



Photogalvanic Effect of Maltose/Methylene Blue System in Aqueous Methanol

RAFIA AZMAT* and FAHIM UDDIN

Department of Chemistry, University of Karachi, Karachi, Pakistan

*Corresponding author: E-mail: rafiasaeed200@yahoo.com

(Received: 20 December 2010;

Accepted: 25 January 2012)

AJC-11015

Photocurrent was observed during reduction of methylene blue with maltose into leuco methylene blue. The dye molecules presumably function as an energy or electron relay. In this study, the details of the novel transmitted light intensity during reduction of methylene blue into leuco form with reducing sugar maltose is reported, including their absorption maxima, quantum yields and lifetimes of the triplet transient species. Results showed that this transmitted light intensity depended upon the concentration of reducing sugar, solution acidity and temperature. High power mercury lamp was used as a source of radiation for this investigation. This is strikingly visible example of the conversion of light to chemical energy and finally into electrical energy which when pass through reaction cell strike on photocell where electrons are generated, measured as a current on a galvanometer.

Key Words: Photocurrent, Transmitted light, Triplet transient species, Galvanometer.

INTRODUCTION

Dyes of thiazine family especially thionine and methylene blue have become more important in recent years, as sensitizers in photogalvanic cells for photo electrochemical utilization of solar energy. The photo voltages and photocurrents in photogalvanic cells containing a dye, toluidine blue [Tb⁺] and reducing agents, Fe(II), EDTA, triethanolamine and triethylamine have been determined and found that photo outputs with EDTA or amines as reducing agents were higher than when Fe(II) is the reducing agent. The efficiency of the EDTA-Tb⁺ photogalvanic cell has been estimated to be about 0.0022 % by cyclic voltametry¹⁻³. The photogalvanic effect arising from photochemical redox reaction of dyes has been studied by many researchers. In which most of the work has been carried out on thionine and Fe²⁺ systems⁴⁻⁶. The effect of incident light intensity on the photogalvanic performance and the action spectrum of the thionine-Fe system investigated in aqueous acetonitrile. According to the experimental results, a mechanism of the oxidation-reduction reaction between the dye and V(III) complexes was proposed in aqueous solution⁷. Bayer *et al.*⁸ reported the photogalvanic effect in electrochemical cell employing aqueous methylene blue and Fe(11)/(111) couple electrolyte and nickel mesh electrodes. Five different standard hydrogen cell configurations were setup by modifying the electrolyte long term open circuit voltage measurements conducted in order to test the stability of the cells. Light on-off reproducibility experiments were also carried out during

lengthy cell operations. Murthy *et al.*³ reported the use of the photogalvanic cell of the photo reduction of riboflavin with ethylenediamine tetraacetic acid. Appreciable photoinduced voltage has been observed. Photochemical and photo physical processes involved in the photoreduction of dyes have been extensively studied by Uddin⁹ and Uddin *et al.*¹⁰ under different optimum conditions with different reductants. Jana and Bhowmik and Mukhopadhyay⁶ studied the photogalvanic effect in phenazine dye-EDTA aqueous systems at different pH. It was found that the photo voltage growth and decay curves follow the functional forms related to the relaxation times and the rate of electrode reaction is pH dependent.

The current research discusses the conversion of light energy into chemical energy during photoreduction of methylene blue with reducing sugar maltose on an especially designed optical processor. The light intensity transmitted during reduction was measured on photocell and reported in term of quantum yield of reaction mixture at different optimum conditions.

EXPERIMENTAL

All reagents used were of (Merck and BDH) AnalaR grade. Stock solutions of dye, reductant, acid, alkali and acetate buffer of known concentration were prepared in deionized water and diluted for desired concentration at the time of experiment. The experiment was divided into following different sessions according to need of photochemical reaction.

Measurement of light intensity: A photocell^{3,11,12} was connected in series with an ammeter to measure the intensity of light beam as described by Azmat and Uddin^{13,14}.

Measurements of acidity: Acidity of reaction was determined by Hammett's acidity function using spectrophotometer.

$$H_o = pK_a + \log \frac{(d_1 - d)}{(d - d_2)} \quad (1)$$

where d_1 and d_2 are absorption of the indicator in extreme acidic and basic solutions and d for a solution of intermediate acidity. Reduction was carried out in inert atmosphere by passing nitrogen gas in reaction mixture which was further purified by Feiser's method as described by Uddin³.

Optical processor: A special optical processor was made to irradiate the reaction mixture (Fig. 1). Mercury Mazda lamp is a convenient lamp to obtain a fine strong beam of light. A parallel beam of light was obtained through convex lenses L_1 and L_2 (onto a small hole (O) 2 mm in a metal plate) and lens L_3 arrangement. Red light was obtained by passing the beam further through a Kodak Wratten filter F. A plain reflecting glass R was used for reflection of a fraction of the filtered light on to a reference photocell (P_2). This light was then passed through reaction cell (C). A magnetic stirrer (M) was used to homogenize the reaction solutions. The photocell (P_1) was used to detect the light after passing through the reaction cell. G_1 and G_2 were used to convert the light signal into electronic current measured in μA or mA from photocell (P_1) and (P_2) respectively^{3,9,10,12}.

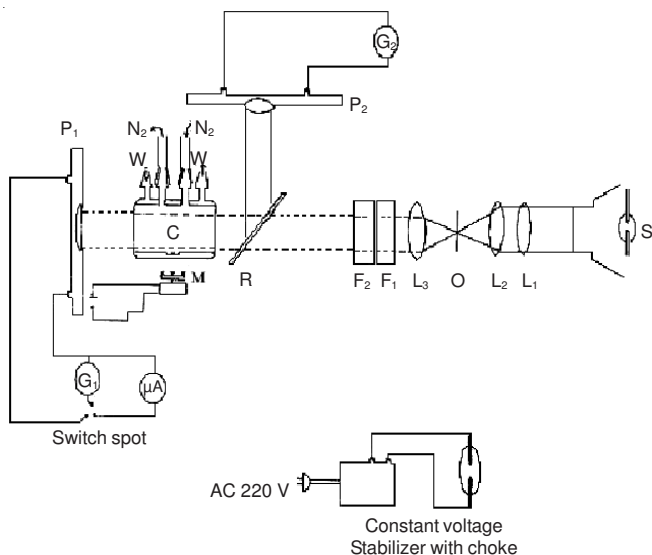


Fig. 1. Arrangement of optical bench

Reaction cell: Reaction mixture was placed in a double walled reaction cell (Fig. 2) having stirring system to homogenize the mixture during flushing of nitrogen before irradiation³.

Experimental procedure: 30 mL of reaction mixture containing known volumes of methylene blue and the buffer solutions in 50 % methanol were pipetted out into the reaction cell at different acidities. The cell was then fitted with the nitrogen retractable bubbler and the outlet tap. The cell was kept

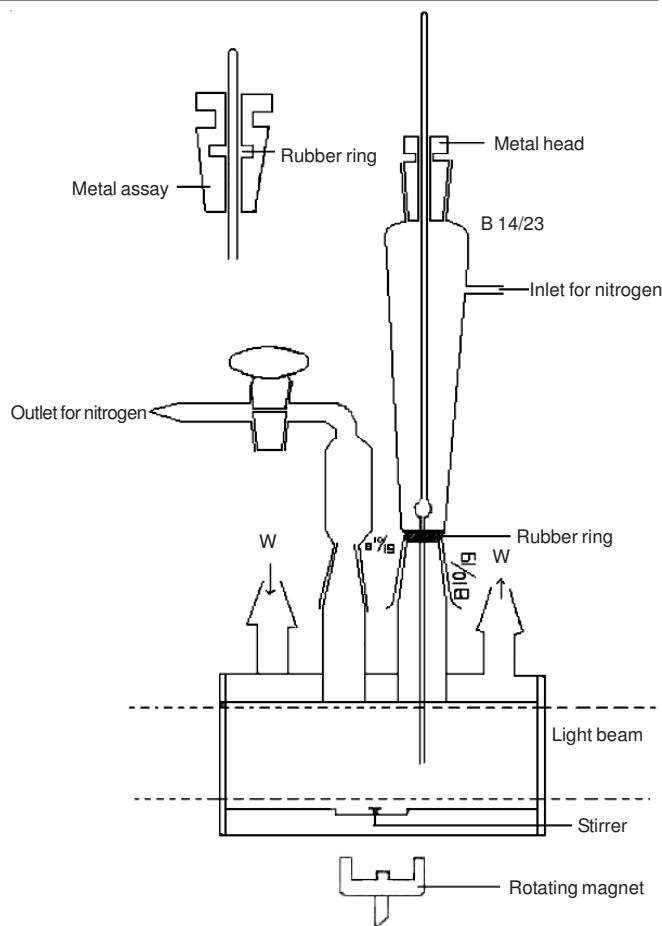


Fig. 2. Reaction cell

in dark with shutters and well stirred magnetically during the flushing and irradiation periods. Oxygen free nitrogen was bubbled for 40 min to the reaction vessel. After degassing the solution, the bubbler was retracted without allowing air to enter into the vessel and the flow of nitrogen was maintained during the run. The lamp was on for 30 min before exposing the reaction solution. Photocell responses from the deflection on the scale of the galvanometer were noted with no cell in the beam (D_o), with the cell containing solvent (D_m) and with the cell containing reaction solutions (D_{ni}). Simultaneous observations were taken on the reference galvanometer. The intensity of the light was measured from the ammeter. The quantum yield was calculated as a function of concentration of reductant, acidity H_o , temperature, concentration of dye and temperature¹².

Calculation of quantum yield (ϕ): Photo reduction of methylene blue in 50 % aqueous methanol with UV-visible/maltose system was investigated for *ca.* 5 min. The deflection on galvanometer upon irradiation of reaction mixture was measured under inert and aerobic condition. The quantum yield was determined by using equation:

$$\log \left(\frac{D_m - D_{nt}}{D_{nt}} \right) = \frac{\epsilon \phi I_o (1 - \alpha) t}{V} + \log \left(\frac{D_m - D_{ni}}{D_{ni}} \right) \quad (2)$$

Eqn. 2 is a straight line equation as the plot of against time 't' is straight line with Slope = $\frac{I_0(1-\alpha)\epsilon\phi L}{V}$ and intercept $\log\left(\frac{D_m - D_{ni}}{D_{ni}}\right)$. The quantum yield (ϕ) was calculated from the slope using eqn. 2 (Fig. 3) as follows:

$$\text{Slope} = \frac{I_0(1-\alpha)\epsilon\phi L}{V} \quad (3)$$

$$\phi = \frac{\text{Slope} \times V}{I_0(1-\alpha)\epsilon L} \quad (4)$$

on the basis of acidity, concentration of dye, concentration of reducing agent and different temperature. In eqn. 4, L is the length of path traveled by the beam in the cell *i.e.* the length of the cell is 7.0 cm, V is the volume of the solution is 0.030 dm³, I₀ is the initial intensity of the beam and (1- α) is the fraction of light transmitted through the window were measured during the experiment¹². The lifetime of triplet transition state was measured through rate constants which appeared in the rate expression of the mechanism of photo reduction of dye, established by Azmat and Uddin^{13,14} and Azmat¹² using quantum yield according to the method described by Wells¹⁵.

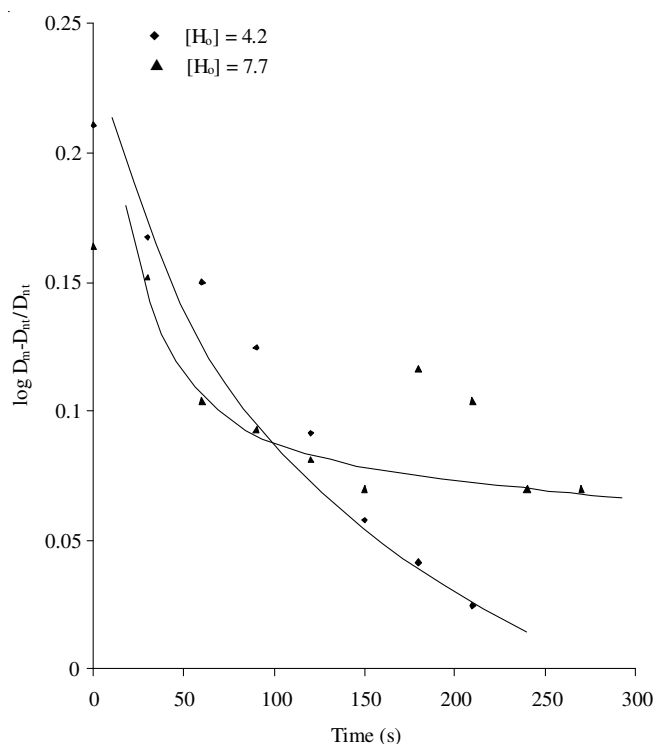


Fig. 3. Plot of $\log D_m - D_{ni}/D_{ni}$ versus time for Maltose at two different pH

RESULTS AND DISCUSSION

The photochemical reduction of methylene blue through high power Hg lamp was investigated initially in aerobic and anaerobic conditions in absence of reducing sugar maltose. The light intensity transmitted through reaction cell showed maximum reduction of dye was obtained in inert atmosphere due to which more photoelectrons were generated in absence

of oxygen. The quantum yield (ϕ) reported in the Table-1 also showed that dissolved oxygen shifts equilibrium in the reverse direction where oxidized (blue) methylene blue generates which may absorb more light, whereas an inert atmosphere results in complete de colouration of the dye (leuco methylene blue)^{9,12,13} results in high intensity of light.

TABLE-1
EFFECT OF AIR/NITROGEN ON QUANTUM YIELD FOR PHOTOCHEMICAL REDUCTION OF METHYLENE BLUE WITH MALTOSE
Solvent = 50 % Aqueous methanol; [MB] = 1×10^6 mol dm⁻³
Maltose = 8×10^{-4} mol dm⁻³; Buffer = Acetate; Temp. = 25 °C

Acidity	Aerobic atmosphere	Nitrogen atmosphere
	ϕ	ϕ
4.2	0.052 ± 0.001	0.151 ± 0.001
7.7	0.023 ± 0.001	0.093 ± 0.001
Decoloration (%)	40	70

The light intensity transmitted through reaction cell was investigated under different parameters like acidity, concentration of reducing sugar and temperature. It was observed that these parameters play an important role in generation of more photoelectrons through photochemical reduction of methylene blue into leuco dye. The photo reduction was studied at different acidities and results are reported in Table-2. Results indicates that quantum yield (ϕ) of photo reduction of dye depends upon acidity of reaction mixture in lower acidity region *i.e.* 4.2. The quantum yield (Table-2) of photo reduction of dye is 0.508 for methylene blue at acidity 4.2 as compared to (0.259) at 7.7. The variation in ϕ versus H₀ (acidity) was observed similar to the reported work²⁻⁶ and representative plots shown in Fig. 4. The plots are curved and show depression from low value of H₀ to high value of H₀ and this transient region show the process of product forming step and an equilibrium between triplet excited states.

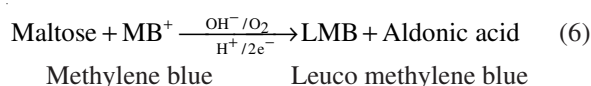


TABLE-2
INFLUENCE OF ACIDITY ON QUANTUM YIELD OF PHOTOCHEMICAL REDUCTION OF METHYLENE BLUE WITH MALTOSE
[MB] = 1×10^6 mol dm⁻³; RCHO = Maltose; Buffer = Acetate; Temp. = 25 °C; Solvent = 50 % methanol

Acidity [H ₀]	I ₀ × 10 ¹⁰ (Einst.s ⁻¹)	Quantum yield ϕ [Maltose] = 8×10^{-4} mol dm ⁻³	Quantum yield ϕ [Maltose] = 6×10^{-3} mol dm ⁻³	I ₀ × 10 ¹⁰ (Einst.s ⁻¹)
	[Maltose] = 8×10^{-4} mol dm ⁻³	[Maltose] = 8×10^{-4} mol dm ⁻³	[Maltose] = 6×10^{-3} mol dm ⁻³	[Maltose] = 6×10^{-3} mol dm ⁻³
4.2	3.855	0.151±0.002	0.508±0.001	3.935
4.7	3.855	0.140±0.001	0.477±0.002	3.935
5.3	3.846	0.131±0.003	0.455±0.002	3.926
6.6	3.843	0.126±0.001	0.424±0.001	3.921
6.9	3.835	0.116±0.002	0.397±0.002	3.899
7.0	3.812	0.106±0.002	0.353±0.001	3.854
7.3	3.812	0.098±0.003	0.318±0.002	3.854
7.4	3.661	0.095±0.006	0.289±0.001	3.853
7.6	3.745	0.093±0.002	0.265±0.002	3.842
7.7	3.723	0.090±0.003	0.259±0.002	3.832

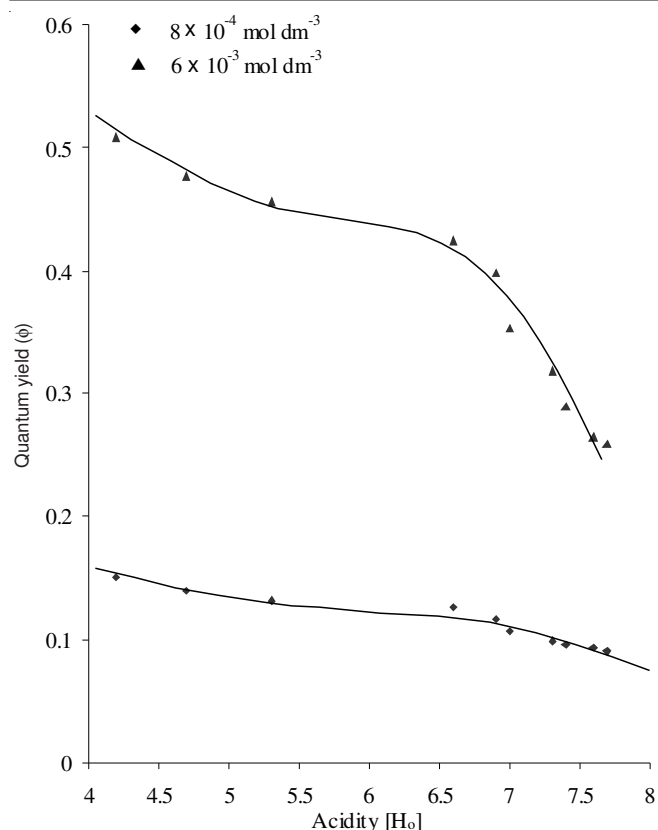


Fig. 4. Plot of ϕ vs. $[H_0]$ for the photo reduction of methylene blue with maltose

To optimize the dye reduction kinetics for maximum intensity of light, a systematic study was carried out by varying

concentration of both the methylene blue and the maltose. Quantum yield of methylene blue with varying concentration of maltose with fixed concentration of methylene blue at two acidities reported in Table-3. It can be seen that the apparent ϕ of the dye reduction directly proportional to the maltose concentration to produce leuco dye¹³. Table-4 showed the effect of varying concentration of methylene blue with fixed concentration of maltose. Reported results indicate that the apparent (ϕ) dye reduction appears to be the same between the concentration range of 1.0×10^{-6} to 4.0×10^{-6} mol dm^{-3} . This indicates that the quantum yield is independent upon the concentration of the dye as shown in Table-4 and less current was recorded due to absorption of light.

The quantum yield of photo reduction of methylene blue with maltose increases gradually as temperature rises in similar way. It was observed that the transmitted light after decolouration is directly related with the temperature (Table-5). The lower value of quantum yield at H_0 7.7 is also in accordance with the other studies¹⁶⁻¹⁸. The average value of temperature coefficient is found to be 1.1647 and 1.1704 at two different pH *i.e.* 4.2 and 7.7 which is comparable with earlier work of Uddin⁵.

Thermodynamic activation parameters like E_a , ΔH^* , ΔG^* and ΔS^* were computed at two different pH (4.2 and 7.7) and tabulated in Table-6 showing that the activation parameters were effected by acidity of reaction mixture¹⁹. The values of E_a for the reduction of methylene blue are 23.26 ± 0.01 and 25.49 ± 0.10 kJ mol^{-1} at acidity 4.2 and 7.7 respectively. The high value at 7.7 indicates that more energy is required for the reduction of methylene blue. The value of ΔS^* reported in the Table-6 ranged from -26.18 ± 0.02 and -26.12 ± 0.04 J mol^{-1} K showed that the highly solvated state of transient complex

TABLE-3
EFFECT OF CONCENTRATION OF REDUCTANT MALTOSE ON QUANTUM YIELD OF METHYLENE BLUE
RCHO = Maltose; Buffer = Acetate; [MB] = 1×10^{-6} mol dm^{-3} ; Temp. = 25 °C; Solvent = 50 % aqueous methanol

10^3 [RCHO] (mol dm^{-3})	$I_0 \times 10^{10}$ (Einst. s^{-1})	Quantum yield ϕ	$10^{-3} \frac{1}{[RCHO]}$ (mol $^{-1}$ dm 3)	$\frac{1}{\phi}$
[H ₀] = 4.2; Confidence interval = 0.115407				
0.8	3.855	0.151 ± 0.002	1.250	6.6137
1.6	3.861	0.189 ± 0.001	0.625	5.2882
2.0	3.882	0.213 ± 0.002	0.500	4.6838
3.0	3.894	0.242 ± 0.001	0.333	4.1322
4.0	3.914	0.302 ± 0.004	0.250	3.3057
5.0	3.935	0.381 ± 0.003	0.200	2.6226
6.0	3.935	0.508 ± 0.001	0.166	1.9673
[H ₀] = 7.7; Confidence interval = 0.5835				
0.8	3.723	0.090 ± 0.003	1.250	11.025
1.6	3.714	0.110 ± 0.001	0.625	9.0909
2.0	3.781	0.121 ± 0.001	0.500	8.2644
3.0	3.812	0.134 ± 0.001	0.333	7.4404
4.0	3.831	0.172 ± 0.004	0.250	5.7836
5.0	3.831	0.226 ± 0.001	0.200	4.4072
6.0	3.832	0.259 ± 0.002	0.166	3.8565

TABLE-4
EFFECT OF CONCENTRATION OF METHYLENE BLUE ON QUANTUM YIELD OF
PHOTOCHEMICAL REDUCTION OF METHYLENE BLUE WITH MALTOSE
RCHO = Maltose 8×10^{-4} mol dm^{-3} ; Buffer = Acetate; [H₀] = 4.2; Solvent = 50 % aqueous methanol

[MB] 10^6 mol dm^{-3}	1.0	1.5	2.0	2.5	3.0	3.5	4.0
ϕ	0.151 ± 0.002	0.151 ± 0.002	0.151 ± 0.002	0.149 ± 0.001	0.151 ± 0.001	0.149 ± 0.001	0.151 ± 0.001
$I_0 \times 10^{10}$ (Einst. s^{-1})	3.855	3.855	3.5321	3.522	3.521	3.520	3.461

TABLE-5
INFLUENCE OF TEMPERATURE ON QUANTUM YIELD OF PHOTOCHEMICAL REACTION OF METHYLENE BLUE WITH MALTOSE
[MB] = 1×10^{-6} mol dm⁻³; [RCHO] = 8×10^{-4} mol dm⁻³; RCHO = Maltose; Solvent = 50 % ethanol; Buffer = Acetate

Acidity [H ₀]	Temperature (°C)					
	20	25	30	35	40	45
Confidence interval = 0.05806						
4.2 φ	0.130 ± 0.001	0.151 ± 0.002	0.194 ± 0.003	0.215 ± 0.001	0.2428	0.277 ± 0.001
I ₀ × 10 ¹⁰ (Einst·s ⁻¹)	3.854	3.855	3.8451	3.8321	3.821	3.812
Confidence interval = 0.04124						
7.7 φ	0.083 ± 0.002	0.090 ± 0.003	0.120 ± 0.001	0.147 ± 0.002	0.162 ± 0.001	0.180 ± 0.002
I ₀ × 10 ¹⁰ (Einst·s ⁻¹)	3.733	3.723	3.724	3.721	3.711	3.710

TABLE-6
THERMODYNAMICS ACTIVATION PARAMETERS AT VARIOUS ACIDITIES [H₀]

Temperature (K) 303/Acidity	E _a (KJ mol ⁻¹)	ΔH [‡] (KJ mol ⁻¹)	ΔS [‡] (JK ⁻¹ mol ⁻¹)	ΔG [‡] (KJ mol ⁻¹)
4.2	23.26 ± 0.01	20.74 ± 0.02	-26.18 ± 0.02	28.67 ± 0.01
7.7	25.49 ± 0.10	22.97 ± 0.02	-26.12 ± 0.04	30.88 ± 0.01

over reactant and support the same mechanism was involved in the reduction of methylene blue with UV/Maltose at two acidities, which involves hydrogen abstraction and electron donation by maltose.

Absorption of methylene blue solution at wavelength of 661 nm results in photo bleaching of the dye molecule, which means the photons cause the methylene blue to break the double bonds and the molecules turn colourless. This is strikingly visible example of the conversion of light to chemical energy. The photogalvanic effect relies on the excitation of dye molecule through light to induce redox reaction with reducing agent yielding high energy product. Such product can loose their energy electrochemically like an ordinary battery. Photooxidation and reduction reaction of dyes can often be used to produce photo current⁷.

In the oxidized form of the dye, there is a conjugation of double bonds across the three rings. The electronic excitation energy for this molecule is within the visible region of the spectrum (Fig. 5). In the reduced form, the double bond on the nitrogen in the middle ring does no longer exist and conjugation is restricted to the two outer rings. Any electronic transitions (such as π bonding to π* antibonding) now have energies in the visible region.

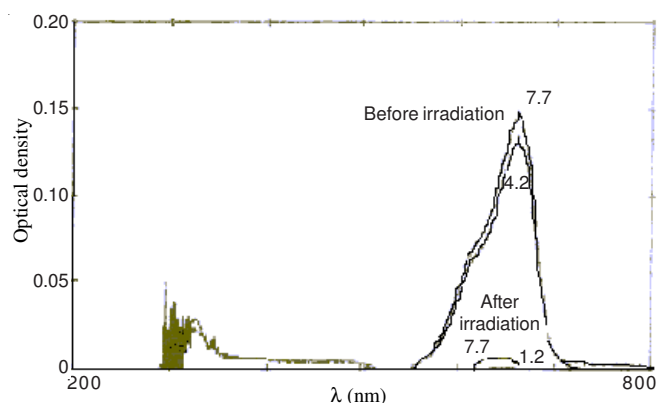


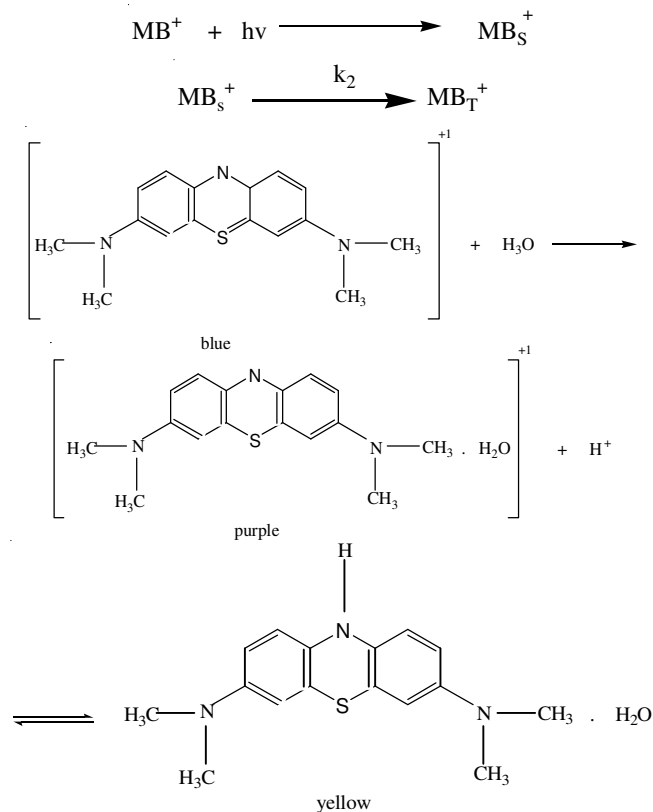
Fig. 5. Spectral change of photo bleaching of methylene blue with maltose before irradiation and after irradiation at pH 4.2 and 7.7

The colourless form of the dye allows the light to pass this energy in from of transmitted light and when transmitted light fall on a photocell, photoelectrons are generated. This generation of photoelectrons through transmitted light by photochemical reduction of dye is directly related to the reaction occurring in reaction mixture.

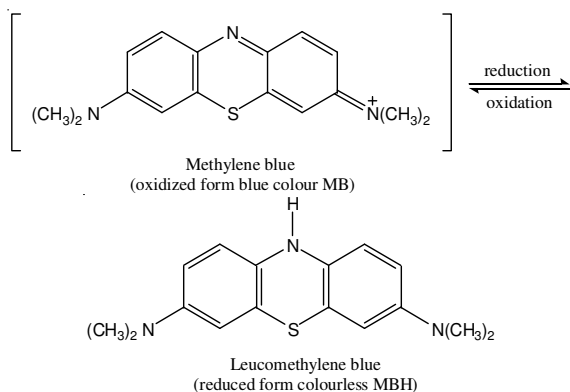
Absorption spectra: The absorption spectra were taken before irradiation and after irradiation to check the reduction (Fig. 5). The sharp peak before irradiation of methylene blue at H₀ = 4.2 at λ_{max} 661 nm mat be related with the brightness of colour of methylene blue. However at H₀ = 7.7 (higher pH range) a broad spectrum was observed with λ_{max} 662 nm and 664 nm for methylene blue/disaccharide system. Such a change in absorbance measurement has been supported by the literature¹⁹ regarding the dimeric form of methylene blue. Spectra showed that at acidity 4.2 decolouration was almost completed with no significant shift in wavelength (662 nm) and indicate that the initial product formed on reduction of methylene blue absorb light at 662 nm. This may be expected due to that the change in buffer composition to maintain acidities at 4.2 and 7.7 were highly dominating due to which no significant shift in λ_{max} were observed after passing radiation from the reaction mixture of methylene blue and verify the reduction of methylene blue into leuco dye. This leuco dye *i.e.*, reduced methylene blue allow to pass the light from colourless solution which generate photoelectrons during photochemical reduction of methylene blue with maltose.

Mechanism of reduction: The reaction between methylene blue and reducing sugar is essentially an oxidation-reduction reaction. Methylene blue oxidizes aldoses into aldonic acid in the presence of acid base equilibria and itself reduces into leuco methylene blue in inert atmosphere but oxygen of the air oxidizes the leuco methylene blue in blue form. The system²⁰ is a clear solution upon passing light but changes to blue colour when shaken, purple when exposed to sunlight and turns yellow when allowed to stand for a day. The duration of the colour change depends upon the length of shaking and light. After 2 days, the yellow colour persists and no changes in colour occur by shaking, if container is opened.

It was observed that dye was highly reactive towards reagents present in the mixture and also interaction with solvent molecule occur. The dye get excited with absorption of photon of light into singlet excited state which may convert into triplet excited state whose lifetime 10.1 μ by internal conversion according to following mechanism.

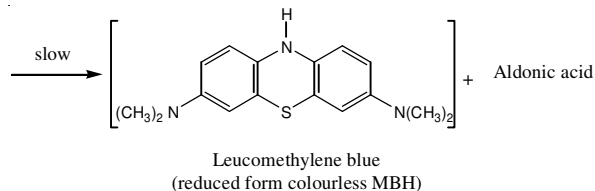
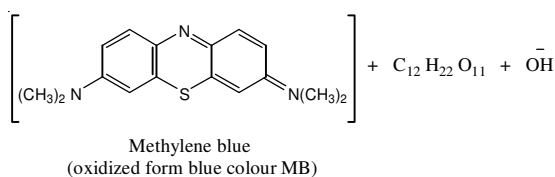


In simple terms, the changes between blue and colourless solution are due to redox cycle between two forms of methylene blue as shown in the following reaction steps¹⁶.

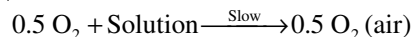


The possible reaction mechanism is outlined below:

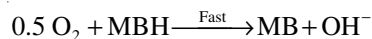
Step-1:



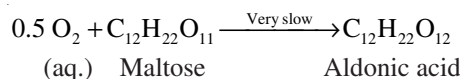
Step-2



Step-3



Net possible oxidation reaction may be:



corresponding aldonic acid may be respective organic acids of oxidation products of maltose.

Conclusion

The above investigation revealed that the generation of photo electrons directly related with transmitted light intensity after reduction of dye at different parameters like acidity, concentration and temperature of reaction mixture. Maximum light intensity was recorded at lower acidity region.

REFERENCES

1. A.S.N. Murthy and K.S. Reddy, *Solar Energy*, **30**, 39 (1983).
2. H. Tsubomura, Y. Shimoura and S. Fujiwara, *J. Phys. Chem.*, **83**, 2103 (1979)
3. A.S.N. Murthy, H.C. Dak and K.S. Reddy, *Int. J. Energy Res.*, **4**, 339 (1980).
4. F. Uddin, Q.Z. Hasnain and M.A.K. Yousufzai, *Arab. J. Sci. Engg.*, **26**, 109 (2001).
5. F. Uddin, *Eur. J. Org. Chem.*, **7**, 1345 (2000).
6. B.B. Bhowmik and M. Mukhopadhyay, *Photochem. Photobiol.*, **78**, 173 (1994).
7. S.T. Hamidi and S.M. Aliwi, *Monatsh. Chem.*, **127**, 339 (1996).
8. I.S. Bayer, Inci Ero lu, Lemi Türker, *Int. J. Energy Res.*, **25**, 207 (2001).
9. F. Uddin, I.M. Adhami and M.A.K. Yousufzai, *J. Saudi Chem. Soc.*, **2**, 47 (1998).
10. F. Uddin and Q.Z. Hasnain, *Kuwait J. Sci.*, **29**, 67 (2002).
11. A.K. Jana and B.B. Bhowmik, *J. Photochem. Photobiol. A*, **110**, 41 (1997).
12. R. Azmat, Reduction of Methylene Blue with Reducing Sugars, Publisher VDM Verlag Dr. Müller e.K. (2009).
13. R. Azmat and F. Uddin, *Can. J. Pure Appl. Sci.*, **2**, 275 (2008).
14. R. Azmat and F. Uddin, *Chin. J. Chem.*, **27**, 1237 (2009).
15. C.H.J. Wells, Introduction to Molecular Photochemistry, Pub. USA, John Wiley & Sons, Inc., New York (1973).
16. A. Sharma, R.D. Rao, S. Mathur and C. Ameta, *J. Photochem. Photobiol. A. Chem.*, **86**, 197 (1989).
17. K.A. Chibison, D.T. Slavnova and H. Gorner, *Chem. Phys. Lett.*, **86**, 301 (2004).
18. R. Azmat, S. Ahmed, S. Qureshi, F.V. Mohammed and F. Uddin, *J. Appl. Sci.*, **6**, 2784 (2006).
19. T. Snchalatha, P. Rajanna and K. Saiperkash, *J. Chem. Educ.*, **74**, 228 (1997).
20. R. Azmat, B. Yasmeen and F. Uddin, *Asian J. Chem.*, **19**, 1115 (2007).