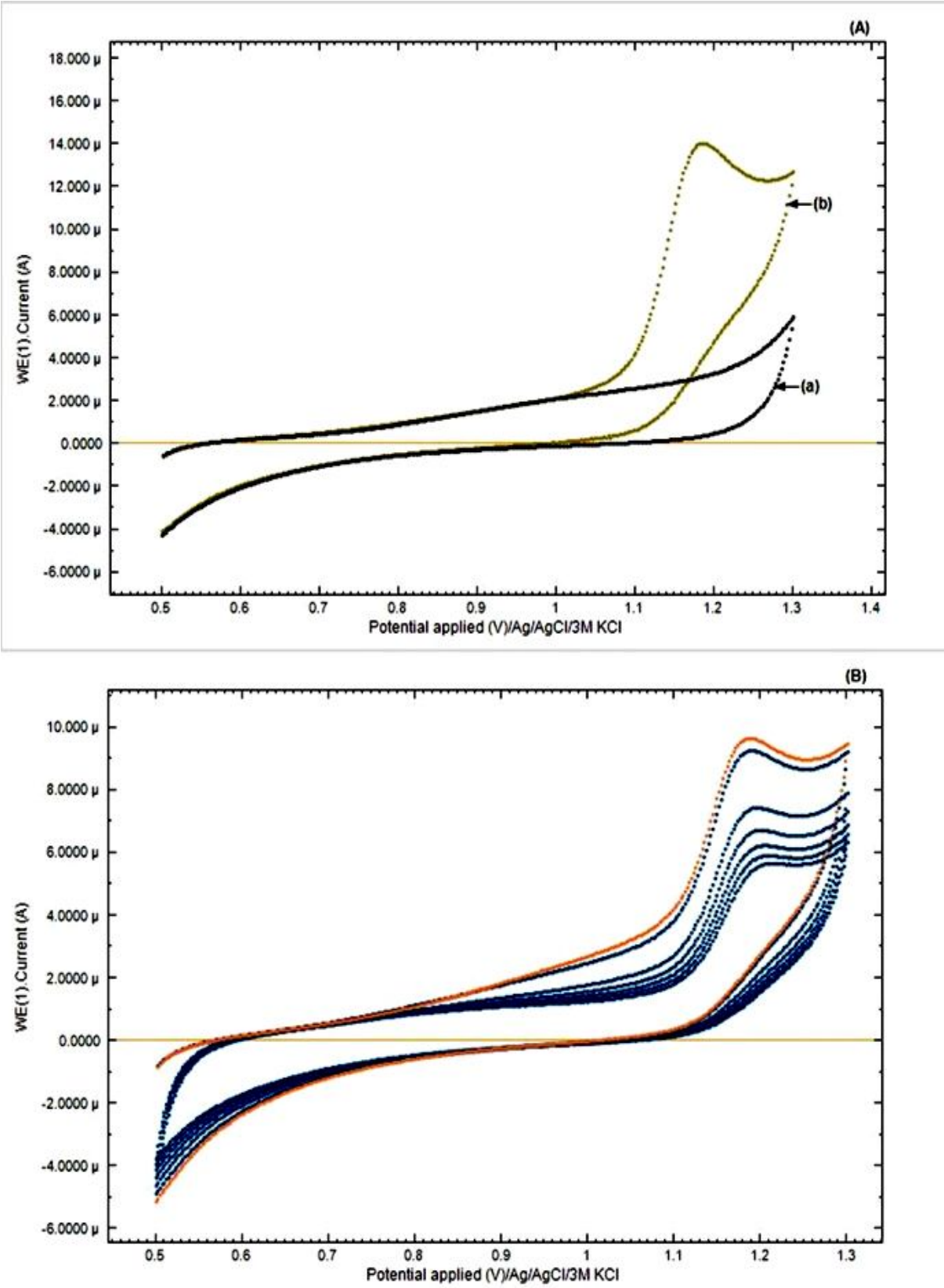



Figure 1.(A) Cyclic voltammograms (CVs) of platinum electrode (PE) (a) in absence of p-NA (b) containing 1mM p-NA, (B) Successive CVs recorded on PE for 1mM of p-NA.[in acidic solution (scan rate 50mVs$^{-1}$)]

©IJRASET (UGC Approved Journal): All Rights are Reserved

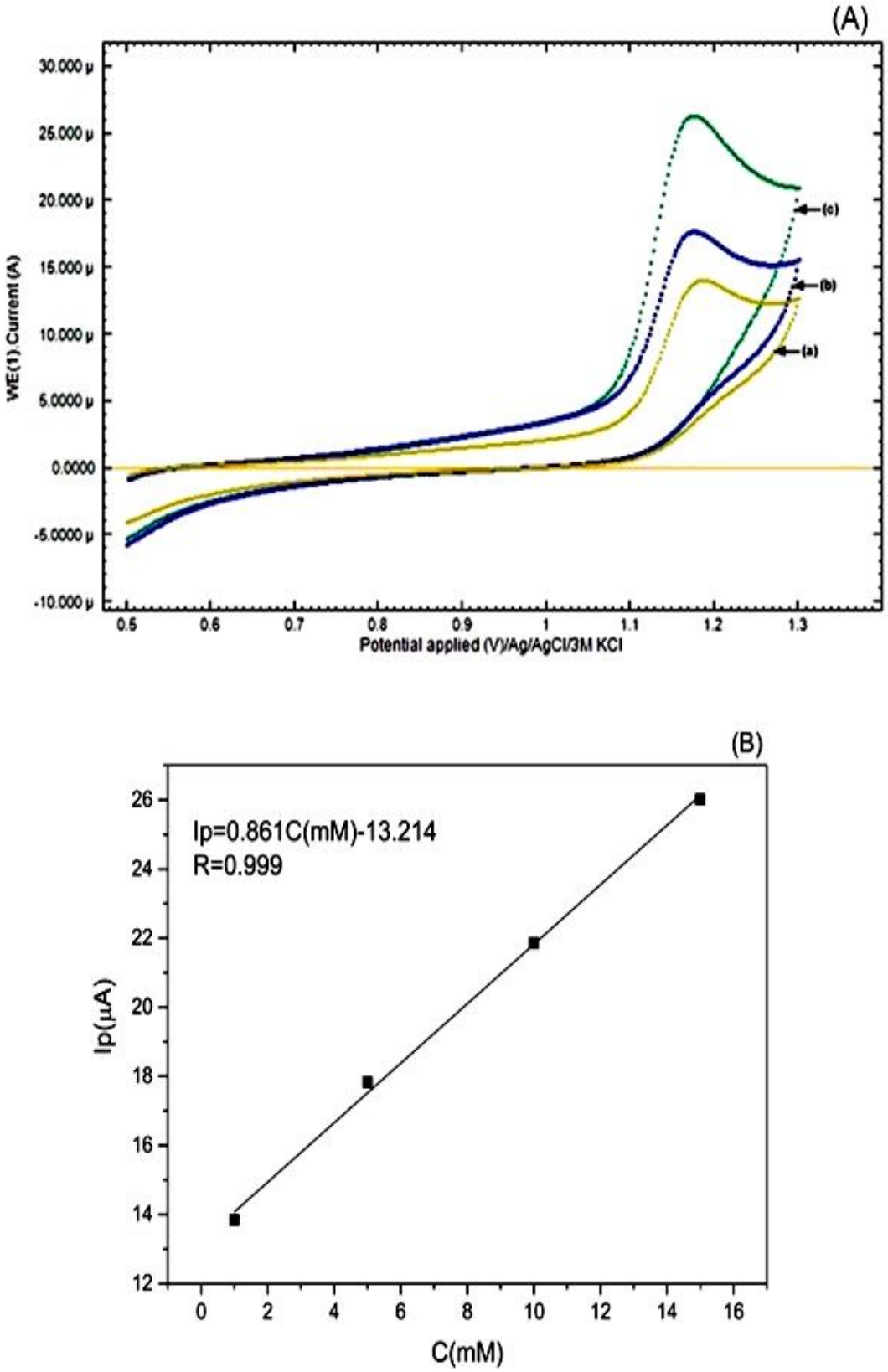



Figure 2. (A) CVs of PE in acidic solution with different concentrations [(a) 1,(b) 5 and (c) 15mmol $L^{-1}$) of p-NA at scan rate 50m$Vs^{-1}$, (B) Dependence of the anodic peak current (Ipa) on p-NA concentrations.

©IJRASET (UGC Approved Journal): All Rights are Reserved

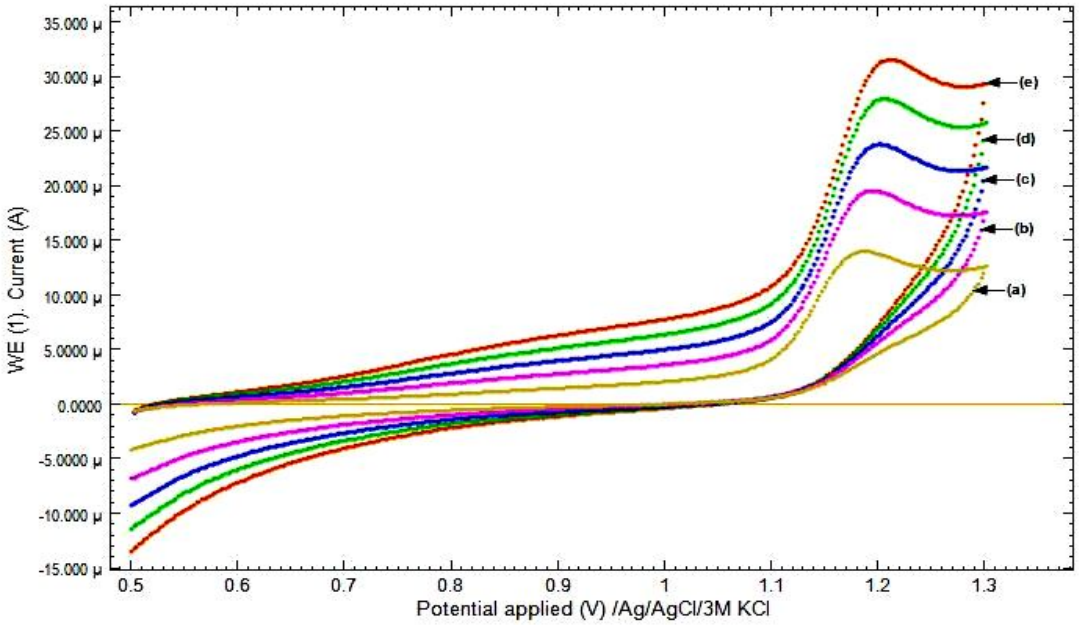



Figure 3 CVs of PE in acidic solution containing 1mM of p-NA at different scan rates (a) 50 (b) 100 (c) 150 (d) 200 (e) 250 $mVs^{-1}$.

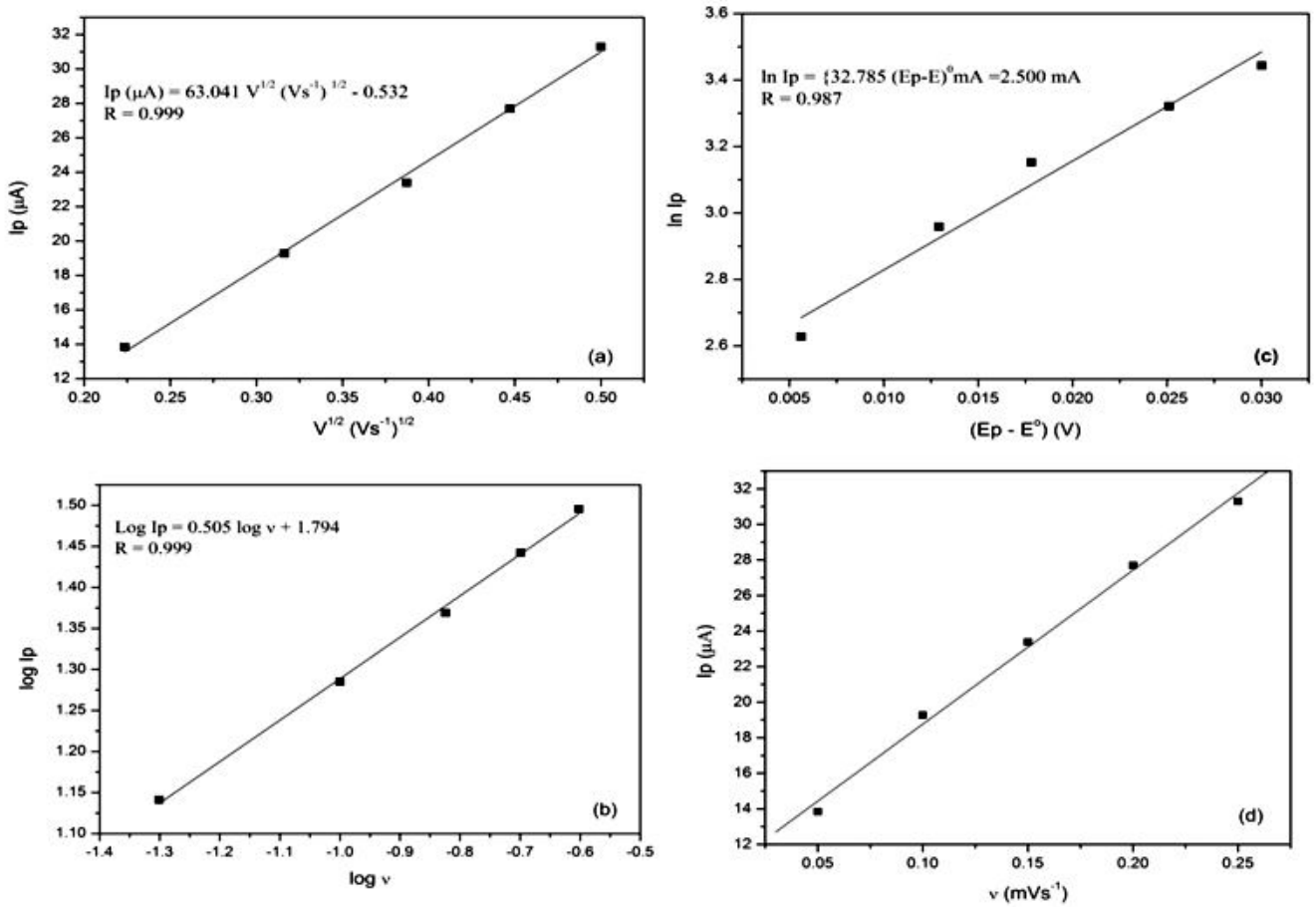



**Figure 4(a)** Logarithm of the peak current (Ip) versus logarithm of the scan rate (ν). **(b)**Showing dependence of peak current (Ip) on the square root of scan rate ($V^{1/2}$). **(c)**Naperian logarithm of Ip versus Ep-$E^0$. **(d)** Showing calibration plot of Ip versus scan rate (ν). (1mmol $L^{-1}$ of p-NA in acidic solution).

©IJRASET (UGC Approved Journal): All Rights are Reserved

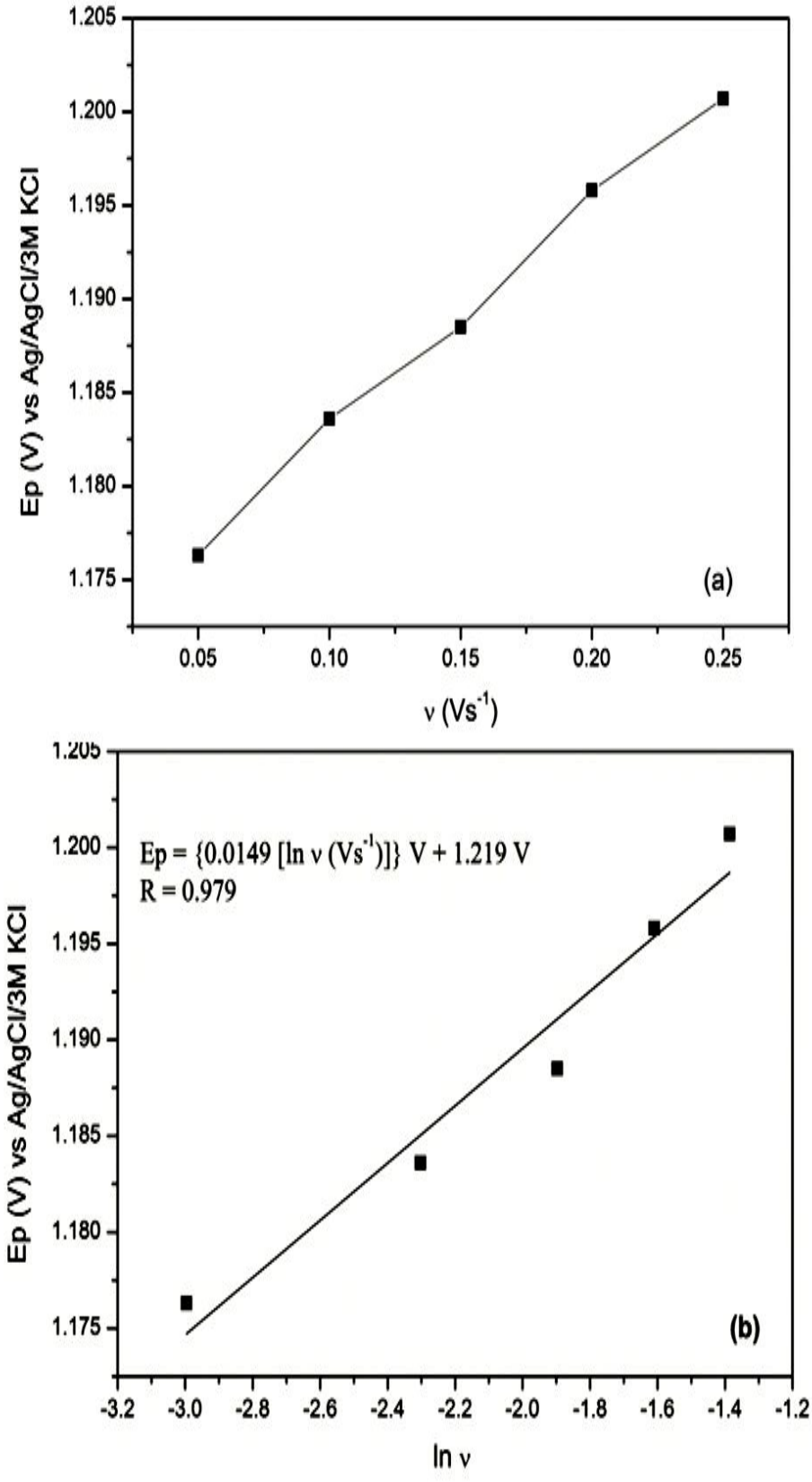
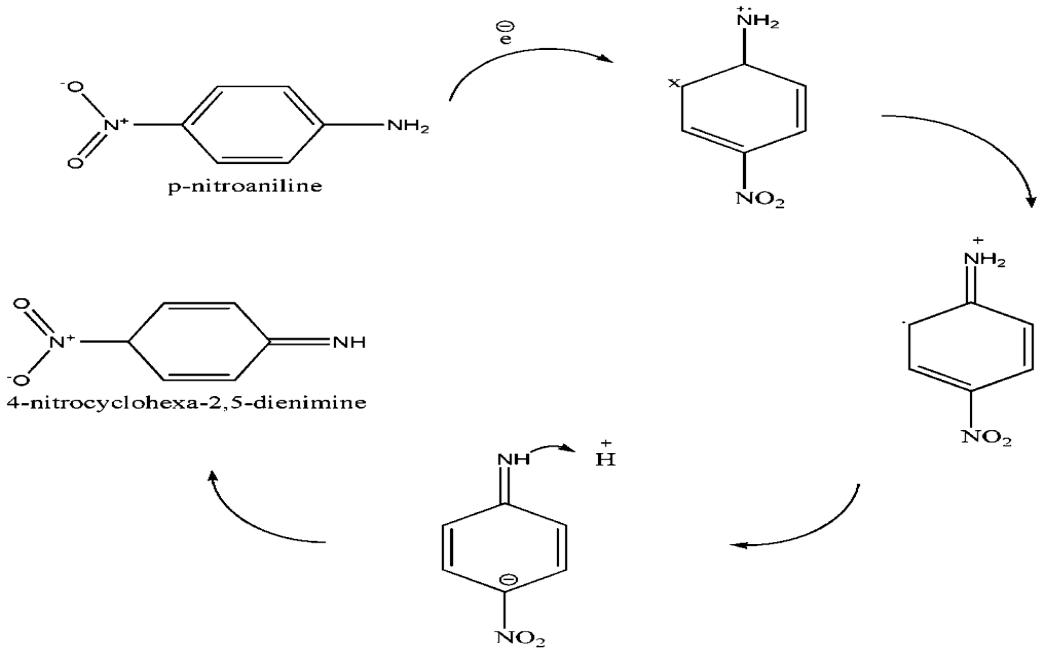



Figure 5. Dependence of peak potential, Ep, (a) on the potential scan rate, ν, (b) on the ln ν for the oxidation of p-NA (1 mmol $L^{-1}$) in acidic solution on PE.

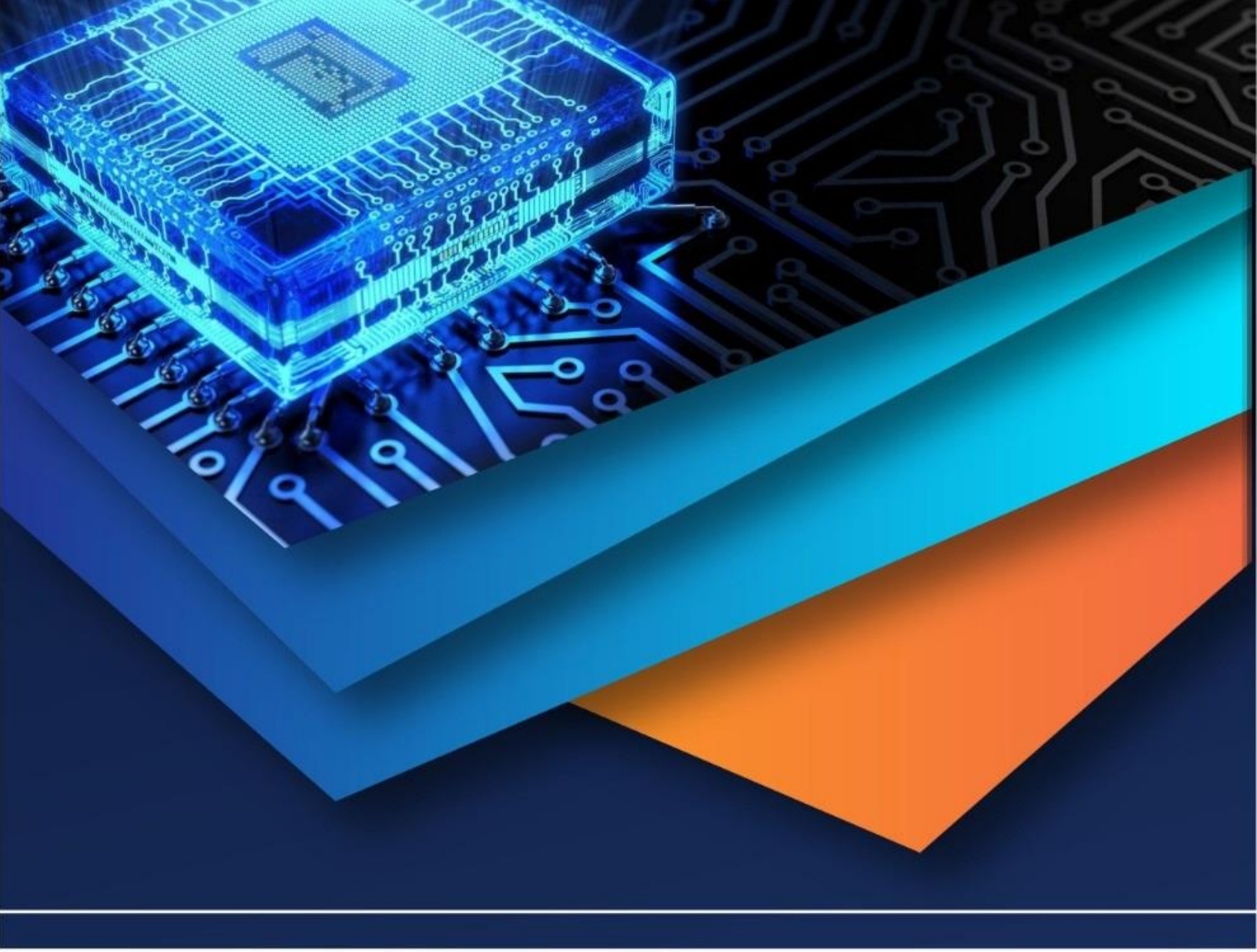
©IJRASET (UGC Approved Journal): All Rights are Reserved

*ISSN: 2321-9653; IC Value: 45.98; SJ Impact Factor :6.887*
*Volume 6 Issue II, February 2018- Available at www.ijraset.com*




Scheme (A)Showing Mechanism of Reaction

©IJRASET (UGC Approved Journal): All Rights are Reserved



10.22214/IJRASET

45.98

IMPACT FACTOR: 7.129

IMPACT FACTOR: 7.429

# INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Call : 08813907089 (24*7 Support on Whatsapp)