DEGRADATION OF TOXIC HETEROCYCLIC COMPOUND 2-AMINOPYRIDINE BY USING VOLTAMMETRIC TECHNIQUE: A KINETIC STUDY

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ABSTRACT

Electro-oxidation of 2-Aminopyridine (2-APy) was carried out on a platinum electrode by employing an eco-friendly electrochemical technique, cyclic voltammetry. The variation of the anodic peak current with scan rate and concentration was investigated for the 2-APy and to find out the control of the reaction, kinetics, electrochemical and analytical parameters of the reaction. The electrochemical behavior of the 2-APy at the platinum electrode was a diffusion-controlled process with the two-electron transfer. Kinetic parameters such as standard heterogeneous rate constant (k^0 , $1.6684 \times 10^3 \text{ s}^{-1}$), anodic electron transfer rate constant (k_{OX} , $2.1455 \times 10^3 \text{ s}^{-1}$), electron transfer coefficient (α , 0.5369) and formal potential (E^0 , 1.0499 V) were calculated under the influence of scan rates. The concentration study in the range of $8.0 \times 10^{-3} \text{ M}$ to $30.0 \times 10^{-3} \text{ M}$ was calibrated, the limit of detection and the limit of quantification were calculated to be $1.9188 \times 10^{-3} \text{ M}$ and $6.3962 \times 10^{-3} \text{ M}$ respectively.

Keywords: 2-Aminopyridine, Cyclic Voltammetry, Kinetic Parameters, Electro-Oxidation, Water Pollution

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INTRODUCTION

The major industrial development increased the number of environmental pollutants, especially in water and soil sources.¹ Pharmaceuticals and personal care products are frequently detected in surface water, groundwaters and wastewater because of their extensive use in a wide range of human activities. Thus, these compounds are known as emerging contaminants receive special attention because of their potential impact on the environment and human health.²⁻⁴

Chronic toxicity and car-cinogenic activity were detected by monoamino-pyridines such as 2-aminopyridine, 3-aminopyridine and 4-aminopyridine. Including the brain, mono aminopyridines are widely distributed in the body because they readily get absorbed by the skin and gastrointestinal tract. Monoaminopyridines are acutely toxic compounds and studies of animals and humans show that they can block K^+ channels.⁵ These are listed by the US Environmental Protection Agency (USEPA) as priority contaminants.⁶

2-APy with the formula $\text{H}_2\text{NC}_5\text{H}_4\text{N}$ is the derivative of heterocyclic organic compound pyridine.^{7,8} In the manufacture of pharmaceuticals, particularly antihistamines and piroxicam, 2-Aminopyridine is used as an intermediate. In the production of ciclopiroxolamine, diphenpyramide, methaqualone, propiram fumarate, pyrilamine, triprolidine, and zomepirac, 2-Aminopyridine may also be an intermediate.⁹⁻¹¹ Of the three monoaminopyridines, the largest production appears to be 2-aminopyridine.¹² Skin irritation, nausea, headache, dizziness, flushing of the extremities, increased blood pressure is caused by the exposure of 2-aminopyridine and high exposure can lead the respiratory failure.¹³

Before discharging into the environment, 2-Aminopyridine must be treated. Thermal incineration and ultrafiltration methods are used to treat the 2-APy, which are not economical.⁷ Fenton and the photo-fenton oxidation process is time consuming.¹⁴ Although, in aerobic and anaerobic conditions 2-Aminopyridine is not expected to be readily biodegradable.¹²

Electroanalytical methods are superior among the various methods and voltammetry is the right choice.^{15,1}

⁶ Cyclic voltammetry is an environmentally safe technique to investigate contaminants and other compounds.¹⁷ Electrochemistry has always given analytical techniques characterized by instrumental

simplicity, moderate cost and portability. These techniques have introduced the most promising methods for specific application.^{18,19} It is widely used to determine the mechanism and kinetic parameters of reactions.^{20,21} In this present work, the kinetic and electrochemical behavior of 2-APy in phosphate buffer has been investigated.

EXPERIMENTAL

Materials and Instrumentation

2-Aminopyridine was bought from Sigma-Aldrich and used without further purification. A stock solution of 2-APy (1.0×10^{-2} M) was prepared in double-distilled water. pH 11.2 Phosphate buffer solution (PBS) 0.2 M was prepared according to the method of Christian and Purdy.²² Other reagents used were of analytical or chemical grade. All solutions were prepared with double-distilled water.

An Autolab model PGSTAT 101 potentiostat/galvanostat at 663 VA Stand (MetrohmAG, Netherlands) was used to record cyclic voltammetric curves. The voltammetric measurements were carried out using a three-electrode cell with the Ag/AgCl /saturated KCl solution (3.0 M) as reference electrode, a platinum wire (Pt) as an auxiliary electrode and a platinum disk electrode (0.031 cm^2), as the working electrode in one compartment. The solution pH calculation was done using Elico LI 120 pH meter (Elico Ltd., India). Before each experiment, the platinum electrode was polished with $0.3 \mu\text{m}$ alumina powder (from Sigma-Aldrich) on smooth polishing pads to get a shiny cleaned surface. All the experiments have been performed at an ambient temperature of $25 \pm 1^\circ\text{C}$

RESULTS AND DISCUSSION

Cyclic voltammetry study of 2-Aminopyridine

The cyclic voltammogram obtained for 1.0×10^{-2} M 2-APy at a scan rate 20 mVs^{-1} shows a well-defined anodic peak at $+1.0492 \text{ V}$ at Pt electrode from potential window range $+0.6$ to $+1.4 \text{ V}$ [Fig.-1B]. No corresponding reduction peak has been found on the reverse scan suggesting that the 2-APy electrode process is an irreversible one.

Fig.-1: Cyclic Voltammogram for 1.0×10^{-2} M 2-APy on Pt electrode in 0.2M phosphate buffer
(A) Blank (B) 2-APy at scan rate (v) = 20 mVs^{-1}

Influence of Scan Rate

The number of successive scans reduces the oxidation current, which maybe because of the adsorption to the electrode surface of 2-APy or its oxidation product [Fig.-2A]. The following CV experiment was to investigate the electrochemical properties of 2APy and the variation of scan rate can give useful information on the electrode process. The effect of applied scan rate for the oxidation of 1.0×10^{-2} M 2-APy was investigated with different scan rates in the range from 20 mVs^{-1} - 180 mVs^{-1} at Pt electrode [Fig.-2B]. As the scan rate was increased, the peak potential (E_{pa}) for oxidation of 2-APy was also increased.

The plot of anodic peak current (I_{pa}) versus scan rate ($v^{1/2}$) [Fig.-3] showed good linearity from the range 20 mV s^{-1} - 180 mV s^{-1} with linear correlation coefficient of $r=0.9886$, Therefore it indicated that the electrode reaction is an irreversible process. Equation can be expressed as:

$$I_{pa} (\mu\text{A}) = 126.5 v^{1/2} (\text{V}^{1/2} \text{s}^{-1/2}) - 4.829 \quad (r=0.9886) \quad (1)$$

Fig.-2: Cyclic Voltammograms on Pt Electrode for 1.0×10^{-2} M 2-APy (A) Successive CV obtained at the $v=60\text{mVs}^{-1}$ (B) CV at different scan rates (20,40,60,80,100,120,140,160 and 180mV s^{-1} respectively) in 0.2 M phosphate buffer (pH 11.2)

Fig.-3: I_{pa} vs $v^{1/2}$

Fig.-4: $\log I_{pa}$ vs $\log v$

A linear relation between logarithm of anodic peak current ($\log I_{pa}$) and the logarithm of scan rate ($\log v$) was observed with the slope value of 0.544 [Fig.-4, Eq.-2]. The observed slope value of 0.544 was comparable with the theoretical value of 0.5^{23,24}. This was expected for a purely diffusion-controlled process:²⁵

$$\log I_{pa} (\mu\text{A}) = 0.544 \log v (\text{V s}^{-1}) + 2.086 \quad (r=0.9891) \quad (2)$$

So the electro-oxidation of 2-APy is diffusion controlled, and with an increase in the scan rate range of $20 \text{ mVs}^{-1} - 180 \text{ mVs}^{-1}$, E_p shifted to a more positive value, a linear relationship between peak potential and scan rate (E_p and $\log v$) has been shown in [Fig.-5]

$$E_p (\text{V}) = 0.057 \log v (\text{V s}^{-1}) + 1.142 \quad (r=0.9849) \quad (3)$$

According to Laviron, Eq. (4)²⁶, for a diffusion-controlled and irreversible electrode process E_p is expressed as:

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

Where, ' α ' is the transfer coefficient, k^0 is the standard heterogeneous rate constant of the reaction, n is the number of electrons transferred, v is the scan rate and E^0 is the formal standard redox potential, Other symbols have their usual meanings.

Thus, the value of αn can be easily calculated from the slope of a plot of E_p versus $\log v$. In our system taking $R=8.314 \text{ JK}^{-1}\text{mol}^{-1}$, $T=298 \text{ K}$, and $F=96480 \text{ C mol}^{-1}$. The value of the αn was determined to be 1.0375.

According to Bard and Faulkner²⁰, α value can be evaluated by using Eq.5.

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

Fig.-5: E_p vs $\log v$

Where, $E_p/2$ is at half the peak current. The average value of the electron transfer coefficient (α) was evaluated to be 0.5369. Furthermore, the number of electrons (n) transferred in 2-APy was calculated to be $1.9323 \approx 2$. k^0 can be calculated from the intercept of Eq.-3 if the value of the formal potential (E^0) is known. Formal potential can be determined from the intercept of the peak potential versus scan rate curve by extrapolating to the vertical axis at $v=0$ ²⁷. k^0 and E^0 were calculated to be $1.6684 \times 10^3 \text{ s}^{-1}$ and 1.0499 V respectively. The electron transfer rate constant $k_{(OX)}$ is a function of the applied potential that can be calculated from the Eq.-6.²⁸

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

The value of $k_{(OX)}$ was calculated to be $2.1455 \times 10^3 \text{ s}^{-1}$.

Effect of 2-APy concentration

The effect of varying concentrations of 2-APy was also studied at Pt electrode in 0.2M PBS pH 11.2 at the scan rate of 20 mVs^{-1} . With increasing concentrations of 2-APy the cyclic voltammograms revealed that the peak current was linearly increasing with the increasing concentration, as shown in [Fig-6A]. A linear 2-APy calibration curve was obtained in the range from $8.0 \times 10^{-3} \text{ M}$ to $30.0 \times 10^{-3} \text{ M}$ [Fig.-6B].

Fig.-6: (A) Cyclic Voltammograms with increasing concentration of 2-APy in pH 11.2 buffer solution on a platinum electrode with 2-APy concentration: (i) 8.0, (ii) 10.0, (iii) 12.0, (iv) 14.0, (v) 16.0, (vi) 18.0, (vii) 20.0, (viii) 24.0, (ix) 26.0, and (x) $30.0 \times 10^{-3} \text{ M}$ (B) Plot of peak current versus concentration of 2-APy

The linear equation was:

$$I_{pa} (\mu\text{A}) = 0.747 C + 7.243 \quad r = 0.9899 \quad (7)$$

By using the equation (8) and (9) Detection limit (LOD) and quantification limit (LOQ) have been determined^{29,30}. The values of LOD and LOQ were $1.9188 \times 10^{-3} \text{ M}$ and $6.3962 \times 10^{-3} \text{ M}$ respectively.

Where m is the slope of the calibration plot (Eq.-7) and S is the standard deviation of the six blank measurements.

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

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

CONCLUSION

The 2-APy voltammetric behavior and anodic oxidation were investigated by CV in a pH 11.2 phosphate buffer solution with a platinum electrode. Based on this study, influences of physicochemical parameters like potential scan rate and concentration were investigated. The 2-APy oxidation is a diffusion-controlled with two-electron transfer irreversible process. Therefore, the cyclic voltammetry can quickly and eco-friendly degrade the toxic compound.

Symbol and Abbreviations

2-APy = 2-Aminopyridine

PBS = Phosphate buffer solution

CV= cyclic voltammetry

E^0 = Formal potential (V)

E_p = peak potential (V)

F = Farady constant ($C \text{ mol}^{-1}$)

Pt= Platinum

I_{pa} = anodic peak current (μA)

k^0 = standard heterogeneous rate constant of the reaction (s^{-1})

n = number of electrons transferred

R = gas constant ($JK^{-1}mol^{-1}$)

r = regression coefficient

$k_{(ox)}$ = electron transfer rate constant

T = temperature (K)

v = scan rate (mVs^{-1})

α = transfer coefficient

LOD= Limit of detection

LOQ= Limit of quantification

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