DEGRADATION AND EVALUATION OF KINETIC PARAMETERS OF P-NITROBENZALDEHYDE: A CYCLIC VOLTAMMETRY STUDY

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ABSTRACT

The electrochemical oxidation of p- Nitrobenzaldehyde (PNBA) was investigated in an aqueous media on a platinum electrode using the eco-friendly cyclic voltammetry (CV) technique. Kinetic and analytical parameters were also evaluated for the reaction, such as standard heterogeneous rate constant (k^0 , $1.2558 \times 10^3 \text{ s}^{-1}$), anodic electron transfer rate constant (k_{OX} , $1.5825 \times 10^3 \text{ s}^{-1}$), electron transfer coefficient (α , 0.4288) and formal potential (E^0 , 0.8567V) were calculated under the influence of scan rates. The concentration study in the range of 1mM to 14mM was calibrated. The limit of detection and the limit of quantification was calculated to be 0.0040mM and 0.0135mM, respectively. It was found that p- Nitrobenzaldehyde displayed irreversible, two-electron transfer and adsorption-controlled reaction. As the analysis in the real sample, cyclic voltammogram shows a good response towards PNBA estimation.

Keywords: Electro-Oxidation, Cyclic Voltammetry, Kinetic Parameters, Platinum Electrode, Water-treatment

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INTRODUCTION

The utilization of new chemicals is rising with the development of modern science, industrialization and technology. As a consequence of this, the lethal effects of chemical pollution and toxicity are undergoing hit to the community, which led the chemical industry and functional agencies to pay attention to the influence of chemicals on the habitat before their deliverance into the ecosphere. Hence in order to secure human's well-being and the habitat, there is a need for abundant and satisfactory knowledge about the toxicity.¹

p-Nitrobenzaldehyde (PNBA) is a nitroaromatic compound. It is used as a mediator in many organic reactions. Skin irritation, eye irritation, respiratory tract irritation and narcosis can be occurred due to exposure to p-NBA.² Currently, nitroaromatic compounds are marked as environmental contaminants. Therefore, the investigation of this compound is essential for the purpose of protecting environment.³ Numerous techniques have been reported for the detection of a nitroaromatic compound such as HPLC with UV/Vis⁴, microextraction combined with gas chromatography⁵, Combination of switchable solvent-based microextraction and electrochemical detection on MWCNTs modified electrode² and few reports are available on the electrooxidation⁶ and electro reduction⁷ of PNBA.

In comparison of above listed methods, electroanalytical method is prominent and voltammetry is prime choice.⁸ It is a powerful analytical technique with high sensitivity, accuracy, precision, rapid response and low operating cost^{9,10}, which is used in the pharmaceutical industry, metal industry, and environmental applications.⁹ Nowadays, cyclic voltammetry is a well-renowned and eco-friendly technique to investigate pollutants and other compounds.¹¹ It is an effective instrument to analyze the electrochemical behavior of a system by a systematic study of current-voltage measurements¹² and it is widely employed to determine the mechanism and kinetic parameters of the reaction.^{13,14} In this work, we present the electrochemical and kinetic behavior of p- Nitrobenzaldehyde in aqueous media using the cyclic voltammetry technique.

EXPERIMENTAL

Material and Methods

p-Nitrobenzaldehyde (Sigma-Aldrich) was used as received. A stock solution of PNBA was prepared with water and ethanol in a volume ratio of 4:1. Acetate buffer (0.1 M) is used as a supporting electrolyte. NaOH and HCl were used to adjust the pH. Other chemicals used were of analytical grade. All solutions were freshly prepared with double distilled water.

Instrumentations

An Autolab model PGSTAT 101 potentiostat/ galvanostat 663 VA Stand (Metrohm AG, Netherlands) was used to perform Cyclic Voltammetry (CV) technique. In this technique, electrochemical cells along with a three-electrode system. Pt disc electrode (PE) (0.031 cm^2) acted as working electrode (WE), Ag/AgCl/3M KCl electrode served as the reference electrode and a Platinum (Pt) wire acted as the counter or auxiliary electrode. The solution pH calculation was done using Elico LI 120 pH meter (Elico Ltd., India). Before each scan working electrode was polished with alumina powder (particle size 0.05 mm) on a cloth polishing pad and washed with doubled distilled water. All the experiments were carried out at room temperature ($25 \pm 1^\circ\text{C}$).

RESULTS AND DISCUSSION

Effect of pH

The electro-oxidation of 8 mM was examined over the pH range of 2.7-11.5 in acetate buffer solution by applying the cyclic voltammetry technique (Fig.-1). However, the finest peak was observed on pH 4.4. Hence further experiment were performed in this range.

Fig.-1: Cyclic Voltammogram of 8 mM PNBA at Different pH Values (a) 2.7, (b) 4.4, (c) 5.6, (d) 7.8 (e) 11.5 at scan rate (v) = 20 mVs^{-1}

Cyclic Voltammetric Study of PNBA

The electrochemical behavior of PNBA was recorded on platinum electrodes using the cyclic voltammetry technique. The CV experiment was performed with a potential window range from +0.4 V to +1.2 V at the 20 mVs^{-1} scan rate shows well defined anodic peak [Fig 2 (b)]. This peak indicates that the irreversible reaction occurred on the platinum electrode surface. On scanning the reverse direction, there was no cathodic peak observed.

Influence of Scan Rate

The influence of scan rate on the electro-oxidation of PNBA was studied at Pt electrode by using cyclic voltammetry technique with different scan rate ranging from 20 mVs^{-1} - 90 mVs^{-1} (Fig.-3). As the scan rate was increased, the peak current (I_{pa}) for oxidation of PNBA was also increased.

The effect of the scan rate (v) on the peak current (I_p) showed a linear relationship from the range 20 mV s^{-1} - 90 mV s^{-1} [Fig.-4a]. Therefore it indicates the adsorption controlled reaction process.¹⁵ The equation can be expressed as:

$$I_{pa} (\mu\text{A}) = 330.65 v (\text{V s}^{-1}) + 4.8904 \quad (r = 0.9877) \quad (1)$$

Fig.-2: Cyclic Voltammogram for 8mM PNBA on Pt Electrode in 0.1M Acetate Buffer (a) Blank (b) PNBA at Scan Rate (v) = 20mVs^{-1}

Fig.-3: Cyclic Voltammograms of 8mM PNBA at Different Scan Rate 20, 30,40,50,60,70,80, and 90 mVs^{-1}

Fig.- 4(a): I_{pa} vs v

Alternatively, linear relationship was observed between $\log I_p$ and $\log v$ (Fig.-4b). Equation can be expressed as:

$$\log I_{pa} (\mu\text{A}) = 0.8176 \log v (\text{V s}^{-1}) + 2.399 \quad (r=0.9927) \quad (2)$$

The slope value of this linear fit (Fig.-4b) is 0.81. It was close to expected value of 1 for purely adsorption controlled process¹⁵⁻¹⁷ with which confirms that the electrooxidation of PNBA was adsorption controlled reaction. With an increase the scan rate range of 20 mVs^{-1} – 90 mVs^{-1} , E_p shifted to more positive value, a linear relationship between peak potential and scan rate (E_p and $\log v$) has been shown in (Fig.-4c).

$$E_p \text{ (V)} = 0.0731 \log v \text{ (V s}^{-1}\text{)} + 0.9741 \quad (r=0.9970) \quad (3)$$

Fig.-4(b): log Ipa vs log v

Fig.-4(c): Ep vs log v

For irreversible electrode process, Laviron¹⁸ equation is given below to define Ep:

$$E_p = E^0 + \left(\frac{2.303RT}{\alpha nF} \right) \log \left(\frac{RTk^0}{\alpha nF} \right) + \left(\frac{2.303RT}{\alpha nF} \right) \log v \quad (4)$$

Where E^0 is the formal standard redox potential, α is the transfer coefficient, n is the number of electrons transferred, k^0 is the standard heterogeneous rate constant of the reaction, v is the scan rate. Thus from the slope of plot E_p vs $\log v$, the value of αn can be easily calculated as 0.8090. α can be expressed by Bard and Faulkner¹⁹ as:

$$\alpha = \frac{47.7}{E_p - E_{p/2}} \text{ mV} \quad (5)$$

Where $E_{p/2}$ is the potential at half –peak current. So the average value of the transfer coefficient of reaction (α) calculated as 0.4288. Further, the number of the transferred electron (n) was calculated from the αn value as 1.88 ~ 2 in the PNBA electro-oxidation. The value of standard heterogeneous rate constant (k^0) can be calculated 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 $v=0$).^{20,21} The formal potential (E^0) and the standard heterogeneous rate constant (k^0) for the reaction were obtained as 0.8567 and $1.2558 \times 10^3 \text{ s}^{-1}$ respectively. The electron transfer rate constant (k_{ox}) can be calculated from the equation:²²

$$k_{(ox)} = k^0 \times \exp \{ -(1 - \alpha)nF(E - E^0)/RT \} \quad (6)$$

So the, k_{ox} was obtained as $1.5825 \times 10^3 \text{ s}^{-1}$

Effect of Concentration

The effect of varying concentrations of PNBA was also studied at Pt electrode in 0.1 M acetate buffer pH 4.4 at the scan rate of 20 mVs^{-1} . With an increasing concentration range of PNBA, the cyclic voltammogram revealed that the peak current was linearly increasing (Fig.-5a). A linear PNBA calibration curve was obtained in the range from 1mM to 14mM (Fig.-5b) and the linear equation was:

$$I_{pa} \text{ (}\mu\text{A)} = 0.9607 C + 1.6197 \text{ (} r = 0.9994 \text{)} \quad (7)$$

The value of the limit of detection (LOD)²³ and limit of quantification (LOQ)²⁴ were 0.0040mM and 0.0135mM, respectively. It was calculated by the below equations:

$$\text{LOD} = 3s/m \quad (8)$$

$$\text{LOQ} = 10s/m \quad (9)$$

Where m is the slope of the calibration plot and s is the standard deviation of the peak current of five blank measurements.

Analytical Application

Real Sample Analysis: Tap Water

This technique is also useful to determine the toxic PNBA in a real sample. A tap water sample was taken for the analysis on a platinum electrode. Further this sample was spiked with PNBA concentration range from 1 mM to 6mM. CV was examined within the same scan potential window range at the 20mVs^{-1} scan rate. CV shows the sharp peak over the blank curve. So, this analytical method is applicable to determine the PNBA with the help of this technique in real sample.

Fig.-5: (a) Cyclic Voltammograms with increasing concentration of PNBA in pH 4.4 buffer solution on a platinum electrode with concentration: (i) 1.0, (ii) 2.0, (iii) 3.0, (iv) 6.0, (v) 8.0, (vi) 14.0 mM (b) Plot of Peak Current versus Concentration of PNBA.

Fig.-6: Cyclic Voltammograms of PNBA in tap water sample at 20mVs^{-1} scan rate with concentration range 1mM, 2mM, 3mM, 5mM, 6mM

CONCLUSION

This work suggested that the electro-oxidation of PNBA in buffer solution by using cyclic voltammetry technique. Kinetic and electrochemical parameters were assessed for the reaction. The electrochemical oxidation process of PNBA was found to be adsorption controlled and the nature of the reaction is irreversible at the platinum electrode. There are two electrons that are transferred during the process with a fast electron transfer rate constant. As the PNBA estimated in the real sample shows a good response. This investigation revealed that the technique is also applicable to analytical chemistry to estimate PNBA in the real sample. Therefore, cyclic voltammetry is an eco-friendly technique that is a convenient method to degrade toxic compounds.

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REFERENCES

1. M. Asadollahi-Baboli, *Environmental Research*, **24(12)**, 1041(2013), <https://doi.org/10.1080/1062936X.2013.840678>

2. H. Ahmar, S.K. Shahvandi, *Electroanalysis*, **31(7)**, 1238(2019), <https://doi.org/10.1002/elan.201800451>
3. P. Mulchandani, C.M. Hangarter, Y.Lei, W.Chen and A. Mulchandani, *Biosensors and Bioelectronics* **21(3)**, 523(2005), <https://doi.org/10.1016/j.bios.2004.11.011>
4. L. Luo, C.Gu, M. Li, X. Zheng and F. Zheng, *Journal of Pharmaceutical and Biomedical Analysis*, **156**, 307(2018), <https://doi.org/10.1016/j.jpba.2018.04.024>
5. J. Rameshgar, K. S. Hasheminasab, L. Adlnasab and H. Ahmar, *Journal of Separation Science*, **40(15)**, 3114(2017), <https://doi.org/10.1002/jssc.201700141>
6. G. Vanmathi, S. Berchmans, K.Srinivasan and A.R. Venkitraman, *Bulletin of Electrochemistry*, **6(11)**, 879 (1990).
7. S. Sharma, M. Kumari and D.K. Sharma, *Nature and Science*, **7(3)**, 84(2009).
8. A. Chatterjee, *Research Journal of Pharmacology and Pharmacodynamics*, **9(2)**, 88(2017), <https://doi.org/10.5958/2321-5836.2017.00015.5>
9. O. A. Farghaly, R. S. Abdel Hameed, and A. A. Abu-Nawwas, *International Journal of Electrochemical Science*, **9(1)**, 3287(2014)
10. N. Kumar, Rosy and R. N. Goyal, *Talanta*, **166(1)**, 215(2017), <https://doi.org/10.1016/j.talanta.2017.01.058>
11. R.S. Nicholson and I. Shain, *Analytical Chemistry*, **36(4)**, 706(1964).
12. P.S Joshi and D.S Sutrave, *International Journal of ChemTech Research*, **11(9)**, 77(2018), <http://dx.doi.org/10.20902/IJCTR.2018.110911>
13. P. Lalitha and S. Sivakamasundari, *Asian Journal of Research in Chemistry*, **3(4)**, 1015(2010).
14. R.G. Compton, C.E. Banks Understanding Voltammetry, Second Edition, Imperial College Press, (2011)
15. N. Kumar, Rosy and R. N. Goyal, *Electrochimica Acta*, **211**, 18(2016), <https://doi.org/10.1016/j.electacta.2016.06.023>
16. C. M. A. Brett and A. M. O. Brett, *Electrochemistry: Principles, Methods and Applications*, Oxford University Press, New York, (1994).
17. P. T. Kissinger and W. H. Heineman, *Laboratory Techniques in Electroanalytical Chemistry*, Second ed., Marcel Dekker, New York, (1996).
18. E. Laviron, *Journal of Electroanalytical Chemistry*, **101(1)**, 19(1979), [https://doi.org/10.1016/S0022-0728\(79\)80075-3](https://doi.org/10.1016/S0022-0728(79)80075-3)
19. A. J. Bard and L. R. Faulkner, *Electrochemical Methods Fundamentals and Applications*, John Wiley & Sons, (2001)
20. L. Fotouhi, M. Fatollahzadeh, and M. M. Heravi, *International Journal of Electrochemical Science*, **7**, (2012) .
21. W. Yunhua, J. Xiaobo and H. Shengshui, *Bioelectrochemistry*, **64(1)**, 95(2004), <https://doi.org/10.1016/j.bioelechem.2004.03.005>
22. J.J. Van Benschoten, J.Y. Lewis, W.R. Heineman, D.A. Roston and P.T. Kissinger, *Journal of Chemical Education*, **60(9)**, (1983)
23. H. M. Rageh, M. M. Abou-Krishna, A. M. Abo-Bakr, and M. Abd-Elsabour, *International Journal of Electrochemical Science* **10**, 4110(2015)
24. K.V. Harisha, B.K. Swamy and E.E. Ebenso, *Journal of Electroanalytical Chemistry*, **823**, 730(2018), <https://doi.org/10.1016/j.jelechem.2018.07.021>

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