

## **Investigation of Electrochemical Behavior of Mordant Dye (C.I. 17135) at Glassy Carbon and Silver Electrodes**

**Necati Menek<sup>1\*</sup>, Serpil Zeyrekl<sup>1</sup> and Yeliz Karaman<sup>2</sup>**

*1- Ondokuz Mayıs University, Sciences and Arts Faculty, Department of Chemistry, 55139, Kurupelit-Samsun, Turkey*

*2- Sinop University, Sciences and Arts Faculty, Department of Chemistry, 57000, Sinop, Turkey*

### **ABSTRACT**

In this study, the electrochemical behaviour of Mordant dye (C.I. 17135) was investigated in Britton-Robinson (BR) buffer (pH 2.0-12.0) media by using different voltammetric techniques: square wave voltammetry (SWV), cyclic voltammetry (CV), differential pulse voltammetry (DPV) and direct current voltammetry (DCV). The electrochemical behavior of the dye has been investigated by using a glassy carbon electrode (GCE) and silver electrode (SE). The broad peak of the azo dye occurred at SW and DP voltammograms, is due to its adsorption on the glassy carbon and silver electrode surfaces. Two reduction peaks were observed at pH < 9.5, and one reduction peak was observed at pH > 9.5 for SWV and DPV techniques at a glassy carbon electrode. From the voltammetric data electrochemical reaction mechanism of the azo dye has been suggested at glassy carbon and silver electrodes.

*Keywords: Azo compound, Mordant dyes, Voltammetry, Reaction mechanism.*

Necati Menek\*: [nmenek@omu.edu.tr](mailto:nmenek@omu.edu.tr)

## Introduction

Azo dyes, which are characterized by the azo functional group (-N=N-), have widespread applications in lots of areas such as textile processing, paper, food, cosmetics, medicine, leather, plastics, varnish, automobiles. The azo dyes are called as monoazo, diazo, triazo, polyazo and azoic dyes, according to the number of azo groups, which is in the same molecule of the dye.

Mordant dyes compose the largest class of synthetic azo dyes, which are extensively employed for the coloration of textile fibers, such as wool, silk, polyester, cotton, and nylon (Yıldız and Boztepe 2002, Pervez et al., 2019). Mordant dyes which contain hydroxyl groups in the ortho position, have capacity to produce metal-dye complexes, by binding the dye molecule to the fibers (Abu-El-Wafa et al., 2005, Ali et al., 2019, Ding and Freeman 2017, Yıldız and Boztepe 2002).

In the literature, there were studies reported about the voltammetric behavior of o-hydroxy azo dyes such as Amaranth and Allura Red AC on silver solid amalgam electrodes and solvent Orange 7 and Eriochrome Black T on glassy carbon electrode and carbon paste electrode, respectively (Chandra et al., 2008, Romanini et al., 2009, Tvorynska et al., 2019).

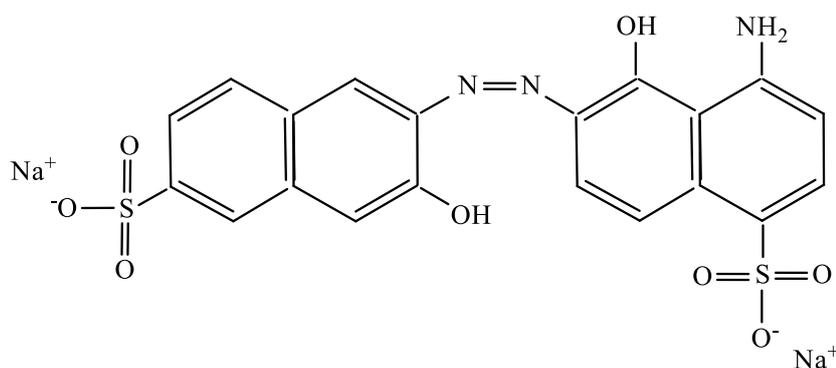
The purpose of this work is to investigate the voltammetric behavior of Mordant dye (C.I. 17135) at a GCE and a SE. The voltammetric techniques employed for the voltammetric analysis of the dye are, SWV, DPV, DCV and CV techniques. At the same time, this present study contributes to previous studies on the voltammetric behavior of azo compounds (Eriksson and Nyholm, 2001, Lucilha et al., 2010, Menek, 1998, Socha et al., 2007). The structure of the Mordant dye (C.I. 17135) is given below (Scheme 1). For Mordant dye (C.I. 17135), no studies have been found so far on glassy carbon and silver electrodes.

## Experimental

6-[2-hydroxy-6-sulfonaphthaleneazo]-3-amino-5-hydroxy-1-naphthalene sulfonic acid disodium salt (Mordant dye C.I. 17135) was purchased from Aldrich and employed without further purification. A  $10^{-3}$  M stock solution of Mordant dye was prepared by dissolving weighted mass of solid in deionized water. The BR (0.04 M) buffer solution employed as the supporting electrolyte was prepared by using 0.04 M phosphoric acid, 0.04 M acetic acid and

0.04 M boric acid and fixed to the desired pH with concentrated sodium hydroxide. All chemicals used for buffer preparation were of p.a. purity.

The Metrohm 757 VA Computrace Electrochemical Analyser was used for the voltammetric measurements of Mordant dye at room temperature. A three-electrode system was employed which consisted of a working electrode (GCE and SE), a Ag/AgCl (saturated KCl) reference electrode and a platinum wire auxiliary electrode. Voltammetric experiments were carried out in the voltammetric cell, where nitrogen gas was passed through the solution for five minutes before the experiments. SWV, DPV, DCV and CV techniques were employed for the voltammetric analysis of the dye. The experimental parameters for the SWV, DPV, DCV and CV techniques were pulse amplitude, 50 mV and potential step 4 mV, DPV was recorded at  $v = 4$  mV/s and pulse time 1 s. For the SWV technique, frequency was 50 Hz and  $v = 200$  mV/s.



**Scheme 1.** Molecular structure of the Mordant dye (C.I. 17135), (6-[2-hydroxyl-6-sulfonaphthaleneazo]-3-amino-5-hydroxy-1-naphthalene sulfonic acid disodium salt).

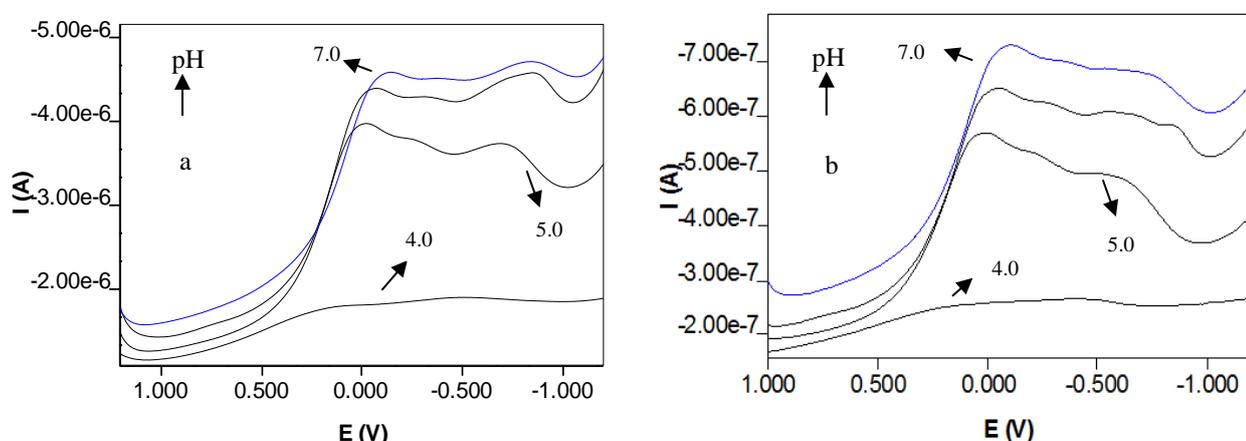
## Results and discussion

### Glassy carbon electrode

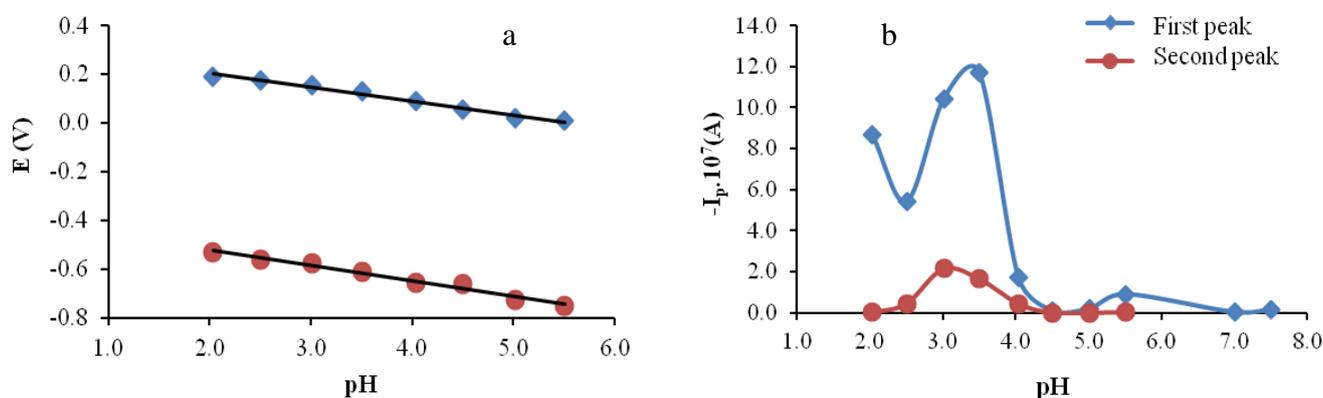
#### SWV and DPV studies

The SW and DP voltammograms of the Mordant dye in BR (pH 2.0-12.0) buffer are presented in Figs. 1 and 3. Two reduction peaks were observed at  $\text{pH} < 9.5$ , and one reduction peak was observed at  $\text{pH} > 9.5$  for SWV and DPV techniques (Fig. 1). The presence of two peaks at  $\text{pH} < 9.5$  and a single reduction peak at  $\text{pH} > 9.5$ , indicated that two-step electrode reaction occurred at  $\text{pH} < 9.5$  and one-step electrode reaction occurred at  $\text{pH} > 9.5$ . The observed shift of the reduction peaks to more negative potentials with increasing pH indicates that protons are involved in the electrode reaction (Fig.2). For SWV and DPV techniques, the current values of the first peak in the acidic media, was much greater than the current values of

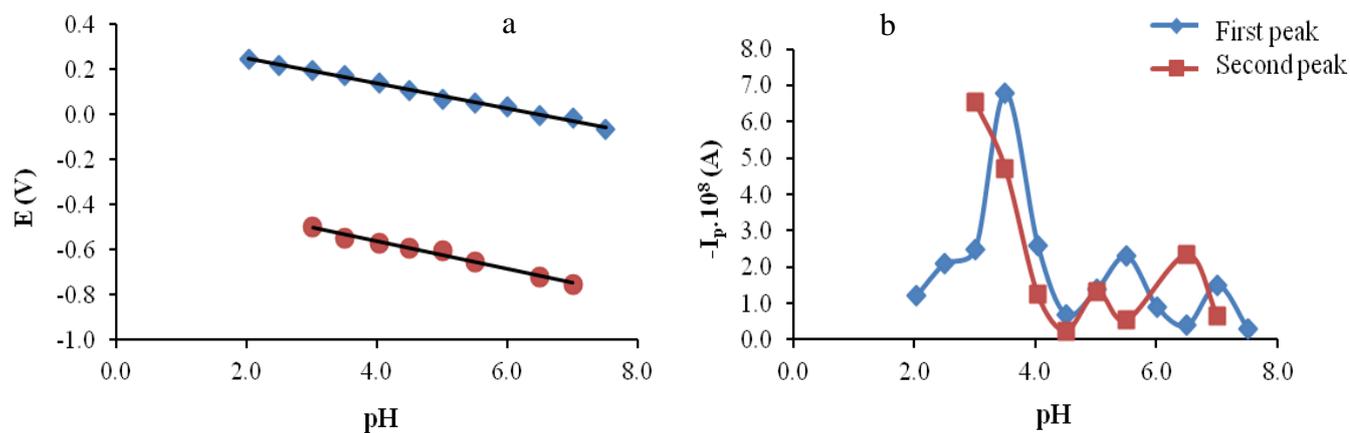
the second peak in the acidic media. Especially in voltammograms obtained in the basic media, the current values are quite low for both peaks (Fig. 1). As seen in Fig. 1, the broad peak of the azo dye occurred is due to its adsorption on the electrode surface (Char et al., 2008, Karaman and Menek, 2012, Karaman, 2014, Ma and Song, 2008, Mirceski and Lovri, 2004, Sun et al., 2005). The linear regression equations of azo dye between the peak potentials and pH were given for the SWV and DPV techniques, respectively, in BR buffer media (Table 1). The data given in Figures 1, 2 and Table 1, show that the addition of protons occurs in the reduction reaction.



**Figure 1.** a) SWV b) DP voltammograms of  $4.76 \times 10^{-5}$  M Mordant dye in BR buffer (0.04 M) pH 4.0, 5.0, 6.0 and 7.0, at GCE.



**Figure 2.** The change in a) cathodic peak potentials and b) cathodic peak currents versus pH in BR buffer obtained for  $4.76 \times 10^{-5}$  M Mordant dye using SWV technique at GCE.



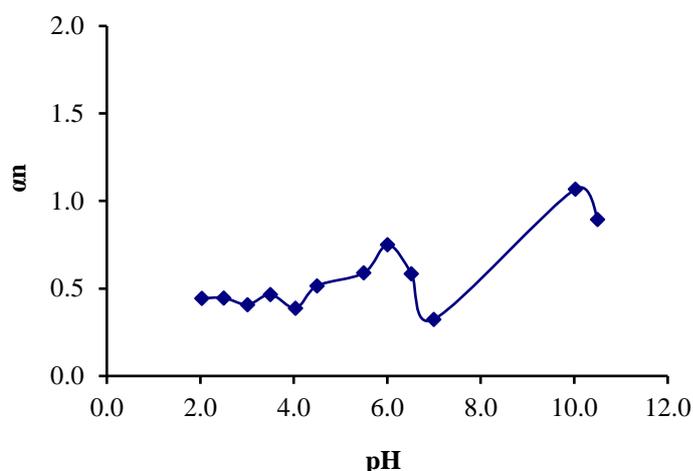
**Figure 3.** The change in a) cathodic peak potentials and b) cathodic peak currents versus pH in BR buffer obtained for  $4.76 \times 10^{-5}$  M Mordant dye using the DPV technique at GCE.

**Table 1.** The change in peak potentials with pH.

Medium	Electrode	Peak	Peak equation	$r^2$ (Regression coefficient)	Technique
BR buffer (pH 2.0-5.5)	GCE	First peak	$E_p$ (V) = $0.317 - 0.0567pH$	0.988	SWV
BR buffer (pH 2.0-5.5)	GCE	Second peak	$E_p$ (V) = $-0.3963 - 0.063pH$	0.981	SWV
BR buffer (pH 2.0-7.5)	GCE	First peak	$E_p$ (V) = $0.3856 - 0.0617pH$	0.989	DPV
BR buffer (pH 2.0-7.0)	GCE	Second peak	$E_p$ (V) = $-0.3182 - 0.0618pH$	0.995	DPV
BR buffer (pH 2.0-12.0)	SE	First wave	$E_{1/2}$ (V) = $-0.0228 - 0.0464pH$	0.983	DCV
BR buffer (pH 3.0-12.0)	SE	Second wave	$E_{1/2}$ (V) = $-0.1454 - 0.0709pH$	0.957	DCV

### **DCV studies**

DC voltammograms of the azo dye in BR buffer media were also studied. One broad reduction wave was observed in the pH range of 2.0 to 12.0. The dependence of the peak potential on pH is given in Table 1. The limiting current is approximately constant in neutral and basic media. Electron transfer coefficient ( $\alpha$ ) was calculated from the Heyrovsky Ilkovic equation. The change  $\alpha$ n versus pH is given in Figure 4. The  $\alpha$ n values are below 1.0 at all pH values.



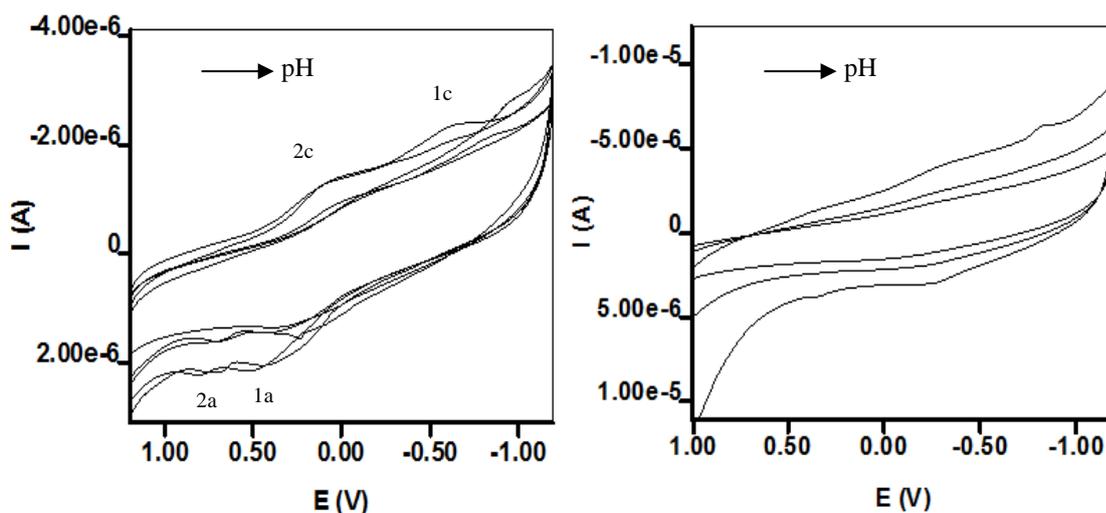
**Figure 4.** The change in  $\alpha n$  with pH for Mordant dye in BR buffer with a GCE.

### **CV studies**

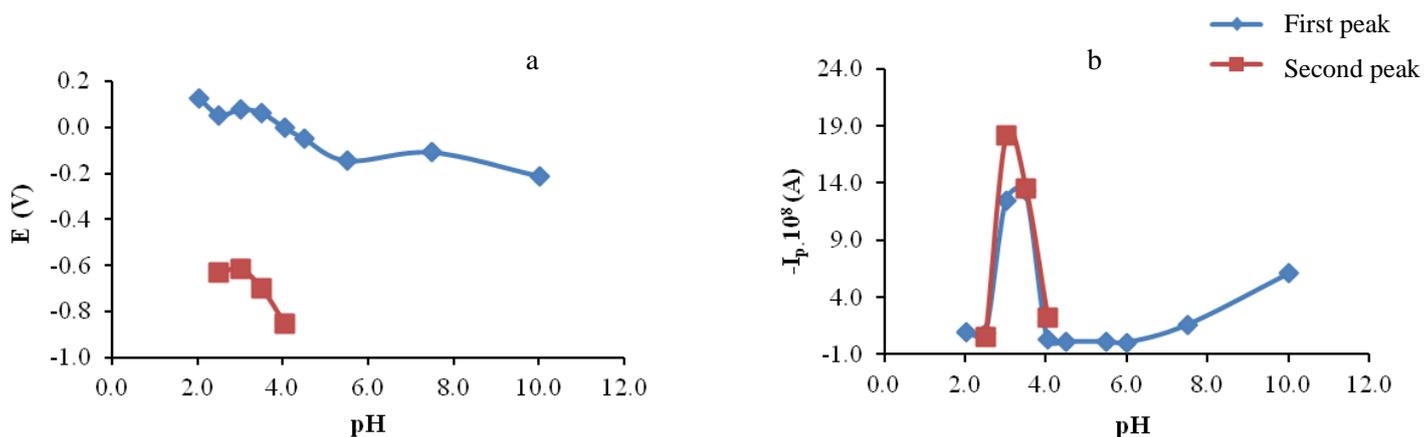
To investigate the electrochemical behavior of the azo dyes, cyclic voltammetry is an important technique that give information about the reversibility or irreversibility of the electrode reactions. For this purpose, the CV voltammograms obtained in BR buffer (pH 2.0-12.0) are given in Fig. 5. During the cathodic potential sweep from 1.2 to -1.2 V, two cathodic peaks (1c, 2c) were seen at 0.097 V and -0.617 V for pH 3.0 in B-R buffer, which were attributed to the reduction of the azo group to amines in acidic media. On the reverse scan from -1.2 to 1.2 V, small corresponding anodic peaks (1a, 2a) were observed at 0.319 and 0.692V for pH 3.0 in BR buffer which were attributed to the oxidation of phenolic hydroxyl groups in the Mordant dye (Fig. 5) (Hattori et al.,2006, Karaman, 2014). As stated in previous studies, amines were produced with the reduction of the azo compounds, which have hydroxyl groups adjacent to an azo group, which was most likely to be reoxidized in the return scan (Yu et al.,

2004). One reduction peak was observed in cathodic scan and one anodic peak was seen in reverse scan in basic media. Peak currents have a sharp increase and decrease in the pH range of 2.0-4.0. After pH 4.0, in the absence of the second peak, the first peak current values increase with increasing pH (Fig. 6).

The peak potential values shifted to more negative values with increasing pH, indicated that protons are involved in the electrode reaction (Fig. 6).

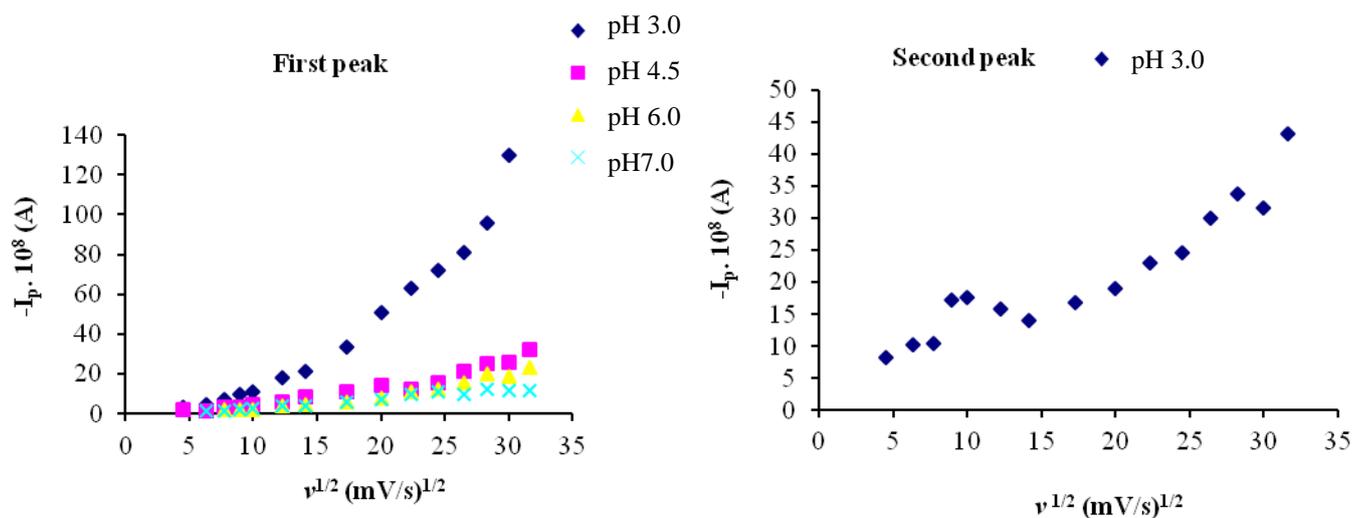


**Figure 5.** CV voltammograms of  $4.76 \times 10^{-5}$  M Mordant dye in BR (0.04 M) buffer at GCE a) pH 2.0, 3.0, 4.0, 5.0, and 6.0 b) pH 9.5, 10.0 and 10.5.



**Figure 6.** The change in a) cathodic peak potentials and b) cathodic peak currents versus pH in BR buffer obtained for  $4.76 \times 10^{-5}$  M Mordant dye using CV technique at GCE,  $\nu = 200$  mV/s.

The effect of square root of scan rate ( $\nu = 20\text{-}1000$  mV/s) on the peak current of the dye at a GCE was examined in BR buffer at different pH values (pH 3.0, 4.5, 6.0 and 7.0) (Fig. 7). Two reduction peaks were observed at pH 3.0 and one reduction peak was observed at pH 4.5, 6.0 and 7.0. The  $I_p$  versus  $\nu^{1/2}$  relation is not linear, and the  $I_p/\nu^{1/2}$  slope increases with increasing scan rate. This result confirms that the azo compound has an adsorption controlled reaction on the electrode surface (Char et al., 2008, Guaratini et al., 2001).



**Figure 7.** The change in cathodic peak currents with square root of scan rate at different pH values at GCE for  $4.76 \times 10^{-5}$  M Mordant dye in BR buffer,  $\nu = 20\text{-}1000$  mV/s.

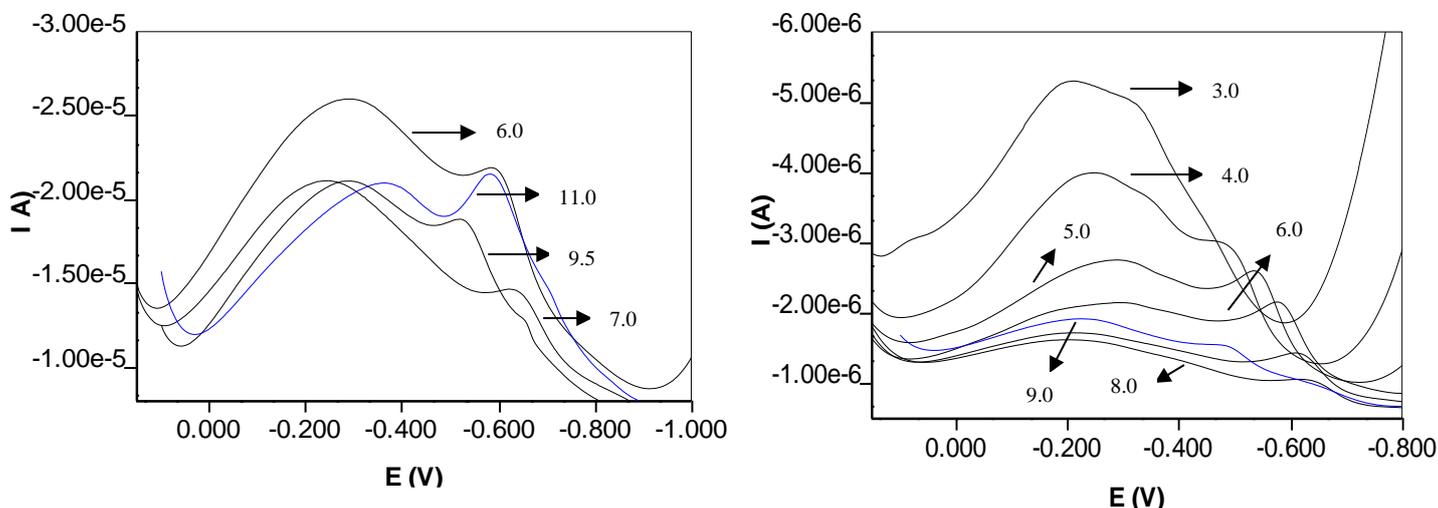
Small anodic peaks were observed at acidic and neutral pH. However, the exponential dependence of peak current with the square root of scan rate is evidence of the kinetic controlling reaction occurring. This indicates that the reaction mechanism is complex.

## Silver Electrode

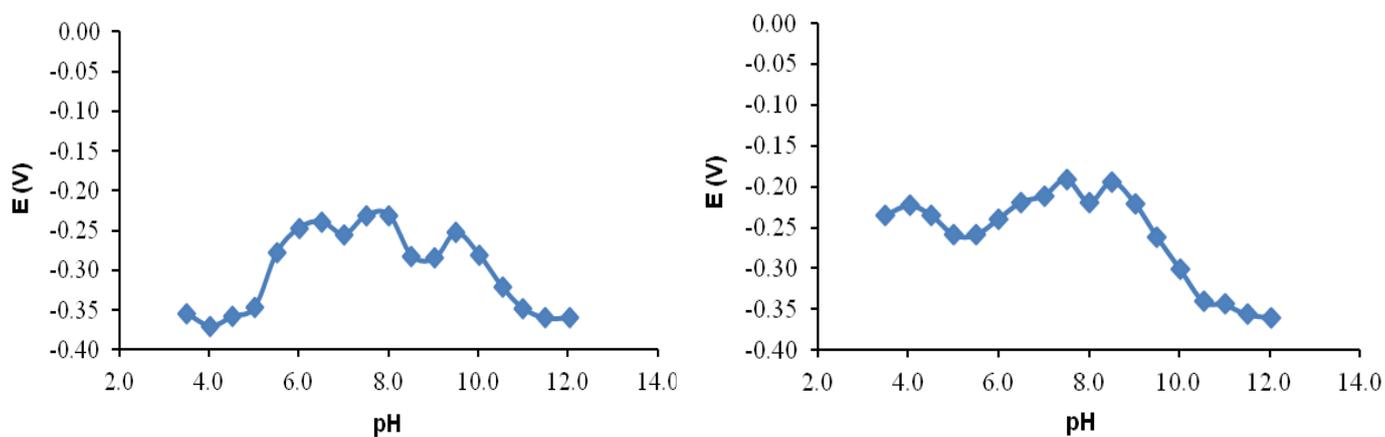
### SWV and DPV studies

The SW and DP voltammograms of the Mordant dye in BR (pH 2.0-12.0) buffer are presented in Figure 8. Two reduction peaks were seen at pH 6.0, 7.0, 9.5 and 11.0 for SWV technique and two reduction peaks were observed at pH 3.0, 4.0, 5.0, 6.0, 7.0, 8.0 and 9.0 for DPV technique (Fig. 8). The presence of two peaks indicated that two-step electrode reaction occurred at the electrode surface. As seen in Fig. 8, the broad peak of the azo dye occurred is

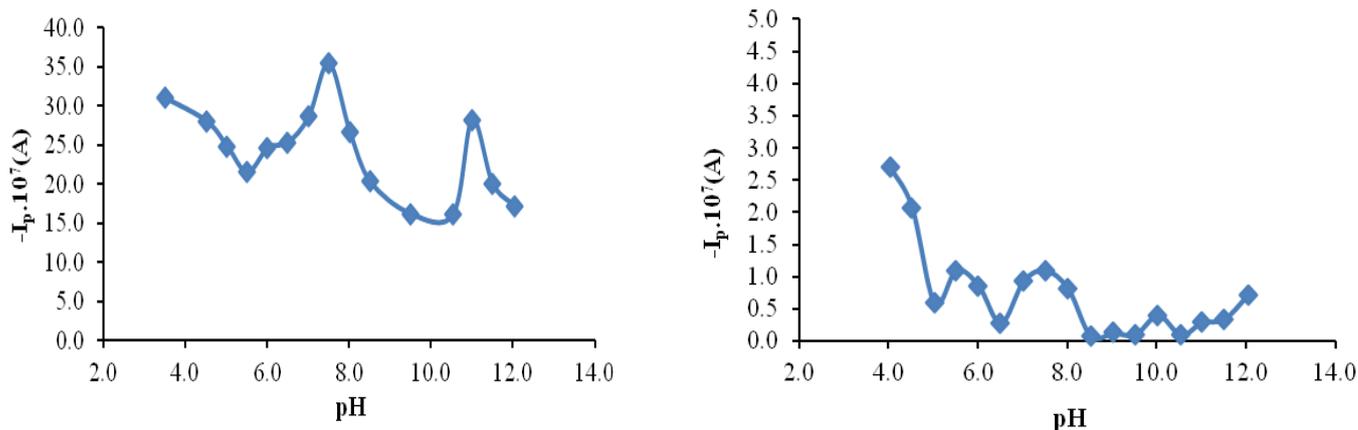
due to its adsorption on the electrode surface (Char et al., 2008, Karaman and Menek, 2012, Ma and Song, 2008, Mirceski and Lovri, 2004, Sun et al., 2005).



**Figure 8.** Voltammograms of  $4.76 \times 10^{-5}$  M Mordant dye in BR buffer (0.04 M) at SE a) SWV, (pH 6.0, 7.0, 9.5 and 11.0,  $\nu = 200$  mV/s) and b) DPV (pH 3.0, 4.0, 5.0, 6.0, 7.0, 8.0 and 9.0).



**Figure 9.** The change in cathodic peak potentials versus pH in BR buffer for Mordant dye at SE a) SWV, b) DPV.

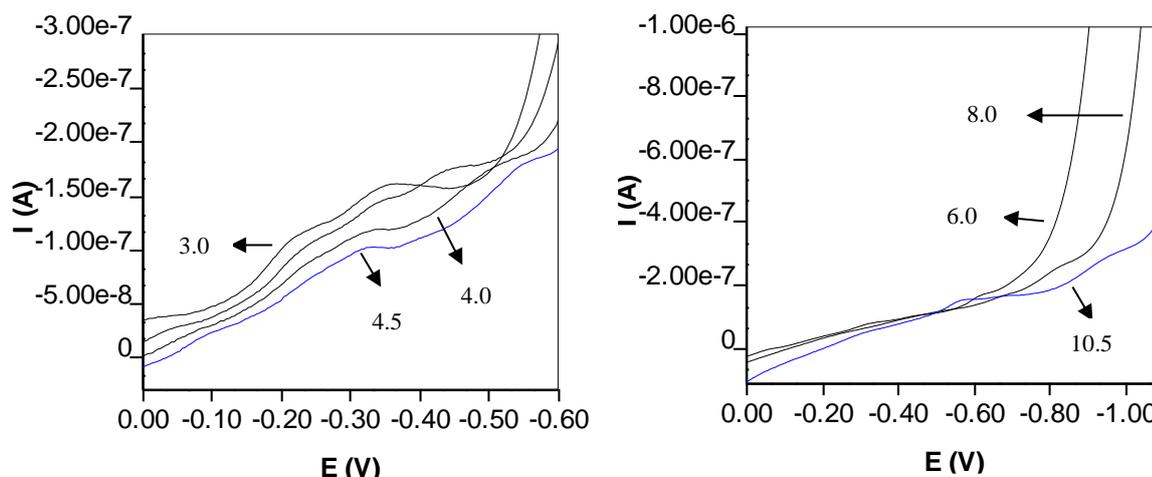


**Figure 10.** The change in cathodic peak currents versus pH in BR buffer for Mordant dye at SE a) SWV, b) DPV.

The change in peak currents versus pH for the azo dye is approximately constant in the range of pH 6.0-9.0 and decreases after pH 9.5 for the SWV technique. However, in DPV technique, it is seen that the peak potential is almost constant in the range of pH 3.5-9.0 and decreases at higher pH values (Fig. 9). As seen in SW and DP voltammograms (Figs. 9, 10), after pH 3.0, the broad peak was observed at negative potentials. These results indicate that there is a two-step reduction reaction occurring on the electrode surface.

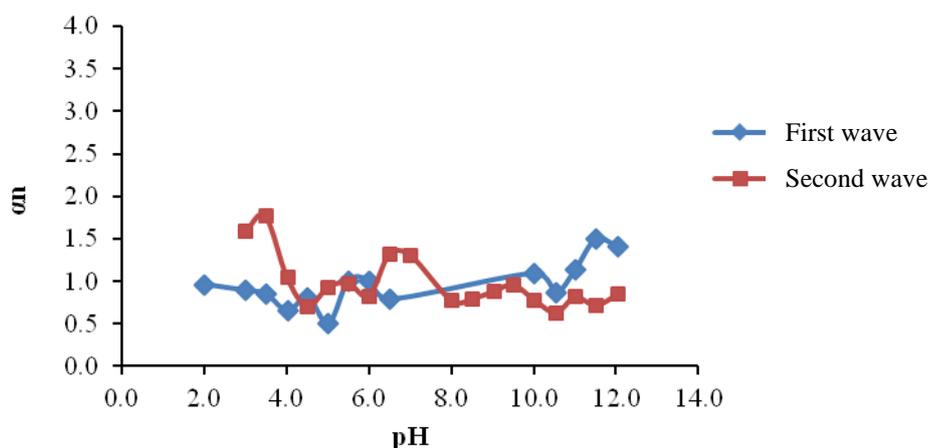
### **DCV studies**

DC voltammograms of the azo dye in BR buffer are shown in Fig. 11. Two reduction waves were seen after pH 3.0 and at pH > 9.0, while one reduction wave was observed at pH 7.0-9.0. As seen in Fig. 11, first and second reduction wave potentials of the dye shifted to more negative values with increasing pH, showing that protons are involved in the electrode reaction. The linear regression equations of azo dye between the half-wave potentials and pH were given for the DCV technique in BR buffer media (Table 1).



**Figure 11.** DC voltammograms of  $4.76 \times 10^{-5}$  M Mordant dye in BR (0.04 M) buffer at SE a) pH 3.0, 3.5, 4.0 and 4.5 b) pH 6.0, 8.0 and 10.5

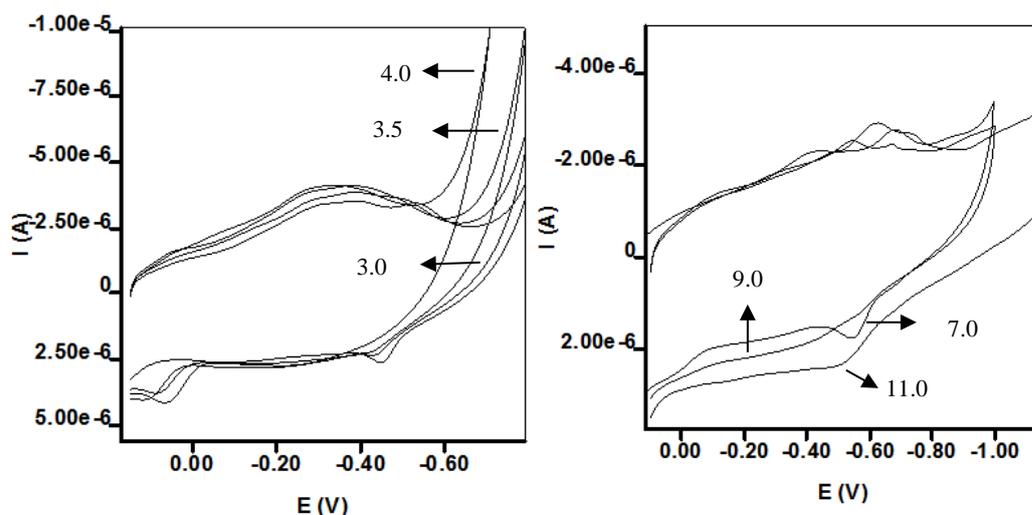
The  $\alpha n$  values were calculated from the logarithmic analyses of the reduction waves by using the Heyrovsky-Ilkovic equation in BR buffer (2.0–12.0). (Bard and Faulkner, 1980, Karaman, 2014, Meites, 1965, Zuman and Perin, 1965). The  $\alpha n$  values of the second wave in the acidic region (pH 3.0, 3.5 and 4.0) are greater than the  $\alpha n$  values of the first wave, although both give similar results in the basic region (pH 10.0, 10.5 and 11.0) (Fig. 12).



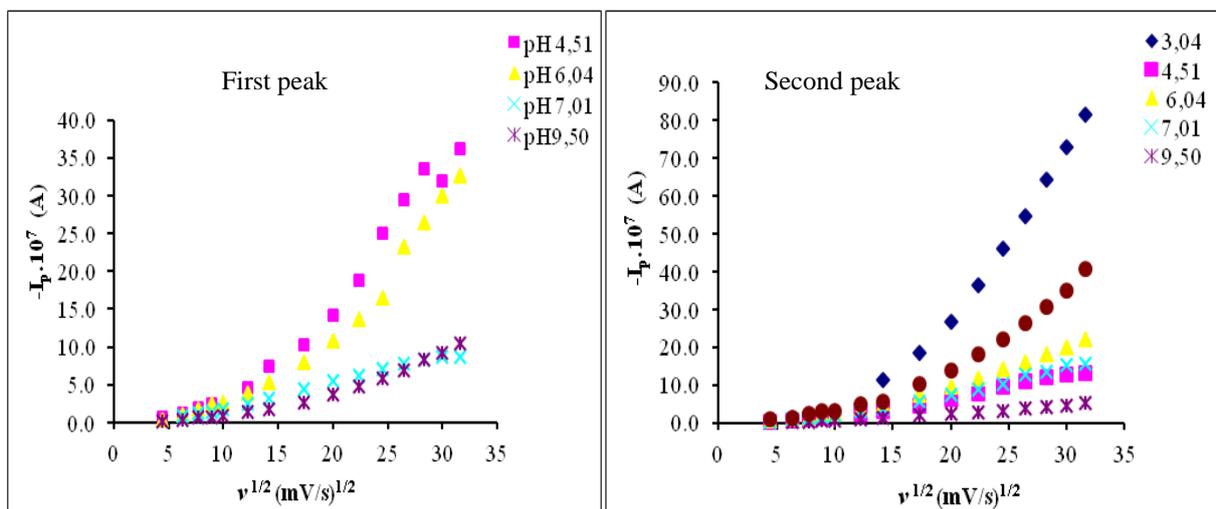
**Figure 12.** The change in  $\alpha n$  with pH for Mordant dye in BR buffer recorded at SE.

**CV studies**

CV voltammograms recorded in BR buffer (pH 2.0-12.0) are given in Fig. 13. Two reduction peaks were observed in cathodic scan, which was attributed to the reduction of the azo group to amines in acidic media, and two anodic peaks were observed in reverse scan in acidic media. One reduction peak was observed in cathodic scan and one anodic peak was seen in reverse scan in basic media.

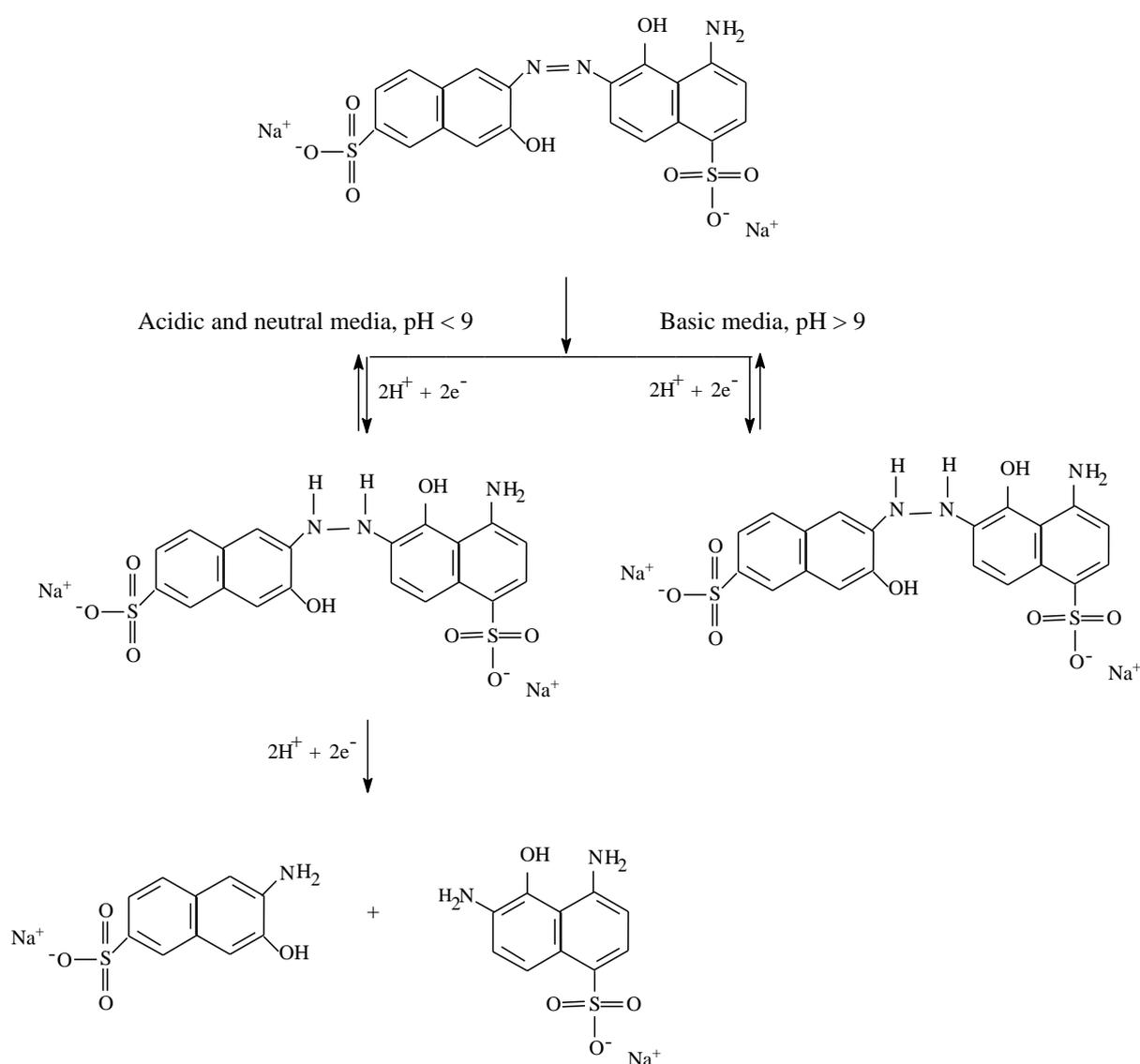


**Figure 13.** CV voltammograms of  $4.76 \times 10^{-5}$  M Mordant dye in BR (0.04 M) buffer at SE a) pH 2.0, 3.0, 3.5, and 4.0, b) pH 7.0, 9.0 and 11.0 solutions.



**Figure 14.** a) The change in cathodic peak currents of Mordant dye with square root of scan rate at different pHs at SE,  $v = 20$ -1000 mV/s.

The effect of square root of scan rate ( $\nu = 20\text{-}1000\text{ mV/s}$ ) on the cathodic peak currents of the dye at a SE was examined in BR buffer at different pH values (Fig. 14). Two reduction peaks were observed at pH 4.5, 6.0, 7.0, 9.5 and 11.0 and one reduction peak was observed at pH 3.0. The linear relation of cathodic peak currents versus  $\nu$  with increasing scan rate, indicating that the azo compound has an adsorption-controlled reaction on the electrode surface (Char et al., 2008, Guaratini et al., 2001, Yu et al., 2004). The reaction mechanism of Mordant dye at glassy carbon and silver electrodes, has been proposed from the voltammetric data (Scheme 2).



**Scheme 2.** The proposed reaction mechanism of Mordant dye.

## Conclusions

The electrochemical behavior of Mordant dye at a glassy carbon electrode and silver electrode has been studied in BR buffer (pH 2.0-12.0) media by using SWV, DPV, DCV and CV techniques. Two reduction peaks were observed at pH < 9.5, and one reduction peak was observed at pH > 9.5 for SWV and DPV techniques with a glassy carbon electrode and silver electrode. The presence of two peaks at pH < 9.5 and a single reduction peak at pH > 9.5, indicated that two-step electrode reaction occurred at pH < 9.5 and one-step electrode reaction occurred at pH > 9.5. The effect of the scan rate on the peak current studies, indicates that the electrode process of the dye at glassy carbon and silver electrodes is adsorption controlled. It was observed from SWV, DPV, DCV and CV techniques that reduction reaction of the Mordant dye corresponds to the cleavage of the azo bond to give the reductive amines.

## Conflict-of-Interest Statement:

None.

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