

ELECTROCHEMICAL OXIDATION OF SUBSTITUTED ANILINE IN ACIDIC SOLUTION

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Abstract: 3-chloro-2-methylaniline (3C2MA) is toxic for Human health and has been used as a precursor in industrial products, drugs, combustion products, pesticides, dyes, plastic, explosives, and rubber. Releasing effluents from these industries contaminates water. In this work, electrochemical degradation of 3C2MA was carried out in acidic solution on a platinum electrode (PE) by employing an eco-friendly technique, cyclic voltammetry. Kinetic parameters were 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 were evaluated under the influence of scan rate. The nature of reaction is found to be adsorption as well as diffusion controlled. The result shows fast kinetics.

Keywords: Water pollution, Voltammetry, Substituted aniline, Redox reaction, Electrode Kinetic

I INTRODUCTION

Anilines are carcinogenic, genotoxic, mutagenic and allergenic so these are harmful for the human health. [1-3] Anilines and substituted anilines are used as a precursor in many industries for commercial purpose to prepare dyestuffs, pesticides, resins, explosives and polymer; plastic etc. These industries release these toxic effluents as wastewater. [4-5] Substituted aniline such as 3-Chloro-2-methylaniline (3C2MA) is used to kill birds. It is so much toxic [6]. It is also used in pharmaceutical Industries. Tolfenamic acid (non-steroidal anti-inflammatory drug) has 3C2MA as impurities [7]. It can change the shape of DNA because it acts as mutagen [8].

Various methods are used to determine or degrade these toxic, UV-VIS spectrophotometry, chromatography; HPLC, electrochemical methods such as Fenton-oxidation, polarography, voltammetry [9]. Electrochemical methods are so efficient which is 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]. It is widely employed to determine the mechanism and kinetic parameters of electrochemical reactions [12-13]. So we employed this technique to degrade this toxic. Many researchers have done work on different substituted aniline. Mono-, di-, and tri chloro substituted aniline was also investigated by researchers in non-aqueous solution [14]. Richa Sharma has also detected o-, m- and p-toluidine [15]. Chloro-substituted aniline has detected by electrochemical techniques by J.C. Suatoni et al. [16] Polarographic [17-18] and voltammetric [19] oxidation and reduction of other substituted aniline have also been studied. But in my knowledge there is no voltammetric determination of kinetic and analytical parameters of this compound while we studied this compound in buffer solution obtaining suitable results [20].

The objective of the study is to find out: 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: α) (b) analytical parameters (linearity, limit of detection: LOD and limit of quantification: LOQ).

II MATERIAL AND METHODS

Chemicals and solutions

All the chemicals such as hydrochloric acid (HCl), potassium chloride (KCl), ethanol, were of analytical grade and were used without further purification. Aqueous solutions of HCl (0.1 mol L^{-1}) and KCl (0.1 mol L^{-1}) were prepared using double distilled water (DDW). Distillation method was used to purify 3C2MA (Merck) in ethanol. After purification the stock solution was prepared in acetone. All experiments were carried out at room temperature ($20\text{-}22^\circ\text{C}$).

Voltammetric Apparatus

An Autolab model PGSTAT 101 potentiostat/galvanostat 663 VA Stand (Metrohm AG, Netherlands) was used to perform cyclic voltammetry. There is three electrode in this system: a Pt disc electrode (PE) (0.031 cm^2) 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_2O_3) before each experiment.

3C2MA voltammetric behaviour

The cyclic voltammetric experiment was performed within the scan potential window range from $+0.2 \text{ V}$ to $+1.2 \text{ V}$ at the 100 mVs^{-1} - 500 mVs^{-1} different scan rates in a voltammetric cell with the 3C2MA solution (1 mmol L^{-1}) in hydrochloric acid solution in presence of KCl as a supporting electrolyte (HCl-KCl).

Electrochemical kinetics

Kinetic parameters were evaluated by the study of the peak current under the influence scan rate. A linear relationship was established between peak currents and scan rates, and between peak potential and scan rates to find out the parameters of the electrochemical reaction.

III. RESULT AND DISCUSSIONS

In the current work, the cyclic voltammetric technique was employed for 3C2MA electrochemical behaviour and to find out the kinetic parameters, control of the reaction, and transfer of number of electron in the reaction.

A. Cyclic Voltammetric experiment for PE

Cyclic voltammogram (CV) of 3C2MA electrochemical oxidation showed only one anodic peak and one cathodic peak at the scan rate 50mVs^{-1} in HCL-KCl when scanning towards positive potential [figure (1a)]. These peaks indicate that the reaction was reversible. But if the peak separation (the difference between the cathodic and anodic peak current) (ΔE_p) can be found out by using following equation:

$$\Delta E_p = E_{pa} - E_{pc}$$

where E_{pa} is anodic peak potential and E_{pc} is cathodic peak potential. The ΔE_p is 0.520Vs^{-1} . So the reaction is found to be quasi-reversible and the number of transferred electron is one.

Successive CVs were performed to find out the activity of PE (figure 1b) in a solution containing 1mM of 3C2MA in HCl-KCl at the scan rate 50Vs^{-1} . The peak current decreased and the peak potential shifted towards the more positive potential indicating the slow rate of the electron transfer with the increasing number of cycles. These numbers of cycles showed the slow redox process due to adsorption of 3C2MA on PE surface. A further increase in the number of cycles may block electrode surface by forming a film on it. So, in this work, the first redox peak of 3C2MA electrochemical oxidation has considered for further analytical experiments.

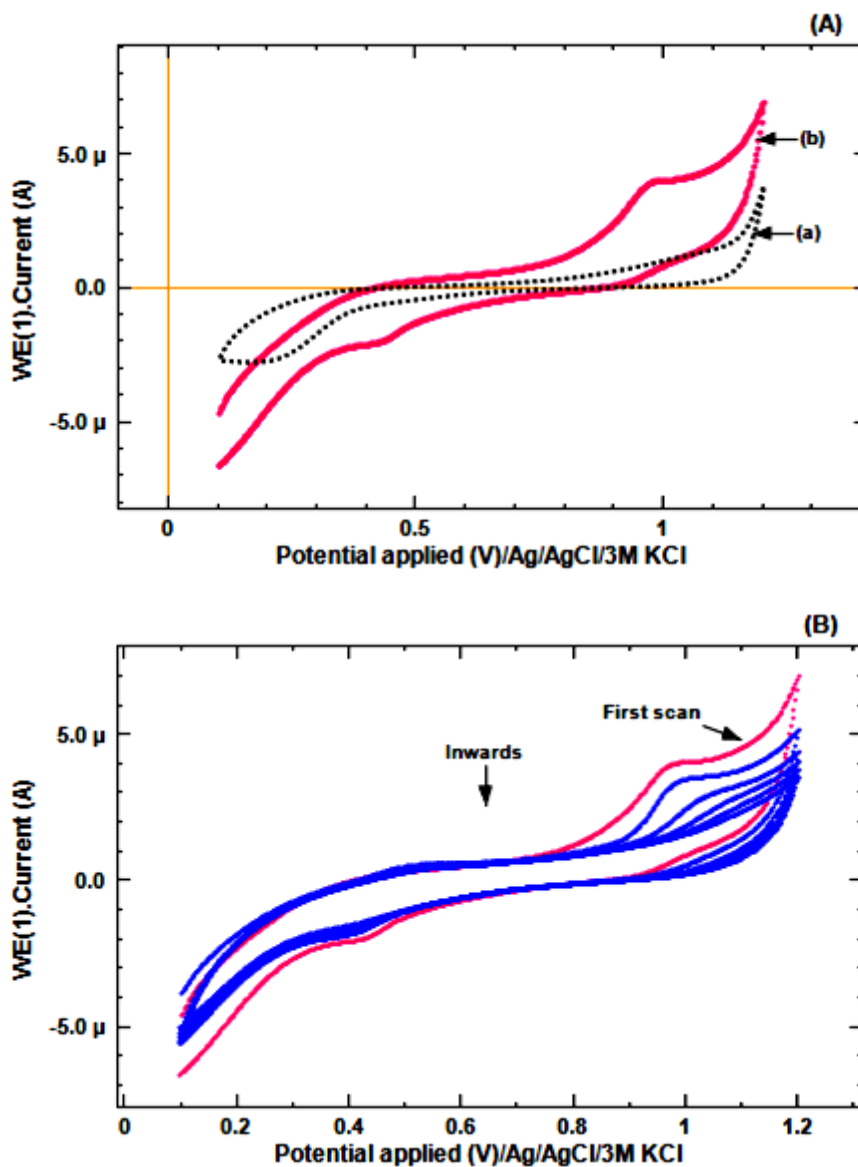


Figure 1 (A) Successive cyclic voltammogram (CV) of platinum electrode (PE) (a) with HCl in presence of KCl as supporting electrolyte (b) containing 3C2MA (1mmol L^{-1}) (B) 6 continuous cycles at the scan rate 50mVs^{-1}

1. Influence of scan rate

For the one electron oxidation the influence of different scan rates on 3C2MA electrochemical behaviour examined by using cyclic voltammetry with the different scan rates ranging from 0.05 to 0.25Vs^{-1} (figure 2). The peak currents and peak potentials were established for the first scan of the 3C2MA electrochemical reaction at different scan rates. An anodic has been examined while scanning at low scan rate. However, with the increasing of scan rate, at 0.15 to 0.25Vs^{-1} , another anodic peak appears which indicates chemical reaction proceeds.

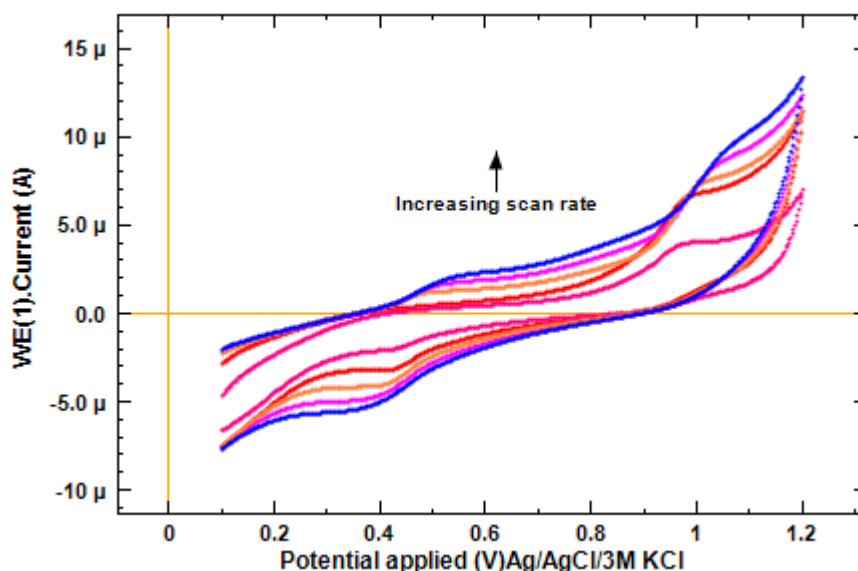


Figure 2 CVs of PE at different scan rates 50-250mvs⁻¹.

The surface coverage of the electrode can be calculated using the sharp et al method: [21]. So the average surface coverage (surface concentration of the electro active species) of electrode is obtained as $0.8 \times 10^{-3} \text{ mol cm}^{-2}$.

Diffusion or adsorption controls the reversibility of electrochemical reaction rate. There are two ways to investigate it: dependence of I_p on $v^{1/2}$ and of $\log I_p$ on $\log v$ [22] [figure 3 (a), (b)].

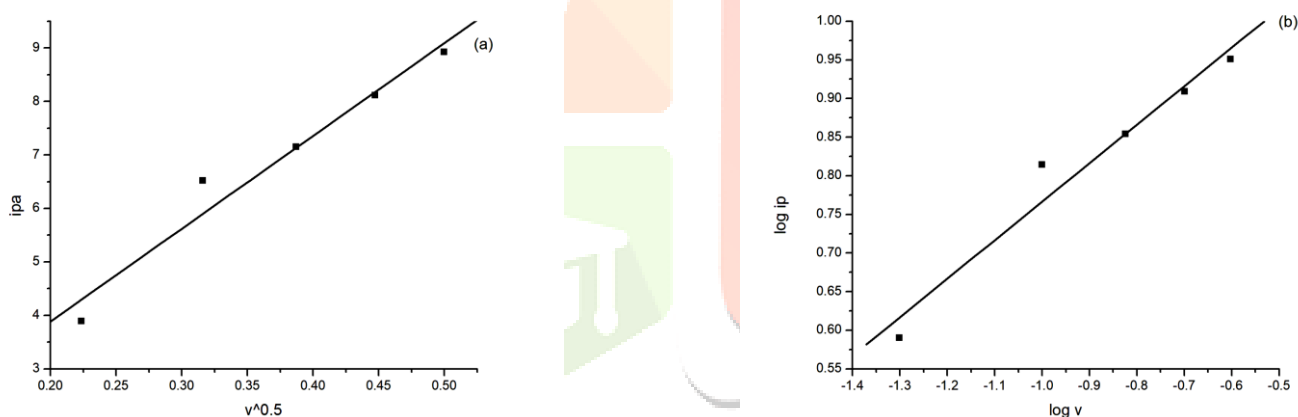


Figure 3(a) (a) Logarithm of the peak current (I_p) versus logarithm of the scan rate (v). (b) Showing dependence of peak current (I_p) on the square root of scan rate ($V^{1/2}$).

Figure 2 shows these plots for the first anodic peak of 3C2MA in HCl-KCl 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. [23]. At various scan rates ranging from 0.05 to 0.25Vs⁻¹, the anodic peak current depends linearly on the square root of scan rate and is described by the following equation:

$$I_p(\mu A) = 17.34 V^{1/2}(Vs^{1/2})^{1/2} - 0.419 \mu A (R = 0.980)$$

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 preceded by a chemical reaction. Alternatively, the dependence of $\log I_p$ on $\log v$ is linear. The slope of this linear fit is 0.498. Therefore according to Bard, Faulkner, and others [12], this process is only controlled by diffusion and is described by the following equation:

$$\log I_p = 0.498 \log v (Vs^{-1})\mu A + 1.265 (R = 0.980)$$

While when the value of a slope is close to 1.0, the process is expected to be an adsorption-controlled process [12, 24, 25]. 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 [26].

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

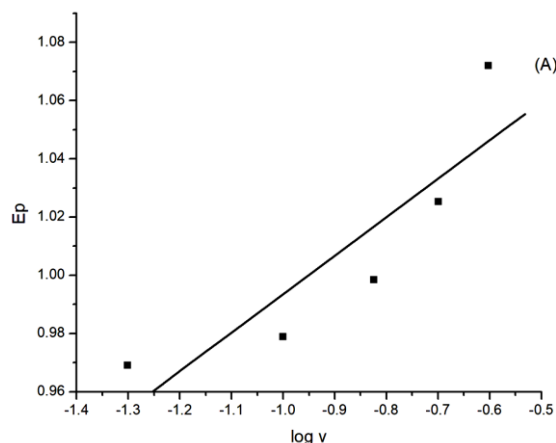


Figure 4 Showing linear relationship between $\log v$ and E_p

A linear relationship and a slope ($b_2 = \partial E_p / \partial (\log v)$) of 0.132 V has determined from the plot of E_p versus $\log v$ in the range from 0.05 to 0.25 V s^{-1} applied potential (figure 4). From the plot, Tafel value (b) is obtained 264 mV for p-NA electro-oxidation. This value exhibits remarkable adsorption for overall reaction. 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 mV [24]. With the increase in scan rate, the peak potential shifted towards a more positive value. It confirms that the oxidation process is irreversible (figure 4). The relationship can be expressed as

$$E_p (V) = 0.132 \log v (Vs^{-1}) + 1.125 (R = 0.900)$$

Kinetic parameters can be evaluated, according to Laviron [26], 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 α 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 4), the value of αn can be determined as 0.448 . According to Bard and Faulkner [19], α 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 and the average value of α is calculated as 0.422 .

Further, the number of the transferred electron (n) was calculated from the αn value as $1.06-1$ in the 3C2MA electrochemical 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 0.44 and $1.22 \times 10^{-1} \text{ s}^{-1}$ respectively. The electron transfer rate constant (k_{ox}) is a function of the applied potential thus can be calculated from the equation [27].

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

So, the k_{ox} was obtained as $9.38 \times 10^3 \text{ s}^{-1}$.

Accordingly, the 3C2MA anodic oxidation is found to be a one-electron process and fast electron transfer rate constant.

IV. CONCLUSION

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

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