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Electrooxidation and Kinetic Study of p-Nitroaniline in Acidic Solution

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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 , $1.761 \times 10^3 \text{ s}^{-1}$), anodic electron transfer rate constant (k_{ox} , $2.136 \times 10^3 \text{ s}^{-1}$), 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: k^0 ; electron transfer rate for anodic reaction: k_{ox} 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)

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 1 mM 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 15 mM 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 reaction when 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 ($\text{LoD} = 3\delta/m$, $\text{LoQ} = 10\delta/m$; 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 0.989 mM and 3.290 mM respectively From the plot of I_p 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

The reversibility of electrochemical reaction rate, controls by diffusion or adsorption, has investigated by two ways: dependence of I_p on $v^{1/2}$ and of $\log I_p$ on $\log v$ [29] [figure 4 (a), (b)]. Figure 4 shows these plots for the first anodic peak of p-NA in A/SA mixture. If I_p changes linearly with $v^{1/2}$, intercepting the origin of the coordinates, then the process is considered as without kinetic interferences. However, for the linear coefficient, if I_p 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 0.25Vs⁻¹, the anodic peak current depends linearly on the square root of scan rate and is described by the following equation:

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

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 $\log I_p$ on $\log v$ 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:

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

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].

$$E_p = b/2 \ln v + \text{constant}$$

FIGURE 4 (a) and (b)

A linear relationship and a slope ($b/2 = \partial E_p / \partial (\log v)$) of 0.034V has determined from the plot of E_p versus $\log v$ in the range from 0.05 to 0.25Vs⁻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

$$E_p (V) = 0.034 \log v (Vs^{-1}) + 1.220 (R = 0.979)$$

Figure 5

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

$$E_p = E^0 + (2.303RT/\alpha nF) \log(RT k^0/\alpha nF) + (2.303RT/\alpha nF) \log v$$

where α is the transfer coefficient, k^0 is the standard heterogeneous rate constant of the reaction, n is the number of electron transferred, v 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 E_p versus $\log v$ (figure 5), the value of αn can be determined as 1.724. According to Bard and Faulkner [19], α can be expressed as

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

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 E_p versus v by extrapolating to the vertical axis at $v=0$) [36-37]. The formal potential (E^0) and the standard heterogeneous rate constant (k^0) for the reaction were obtained as 1.171 and $1.761 \times 10^3 \text{ s}^{-1}$ 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 $2.136 \times 10^3 \text{ s}^{-1}$.

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.

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Figures

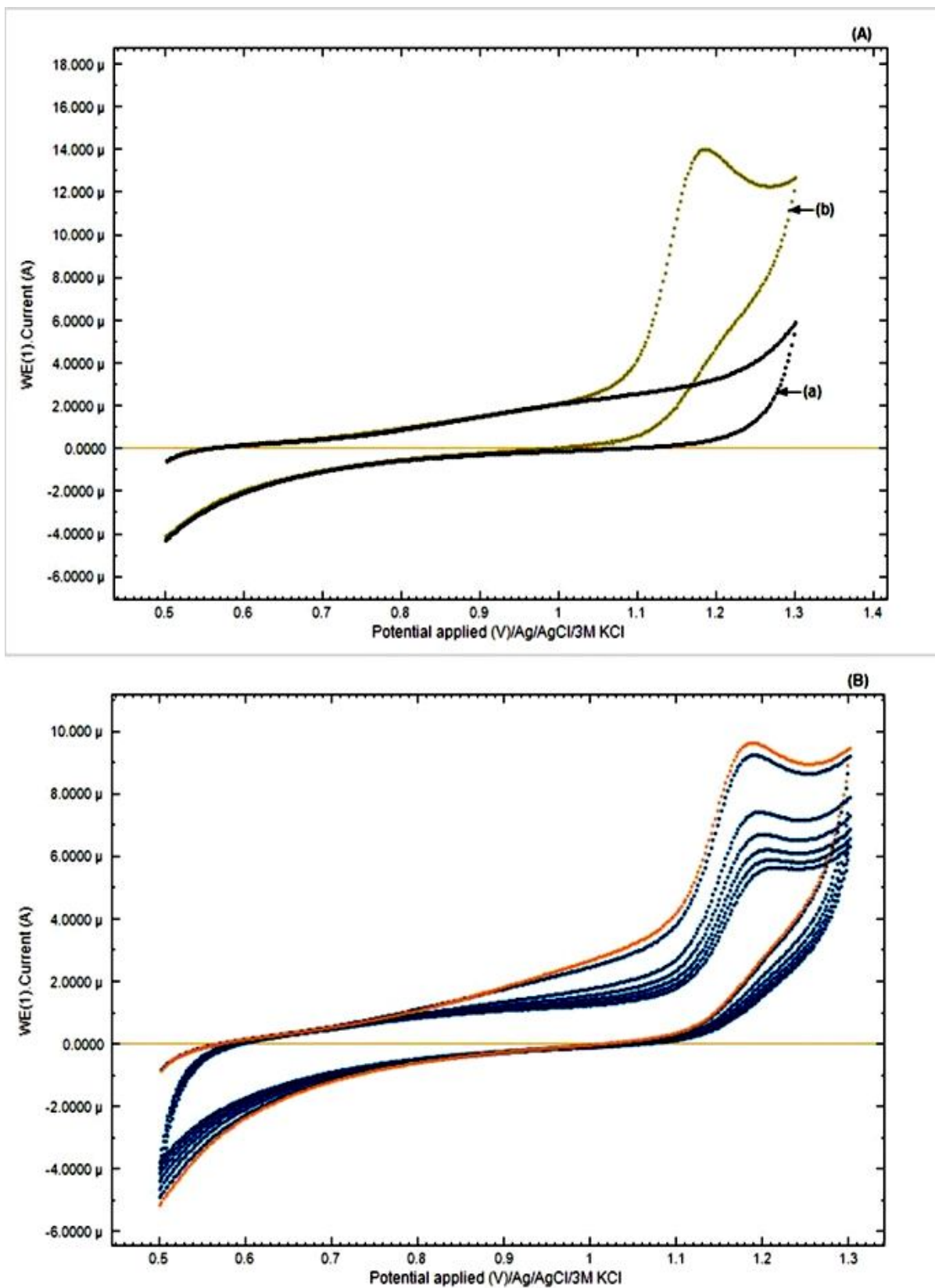


Figure 1.(A) Cyclic voltammograms (CVs) of platinum electrode (PE) (a) in absence of p-NA (b) containing 1mM p-NA, (B) Successive CVs recorded on PE for 1mM of p-NA.[in acidic solution (scan rate 50mVs⁻¹)]

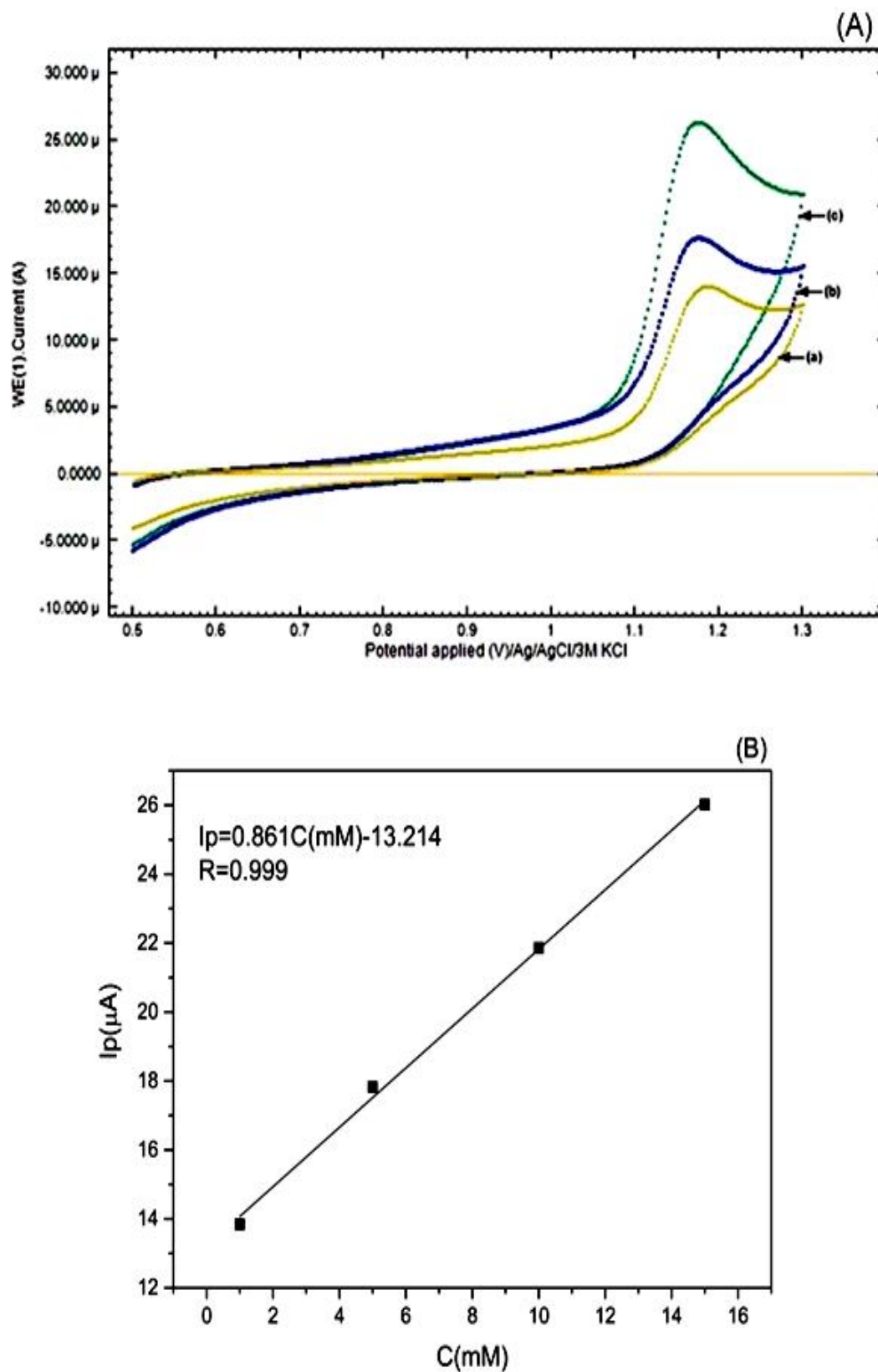


Figure 2. (A) CVs of PE in acidic solution with different concentrations [(a) 1, (b) 5 and (c) 15 mmol L^{-1}] of p-NA at scan rate 50 mVs^{-1} , (B) Dependence of the anodic peak current (I_{pa}) on p-NA concentrations.

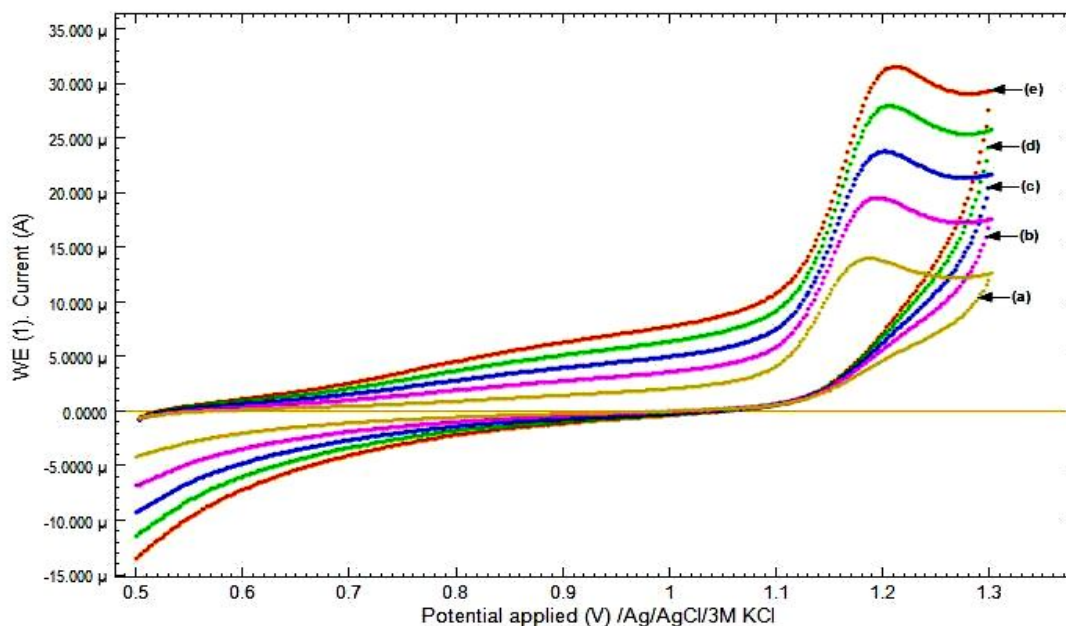


Figure 3 CVs of PE in acidic solution containing 1mM of p-NA at different scan rates (a) 50 (b) 100 (c) 150 (d) 200 (e) 250 mVs⁻¹.

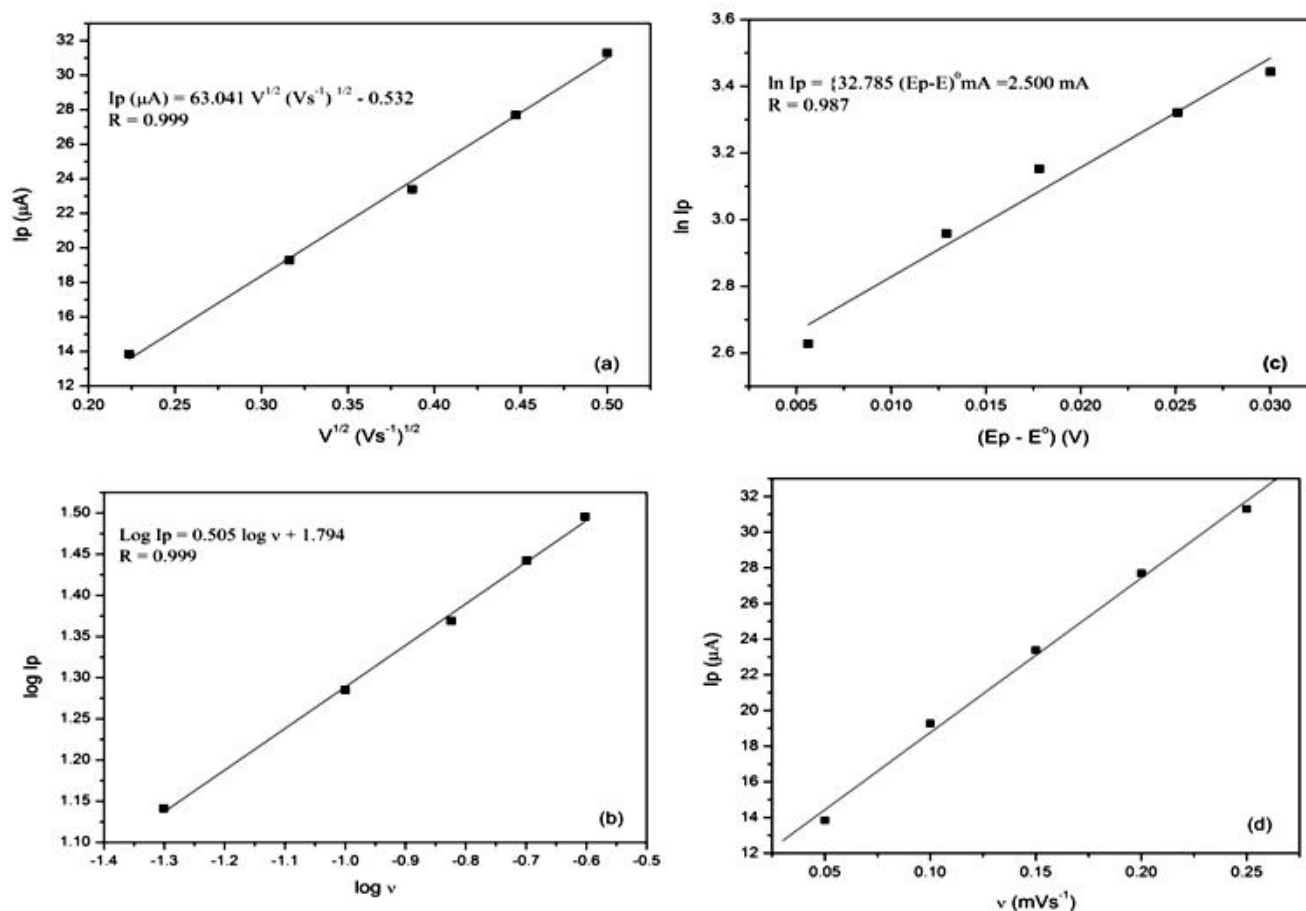


Figure 4(a) Logarithm of the peak current (I_p) versus logarithm of the scan rate (v). (b) Showing dependence of peak current (I_p) on the square root of scan rate ($V^{1/2}$). (c) Naperian logarithm of I_p versus $E_p - E^0$. (d) Showing calibration plot of I_p versus scan rate (v). (1mmol L⁻¹ of p-NA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

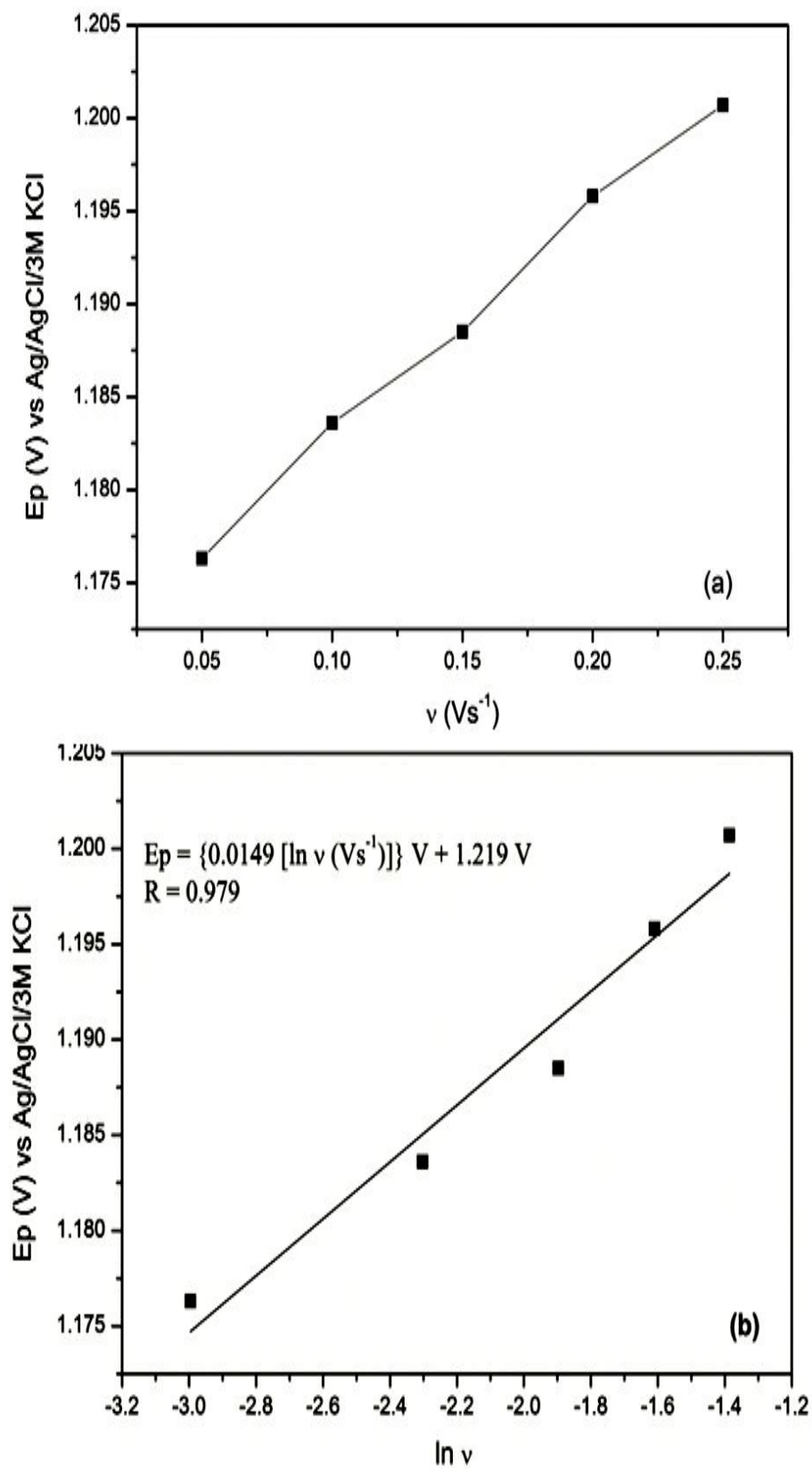
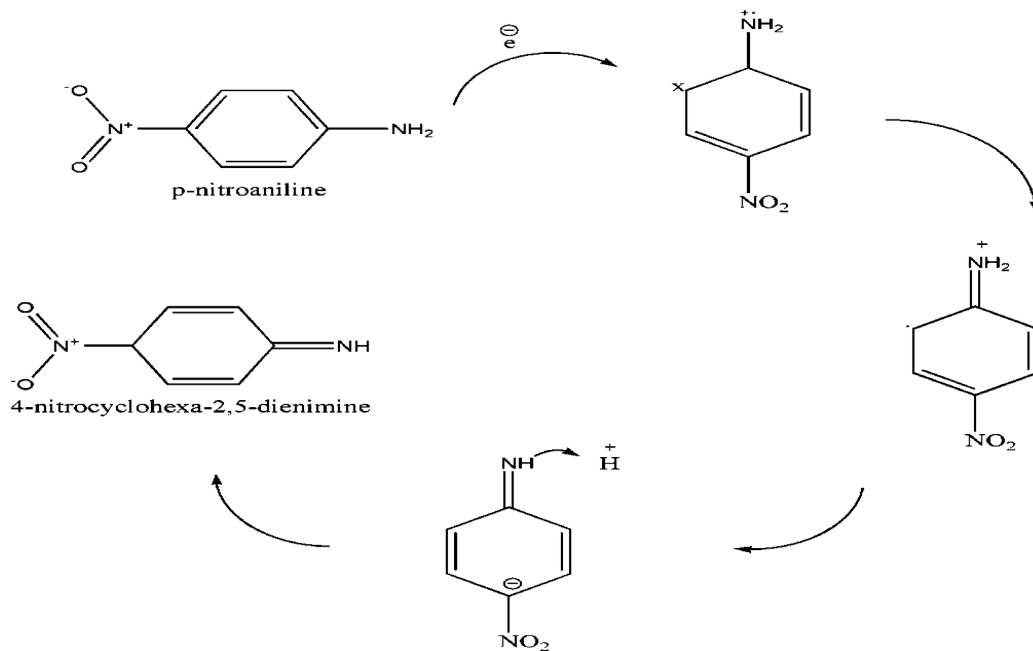


Figure 5. Dependence of peak potential, E_p , (a) on the potential scan rate, v , (b) on the $\ln v$ for the oxidation of p-NA (1 mmol L^{-1}) in acidic solution on PE.



Scheme (A) Showing Mechanism of Reaction



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