

Full Paper

The Electrochemical Redox Behaviour of Acid Blue 25 and its Quantitative Measurement at Carbon Paste Electrode: A Voltammetric Study

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Abstract- The electrochemical oxidation and reduction behavior of Acid Blue 25 (AB 25) at carbon paste electrode (CPE) was investigated by employing cyclic voltammetry (CV) and differential pulse voltammetry (DPV) techniques. AB 25 was an anthraquinonic and anionic dye and it gives two reversible redox systems at potential values ≈ 0.2 V and ≈ 0.56 V respectively. The effect of pH on the anionic dye was studied and it was conformed that the pH-7.0 of phosphate buffer solution (PBS) was the suitable supporting electrolyte for further studies. We have studied the effect of accumulation time, scan rate, concentration, and repeatability. We have proposed a mechanism for the redox behavior of AB 25. It was conformed that one system at 0.2 V was diffusion controlled, where as the other system at 0.56 V was controlled by adsorption process. We have determined the limit of detection (LOD) and limit of quantification (LOQ) values as 3.248×10^{-8} M and 10.22×10^{-8} M respectively. By using electrochemical impedance spectroscopic (EIS) study we have observed the surface nature of the different electrodes.

Keywords- Acid Blue 25, Cyclic voltammetry, Differential pulse voltammetry, Electrochemical impedance spectroscopy, Carbon paste electrode

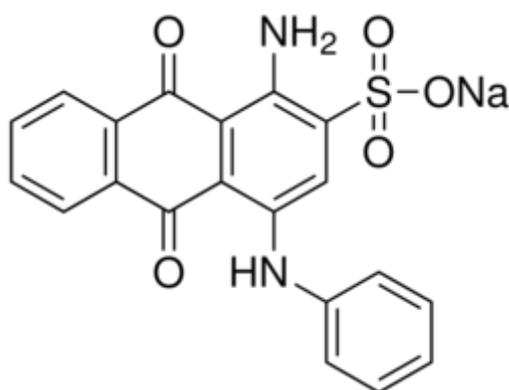
1. INTRODUCTION

Dyes are colored compounds, which were used to give away color to various substrates, including leather, paper, hair, drugs, cosmetics, waxes, greases, plastics and textile materials [1,2]. The oldest known dye is Indigo and it was used to mummy clothes by the ancient Egyptians [3]. In general the dyes are chemically bonded to the substance and become a part of the material on which it was applied. The structures which was necessary for color were called as chromophors, the color change was due to π - π^* and n - π^* transitions in the unsaturated double bonds, if the color intensity of the molecule enhances by the presence of other groups, then these groups are called as auxochromes [4].

In our daily life the usage of dyes was increased more rapidly because of its wide range of applications. The dyes are toxic in nature, and water gets contaminated with effluents eluted from the industries [5,6]. The water contamination with dyes causes severe health diseases [7]; hence selective determination, separation and quantification of dyes are of importance [8]. AB 25 (1-amino-9,10-dihydro-9,10-dioxo-4-(phenylamino)-2-anthracenesulfonic acid, monosodium salt) (SCHEME-I) [9,10] comes under the anthraquinone dyes, and it is an acidic dye. AB 25 is widely used in textile dyeing [11,12].

CV was the technique which was widely used in many fields of chemistry. This technique is based on current response against applied potential. By using this technique we can predict the redox mechanism of analyte. DPV is a sensitive technique in comparison with CV, because it minimizes the migration current. Carbon paste electrodes (CPE) has been used by many number of electrochemists, in our present study, we have used CPE as a working electrode due to its low cost and ease of preparation.

Several methods have been employed for the quantitative determination of dyes, such as voltammetric [13-25], chromatographic [26-28], capillary electrophoresis [29-31], spectrophotometry [32] and raman spectroscopy [33] methods. Among the all, electroanalytical techniques such as CV and DPV were widely used for the quantification of the analyte.



Scheme 1. Molecular structure of Acid blue 25

In our present work, we have studied the redox behavior of AB 25 and proposed a redox mechanism (SCHEME-II). We have studied the redox nature of AB 25 in different pH values, scan rate and concentration. Electrochemical impedance spectroscopy was employed for the determination of surface nature of the working electrode.

2. EXPERIMENTAL

2.1. Apparatus

CHI-660D (CH-Instruments) electrochemical work station was used for CV, DPV and EIS experiments. The experiments were done with a conventional three electrode electrochemical cell. In the three electrode system carbon paste electrode (CPE) was used as a working electrode, Pt - wire and Saturated Calomel Electrode (SCE) were used as counter and reference electrode respectively. A model LI 120 (ELICO) pH meter was used for the preparation of various pH buffer solutions.

2.2. Chemicals

AB 25 was obtained from Sigma Aldrich and dissolved in water to prepare 0.1 mM L⁻¹ standard stock solution. 0.1 M phosphate buffer solution was prepared from NaH₂PO₄·2H₂O and Na₂HPO₄. Fine graphite powder was received from Loba Chemie Pvt. Ltd, Mumbai (India) and Silicon oil was obtained from Scientific India Pvt. Ltd, Mumbai. All other chemicals used were of analytical grade quality.

2.3. Preparation of carbon paste electrode

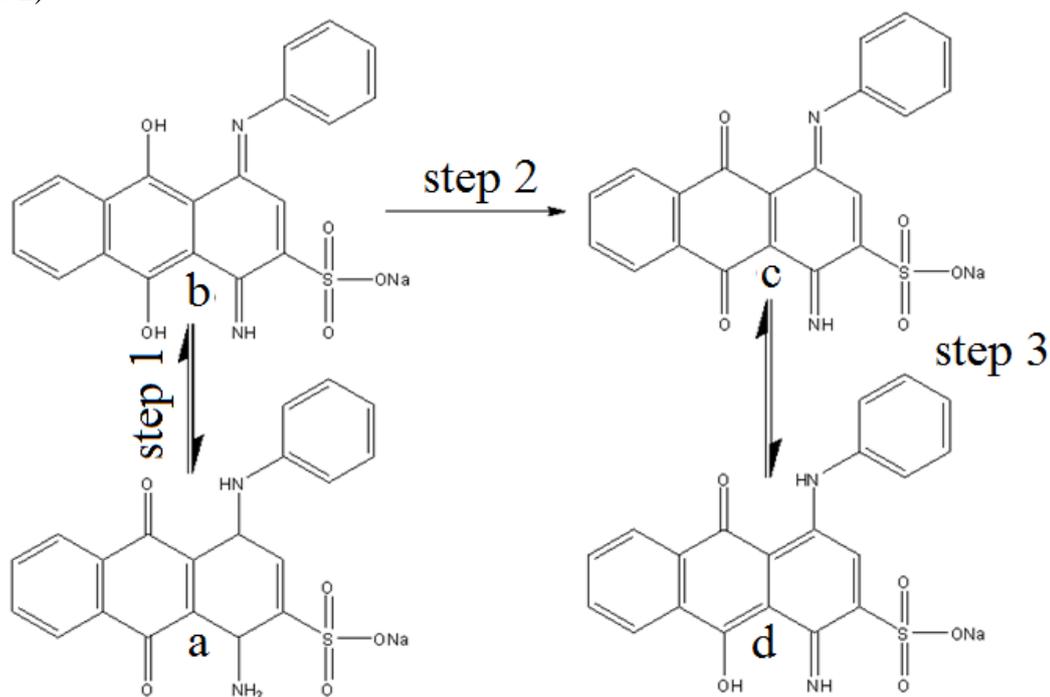
The CPE was made by hand mixing of 85% graphite powder and 15% of silicon oil using agate mortar for 45 minutes in order to form homogeneous paste. This carbon paste was introduced into 2 mm diameter of Teflon tube and electrical contact was made through a copper wire through the tube. The prepared electrode was smoothed on a piece of soft filter paper before making measurements.

3. RESULTS AND DISCUSSION

3.1. Electrochemistry of Acid Blue 25

The electrochemistry of AB 25 at CPE in pH-7.0 of PBS solution was studied by employing CV and DPV techniques. The surface nature of the working electrode was observed by EIS studies. The impedance results showed that the CPE was the suitable working electrode than the glassy carbon electrode (GCE) and Pt electrodes. The CV results

of 1×10^{-4} M solution of AB 25 showed two reversible systems at potentials 0.2 V and 0.56 V respectively. Fig. 1A and 1B shows the CV and DPV of 1×10^{-4} M solution of AB 25 at CPE working electrode. The redox behavior of AB 25 was dependent on the pH of the supporting electrolyte and also dependent on the scan rate. It was observed that one of the reversible systems of AB 25 was controlled by diffusion and other was controlled by adsorption. Based on the results obtained, we have proposed an electrochemical redox mechanism for AB 25 (Scheme 2).



Scheme 2. Proposed electrochemical redox mechanism for AB 25 at carbon paste electrode

The proposed electrochemical redox mechanism of AB 25 proceeds as follows: AB 25 (a) was first reversibly reduced to form compound (b), further it was oxidized irreversibly to form a corresponding compound (c). The product (c) formed in the second step was reversibly reduced to form the compound (d).

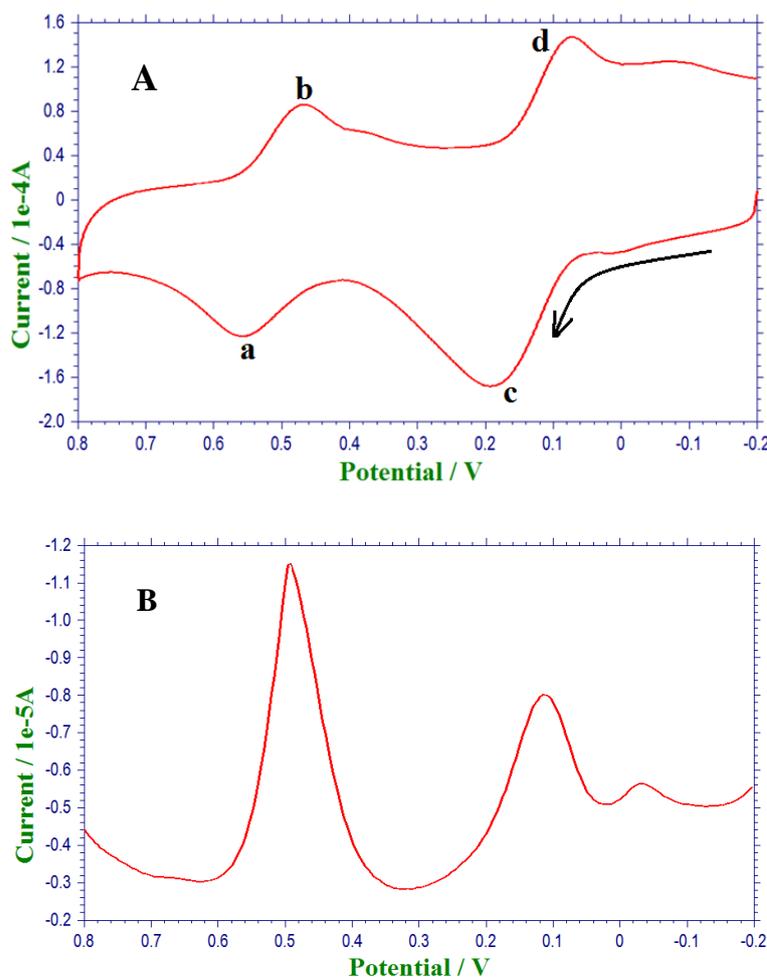


Fig. 1. (A) The Cyclic voltammogram of 1×10^{-4} M AB 25 in phosphate buffer solution of pH-7.0 with a scan rate of 100 mVs^{-1} at carbon paste electrode (working electrode) versus saturated calomel electrode (reference electrode) (B) The Differential pulse voltammogram of 1×10^{-4} M AB 25 in phosphate buffer solution of pH-7.0 at carbon paste electrode (working electrode) versus saturated calomel electrode (reference electrode)

3.2. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) was an important technique for the determination of surface nature of the working electrode. In this experiment we have observed different types of working electrode surfaces towards the determination of AB 25, the nature of CPE working electrode, glassy carbon electrode, Pt electrode was tested between the frequency ranges from 1 Hz to 1,00,000 MHz's. From Fig. 2A, it shows that the nyquist plot of three different electrodes, from figure CPE working electrode (red starred symbols) shows better electron transfer rate than the other GCE (blue square boxes) and Pt (grey diamond boxes) working electrodes. Fig. 2B was the bode plot of three different

electrodes in which black square's represents CPE working electrode, red circles represents GCE working electrode and blue stars represents Pt working electrode [34,35].

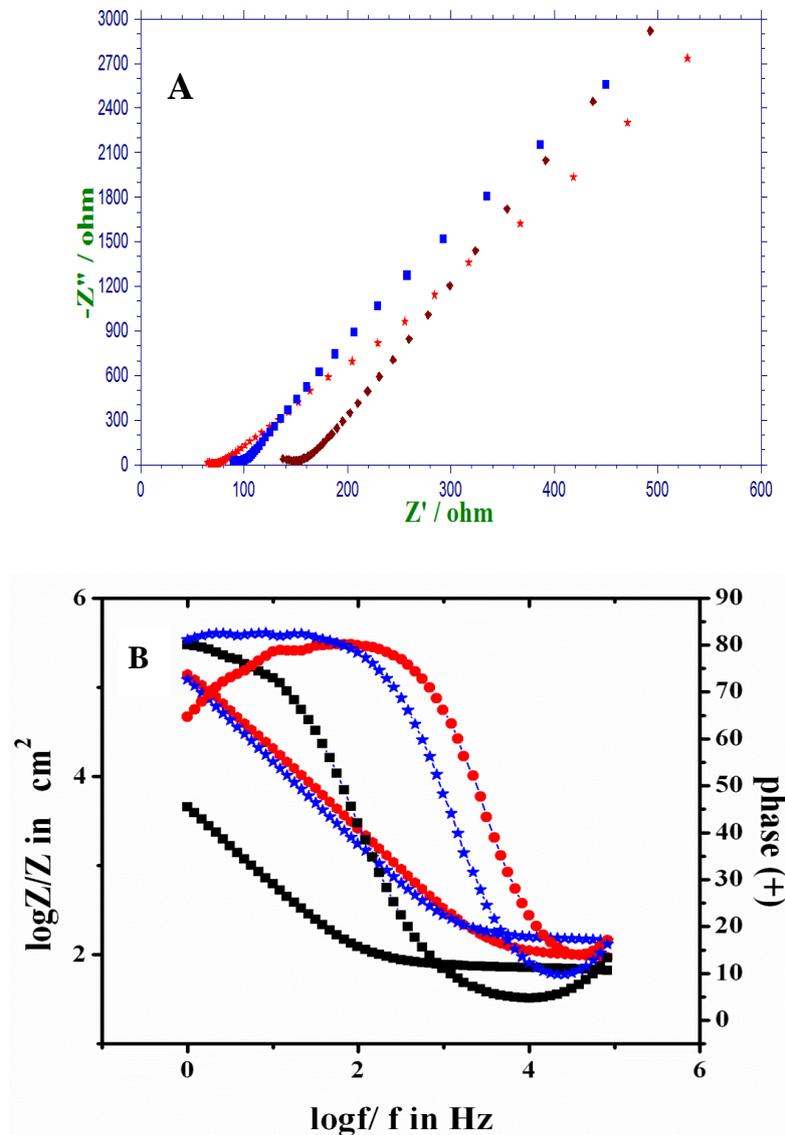


Fig. 2. (A) The nyquist plot of EIS representing three different electrodes, red colored (CPE), blue colored (GCE) and grey colored (Pt electrode) (B) The bode plot of three different electrodes, black square's represents CPE, red circles represents GCE and blue stars represents Pt electrode

3.3. Effect of pH

We have studied the effect of pH on the redox behavior of 1×10^{-4} M solution of AB 25 at CPE. In this study we have used phosphate buffer solution between the pH ranges from pH-5.0 to pH-8.0. At pH-5.0 it was observed that there were two redox systems at potentials 0.2 V and 0.56 V. Further as the pH of the solution was increased the peak potentials of the system was shifted towards the less positive potentials, from this we have concluded that the

redox reaction of AB 25 was dependent on the pH of the supporting electrolyte. As the pH of the supporting electrolyte was increased the peak currents of first system (i.e. at 0.2 V) decreased and after pH-7.0 (i.e. at basic medium) no peak was observed. For the second system (i.e. at ~0.56 V) the peak currents first increased and after pH-7.0 it was decreased. Therefore we have observed the maximum peak currents at pH-7.0 and we have used pH-7.0 as an optimum pH for further studies. Fig. 3 was the CV's of AB 25 at different pH values [36].

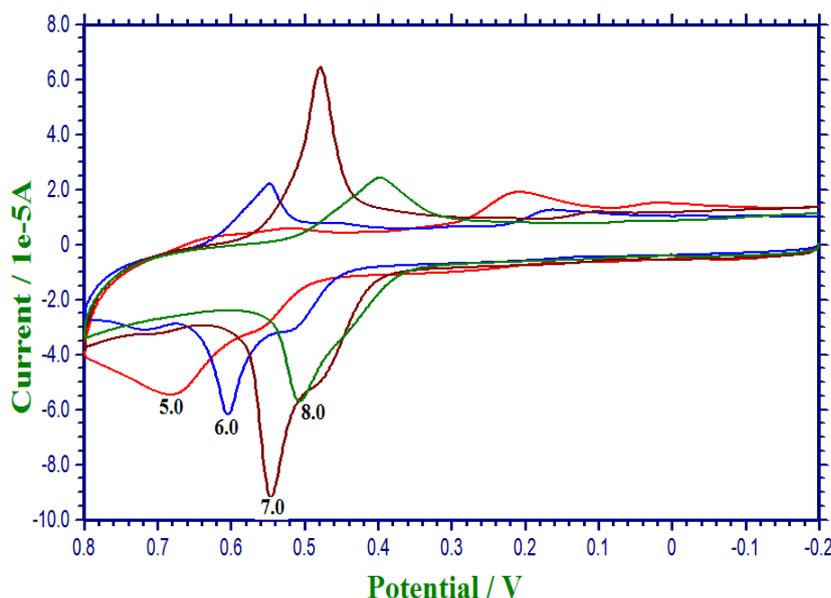


Fig. 3. The Cyclic voltammograms of 1×10^{-4} M AB 25 in phosphate buffer solutions of pH-5.0, pH-6.0, pH-7.0, pH-8.0 with a scan rate of 100 mVs^{-1} at carbon paste electrode (working electrode) versus saturated calomel electrode (reference electrode)

3.4. Effect of Accumulation time

We have studied the effect of accumulation time on the peak currents of 1×10^{-4} M solution of AB 25 in the PBS of pH-7.0 at CPE. We have observed an interesting result, the time of accumulation was influenced greatly on the peak currents of one system (0.2 V) and other system was less affected. As the time of accumulation was increased the peak currents of first system (0.2 V) was gradually increased, whereas the peak currents of the other system (0.56 V) was slightly decreased. The proposed electrochemical redox mechanism (scheme 2) suggests that compound (c) was formed from compound (b) and increase in the concentration of compound (b) occurs continuously with accumulation time and this was due to the irreversible step (2). Hence the step (2) was responsible for the linear increase of current with accumulation time of first the redox system (0.2 V). Whereas the peak currents of second redox system decreases and it was due to the decrease in the concentration of

compound (b). Fig. 4 was the plot drawn between the peak currents on y-axis and accumulation time on x-axis, from Fig. 4 black square boxes are peak currents corresponds to first redox system and red circles are for the peak currents of second redox system.

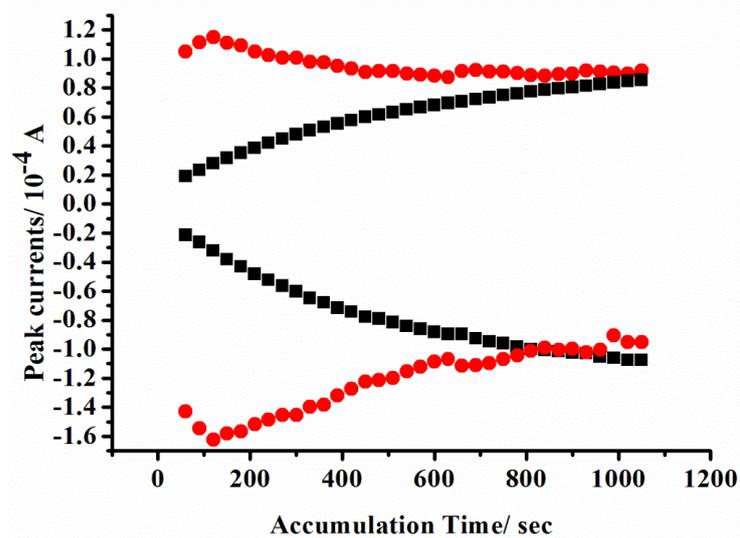


Fig. 4. A plot drawn between accumulation time (in sec) and their respective peak currents black square boxes represents first redox system and red circles represents second redox system

3.5. Effect of scan rate

The effect of different scan rates on the peak currents of 1×10^{-4} M solution of AB 25 in PBS of pH-7.0 was studied by varying the scan rates from 10 mV s^{-1} to 150 mV s^{-1} with an initial pre concentration time of 20 minutes. A typical observation was found for the AB 25, the first redox system (at 0.2 V) was linearly increased with square root of scan rate, suggesting diffusion controlled process. The linear regression equations and correlation coefficients were found to be as $(I_{p_{a1}} \text{ in } 10^{-5} \text{ A}) = 1.61v^{1/2} - 4.045$ and $(I_{p_{c2}} \text{ in } 10^{-5} \text{ A}) = 1.278v^{1/2} - 2.74$, $r^2 = 0.997$ and 0.9985 respectively. Whereas the other redox system (at 0.56 V) was linearly increased with the scan rate suggesting the adsorption controlled process, the linear regression equations and correlation coefficient values was found to be as $(I_{p_{a2}} \text{ in } 10^{-5} \text{ A}) = 0.0379v + 1.212$ and $(I_{p_{c1}} \text{ in } 10^{-5} \text{ A}) = 0.0595v + 0.231$ and $r^2 = 0.9988$ and 0.9997 respectively. Fig. 5A was the cyclic voltammograms of 1×10^{-4} M solution of AB25 for different scan rates and Fig. 5B was the plot drawn between peak currents of first redox system on y-axis and square root of scan rate on x-axis, Fig. 5C was the plot of second redox system on y-axis and their scan rates on x-axis [37].

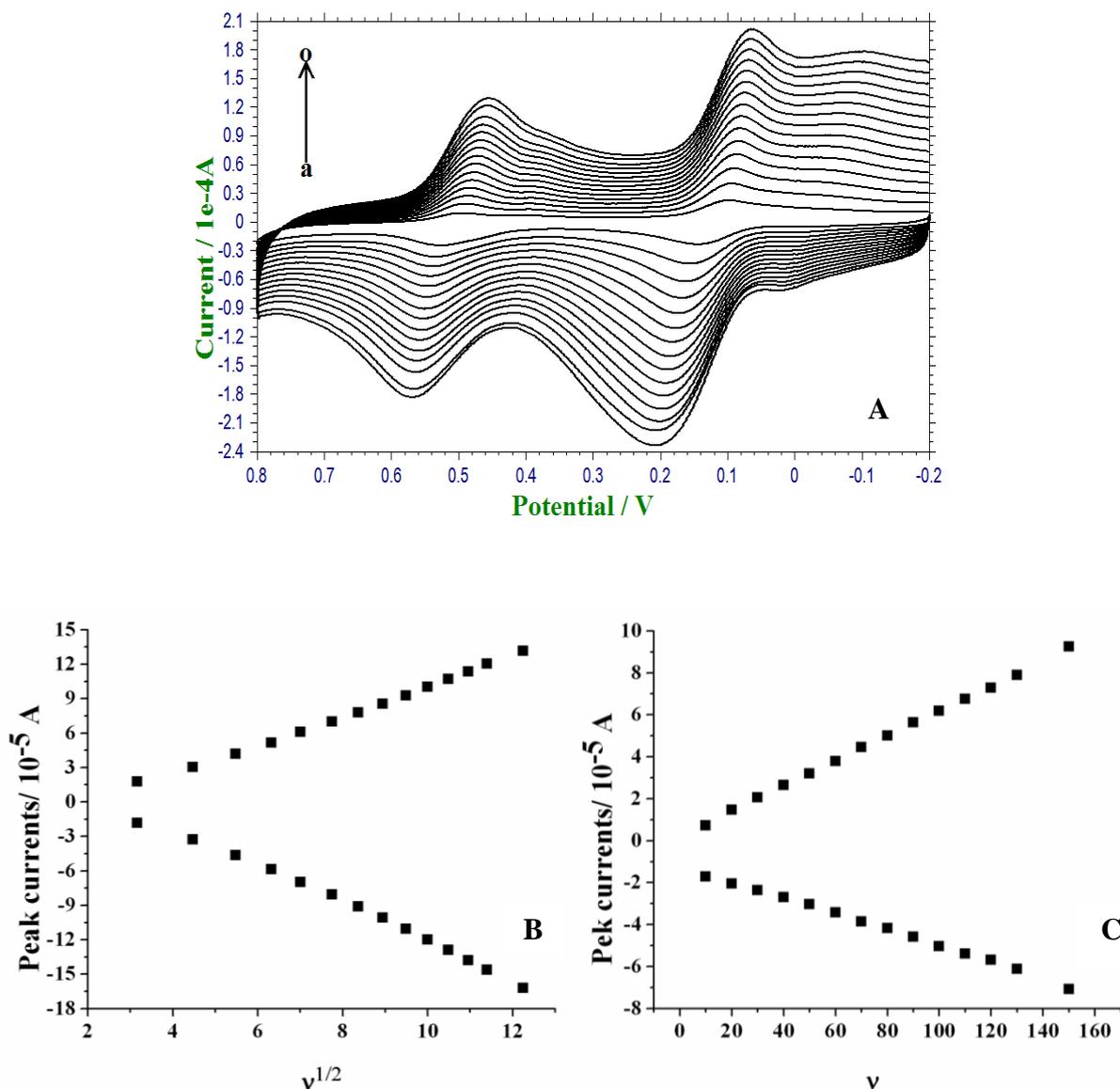


Fig. 5. (A) The Cyclic voltammograms of 1×10^{-4} M AB 25 in phosphate buffer solution of pH-7.0 with scan rates (a): 10 mVs^{-1} , (b): 20 mVs^{-1} , (c): 30 mVs^{-1} , (d): 40 mVs^{-1} , (e): 50 mVs^{-1} , (f): 60 mVs^{-1} , (g): 70 mVs^{-1} , (h): 80 mVs^{-1} , (i): 90 mVs^{-1} , (j): 100 mVs^{-1} , (k): 110 mVs^{-1} , (l): 120 mVs^{-1} , (m): 130 mVs^{-1} , (n): 140 mVs^{-1} and (o): 150 mVs^{-1} at carbon paste electrode versus saturated calomel electrode with an initial pre concentration time of 20 minutes (B) A plot between square root of scan rate and peak currents of first redox system at 0.2 V (C) The plot between scan rate and their peak currents of second redox system at 0.56 V

3.6. Effect of concentration

The effect of AB 25 concentration on peak currents in PBS solution of pH-7.0 at CPE was studied by using CV and DPV techniques. DPV has shown more accurate results than that of CV technique. Fig. 6A shows the differential pulse voltammograms of different concentrations of AB 25 and Fig. 6B shows the plot drawn between the concentration of AB

25 on x-axis and their peak currents on the y-axis. From the Fig. 6B the peak currents were gradually increased with increase in the concentration of AB 25. The effect of concentration has shown two linearity's with correlation coefficient values of 0.996 and 0.990. The linear regression equations were found to be as $(I_{pa2} \text{ in } 10^{-5} \text{ A}) = 0.0591(\text{concentration of AB 25}) + 0.196$ and $(I_{pa2} \text{ in } 10^{-5} \text{ A}) = 0.0344(\text{concentration of AB 25}) + 1.16$ respectively. The change in the linearity's occurred may be due to the saturation of electrode with AB 25 [38]. Based on following equations we have found the limit of detection (LOD) and limit of quantification (LOQ) as $3.248 \times 10^{-8} \text{ M}$ and $10.22 \times 10^{-8} \text{ M}$ respectively. Where S_b was the standard deviation and 'm' was the slope of calibration curve [39,40].

$$\text{LOD} = 3S_b/m \quad (1)$$

$$\text{LOQ} = 10 S_b/m \quad (2)$$

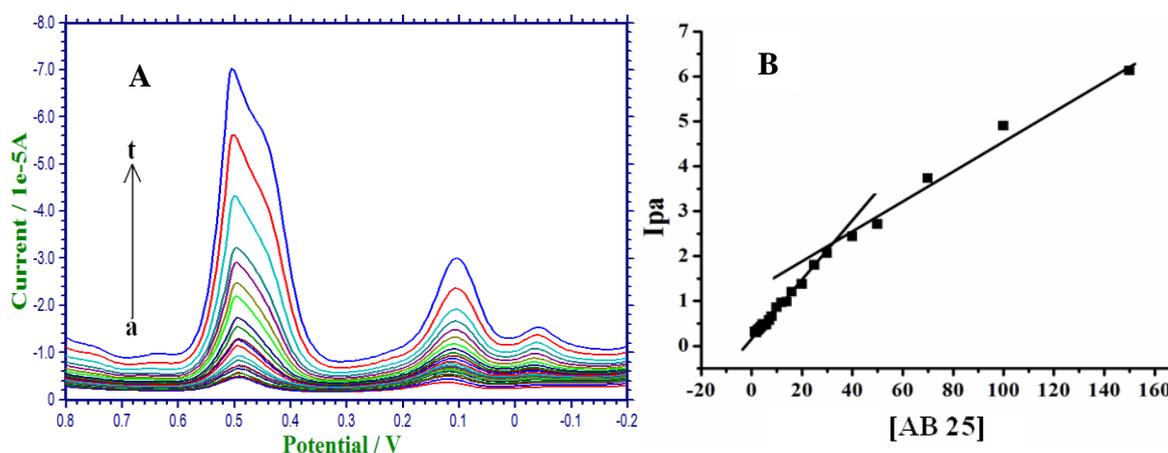


Fig. 6. (A) The Differential pulse voltammograms of AB 25 with different concentrations of (a): $1.6 \times 10^{-8} \text{ M}$, (b): $2.5 \times 10^{-8} \text{ M}$, (c): $4 \times 10^{-8} \text{ M}$, (d): $4.5 \times 10^{-8} \text{ M}$, (e): $5 \times 10^{-8} \text{ M}$, (f): $6 \times 10^{-8} \text{ M}$, (g): $7 \times 10^{-8} \text{ M}$, (h): $8 \times 10^{-8} \text{ M}$, (i): $10 \times 10^{-8} \text{ M}$, (j): $12 \times 10^{-8} \text{ M}$, (k): $14 \times 10^{-8} \text{ M}$, (l): $16 \times 10^{-8} \text{ M}$, (m): $20 \times 10^{-8} \text{ M}$, (n): $25 \times 10^{-8} \text{ M}$, (o): $30 \times 10^{-8} \text{ M}$, (p): $40 \times 10^{-8} \text{ M}$, (q): $50 \times 10^{-8} \text{ M}$, (r): $70 \times 10^{-8} \text{ M}$, (s): $100 \times 10^{-8} \text{ M}$ and (t): $150 \times 10^{-8} \text{ M}$ at a carbon paste electrode versus saturated calomel electrode (B) A plot between the anodic peak currents against different concentrations of AB 25

4. CONCLUSION

In our present work, we have explained the electrochemical determination of AB 25 at CPE. It was found that the redox mechanism was dependent on the pH of the solution. Based on the effect of scan rate studies an interesting result was observed, the first redox system was controlled by diffusion process and the second redox system was controlled by

adsorption process. Based on the results obtained from pH effect, scan rate effect and accumulation time, we have proposed an electrochemical mechanism for redox reaction of AB 25 and the LOD and LOQ values were evaluated. By employing EIS spectroscopy, we have found that CPE was the suitable electrode for the determination of AB 25.

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REFERENCES

- [1] Y. Yang, D. Jin, G. Wang, D. Liu, X. Jia, and Y. Zhao, *Colloids. Surf. B* 88 (2011) 521.
- [2] Y. Yang, D. Jin, G. Wang, S. Wang, X. Jia, and Y. Zhao, *Bioresour. Technol.* 102 (2011) 7429.
- [3] A. Vuorema, P. John, M. Keskitalo, and F. Marken, *J. Appl. Electrochem.* 38 (2008) 1683.
- [4] L. Xu, C. Liu, Z. Qin, R. Jiang, and Y. Li, *Eur. J. Org. Chem.* 2013 (2013) 300.
- [5] A. Radi, M. R. Mostafa, T. A. Hegazy, and R. M. Elshafey, *J. Anal. Chem.* 67 (2012) 890.
- [6] A. Kuleyin, and F. Aydin, *Environ. Prog. Sustain. Energy.* 30 (2011) 141.
- [7] A. N. Chowdhury, S. R. Jesmeen, and M. M. Hossain, *Polym. Adv. Technol.* 15 (2004) 633.
- [8] F. Renault, N. M. Crini, F. Gimbert, P. M. Badot, and G. Crini, *Bioresour. Technol.* 99 (2008) 7573.
- [9] P. Tang, Y. Feng, and D. Li, *J. Phys. Chem. Solid.* 73 (2012) 1505.
- [10] I. Bouzaida, C. Ferronato, J. M. Chovelon, M. E. Rammah, and J. M. Herrmann, *J. Photochem. Photobiol. A.* 168 (2004) 23.
- [11] M. Kousha, E. Daneshvar, A. R. Esmaeli, M. Jokar, A. R. Khataee, *Int. Biodeterior. Biodegrad.* 69 (2012) 97.
- [12] H. Ghodbane, and O. Hamdaoui, *Ultrason. Sonochem.* 16 (2009) 455.
- [13] D. Mahanta, N. Munichandraiah, S. Radhakrishnan, G. Madras, and S. Patil, *Synth. Met.* 161 (2011) 659.
- [14] C. C. I. Guaratini, A. G. Fogg, and M. V. B. Zanoni, *Electroanalysis.* 13 (2001) 1535.
- [15] P. J. Almeida, J. A. Rodrigues, A. A. Barros, and A. G. Fogg, *Anal. Chim. Acta.* 385 (1999) 287.
- [16] A. R. H. M. Yusoff, A. G. Fogg, and R. Ahmad, *Talanta* 47 (1998) 797.
- [17] A. G. Fogg, A. Rahim, H. M. Yusoff, and R. Ahmad, *Talanta* 44 (1997) 125.
- [18] M. Valnice, B. Zanoni, and A. G. Fogg, *Anal. Proc.* 31 (1994) 217.

- [19] M. V. B. Zanoni, A.G. Fogg, J. Barek, and J. Zima, *Anal. Chim. Acta* 315 (1995) 41.
- [20] M. V. B Zanoni, A. G. Fogg, and C. C. I. Guaratini, *Dyes Pigments*. 50 (2001) 211
- [21] M.V.B. Zanoni, A.G. Fogg, J. Barek, J. Zima, *Anal. Chim. Acta* 349 (1997) 101.
- [22] A. E. Radi, M. Mostafa, T. Hegazy, and R. Elshafey, *Port. Electrochim. Acta* 28 (2010) 417.
- [23] H. Yin, Y. Zhou, X. Meng, T. Tang, S. Ai, and L. Zhu, *Food Chem.* 127 (2011) 1348.
- [24] A. G. Fogg, and M. V. B. Zanoni, *Anal. Proc.* 31 (1994) 173.
- [25] M. E. Osugi, P. A. Carneiro, and M. V. B. Zanoni, *J. Braz. Chem. Soc.* 14 (2003) 660-665.
- [26] M. A. Mottaleb, and D. Littlejohn, *Anal. Sci.* 17 (2001) 429.
- [27] J. C. Jones, D. Littlejohn, and P. R. Griffiths, *Appl. Spectrosc.* 53 (1999) 792.
- [28] A. Hansa, V. L. Pillay, and C. A. Buckley, *Water Sci. Technol.* 39 (1999) 169.
- [29] A. I. Revilla, H. C. Keull, and J. Havel, *J. Capillary. Electrophor.* 7 (2002) 67.
- [30] T. Poiger, S. D. Richardson, and G. L. Baughman, *J. Chromatogr. A* 886 (2000) 271.
- [31] K. N. Tapley, *J. Chromatogr. A.* 706 (1995) 555.
- [32] E. Halamek, and Z. Koblíha, *Collect. Czech. Chem. Commun.* 57 (1992) 1221.
- [33] S. Kokot, Nguyen Anh, and L. Tuan, *Rintoul. Appl. Spectrosc.* 51 (1997) 387.
- [34] K. Reddaiah, T. M. Reddy, P. Raghu, and P. Gopal, *Anal. Bioanal. Electrochem.* 4 (2012) 372.
- [35] K. Reddaiah, T. M. Redday, and P. Raghu, *J. Electroanal. Chem.* 682 (2012) 164.
- [36] P. Raghu, B. E. K. Swamy, T. M. Reddy, B. N. Chandrashekar, and K. Reddaiah, *Bioelectrochemistry* 83 (2012) 19.
- [37] K. Reddaiah, T. M. Reddy, P. Raghu, and B. E. Kumaraswamy, *Anal. Bioanal. Electrochem.* 4 (2012) 122.
- [38] P. Gopal, T. M. Reddy, K. Reddaiah, P. Raghu, and P. V. Narayana, *J. Mol. Liq.* 178 (2013) 168.
- [39] P. Raghu, T. M. Reddy, B. E. K. Swamy, B. N. Chandrashekar, and K. Reddaiah, *J. Electroanal. Chem.* 665 (2012) 76.
- [40] T. M. Reddy, M. Sreedhar, and S. J. Reddy, *J. Pharm. Biomed. Anal.* 31 (2003) 811.