



## Potentiometric Reduction of methylene Blue in Acidic Medium at Carbon Electrode

TALAT MAHMOOD  
AHMAD ALI  
IFFAT MAHMOOD  
SANA MUSTAFA

Department of Chemistry  
Federal Urdu University of Arts, Science and Technology  
Karachi, Pakistan

ARIF ZUBAIR  
Department of Environmental Science  
Federal Urdu University of Arts, Science and Technology  
Karachi, Pakistan

### Abstract:

*The study has focused on the development of a treatment technique and method for dye wastewater, such as an oxidation reduction process. The potentiometric study of voltage sensitive methylene blue dye was performed in acidic medium at carbon electrodes. It was found that the carbon electrode shows sensitivity and durability for the retardation of dye. From the results it is revealed that the time of retardation decreases with increasing applied potential. The spectral study of methylene blue dye shows that as the applied potential increases the absorbance of dye content also decreases linearly and the color intensity faded out with due course of time and finally to a colorless solution. The effect of concentration of dye shows the direct relation of concentration and retardation time. The extent of retardation of the large decrease in absorbance was observed in  $6.0 \times 10^{-6}$  M solution at different applied potentials. It was found that as the dilution of methylene blue was increasing the  $\lambda_{max}$  was slightly shifted linearly with higher wavelength which shows a bathochromic shift. The kinetics of the retardation of basic blue dye were found to be first order with respect to concentration of dye at room temperature.*

**Key words:** Potentiometric behavior, Methylene blue, Bathochromic Shift, Applied Potential, Carbon Electrode, Acidic medium

## Introduction

S.K. Deb and Chopoorian discovered electrochromism in 1968 and this has had a wide range of commercial applications. Dyes are colored aromatic organic compounds. Color in dyes is variably explained as a consequence of the presence of chromospheres. Because of the extensive environmental contaminations from dyeing operations, environmental research has paid special attention to dye compounds. There are several methods for the treatment of the dye effluent. Electrochemical methods, reduction and oxidation the decolorization of dyes in the presence of reductants, were studied by many workers<sup>1-7</sup>. In chemical methods, photocatalytic processes are widely recognized as viable solutions to environmental problems and effluent treatment<sup>8-15</sup>.

Methods of decolorization have therefore become important in recent years. The main purpose of our work was to study the potentiometric effect of voltage sensitive dye in HCl at carbon electrode. It was found that the use of carbon electrode shows improved sensitivity and durability for the retardation of dyes.

## Materials and Methods

The potentiometric reduction of methylene blue [C<sub>16</sub>H<sub>18</sub>N<sub>3</sub>SCl] dye in acidic medium was performed. A stock solution of dye was prepared in 0.1M HCl and it is diluted by using distilled water. A 100 mL dye solution was taken and transferred to the beaker. Two identical carbon electrodes made of similar material of carbon rods, 4cm long and 0.75cm in diameter, were used. Both electrodes were sealed from one end by an electrical wire that makes the electrical connection. Spectrophotometer UV 2600 BMS (Biotechnology Medical Services) was used to record the spectrum of the dye. A DC potential was applied in the range from 1.5V to 12V. The spectrums of various standard solutions of dye performed in acidic medium for the quantitative estimation of dye. After

applying the voltage, the color intensity faded to a colorless solution. The  $\lambda_{\max}$  of methylene blue is 665nm and its molar absorptivity ( $\epsilon$ ) is 56201. The same procedure was repeated for different concentrations of dye. The extent of reduction of basic dye was observed in each case in terms of a linear decrease in the absorbance. This decrease in absorbance was calculated with different intervals of time keeping the applied potential fixed.

## Result and Discussion

The potentiometric behavior of voltage sensitive dye was performed at carbon electrodes. In the present study the effect of various parameters like concentration and applied potential were taken into consideration. The kinetics of potentiometric study were also performed for the determination of reaction rates and their order. The spectrum of various standard solutions of dye was taken for the confirmation of Beer's law. Figure 1 shows a calibration curve for the quantitative estimation of dye. The  $\lambda_{\max}$  of methylene is 665nm and its molar absorptivity ( $\epsilon$ ) is 56201. The validity of Beer's Law supports the presence of a monomeric form of dye in solution. It was found that as the dilution of dye increase the  $\lambda_{\max}$  was slightly shifted linearly to higher wavelength, which shows a bathochromic shift. The potentiometric behavior of dye at carbon electrodes in 0.1M HCl was performed at different applied potentials ranging from 3 — 12 DC Volts of three different concentrations. The extent of reduction of basic dye was observed in each case in terms of a linear decrease in the absorbance at maximum wavelength. This decrease in absorbance was calculated with different intervals of time keeping the applied potential fixed. The dye was completely faded out or colorless when its absorbance was approximately zero. The results are represented for three different concentrations in fig.2-7.

Kinetics of potentiometric study of methylene blue were studied for the determination of the rate constant values of dye at carbon electrodes at different applied potentials. A graph of  $\ln(a-x)$  of dye was plotted against time on the basis of the change in concentration at different reduction time shows

almost straight line. The kinetics of the retardation of basic blue dye were found to be first order with respect to concentration of dye at room temperature as shown in Figures 8-10.

Retardation of methylene blue was done at different applied voltages ranges from 3.0 V to 12.0V. It was found that time of retardation decreases with increasing applied potential. There is an inverse relation between the applied voltage and time of retardation. Table 2 and Figure 11 show that as we increasing applied potential time of retardation, this decreased gradually. Experimental work has been done at three different concentrations and it is observed that time of the retardation of dye increases by increasing concentration.

## **Conclusion**

Dyes and pigments are mostly colored substances used for coloration. The chemicals used for their synthesis are hazardous to human life. The major environmental problem of colorants is the removal of dyes from effluents. Untreated waste water from industries and textile mills may be highly colored and thus particularly dangerous if discharged to open water. Methods of decolorization have therefore become important in recent years. In the present study the potentiometric study of voltage sensitive dye was performed in HCl at carbon electrode. It was found that the use of carbon electrode shows improved sensitivity and durability for the retardation of dyes.

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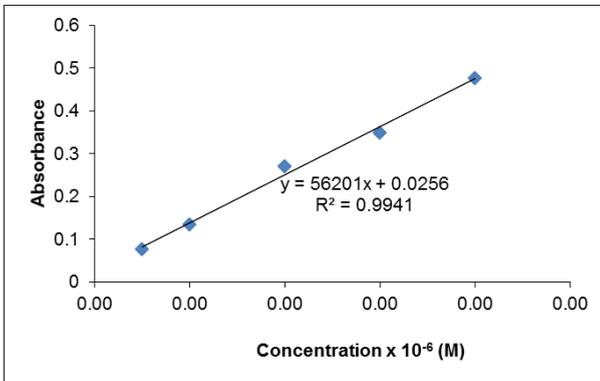
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## ANNEXES

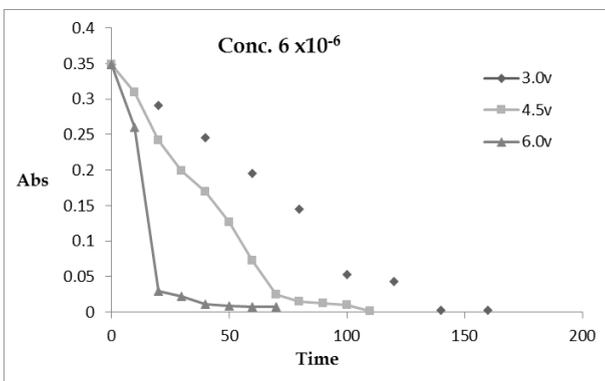
**Table 1 - Calibration curve of Methylene blue**

Concentration(M)	Absorbance
$1 \times 10^{-6}$	0.077
$2 \times 10^{-6}$	0.135
$4 \times 10^{-6}$	0.270
$6 \times 10^{-6}$	0.349
$8 \times 10^{-6}$	0.477

**Fig. 1 Calibration Curve of methylene blue dye**



**Effect of voltage on different concentration of Methylene blue**



**Figure 2.**

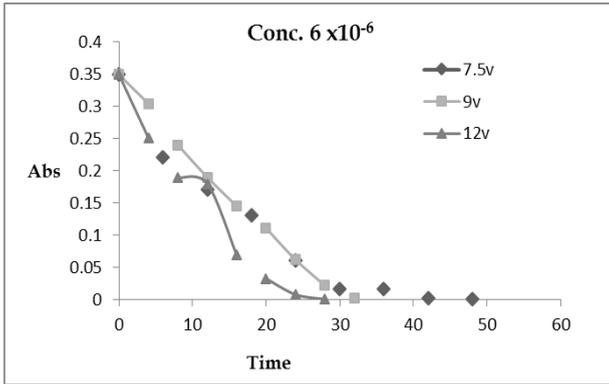


Figure 3.

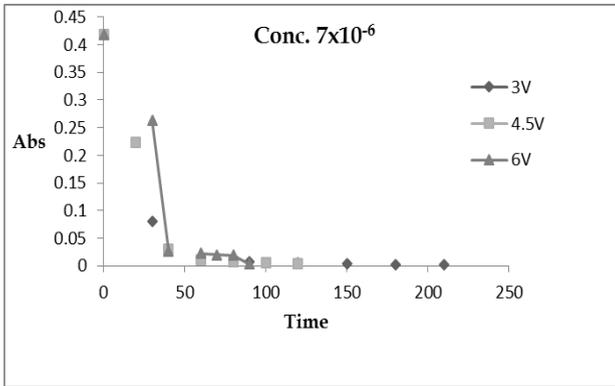


Figure 4.

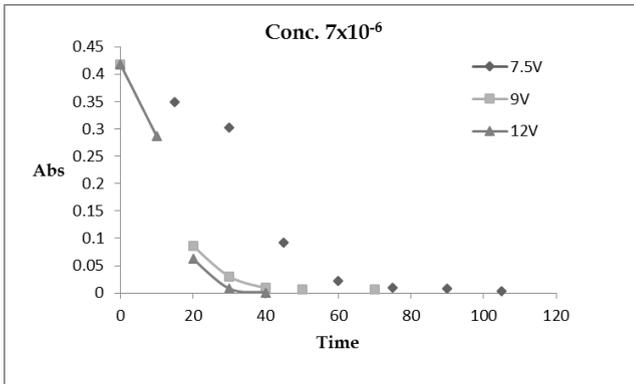


Figure 5.

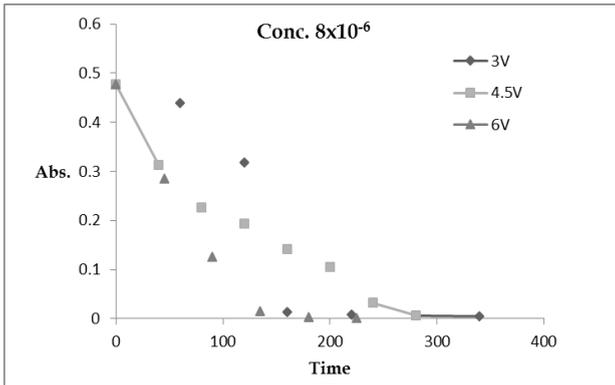


Figure 6.

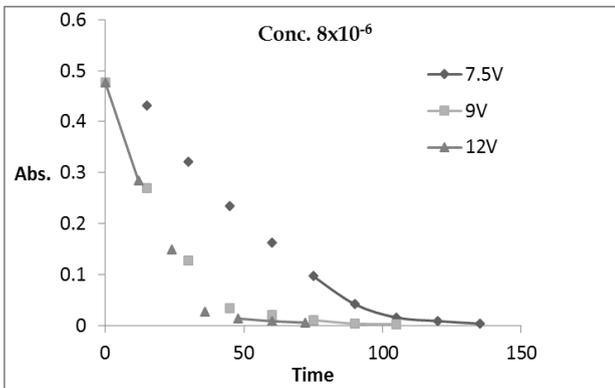


Figure 7.

**Kinetics of Methylene blue**  
**Concentration =  $8.0 \times 10^{-6}$  M**  
**Voltage = 9.0V**

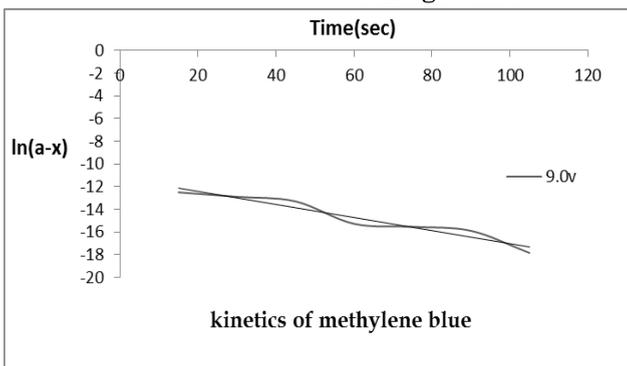
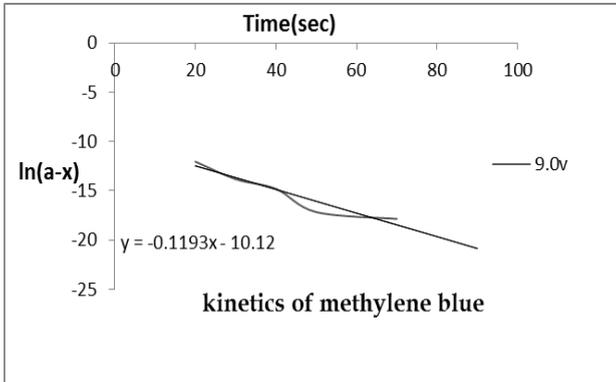


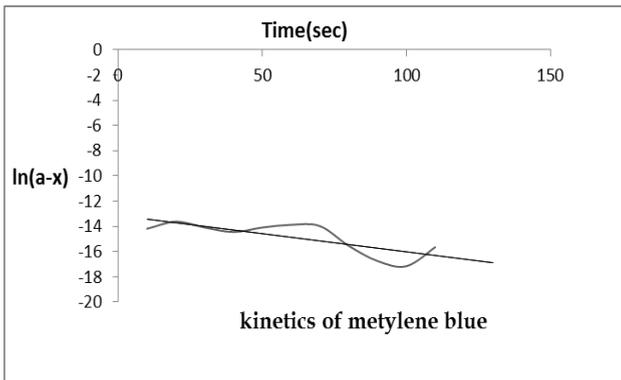
Figure 8.

**Concentration=  $7.0 \times 10^{-6}$  M**  
**Voltage= 9.0V**



**Figure 9.**

**Concentration=  $6.0 \times 10^{-6}$  M**  
**Voltage= 9V**



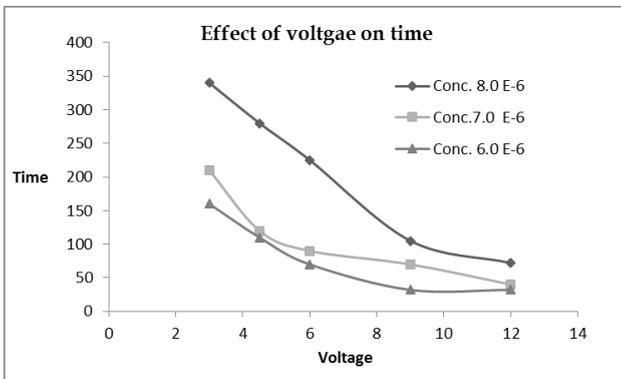
**Figure 10.**

**Retardation of methylene blue at different applied voltages**

Voltage(V)	Concentration $8.0 \times 10^{-6}$ M Time(sec)	Concentration $7.0 \times 10^{-6}$ M Time(sec)	Concentration $6.0 \times 10^{-6}$ M Time(sec)
3.0	340	210	160
4.5	280	120	110
6.0	225	90	70
9.0	105	70	32
12.0	72	40	32

**Table 2.**

**Retardation of methylene blue at different applied voltages**



**Figure 11.**