Cyclic Voltammetric Study of Reactive Black 5 Dye at a Mercury Electrode

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ABSTRACT: A cyclic voltammetry (CV) study of Reactive Black 5 Dye (RB5) in Britton-Robinson buffer (BRB) using a hanging mercury drop electrode (HMDE) is described. CV was carried out by anodic and cathodic potential scan through within the range of + 200 to - 950 mV with no accumulation time. The effect of the different scan rates and pH of BRB on the peak height and peak potential of the analyte were also studied. The results show that in pH 2 to 5, reduction process on the hanging mercury electrode gave three cathodic peaks at + 75 to -151 mV for the first peak, - 98 to - 330 mV for the second peak and – 395 to -630 mV for the third peak. Only single reduction peak was obtained at -460 to -675 mV in pH 6 to 8 and two reduction peaks were obtained at - 530 to -640 mV for the first peak and -730 to -840 mV for the second peak in pH 9 to 12. All potentials were referred against Ag/AgCl as the reference electrode. The BRB pH 4.0 was noted as the best condition for the detection of RB5 in acidic medium and pH 9.0 in basic medium since both media gave maximum peak current. Effect of the scan rate and pH of BRB on both responses have proved that the reduction of RB5 is an irreversible reaction, pH dependent and the limiting current is adsorption controlled. Future work will cover study of cathodic stripping voltammetry of RB5 at the same type of electrode.

Keywords : Cyclic voltammetry, Britton-Robinson buffer, hanging mercury dropping electrode (HMDE) and Reactive Black 5 (RB5)

Introduction

In the recent years, growing concern and awareness about issues on environment have brought together both analytical and material science researchers to investigate appropriate process or method in removing and monitoring various pollutants worldwide.

Dyes become one of these pollutants as about 9% of the 45 × 10^4 tonne of dyestuffs produced where their presence in waste aqueous effluents can contribute serious environmental and human health damage (Tonlé *et al.,* 2007). Dyes are generally be defined as coloured substances which have the affinity to the applied substrates. According to PeláezCid *et al.* (2008) dyes are compounds produced worldwide annually in large amount which are more than 7 × 10^8 kilograms and used in nutritional, cosmetics, paper, pharmaceutical, printing inks, textile and tannery which is textile industry consumes half of the overall dye production.

[2, 7-naphthalenedisulfonic acid, 4-amino -5-hydroxy-3,6-bis((4((2(sulfooxy) ethyl) sulfonyl) phenyl) azo)-tetrasodium salt] or Reactive Balck 5 (RB5) dye in **FIGURE 1,** is categorized in vinyl sulphonate azodye due to the presence of

–N=N- bonds combined with vinylsuiplhone as the reactive group (Tunc *et al.,* 2009). Textile, printing, and pharmaceutical industry are major users of RB5 (Karipcin *et al.,* 2009).

Concentrations of RB5 in range 10-100 mg/L is toxic to fish, the concentration of RB5 above 1000 mg/L leads to inhibition of wastewater bacteria activity and it release approximately 0.3% nitrogen which can contribute to eutrophication.

This paper describes the cyclic voltammetric (CV) study of RB5 dye using hanging mercury dropping electrode (HMDE) as the working electrode. CV becomes the most widely used technique to acquire qualitative information on electrochemical reactions because of its ability in providing considerable information about the kinetic of the system, number of electron transferred, reversibility of the system as well as adsorption and diffusion characteristic (Hadzri *et al.,* 2010).

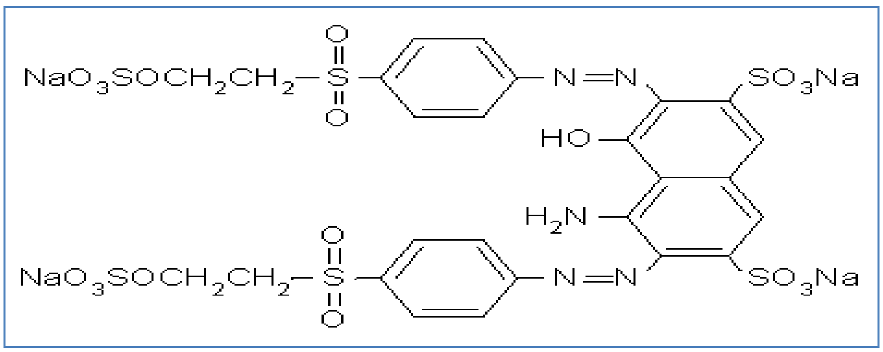

FIGURE 1: Chemical structure of RB5 dye

Materials and methods

Reagents

All solutions were prepared using double distilled water and analytical grade reagents. 0.10 g of RB5 dye was dissolved in 50.0 mL double distilled water to produce 2000 ppm RB5 dye stock solution. A stock of Britton-Robinson-Buffer (BRB) solution (0.04 M) as supporting electrolyte prepared as follows; 2.47 g boric acid (Fluka), 2.30 mL acetic acid (Merck) and 2.70 mL orthophosporic acid (Ashland Chemical) were diluted to 1 L with double distilled water. 1 M sodium hydroxide or 1 M hydrochloride acid was used to adjust the pH of the BRB solution to the desired value. High purity mercury, (99.999%) was used for hanging mercury dropping electrode (HMDE).

Measurement methods

Cyclic voltammetry (CV) was performed using an electrochemical workstation. All voltammogrammes were recorded with a Voltammetry Analyser (VA 757) combined with VA stand equipped with three electrode system consisting of a HMDE as the working electrode, an Ag/AgCl as the reference electrode and platinum wire counter electrode. In all voltammetric analysis, 10 mL supporting electrolyte solution was deaerated by a stream of nitrogen for at least 20 mins. The RB5 dye solution was purged by gas for 5 mins and allowed to stand for 3 s in order to obtain cyclic voltammogrammes. Other parameters used are medium drop size, stirrer speed (2000rpm), initial potential, E_i (200 mV), end potential, E_f (800 mV) for acidic medium;and (950 mV) for basic medium. The concentration of RB5 dye in cell is 200 ppm.

Results and Discussion

In BRB pH 2-5, reduction process of RB5 dye exhibited three well defined electroreduction peaks at +75 to -151 mV, -98 to -330 mV, -395 to -630 mV, respectively. Only single electroreduction peak was obtained at -460 to -670 mV in BRB of pH 6-8. Two electroreduction peaks were observed (-530 to -640 mV and -730 to -840 mV) in BRB pH 9-12. Cathodic cyclic voltammogrammes obtained at HMDE in 0.04 M BRB solution respectively at pH 4.0, 7.0 and 9.0 respectively with a scan rate of 25 mV/s were shown in **FIGURE 2a, 2b** and **2c.**

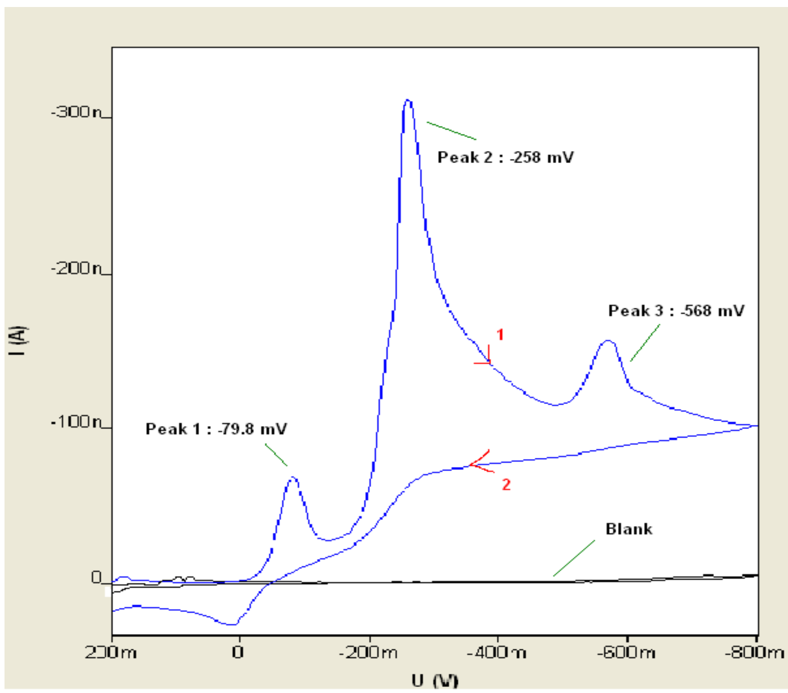

FIGURE 2a : Cathodic cyclic voltammogram of 200 ppm RB5 dye in 0.04 M BRB solutions pH 4

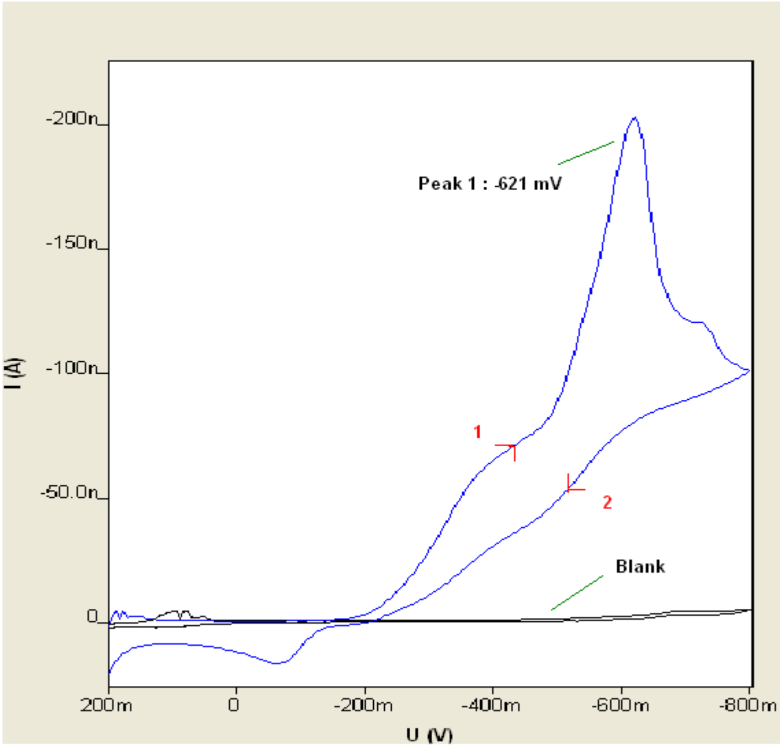

FIGURE 2b: Cathodic cyclic voltammogram of 200 ppm RB5 dye in 0.04 M BRB solutions pH 7

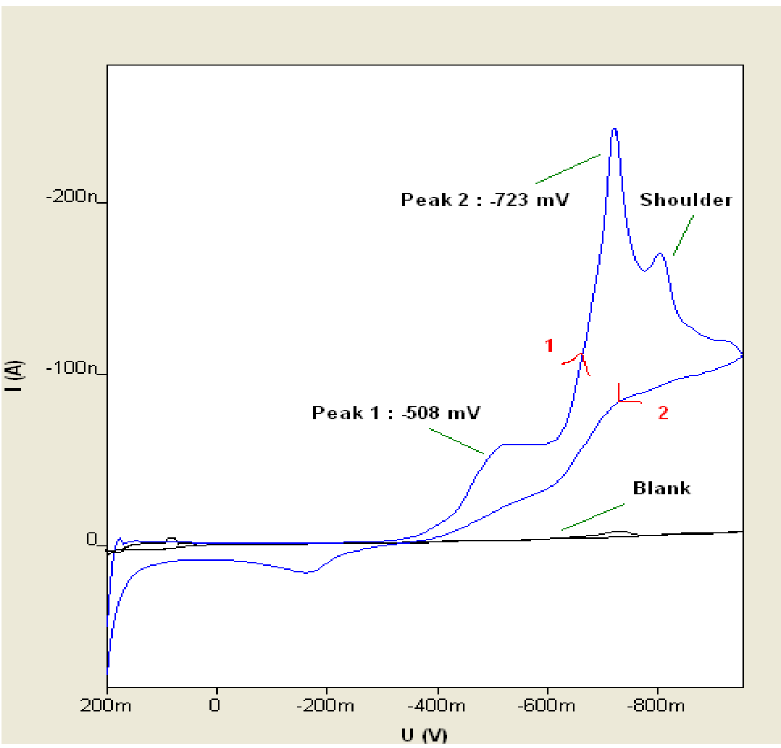

FIGURE 2c : Cathodic cyclic voltammogram of 200 ppm RB5 dye in 0.04 M BRB solutions pH 9

No peak was observed in anodic direction of the reverse scans in all pH of BRB solution suggesting that the irreversible nature of an electrode process (Gupta *et al*, 2010; Gupta *et al*, 2010; Jain *et al.,* 2007). A suggested mechanism for the irreversible reduction of RB5 dye at the mercury electrode surface is shown by Equation (1) below.

$$2e^{-} + 2H^{+} + (R–N{=}N–R1) \rightarrow (R–NH–NH–R1) \qquad (1)$$
$$2e^{-} + 2H^{+} + (R–NH–NH–R1) \rightarrow (R–NH_2) + (R1–NH_2) \qquad (2)$$

Equation 1: Suggested mechanism for the irreversible reduction of RB5 dye

A mechanism for azo reduction involves two stages as given in reaction (1) and (2) above (Karatas *et al*., 2009). An unstable colourless compound is the intermediate product of reaction (1) and the azo bond can reform upon oxidation and regain the colour. R and R1 are variously substituted phenyl and naphthol residues. Azo compounds which play part as terminal electron acceptors are utilized by carriers in the electron transport chain. Hence, they regenerate themselves, fortuitously reducing azo bond and finally breaking the RB5 dye chromophore.

Effects of pH

The influence of pH of BRB on the cyclic voltammetric behavior of RB5 dye has been studied in the pH range of 2-12 with a scan rate of 25mV/s. The results show that peak potential, (E_p) of RB5 dye shifts to a more negative potential with increasing pH (**FIGURE 3**) indicating that the reduction process is pH dependent. The reduction process involves the coupling of hydrogen ion, H^+ (Sarigul and Inam, 2009). In addition, the shifting of E_p is towards a more negative value with increasing H^+ in the electrode reduction process (Jain *et al.*, 2007; Zanoni *et al.,*1997).

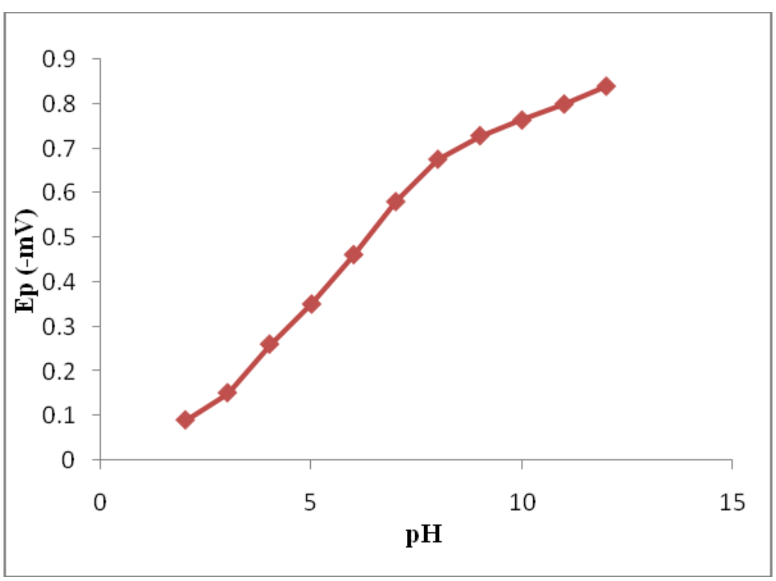

FIGURE 3: Effect of various pH of BRB on E_p of RB5 dye

In acidic medium, maximum peak current, I_p of 297 nA was observed at pH 4.0 (**FIGURE 4a**). In the basic medium, maximum I_p of 180 nA is obtained at pH 9.0 (**FIGURE 4b**). Therefore, pH 4.0 and 9.0 were used throughout this experiment.

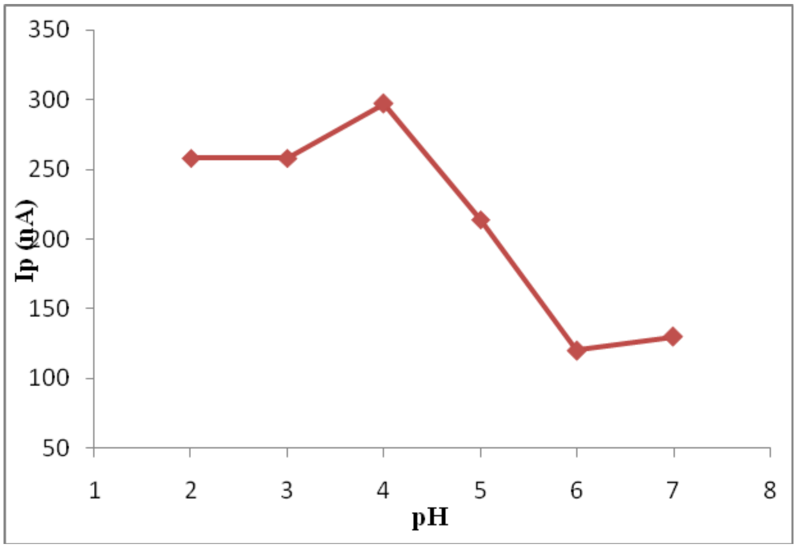

FIGURE 4a: Effects of pH 2-7 of BRB on I_p of RB5 dye

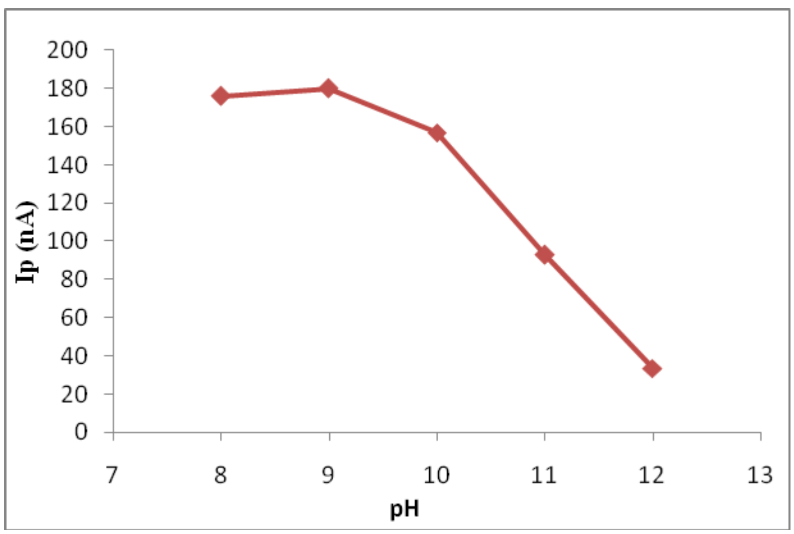

FIGURE 4b: Effects of pH 8-12 of BRB on I_p of RB5 dye.

Effects of scan rate

Effect of scan rate, (v) has been studied from v of 25 to 200 mV/s using fixed concentration of RB5 dye at 200 ppm. The v is found to affect on both I_p and E_p. When v, is increased the E_p shifted towards more negative direction and accompanied by an increase of I_p. Examination on the linear relationship between I_p versus v (**FIGURE 5**) indicates that RB5 dye was adsorbed on the electrode surface (Bard and Faulker,1980).

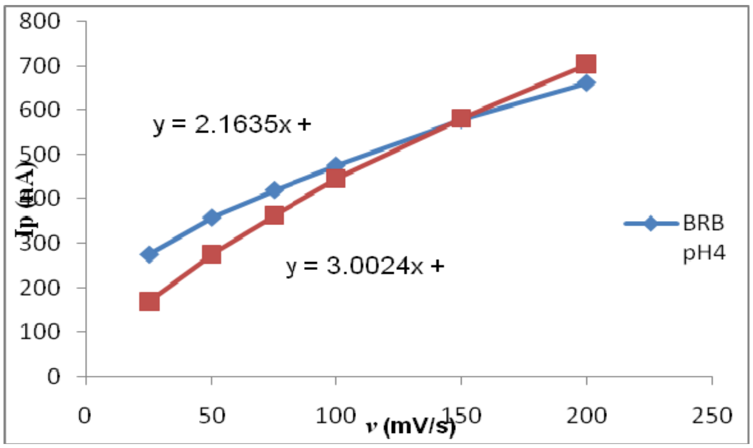

FIGURE 5 : Plot of I_p versus v for 200 ppm RB5 dye in BRB pH 4.0 and 9.0

The linear plot of log I_p versus log v as shown in **FIGURE 6** with a slope of 0.5088 (R^2 = 0.9998, n = 10) for BRB pH 4.0 and 0.6834 (R^2 = 0.9998, n = 10) for BRB pH 9.0. The slope of more than 0.5 indicates that the reduction process of RB5 dye in both media is mainly controlled by diffusion with slight adsorption contribution (Qiu and Yong, 2008; El-Sayed *et al.*,2010). It means that the mercury surface is rapidly and completely covered with the electroactive species (Badawy *et al.,* 2010).

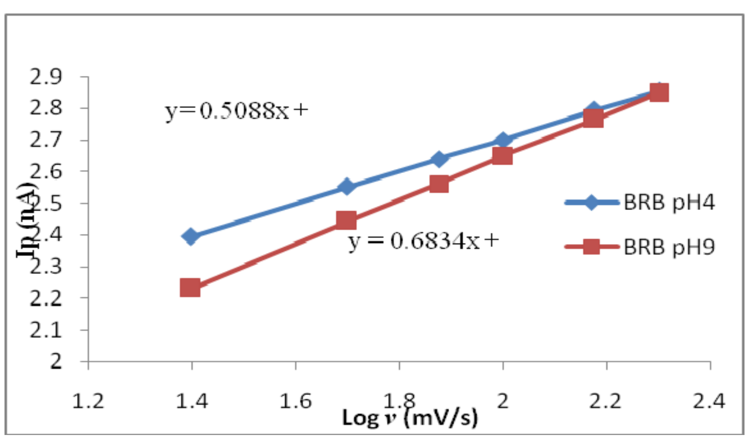

FIGURE 6 : Plot of log I_p versus log v for 200 ppm RB5 dye in BRB pH 4.0 and 9.0

The linear relationship was found between I_p and the square root of *v* (**FIGURE 7**), indicating that the reduction process is diffusion controlled (Masek *et al.*, 2011; Ambrosi *et al.*,2005).

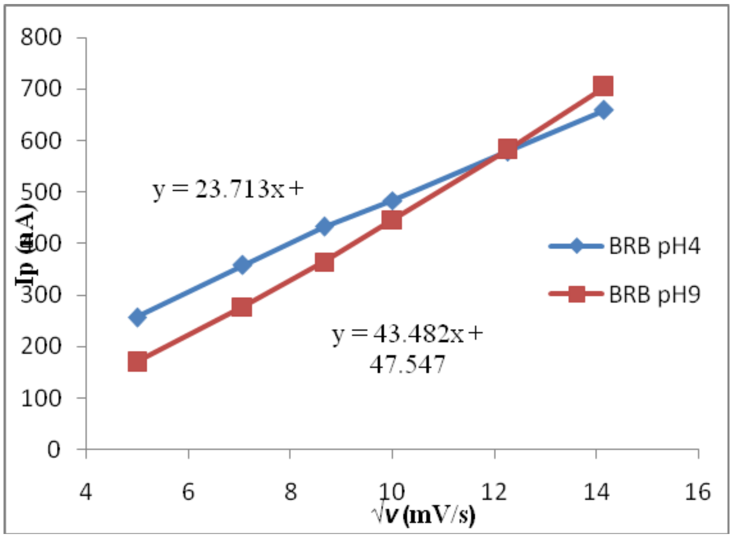

FIGURE 7 : Plot of log I_p versus square root *v* for 200 ppm RB5 dye in BRB pH 4.0 and 9.0

A linear plot of E_p versus log *v* as shown in **FIGURE 8a** and **FIGURE 8b** confirmed that in BRB pH 4.0 and 9.0, the reduction of RB5 dye on the electrode surface is totally irreversible. The confirmation of the irreversible nature of reduction process was also done by observing the shift of E_p to a more negative value with increasing of *v* value (Okumura and Stradiotto, 2007).

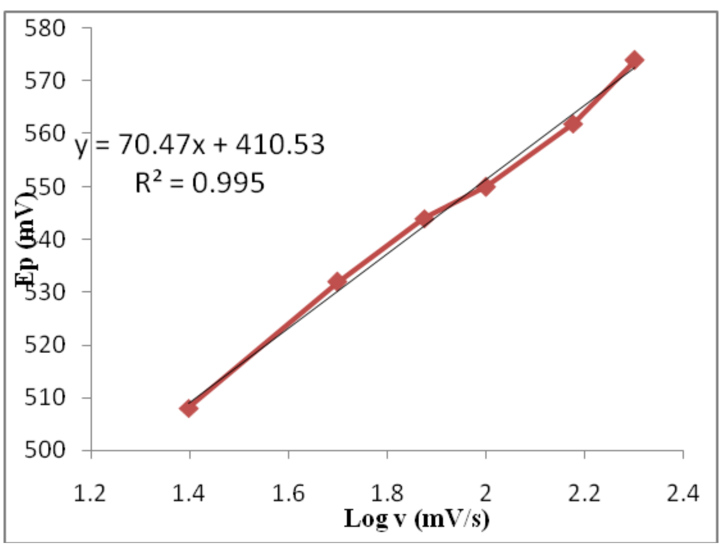

FIGURE 8a : Plot of E_p versus log *v* for 200 ppm RB5 dye in BRB pH 4.0

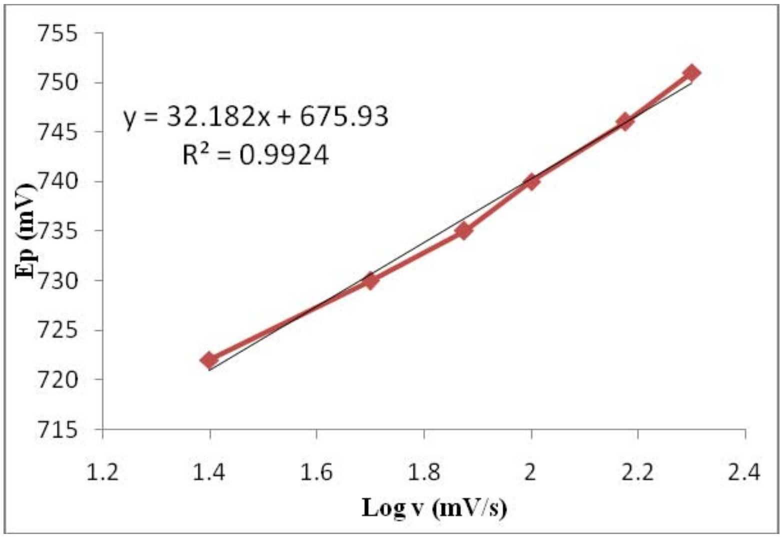

FIGURE 8b : Plot of E_p versus log *v* for 200 ppm RB5 dye in BRB pH 9.0

Conclusion

RB5 dye undergoes irreversible reduction at the mercury electrode and was found to be pH dependence. The limiting current is an adsorption controlled. The maximum reduction peaks of RB5 dye were observed in BRB of pH 4 and 9.

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