

# Anodic oxidation of 3-chloro 2-methylaniline in buffer solution

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## ABSTRACT

*In this work, anodic oxidation of 3-chloro-2-methyl aniline (3C2MA) was carried out in phosphate buffer solution (PBS) on a platinum electrode (PE) by employing an eco-friendly technique, cyclic voltammetry (CV) to degrade it because it has been used as a precursor in industries which is toxic for Human health. Kinetic parameters for the reaction such as standard heterogeneous rate constant at the rate determining step, anodic electron transfer rate constant, electron transfer coefficient of reaction, formal potential, and the surface coverage of electrode were evaluated under the influence of scan rate ( $v$ ).*

**Keywords:** Cyclic voltammetry, Kinetic parameters, Electrode kinetic, Water pollution

## INTRODUCTION

Anilines are harmful to the human health due to carcinogenic, genotoxic, mutagenic and allergenic inequalities [1-3]. Commercially, anilines are used as a precursor to produce dyestuffs, pesticides, and explosives etc in many industries. These toxic effluents are released as wastewater by these industries [4-5]. Substituted aniline (SA), for instance, 3C2MA is used to kill population of birds as it is extremely toxic in nature [6]. Moreover, it is also used in pharmaceutical industries as a precursor. It is found in non-steroidal anti-inflammatory drug (Tolfenamic acid) as impurities [7]. It acts as mutagen; therefore, it can change the shape of DNA and has considered being harmful to mankind [8].

To determine these toxics, various methods: UV-VIS spectrophotometry, chromatography, electrochemical: Fenton-oxidation, polarography, voltammetry are used [9]. Electrochemical technique is the most proficient technique since it provides a very consistent, accurate, and highly sensitive outcome. It is simple to operate, and the results obtained from it can readily be interpreted [10]. Currently, voltammetry is an eco-friendly technique to examine pollutants [11] and to determine the mechanism and kinetic parameters of electrochemical reactions [12-13]. Furthermore, many researchers have done polarographic [14-15] and voltammetric [16] oxidation and reduction of different SA [17-20].

It is stated, there is no literature on voltammetric determination of this compound till date. However, we have studied in our previous research work [21, 22]. Finally, the electrochemical oxidation parameters of 3C2MA: the nature of the reaction: diffusion and adsorption control; kinetic parameters are reported in this paper.

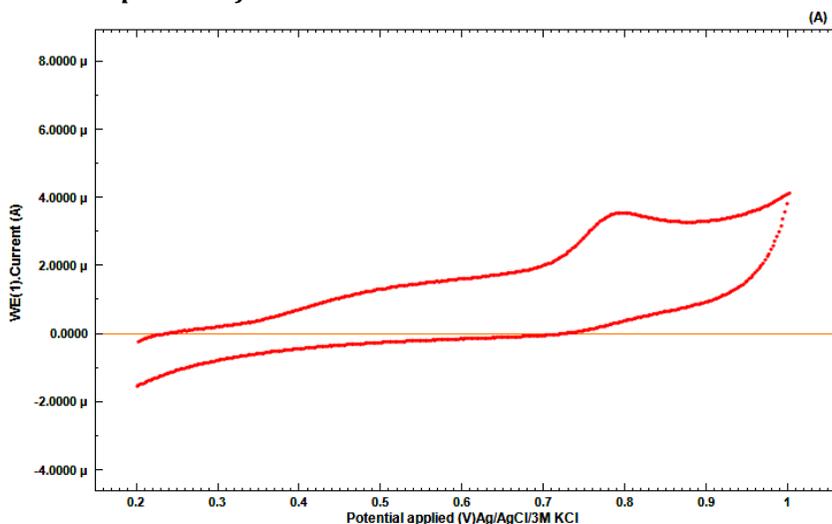
## MATERIAL AND METHODS

All the chemicals: ethanol, 3C2MA (Merck), dipotassium hydrogen phosphate ( $K_2HPO_4$ ), potassium dihydrogen phosphate ( $KH_2PO_4$ ), NaOH, were of AR grade and were used without purification. PBS was prepared using double distilled water (DDW). Distillation method was used to purify 3C2MA in ethanol and the stock solution was prepared in acetone. An Autolab model PGSTAT 101 potentiostat/galvanostat 663 VA Stand (Metrohm AG, Netherlands) was used to perform CV. This is three electrode system: a Pt disc electrode (PE) as the working electrode (WE), Ag/AgCl/3M KCl electrode as the reference and a Pt wire as the counter electrode. The WE was polished with alumina powder ( $Al_2O_3$ ) before each experiment.

## RESULT AND DISCUSSIONS

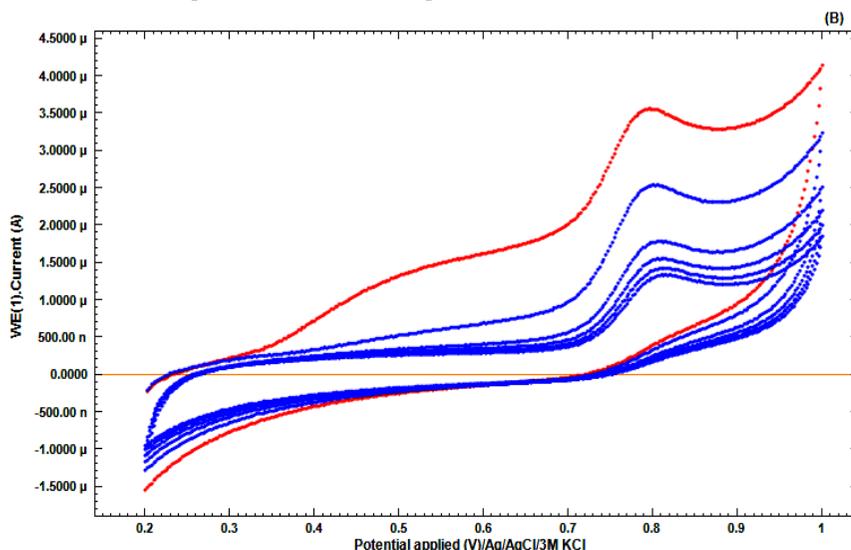
Herein, the CV technique was employed for 3C2MA electrochemical behaviour. The CV experiment was performed within the scan potential window range from +0.2 V to +1.0 V at the 100  $mVs^{-1}$ -1000  $mVs^{-1}$  different  $v$  in a voltammetric cell with the 3C2MA solution (1 mM) in PBS in presence of NaOH as a supporting electrolyte. Kinetic parameters were determined by the peak current ( $I_p$ ) under the influence of  $v$ . A linear relationship was recognized between  $I_p$  and  $v$ , and between peak potential ( $E_p$ ) and  $v$ .

### A. Cyclic Voltammetric experiment for PE



**Figure 1 (A) Voltammogram in PBS containing 3C2MA**

CV of 3C2MA shows only one anodic peak at the  $v=100\text{mVs}^{-1}$  [figure(1a)]. This peak indicates that the irreversible reaction was occurred on the PE surface. Successive scans were performed to find out the activity of PE (figure 1b) towards 3C2MA at the  $v=100\text{Vs}^{-1}$ . The  $I_p$  decreased and the  $E_p$  shifted towards the more positive potential indicating the slow rate of the electron transfer with the increasing number of scans and showed the slow redox process due to adsorption of 3C2MA on PE surface.

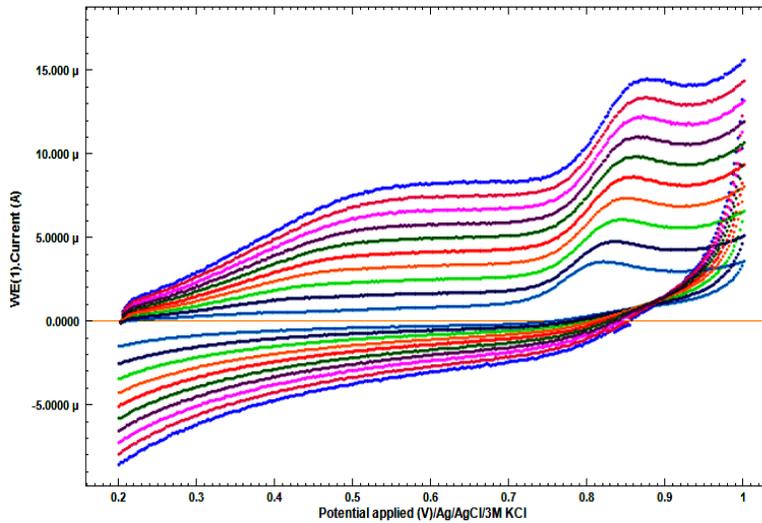


**Figure 1 (B) 6 continuous cycles at the scan rate  $100\text{mVs}^{-1}$**

A further increase in the number of scans may block PE surface by forming a film on it. Therefore, in present work, the first redox peak of 3C2MA anodic oxidation has considered for further analytical experiments.

#### **Influence of scan rate**

The influence of different  $v$  on 3C2MA examined by using CV (figure 2). The  $I_p$  and  $E_p$  were established for the first scan of the 3C2MA electrochemical reaction. The surface coverage ( $\Gamma$ ) of the electrode can be calculated using the sharp et al method: [23]. Therefore,  $\Gamma$  is obtained as  $0.414 \times 10^{-4} \text{ mol cm}^{-2}$ . Diffusion or adsorption controls the reversibility of electrochemical reaction rate, therefore, relationship is stabilised between  $I_p$  and  $v^{1/2}$  and between  $\log I_p$  and  $\log v$  [24] [figure 3(a),(b)]. Figure 3 reports these plots for the first anodic peak of electrochemical reaction. If  $I_p$  changes linearly with  $v^{1/2}$ , intercepting the origin of the coordinates, then the process is considered as without kinetic interferences.



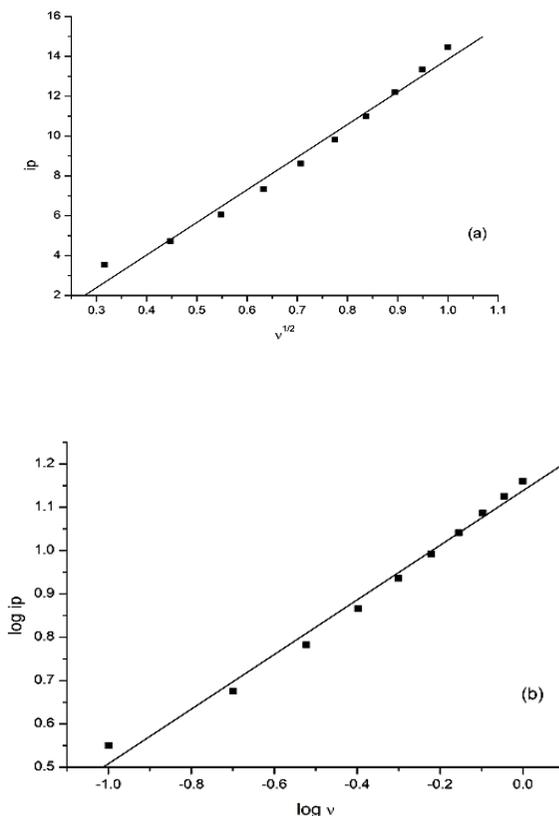
**Figure 2 CVs of PE with 3C2MA at different scan rates.**

However, the origin of the coordinates is not intercepted by this linear fit, [figure 3 (a)], the electrode process is diffusion-control in nature and is proceeded by a chemical reaction[25]. At various  $v$ ,  $I_p$  depends linearly on the square root of  $v$  (equation below):

$$I_p(\mu A) = 16.369 V^{1/2} (v_s^{1/2})^{1/2} - 2.516 \mu A (R = 0.992)$$

Alternatively, the dependence of  $\log I_p$  on  $\log v$  is linear. The slope of this linear fit is 0.630. Therefore according to Bard, Faulkner, and others [12], this process is only controlled by diffusion (equation below):

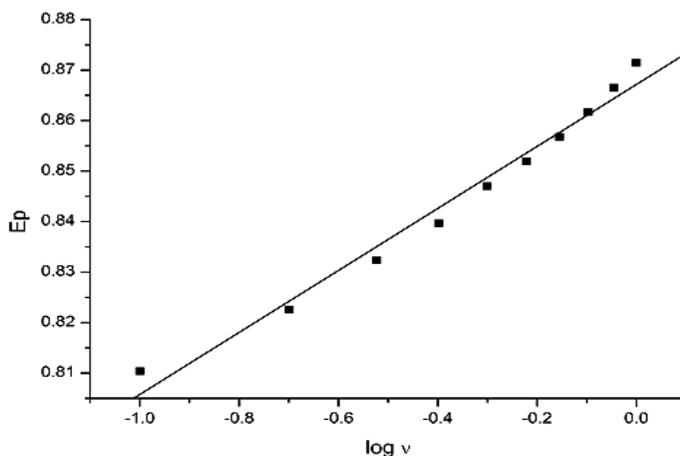
$$\log I_p = 0.630 \log v (Vs^{-1}) \mu A + 1.138 (R = 0.994)$$



**Figure 3 showing(a)  $I_p$  vs  $v^{1/2}$  (b)  $\log I_p$  vs  $\log v$**

While when the value of a slope is close to 1.0, the process is expected to be an adsorption-controlled process [12, 26, 27]. Because for the first scan at all scan rate reaction is found to be diffusion controlled then the Tafel slope,  $b$ , has determined by using the following equation for the reaction [28].

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



**Figure 4 Showing log v vs Ep**

From the slope of plot (figure 4), Tafel value ( $b$ ) is obtained 122mV that exhibits remarkable adsorption for overall reaction or the participation of reaction intermediates on the PE surface for a one-electron process in the rate determining step [26] (figure 4) (equation below):

$$E_p(V) = 0.061 \log v (Vs^{-1}) + 0.867 (R = 0.990)$$

$E_p$  is defined as

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

where  $\alpha$  is the transfer coefficient,  $k^0$  is the standard heterogeneous rate constant of the reaction,  $n$  is the number of electron transferred and  $E^0$  is the formal potential. Other symbols should be considered as conventional [28]. Consequently, from the value of  $\alpha n$  can be determined as 0.963 and  $\alpha$  is calculated as 1.149.

Further,  $n$  was calculated from the  $\alpha n$  value as 1.  $E^0$ ,  $k^0$  [27-28] and  $k_{ox}$  [29] for the reaction were obtained as 0.811,  $3.120 \times 10^2 s^{-1}$  and  $8.362 \times 10^2 s^{-1}$  respectively.

## CONCLUSION

3C2MA electrochemical oxidation is found to be one electron transfer process of diffusion as well as adsorption controlled in which high scan rate chemical reaction also involved. Therefore, this toxic compound can be degraded with the help of an eco friendly electrochemical treatment, cyclic voltammetry easily.

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