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Voltammetric Behavior of 2-bromo-4, 6-dinitroaniline and 3-chloro-2-methylaniline in Aqueous Medium

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Abstract: Herein, anodic oxidation of 2-Bromo 4, 6-dinitroaniline (2B46DNA) was performed in an aqueous medium on a platinum electrode (PE) using cyclic voltammetry. The anodic reaction was found to have diffusion as well as adsorption-controlled nature with an overall coupled-electron transfer. Kinetic and analytical parameters were also evaluated for the reaction. Kinetic parameters such as standard heterogeneous rate constant at the rate determining step, anodic electron transfer rate constant electron transfer coefficient of reaction, and formal potential and Surface coverage of electrode were evaluated under the influence of scan rate. Further, 2B46DNA-chemically-modified PE (CMPE) was employed to perform electro-oxidation of 3-chloro 2-methylaniline (3C2MA) in acidic solution. A Very intense peak of 3C2MA electro-oxidation was observed on CMPE while weak peak on PE. As the analysis in the real sample, both PE and CMPE show good response towards 3C2MA estimation..

Keywords: Kinetic parameters, Chemically-modified electrode, substituted aniline, Water pollution

I. INTRODUCTION

Anilines having carcinogenic, genotoxic, mutagenic and allergenic inequalities, is harmful to the human health [1-3]. Aniline and its derivatives are the simplest of the primary aromatic amines an organic base used to make dyes, drugs, explosives, plastics and chemicals for the rubber industry as a precursor.

These toxic effluents are released as wastewater by these industries [4-6]. Substituted aniline (SA), for instance, 2B46DNA and 3C2MA have been preferred to analyse in this article. These compounds are aniline derivatives with additional bromine, nitro4 and chloro and methyl substituents respectively.

Eric J Weber et al [7] reported 2B46DNA may undergo reduction in some natural anoxic sediments, as a result the subsequent release of potentially hazardous aromatic amines to the water column whereas 3C2MA is extremely toxic in nature since it is used to kill population of birds [6]. Moreover, it is also used in pharmaceutical industries as a precursor and found in non- steroidal anti-inflammatory drug (Tolfenamic acid) as impurities [8]. Also, it acts as mutagen and can change the shape of DNA so it has considered being harmful to mankind [9]. To determine these toxics, various methods: UV-VIS spectrophotometry, chromatography, electrochemical: Fenton-oxidation, polarography, voltammetry are used [10]. At present, voltammetry, an eco-friendly technique, is used to examine pollutants [11] and is employed to determine the mechanism and kinetic parameters of electrochemical reactions [12, 13]. Voltammetric technique is the most proficient technique as it simple to operate and provides a very consistent, accurate, and highly sensitive outcome that can readily be interpreted14. Further, many researchers have done polarographic [15, 16] and voltammetric [17] oxidation and reduction of different substituted aniline [18-21]. To the best of my knowledge, there is no literature on voltammetric determination of these compounds till date. However, 3C2MA has been studied in our previous research work [22, 23].

It has now been in trend for many years that in electrochemical studies, chemically-modified electrodes and nanoparticle modified electrodes are used to enhance the sensitivity of electrode towards redox reaction and electro-deposition [24, 25] and these electrodes are employed in different analytical applications [26]. Further, chemical sensor electrode has been also used for oxidation of substituted aniline [27].

Finally, in this paper, the electrochemical oxidation parameters of 2B46DNA: **(a)** the nature of the reaction: diffusion and adsorption control; **(b)** kinetic parameters; standard rate constant (ko), electron transfer rate for anodic reaction (kox) and transfer coefficient (α) **(c)** activity of 2B46DNA-chemically-modified platinum electrode (CMPE).

II. EXPERIMENTAL

A. Chemicals and Solutions

All the chemicals, ethanol, acetone, and sulphuric acid (H_2SO_4) (as supporting electrolytes) are of AR grade and were used as received. Potassium dihydrogen phosphate and dipotassium hydrogen phosphate was used to prepare phosphate buffer (pH=7.0). Double distilled water (DDW) was used to prepare all aqueous solutions. 3C2MA (Merck) was distilled and 2B46DNA (Merck) was recrystallized for purification by using ethanol before use. All experiments were carried out at room temperature (25-27°C).

B. Voltammetric Experiments

An Autolab model PGSTAT 101 potentiostat/galvanostat 663 VA Stand (Metrohm AG, Netherlands) was employed to perform cyclic voltammetry consisted of three electrode system a Pt disc electrode (PE) (0.031 cm^2) as a working electrode, Ag/AgCl/3M KCl reference electrode and a Pt wire as a counter electrode. All potentials mentioned in this work as referred to a reference electrode. Electrodes were pretreated before each voltammetric experiments.

1) *Voltammetric behaviour*: With the help of pre-mentioned voltammetric setup, the nature of process was observed. Process may be either of adsorption-controlled or of diffusion-controlled and either cathodic or anodic or both in nature.
2) *2B46DNA electrooxidation*: The cyclic voltammetric experiment was conducted within the scan potential window range between 0.0 V and 1.4 V vs Ag/AgCl (3M KCl) at 50 mVs^{-1} scan rate in a voltammetric cell with the 4mmol L^{-1} 2B46DNA solution in buffer solution.

C. Electrochemical kinetics

A linear relationship was established between peak potential and scan rates to evaluate the kinetic parameters under the influence of different scan rates 50-250 mVs^{-1}. The determination of 2B46DNA anodic oxidation was also carried out.

D. Electrode Modification

The cyclic voltammetric experiment was conducted to polymerize PE. For modification of electrode, 32 repeated cycles of a 4mmol L^{-1} 2B46DNA were performed at 100 mVs^{-1} scan rate in buffer solution. After polymerization, CMPE was rinsed with double distilled water dried in air and was used for further experiment.

E. 3C2MA voltammetric behavior

A 1.66 mmol L^{-1} 3C2MA solution in 0.5M sulphuric acid was electrolysed at 100mVs^{-1} scan rate on CMPE to find out the behavior of 3C2MA.

III. RESULTS AND DISCUSSIONS

A. Cyclic voltammetric study of 2B46DNA

Cyclic voltammogram (CV) of 2B46DNA showed one anodic peak at scan rate 50mVs^{-1} when scanning towards positive potential whereas no analogous cathodic peak observed on the reverse scan [figure 1(a)]. So the reaction is found to be irreversible in nature. 6 consecutive CVs in a solution containing 4mM of 2B46DNA at the scan rate 100Vs^{-1} were conducted [figure 1(b)] to find out the activity of bare PE. With the increasing the number of cycles, the peak current falls down slowly and the peak potential shifted towards the more positive potential and after fifth scan, no sharp peak has been observed. It indicates adsorption on PE surface which inhibits the oxidation process slowly and a further increase in number of cycles may cause the blockage of electrode surface by development of a layer on it. So, only the first oxidation peak of 2B46DNA was measured in this study at different scan rates for further analytical experiments.

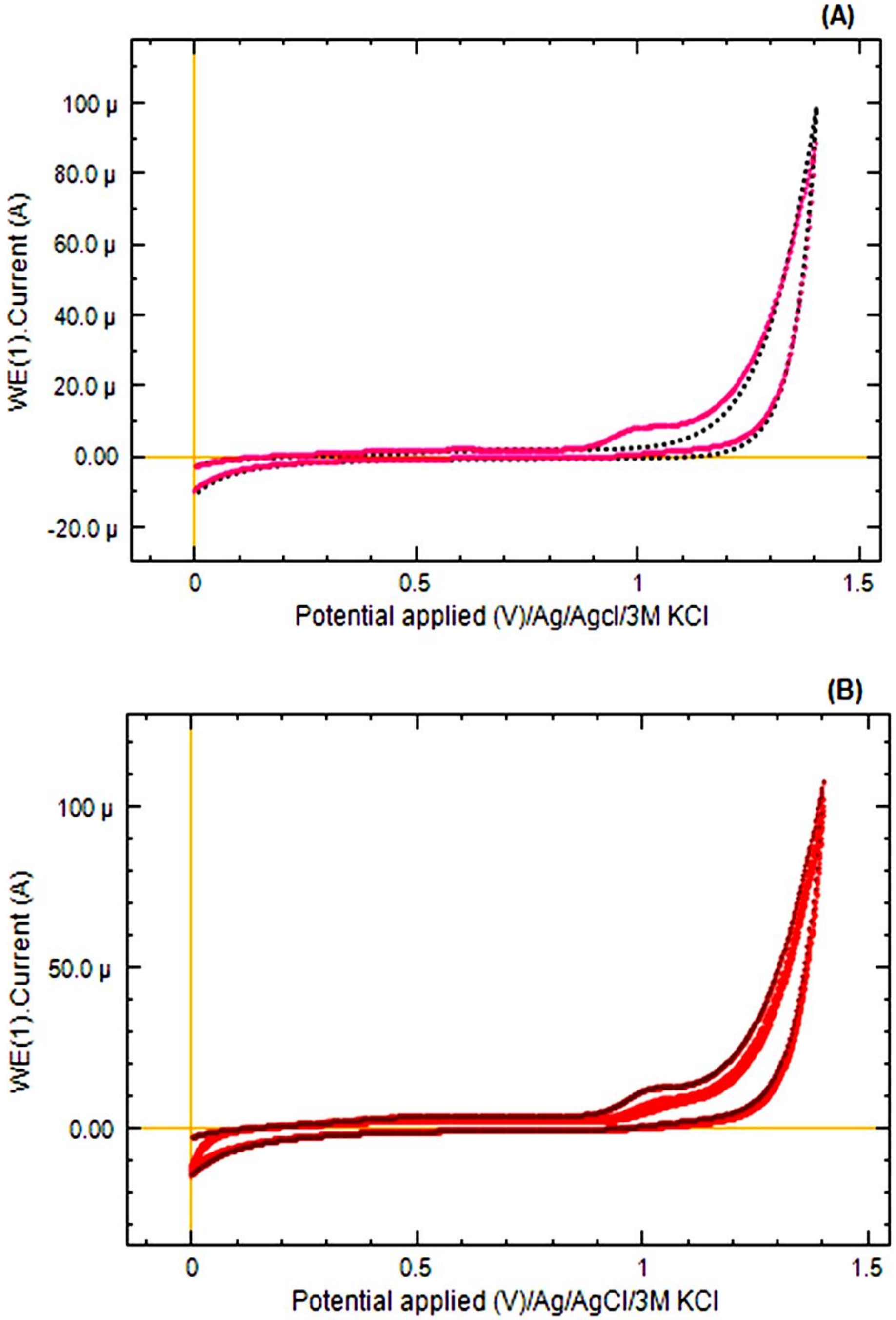

Figure 1 (A) Cyclic voltammogram (CV) of pt electrode (PE) (a) in absence and (b) presence of 4mmol L^{-1} 2B46DNA at 50 mVs^{-1}, (B) 6 Successive CVs recorded at scan rate 100mVs^{-1}

1) *Surface Coverage*: The surface coverage of the electrode can be calculated using the sharp et al [28]. So the average surface coverage (surface concentration of the electro active species) of electrode is obtained as 0.7 × 10^{-3} mol cm^{-2}.
2) *Influence of Scan Rate*: The effect of scan rate on 2B46DNA electro-oxidation was investigated by cyclic voltammetry with scan rates of 0.05-0.25Vs^{-1} (figure 2).

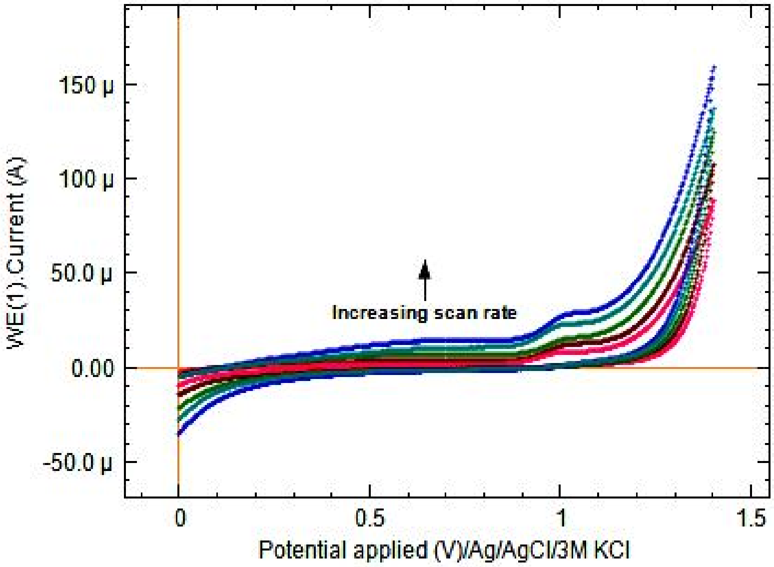

Figure 2 CVs of PE in mixed medium solution containing 4mM of 2B46DNA at different scan rates 50-250mVs^{-1}

The reversibility of electrochemical reaction rate is controlled by diffusion or adsorption. A linear relationship is established between Ip and $\nu^{1/2}$ and log Ip and log ν [29] (figure 3 a, b).

Figure 3 shows these plots for the first anodic oxidation peak of 2B46DNA. At various scan rates, the anodic oxidation peak current depends linearly on the square root of scan rate and is described by the following equation:

$$Ip(\mu A) = 64.62532\,\nu^{1/2}\left(Vs^{1/2}\right)^{1/2} - 8.08257\mu A\ (R = 0.97399)$$

Since the linear coefficient has a value of intercept which is not zero, then it is considered that the 2B46DNA anodic reaction is preceded by a chemical reaction and was diffusion-controlled in nature [30].

Alternatively, a linear relationship between log Ip vs log ν shows linearity and is described by the following equation:

$$\log Ip = 0.73057 \log \nu\ (Vs^{-1})\mu A + 1.81528\mu A\ (R = 0.98142)$$

The slope of this linear fit is close to 0.7, according to Bard, Faulkner and others; the process is both controlled by diffusion as well as adsorption [12, 31, 32]

Further, the Tafel slope b was determined using the following equation for totally irreversible diffusion-controlled reaction [33].

$$Ep = b/2 \ln \nu + constant$$

From the plot, Tafel value (b) of 45.20mV, this low Tafel value shows no remarkable adsorption for first oxidation peak at different scan rates [34]. With an increase in scan rate, the peak potential shifted to a positive value, it confirms the oxidation process was irreversible, and a linear relationship was observed in the range of 0.05-0.30Vs^{-1} in figure 4. The relationship can be expressed as

$$Ep\ (V) = 0.0226 \log \nu\ (Vs^{-1}) + 1.01867\ (R = 0.96275)$$

As for an irreversible electrode process, according to Laviron [35], Ep is defined as

$$Ep = E^0 + (2.303RT/\alpha nF)\log(RTk^0/\alpha nF) + (2.303RT/\alpha nF)\log \nu$$

Here symbols should be considered as usual. So the value of αn was calculated to be 2.6168 (figure 4). According to Bard and Faulkner equation [12], the average value of α was calculated as 1.2182. Further, the number of electron (n) transferred in the electro-oxidation of 2B46DNA was calculated to be 2. The value of k^0 can be determined by knowing the value of E^0 (from the intercept of the plot Ep versus ν) [35, 36]. E^0 was obtained as 0.98752 so the k^0 was calculated as $2.0786 \times 10^2\ s^{-1}$. The electron transfer rate constant (k_{ox}) for this oxidation process is a function of the applied potential and can be described as [37]

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

So, the k_{ox} was calculated as $2.295 \times 10^2 s^{-1}$.

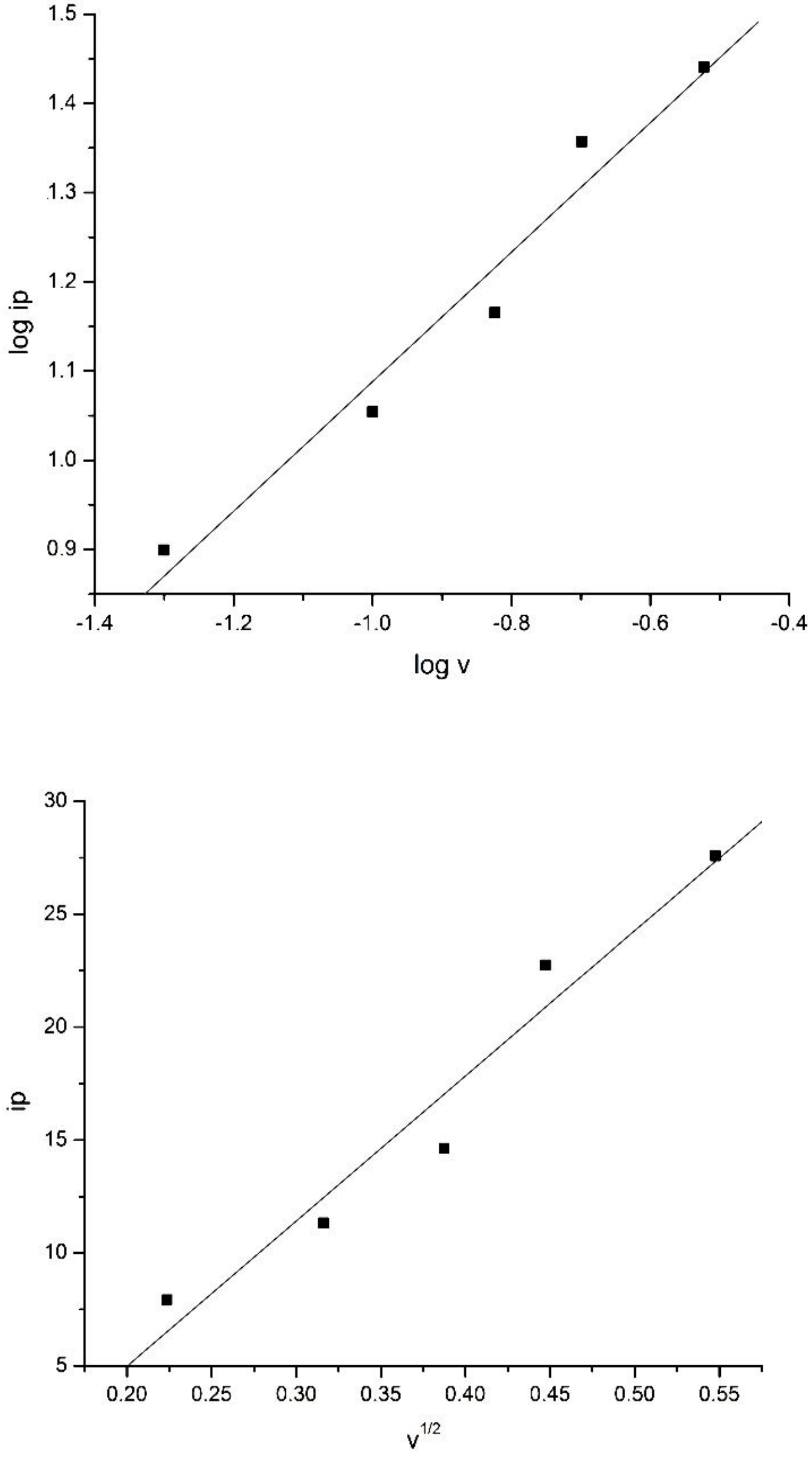

Figure 3 (a) Logarithm of the peak current (Ip) versus logarithm of the scan rate (ν). (b) Showing dependence of peak current (Ip) on the square root of scan rate ($V^{1/2}$).

B. *Cyclic voltammetric study for chemically- modified Pt electrode (CMPE)*

Modification of electrode was taken into place to find out the activity of polymer film formed during the cyclic voltammetric experiments and the stability of electrode towards the 3C2MA anodic reaction.

1) *Modification of PE*: Prior to modification, electrode was pretreated by polishing with alumina to a mirror-like finish and was rinsed with double distilled water. After pretreatment, 25 consecutive cycles were run in the range of 0.0-1.4V/Ag/AgCl/3M KCl at the scan rate of 100mVs^{-1}. In this study, 2B46DNA (4mmol L^{-1}) was used with mixed medium to modify the PE surface to produce 2B46DNA/PE. CV shows that the peak current was condensed with increasing the number of cycles since it gradually condensed and peak potential was not changed during the repeated cycles indicates the surface was electro-polymerized.

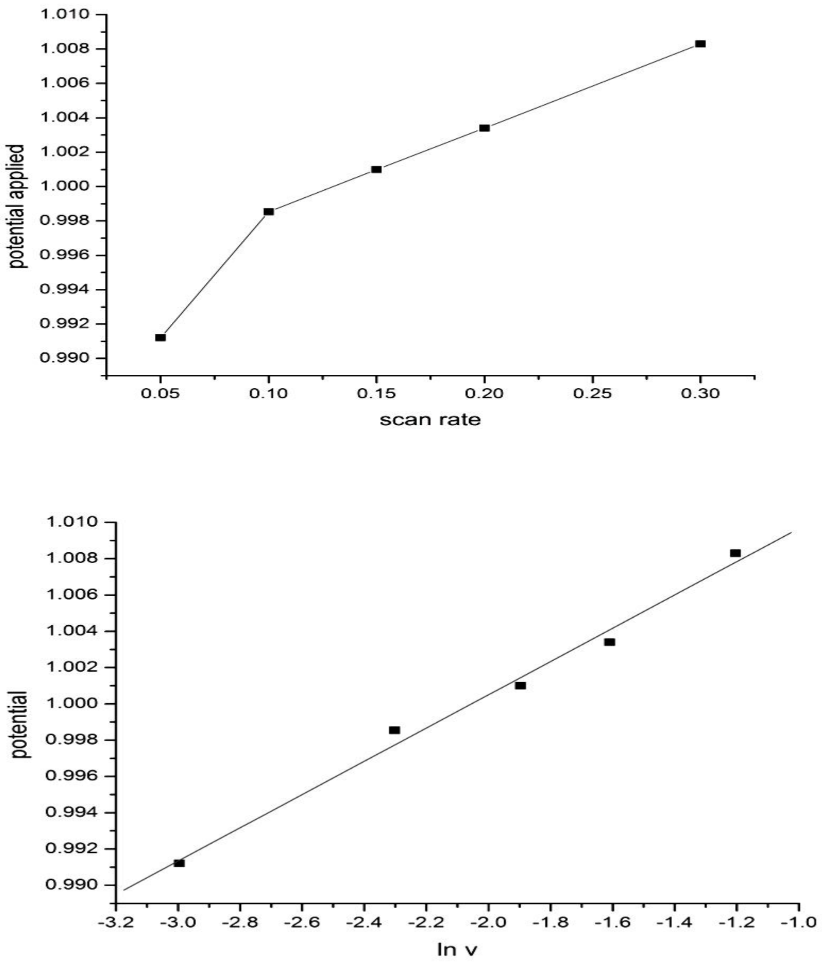

Figure 4. Dependence of peak potential, Ep, (a) on the potential scan rate, ν, (b) on the ln ν

2) *Characterization of CMPE:* CMPE was further used for electro-oxidation of 3C2MA to find out its activity towards the anodic process. 1.66 m mol L^{-1} 3C2MA solution 0.5 M H_2SO_4 was used for the experiment in the potential range from 0.0-1.4V/Ag/AgCl/3M KCl at the scan rate of 100mVs^{-1}. On bare electrode, there was slight peak while it is observed that the peak current was very sharp on modified electrode in comparison to bare electrode. So more 3C2MA electro-oxidation has been observed when process run on CMPE. This is due to the formation of conductive polymer film on the surface of PE which exhibits the activity of the PE towards the electro-oxidation of 3C2MA. So, the activity of produced electrode is more towards the 3C2MA anodic process. CVs response was shown in figure 5 for both bare (a) and modified electrode (b).

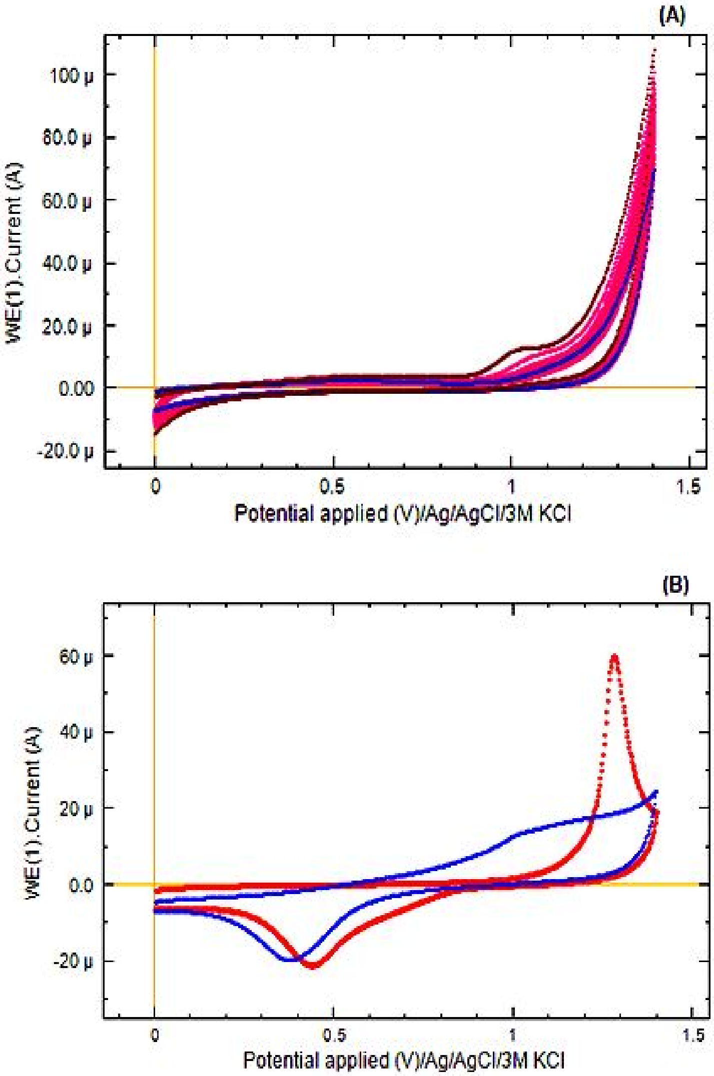

Figure 5. (A) 32 Repeated cycle showing of 2B46DNA in 0.5M H_2SO_4. (B) showing CVs (a) on bare pt electrode (blue) (b) on CMPE (red) in 1.66mM 3C2MA at scan rate 100 mVs^{-1}.

IV. CONCLUSIONS

Electro-oxidation of 2B46DNA is of two electron oxidation to form cation radical at high rate constant at bare electrode. 2B46DNA polymer-modified electrode is very useful for the electro-oxidation of 3C2MA in comparison to bare PE due to formation of conductive polymer film on the electrode surface which enhances the activity of bare electrode towards 3C2MA electrooxidation.

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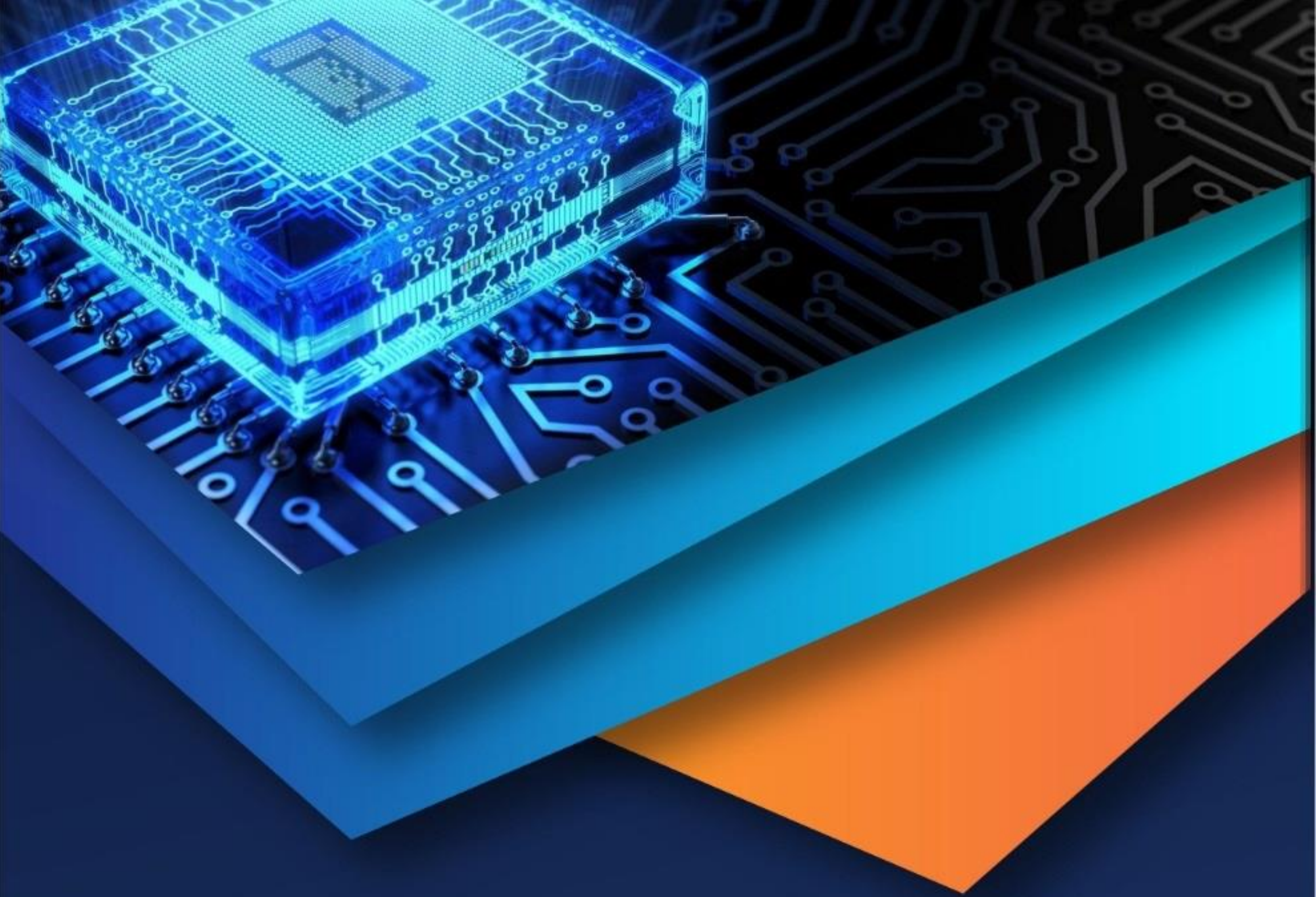

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