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## Voltammetric Behavior Of 3-Chloro 2-Methyl Aniline In Aqueous Medium.

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### ABSTRACT

Substituted anilines have been used as a precursor in various industrial products such as drugs, pesticides, dyes, plastic, etc. It is an environmental concern that carcinogenic effluents and toxics released as the end products of the degradation of these products in water from different industries are the main cause of enhancing toxicity in water. An eco-friendly technique, cyclic voltammetry was employed to degrade these toxics. In this work, electro-oxidation of 3-chloro 2-methyl aniline (3C2MA) was carried out in an aqueous medium (Thiel, Schultz, and Koch buffer) on a platinum electrode. Kinetic and analytical parameters were also evaluated for the reaction such as standard heterogeneous rate constant at the rate determining step, anodic electron transfer rate constant, electron transfer coefficient of reaction, and formal potential, the surface coverage of electrode, and linearity were evaluated under the influence of scan rate. As the analysis in the real sample, cyclic voltammogram shows good response towards 3C2MA estimation.

**Keywords:** 3-chloro 2-methyl aniline, Kinetic parameters, Cyclic voltammetry, pollution, water treatment

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## INTRODUCTION

Aromatic amine includes aniline and substituted anilines [1]. Substituted anilines has used as a precursor in various industrial products such as drugs, pesticides, dyes, plastic, explosives, rubber, and epoxy polymers and combustion products [2,3]. It has harmful effects such as genotoxic, allergenic, mutagenic, and carcinogenic on human health [4-6]. Various manufacturers of herbicides, pesticides, dyes, and pharmaceuticals industries release toxic effluents consisting of 3-Chloro-2-methylaniline (3C2MA) in it [6]. 3C2MA could be released to the environment in wastewater emissions from azo dye manufacturing sites using it as an intermediate [7]. 3C2MA is a mutagen that changes the shape of DNA [8]. It is an environmental concern that mutagenic and 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.

Chloro substituted aniline has detected by electrochemical techniques by J.C. Suatoni et al. [9] Electrochemical technique is the most proficient technique since it provides a very consistent outcome, simple to operate, highly sensitive, accurate, rapidly analyzed [10]. Voltammetry is an eco-friendly technique to investigate pollutants and other compounds [11]. Ryan developed cyclic staircase voltammetry in the late seventies [12]. It is widely used to determine the mechanism and kinetic parameters of reactions [13-14]. Jeff Bacon showed the anodic oxidation of p-nitroaniline [15]. Mono-, di-, and tri chloro substituted aniline was also detected by researchers in non-aqueous solution [16]. Richa Sharma has also detected o-, m- and p-toluidine [17]. There has no work been done in my knowledge to determine the voltammetric parameters for 3C2MA.

The aim of this study is to find out: (1) the electro-oxidation parameters of 3C2MA: (a) kinetic parameters (standard rate constant:  $k_0$ ; electron transfer rate for anodic reaction:  $k_{ox}$  and transfer coefficient:  $\alpha$ ) (b) analytical parameters (linearity, limit of quantification: LOQ and limit of detection: LOD), (2) the applicability of the method towards estimation of 3C2MA in real sample. So this work provides kinetic parameters of electro-oxidation and estimation of 3C2MA in real sample.

## MATERIAL AND METHODS

### Chemicals and solutions

All the chemicals were of analytical grade. Ethanol and acetone (as solvent) were used without further purification. Distillation was used to purify 3C2MA (3-chloro, 2-methyl aniline) (Merck) in ethanol. After purification of chemical, the stock solution was prepared in acetone. Thiel, Schultz and Koch buffer [18] consisting of different volumes of 0.05 M oxalic acid, 0.02 M boric acid, 0.05 M succinic acid, 0.05 M sodium sulphate and 0.05 M borax, was used for maintaining the pH. All these chemicals were of CDH. All experiments were carried out at room temperature (24-26°C).

### 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<sup>2</sup>) 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<sub>2</sub>O<sub>3</sub>) before each cyclic voltammetric experiments.

### 3C2MA electro-oxidation

The cyclic voltammetric experiment was conducted within the scan potential window range from 0.5 V to +1.2 V at the 100 mVs<sup>-1</sup>-1000 mVs<sup>-1</sup> different scan rates in a voltammetric cell with the 3C2MA solution (1.992 mmol L<sup>-1</sup>) in buffer solution using the aforementioned voltammetric setup.

### 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 1.992 to 8.335 mmol L<sup>-1</sup>), between anodic peak currents and scan rates, and between peak potential and scan rates to find out the kinetic parameters of 3C2MA electro-oxidation.

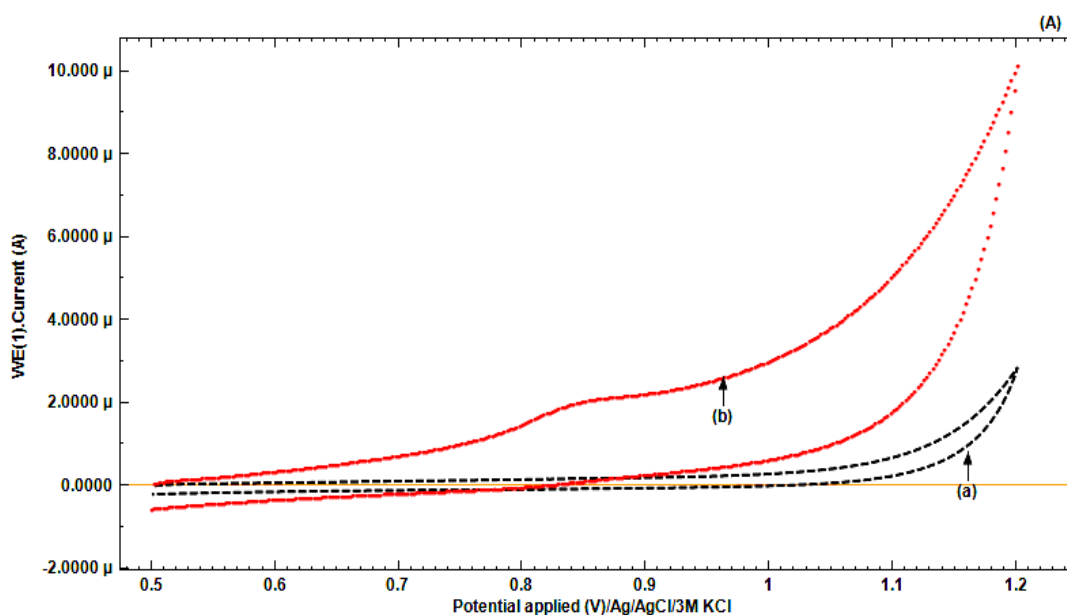
### RESULT AND DISCUSSIONS

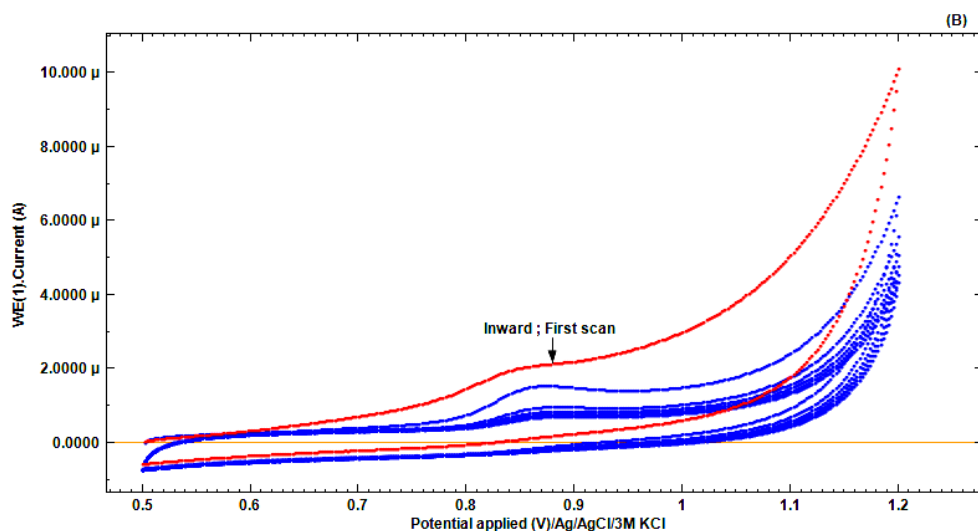
In the present work, the cyclic voltammetric technique was employed for 3C2MA electro-oxidation and to find out the control of the reaction, transfer of electron in the reaction, kinetic and analytical parameters.

#### Cyclic Voltammetric study of 3C2MA

Cyclic voltammogram (CV) of 3C2MA electro-oxidation showed only one anodic peak at the scan rate 100mVs<sup>-1</sup> in buffer solution 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 1.992mM of 3C2MA in buffer solution at the scan rate 100Vs<sup>-1</sup> were performed to find out the activity on platinum electrode (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 3C2MA 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 3C2MA electro-oxidation has considered for further analytical experiments in this study.



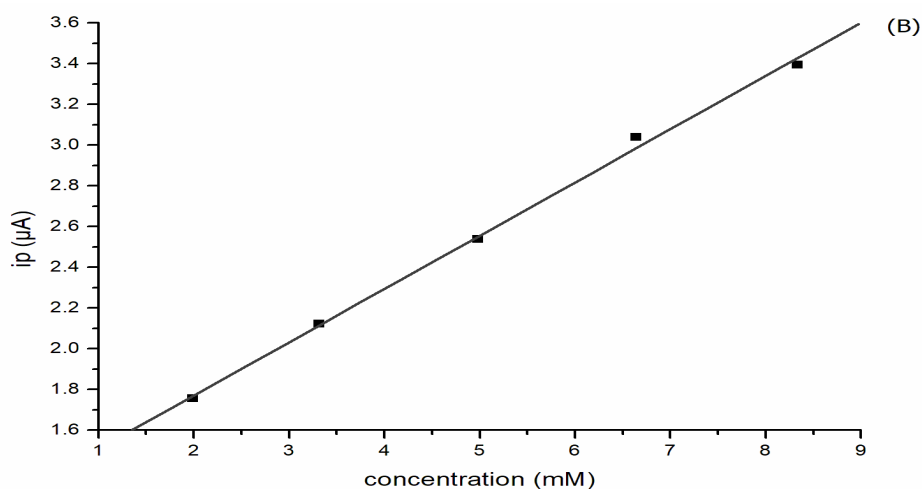


**Figure 1: (A) CV of PE (a) blank (buffer solution) (b) containing 3C2MA (1.992mM) (B) 6 consecutive CVs of PE in buffer solution containing 3C2MA (1.992mM) at the scan rate of 100mv/s vs Ag/AgCl/3M KCl.**

### Influence of concentration

The CV of different concentrations of 3C2MA ranging from 1.992 to 8.335mM in buffer solution at the scan rate of  $100\text{mVs}^{-1}$  has shown in Figure 2 (a). The peak potential is proportional to the concentration of 3C2MA for the reaction when scanning towards positive potential. It shifts towards negative potential while concentration increases. It indicates the expertise of electro-oxidation of 3C2MA 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.

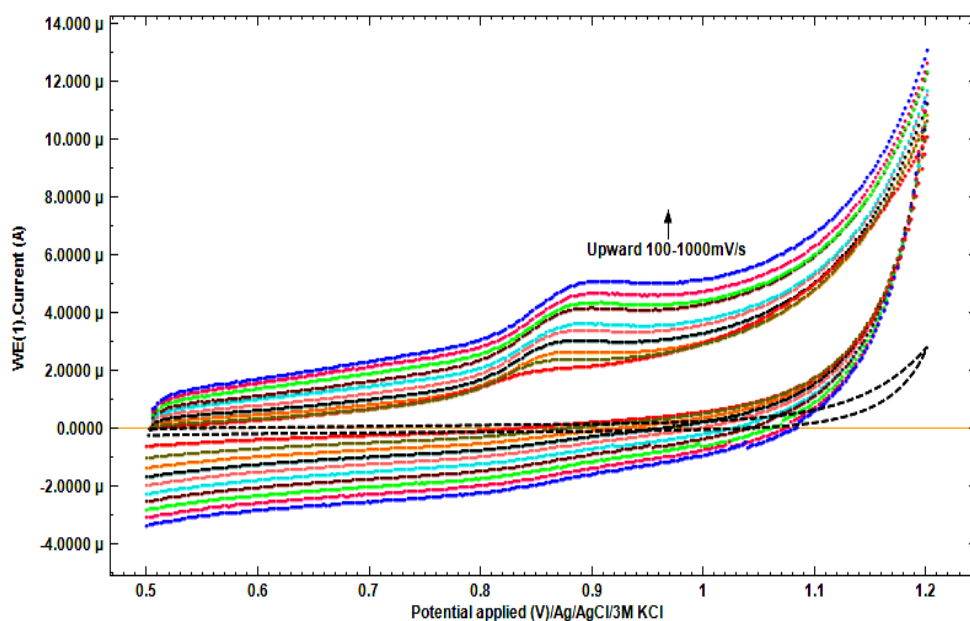
The value of the limit of detection and the limit of quantification ( $\text{LoD} = 3\delta/m$ ,  $\text{LoQ} = 10\delta/m$ ; where  $\delta$ =the standard deviation of the intercept of the y-coordinates from the line of best fit, and  $m$  the slope of the same line) is found to be 0.442mM and 1.475mM respectively From the plot of  $i_p$  versus concentration [figure 2 (b)].



**Figure 2: (A) CV of PE in buffer solution with different concentrations (1.992, 3.320, 4.980, 6.640 and 8.335mM) of 3C2MA at scan rate  $100\text{mVs}^{-1}$  vs Ag/AgCl/3M KCl, (B) Dependence of the anodic peak current ( $i_p$ ) on concentrations.**

### Influence of scan rate

The influence of different scan rates on 3C2MA electro-oxidation investigated by using cyclic voltammetry with the different scan rates ranging from 0.100 to 1.000Vs<sup>-1</sup> (figure 3). The peak currents and peak potentials were ascertained for the first scan of 3C2MA electro-oxidation at different scan rates. There was no cathodic peak has examined while scanning reverse direction.



**Figure 3: CVs of PE in buffer solution containing 1.992mM 3C2MA at different scan rate of 100-1000mv/s vs Ag/AgCl/3M KCl. (dashed line showing blank)**

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  $\log v$  [19] [figure 4 (a), (b)]. Figure 4 shows these plots for the first anodic peak of 3C2MA in buffer solution. 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. [20]. At various scan rates ranging from 0.1 to 1.0Vs<sup>-1</sup>, the anodic peak current depends linearly on the square root of scan rate and is described by the following equation:

$$I_p(\mu A) = 0.329 V^{1/2}(Vs^{1/2})^{1/2} + 4.487\mu A (R = 0.985)$$

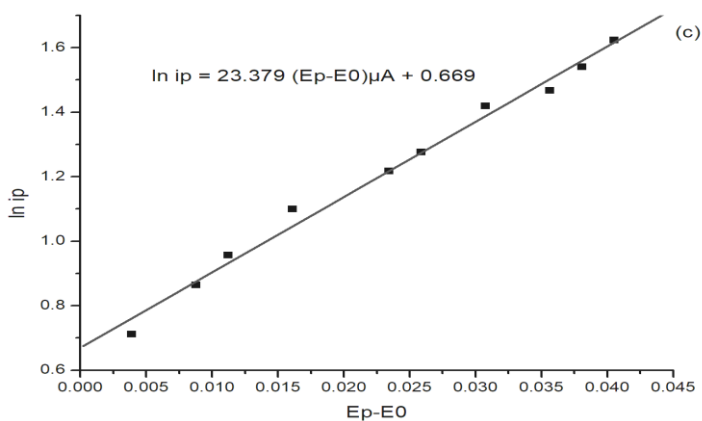
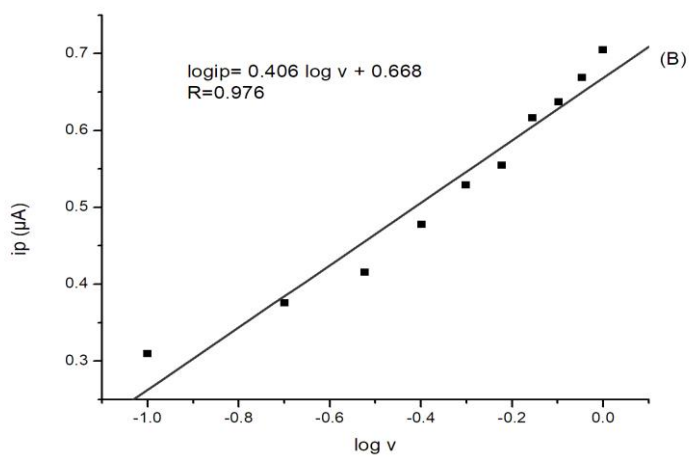
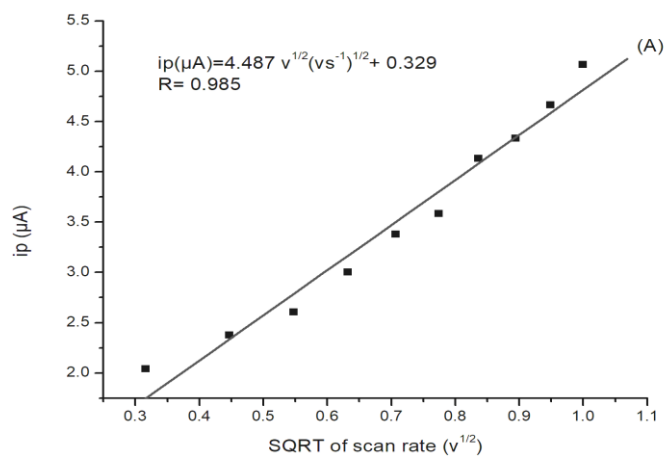
The origin of the coordinates is not intercepted by this linear fit, [figure 4 (a)], the electrode process is diffusion-control in nature and is proceeded by a chemical reaction. Alternatively, the dependence of  $\log I_p$  on  $\log v$  is linear. The slope of this linear fit is 0.329. Therefore according to Bard, Faulkner, and others [13], this process is only controlled by diffusion and is described by the following equation:

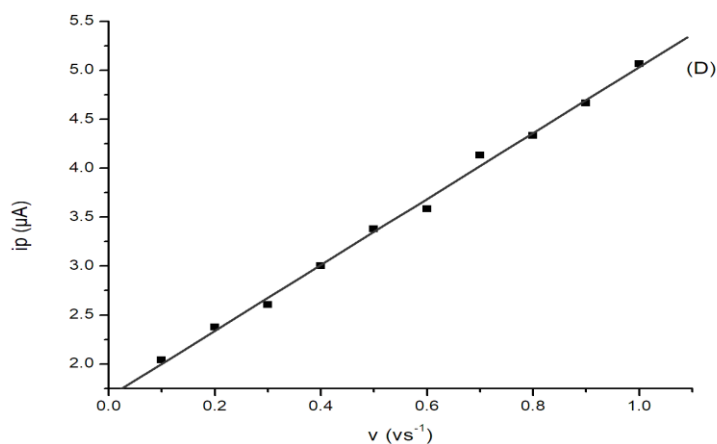
$$\log I_p = 0.406 \log v (Vs^{-1})\mu A + 0.668(R = 0.976)$$

While when the value of a slope is close to 1.0, the process is expected to be an adsorption-controlled process [13, 21, 22].

Further, the Tafel slope,  $b$ , has determined by using the following equation for an irreversible diffusion-controlled reaction [23].

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

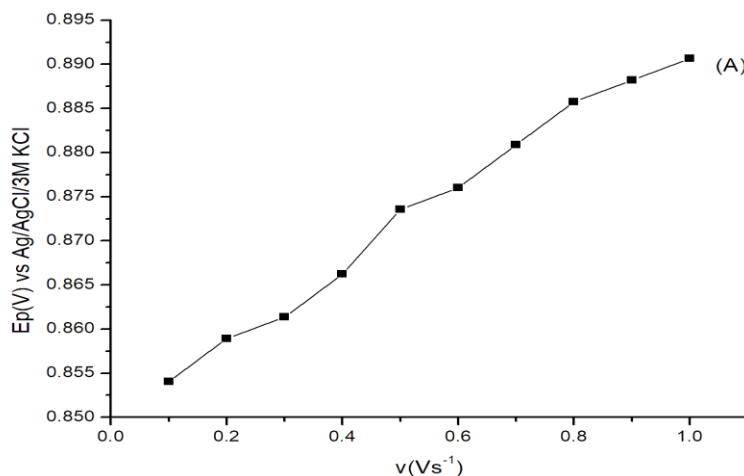




**Figure 4: (A) Logarithm of the peak current ( $I_p$ ) versus logarithm of the scan rate ( $v$ ). (B) Showing dependence of peak current ( $I_p$ ) on the square root of scan rate ( $V^{1/2}$ ). (C) Napierian logarithm of  $I_p$  versus  $E_p - E^0$ . (D) Showing calibration plot of  $I_p$  versus scan rate ( $v$ ). ( $1\text{mmol L}^{-1}$  of p-NA in mixed medium).**

A linear relationship and a slope  $(b/2) = \partial E_p / \partial (\log v)$  of  $0.039\text{V}$  has determined from the plot of  $E_p$  versus  $\log v$  in the range from  $0.100$  to  $1.000\text{Vs}^{-1}$  applied potential (figure 5). From the plot, Tafel value ( $b$ ) is obtained  $78\text{mV}$  for 3C2MA 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  $118\text{ mV}$  [21]. 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

$$E_p (V) = 0.039 \log v (Vs^{-1}) + 0.887 (R = 0.956)$$



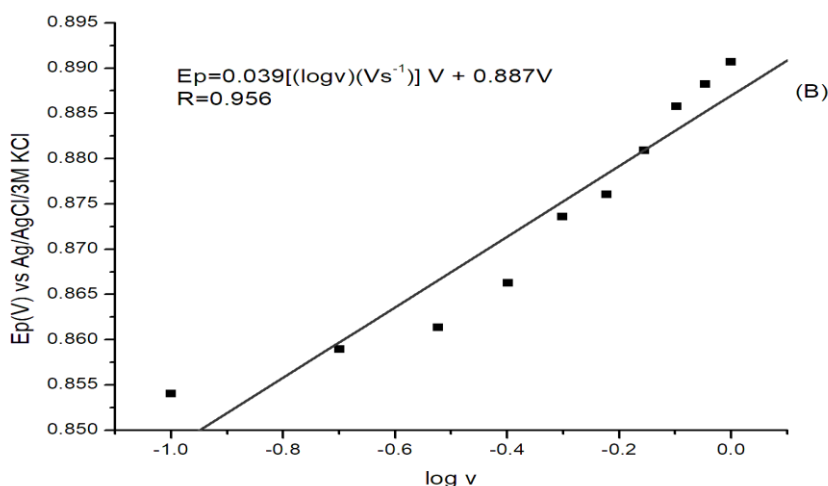


Figure 5: Dependence of peak potential,  $E_p$ , (A) on the potential scan rate,  $v$ , (B) on the  $\ln v$  for the oxidation of 3C2MA (1.992 mM) in buffer solution on PE.

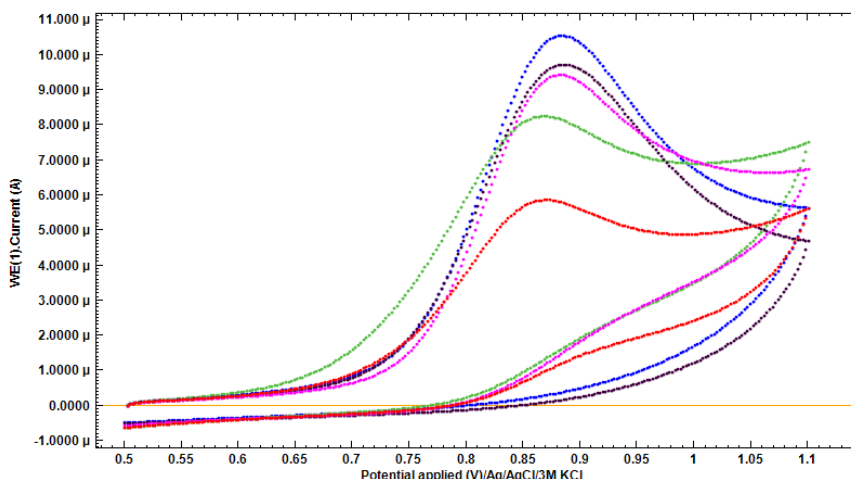


Figure 6: CVs of PE in 3C2MA in tap water sample 200 mV/s scan rate 10mM, 15mM, 18mM, 20mM, 25mM

As for an irreversible electrode process, according to Laviron [24],  $E_p$  is defined as

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

where  $\alpha$  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  $\alpha n$  can be determined as 1.518.

According to Bard and Faulkner [13],  $\alpha$  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  $\alpha$  is calculated as 1.282.



Further, the number of the transferred electron ( $n$ ) was calculated from the  $\alpha n$  value as 1.184-1 in the 3C2MA 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 0.850 and  $5.215 \times 10^2 \text{ s}^{-1}$  respectively. The electron transfer rate constant ( $k_{ox}$ ) is a function of the applied potential thus can be calculated from the equation [25].

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

So, the  $k_{ox}$  was obtained as  $6.977 \times 10^3 \text{ s}^{-1}$ .

Accordingly, the 3C2MA anodic oxidation is found to be a one-electron process.

#### Analytical application: Real sample analysis

This method is also important to determine the toxic 3C2MA in a real sample. The determination was carried out using cyclic voltammetry in a tap water sample on PE. A tap water sample is taken for analysis. Further this sample is unspiked with distilled water and spiked with 1.992mM concentration of 3C2MA. CV was carried out within the same scan potential window range at the  $100\text{mVs}^{-1}$  scan rate. A blank was obtained, then unspiked and spiked solution were observed. CVs show the sharp peak over the blank curve (Figure not shown). So, this analytical method is applicable to determine the 3C2MA with the help this technique in real sample.

#### CONCLUSIONS

This study suggests that the electro-oxidation of 3C2MA in buffer solution is a one-electron irreversible oxidation to form cation radical at the high rate constant on PE. Kinetic parameters were evaluated for the reaction. 3C2MA was also estimated in real sample. This indicates method is applicable to analytical chemistry to estimate 3C2MA in the real sample.

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