DEGRADATION AND EVALUATION OF KINETIC PARAMETERS OF ANTIPYRINE IN BUFFER SOLUTION BY CYCLIC VOLTAMMETRY

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ABSTRACT

In this work, anodic oxidation of antipyrine was carried out in phosphate buffer on a platinum electrode by employing an eco-friendly technique, cyclic voltammetry. A well defined anodic peak was shown by antipyrine in phosphate buffer at pH 9.0. The oxidation process was shown to be irreversible and the number of electrons (n) transferred in the process was calculated. Kinetic parameters for the reaction such as standard heterogeneous rate constant at the rate determining step, electron transfer rate constant, electron transfer coefficient of the reaction and formal potential of the electrode were calculated under the influence of scan rate (v).

KEY WORDS : Antipyrine, Cyclic voltammetry, Electro-oxidation, Degradation, Kinetic parameters, Water pollution.

INTRODUCTION

Pharmaceutical and personal care products are often found in surface water, ground water and wastes in wide range due to the human activities. Their presence has been also noticed in meat and dairy food products because they are used in animal food preparation. Thus, these compounds are known as emerging contaminants which receive special attention because of their potential impact on the environment and human health (Loss *et al.*, 2013, Tran *et al.*, 2014 and Sui *et al.*, 2015). Antipyrine commonly detected in the aquatic environment because of very active pharmaceutical compound (Wiegel *et al.*, 2004 and Durán *et al.*, 2013). Antipyrine (ANT) also known as Phenazone a powerful analgesic, antipyretic and anti-inflammatory drug (Miao *et al.*, 2015), is selected as the target compound owing to its wide use, removal resistance , frequent detection and insufficient toxicity information (Monteagudo *et al.*, 2016). Due to comparatively poor human body absorption, unignorable amounts of ANT are released by the urban drainage system into the marine ecosystem (Cai *et al.*, 2013). Lungs and other target organs were reported vulnerable to ANT exposure, as a result,

The serious threat to human bodies of long-term ANT exposure is not neglected although its concentration in aquatic environment is low (Tan *et al.*, 2013). Many different oxidative treatment processes has been used to investigate the degradation of phenazone, such as Sono-photo-Fenton treatment of antipyrine aqueous solution (Yuan *et al.*, 2009 and Durán *et al.*, 2013), direct photolysis and UV/H$_2$O$_2$ (Tan *et al.*, 2013), traditional aerobic biological treatment (Zuehlke *et al.*, 2006), degraded by chlorination with 0.4 mg/L chlorine (Rodil *et al.*, 2012), In another related work, a ferrioxalate assisted solar photo-Fenton process (Durán *et al.*, 2013) and in synthetic urban wastewater (Durán *et al.*, 2014) respectively, indicating a negative effect of the used wastewater matrix on mineralization efficiency.

Because of many advantage of electrochemistry, it is an appealing choice for pharmaceutical analysis (Nigoviæ *et al.*, 2003 and Uslu *et al.*, 2004). Electrochemistry has always given analytical technique characterized by instrumental simplicity, moderate cost and portability. These techniques have introduced the most promising methods for specific application (Jain *et al.*, 2006 and Jain *et al.*, 1997). Cyclic voltammetry is an environmentally

safe technique to investigate contaminants and other compounds (Nicholson *et al.*, 1964) Because of the resemblance of electrochemical and biological reaction, an electrode and a body oxidation/reduction pathways share common concept, it might be supposed. Biologically important molecules can be investigated electroanalytically by voltammetry in order to determine the molecule in different ways, additional applications of electrochemistry include the determination of electrode mechanisms. The redox properties of drugs can give us insight to their metabolite fate in *in vivo* redox process or pharmacological activity (Wang *et al.*, 1988). In the late seventies, Rayan developed cyclic staircase voltammetry (Ryan *et al.*, 1977), which is widely used to determine the mechanism and kinetic parameters of reactions (Allen *et al.*, 2001 and Compton *et al.*, 2011).

Experimental Section

Reagents and Chemicals

Antipyrine was purchased from Sigma-Aldrich and used without further purification. A stock solution of ANT (10mM) was prepared in triple distilled water. Phosphate buffer (PB) 0.2M of pH 9.0 was prepared according to the method of Christian and Purdy (Christian *et al.*, 1962). Other reagents were used of analytical or chemical grade. All solutions were prepared with triple distilled water.

Instrumentation and Analytical Procedures

All the Electrochemical measurements were carried out on an Autolab model PGSTAT 101 potentiostat/galvanostat 663 VA Stand (MetrohmAG, Netherlands). Voltammetric measurements were carried out in a single-compartment three-electrode glass cell with a platinum disc electrode (0.031 cm^2) electrode as the working electrode, a platinum wire as the counter electrode, and Ag/AgCl (3.0 M KCl) as the reference electrode. Alumina powder (Al$_2$O$_3$) from Sigma-Aldrich was used to polish working electrode before each experiment. All the experiments were carried out at an ambient temperature of 25 ± 0.1 °C

RESULTS AND DISCUSSION

Cyclic voltammetric experiment of ANT for platinum electrode

Electro-oxidation of ANT at a platinum electrode was studied by CV in 0.2M Phosphate buffer at pH=9.0, at different scan rates and potential window range from +0.6 to +1.6 V. As on reverse scan no cathodic peak was observed, it suggests that process was irreversible. First cyclic voltammogram at the scan rate v = 20 mVs^{-1} shows an anodic peak with the peak potential (Ep) = +1.3098 V (Figure 1 B).

The oxidation current reduces with the number of successive scans which may be because of the adsorption to the electrode surface of ANT or its
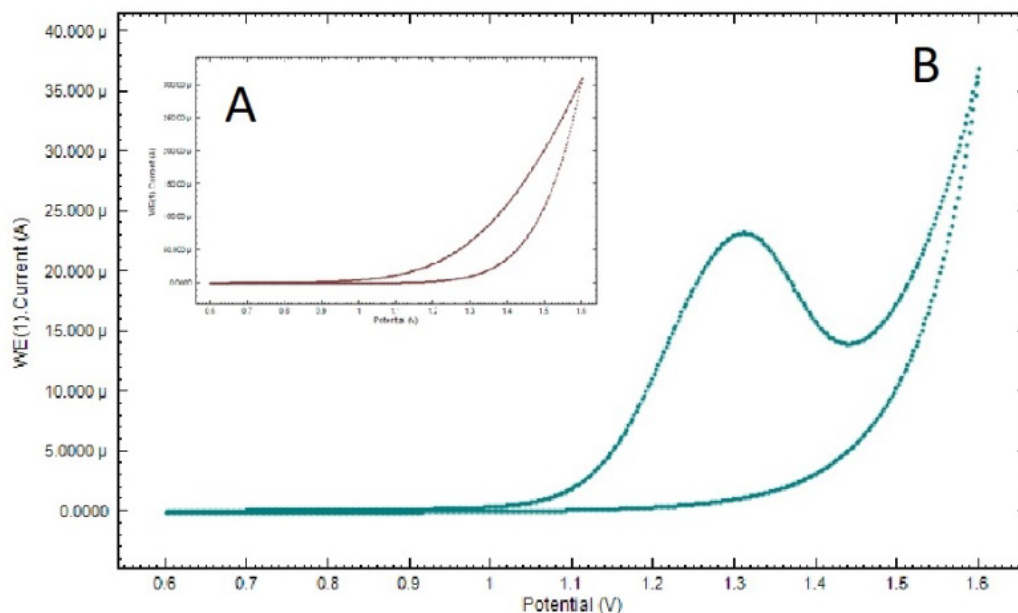

Fig. 1. Cyclic vpltammogram for 10mM ANT on Pt electrode in 0.2M phosphate buffer (A) Blank (B) ANT at scan rate (v) = 20mVs^{-1}

oxidation product (Figure 2 A). CV explored the effect of different scan rates on the electro-oxidation of ANT as shown in (Figure 2 B).

Effect of Scan Rate:

The effect of the square root of the scan rate on the peak current was found to be linear from 20 mV s^{-1} -180 mV s^{-1}, if there is a linear change in Ip with $v^{1/2}$, the origin of the co-ordinates intercepted, it is believed that the process would not have kinetic interference. However, if Ip has an intercept value that is not zero for the linear coefficient, then the process is accompanied by homogeneous chemical reaction (Wudarska *et al.*, 2013). By this linear fit origin of the coordinates is not intercepted (Figure 3), the electrode process is diffusion-control in nature and can be expressed as:

Ipa (µA) = 190.9 $v^{1/2}$ ($V^{1/2} s^{-1/2}$) - 6.822 (r=0.9931)

A linear relationship between log Ipa and log v has been observed (Figure 4), corresponding to the equation

log Ipa (µA) = 0.552 log v (V s^{-1}) + 2.277 (r=0.9933)

As the theortical value for diffusion controlled current process is 0.5, In our system the slope value is 0.55 which is close to theoretically value (Gosser *et al.*, 1993). So the electro-oxidation of ANT is diffusion controlled, and with an increase the scan rate range of 20 m Vs^{-1} - 180m Vs^{-1}, Ep shifted to
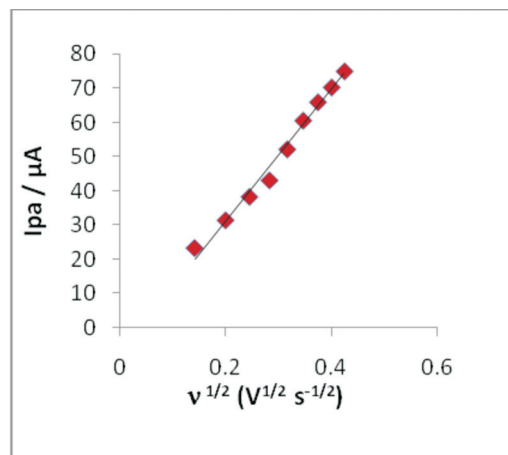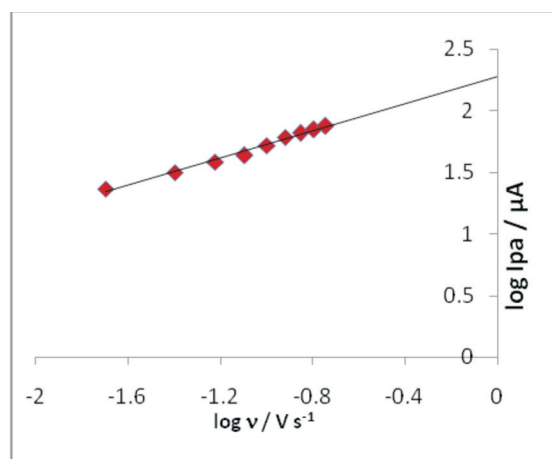

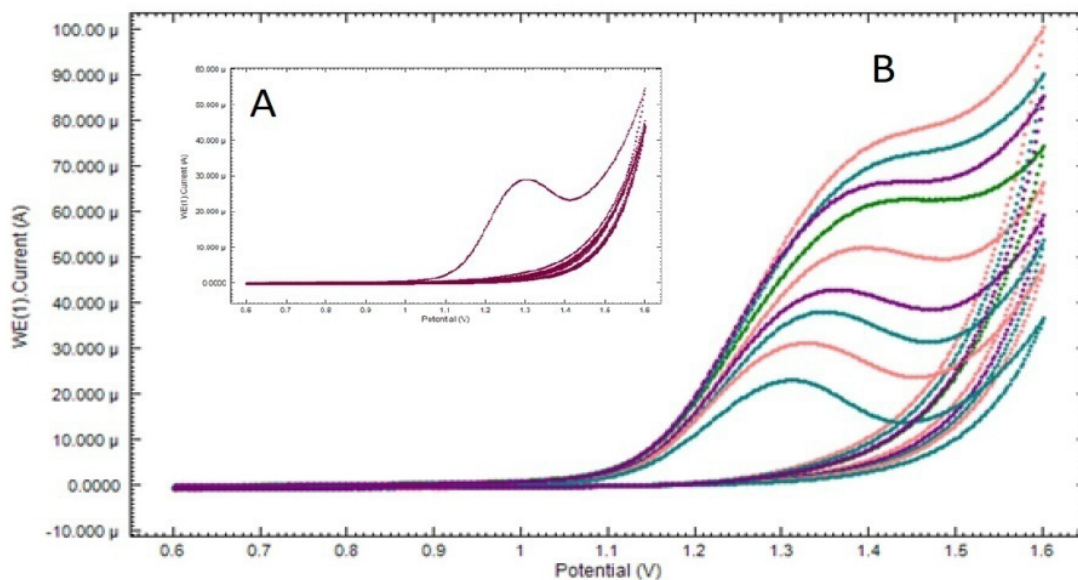**Fig. 3.** Ipa vs $v^{1/2}$

Fig. 4. log Ipa vs log v

Fig. 2. Cyclic voltammograms on Pt electrode for 10mM ANT (A) Successive cyclic voltammograms obtained for 10 mM ANT at the v= 40mVs^{-1} (B) Cyclic voltammograms of 10mM ANT at different scan rates (20,40,60,80,100,120,140,160 and 180 mVs^{-1}, respectively) in 0.2 M phosphate buffer (pH 9.0).

more positive value, a linear relationship between peak potential and scan rate (Ep and log v) has been shown in (Figure 5).

Ep (V) = 0.108 log v (V s^{-1}) +1.486   (r=0.9927)

According to Laviron, (Laviron *et al.,* 1979) Ep is defined as for an irreversible electrode process

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

where E^0 is the formal standard redox potential, 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, Other symbols have their usual meanings. Thus, the value of αn can be easily calculated from the slope of a plot of Ep versus log v. The value of αn was evaluated to be 0.5475.

According to Bard and Faulkner (Allen *et al.,* 2001) α can be expressed as:

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

Where Ep is peak potential, Ep$_{/2}$ is the potential when peak current is half.

The average value of electron transfer coefficient (α) was evaluated to be 0.4880 and number of electrons (n) transferred in ANT was calculated to be 1.12 ≈ 1. Consequently, the standard heterogeneous rate constant (k^0) can be calculated by knowing the value of the formal potential (E^0), as E^0 can be obtained from the intercept of the peak potential versus scan rate curve by extrapolating to the vertical axis at v=0 (Wu *et al.,* 2004). E^0 and k^0 was calculated to be 1.3099 V and 8.488 x 10^{2}s^{-1} respectively. The electron transfer rate constant (k$_{OX}$) is a function of the applied potential can be calculated from the equation (Van Benschoten *et al.,* 1983)

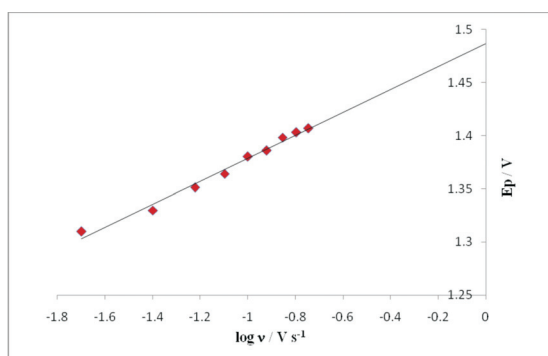$$k_{(ox)} = k^0 \times exp\ \{-(1-\alpha)nF\ (E - E^0)/RT\}$$

So, the value of K$_{(ox)}$ was calculated to 8.641 x 10^{2}s^{-1}.

CONCLUSION

The electro-oxidation process of Antipyrine was found to be purely diffusion controlled and one electron is transferred during process. The nature of reaction is irreversible at the platinum electrode. Therefore, this compound can be degraded with the help of cyclic voltammetry easily and eco-friendly.

ACKNOWLEDGMENTS

Symbol and abbreviations

ANT= Antipyrine
CV= cyclic voltammetry
E^0= Formal potential (V)
Ep= peak potential (V)
F= Farady constant (C mol^{-1})
Pt= Platinum
Ipa= 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

Fig. 5. Ep vs log v

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