Photometric Study of Oxidation of Ascorbic Acid by Methylene Green in Aqueous Alcoholic System

[1]Sameera Razi Khan*, [2]Rehana Saeed, [2]Maria Ashfaq, [2]Summyia Masood
[1]*Department of Chemistry, Federal Urdu University of Science, Arts & Technology, Gulshan-e-Iqbal, Karachi.*
[2]*Department of Chemistry, University of Karachi.*
sameerarazi.khan@gmail.com, sameerarazi_khan@yahoo.com

(Received on 17th January 2018, accepted in revised form 13th August 2018)

Summary: The photochemical study for oxidation of ascorbic acid with methylene green was studied in aqueous and aqueous methanol, ethanol, and isopropanol at temperature ranges from 303-318 K in acidic medium. The quantum yield of the photochemical oxidation of ascorbic acid with methylene green was determined by irradiation of reaction mixture by monochromatic light of 657 nm and transmitted light was recorded by photocell response as electrical signals on galvanometer. The rate of reaction mixture in terms of quantum yield was determined and found independent of variation in methylene green concentration and had increased with the concentration of ascorbic acid. The effect of dielectric constant was studied by varying the compositions of alcohol and the results obtained revealed that the quantum yield decreased with the decrease of the polarity of system in acidic medium. On the basis of kinetics the reaction follow pseudo first order and mechanism has been proposed. Thermodynamic parameter such as energy of activation (E_a^*), change in enthalpy of activation (ΔH^*), change in free energy of activation (ΔG^*), and change in entropy of activation (ΔS^*) were also calculated.

Keywords: Photochemical; Quantum Yield; Methylene Green; Ascorbic Acid; Alcohols; Thermodynamic Parameters.

Introduction

Thiazine dyes are widely used in various processes such as adsorption processes, dying in textile, heterogeneous catalysis and chromatographic analysis. Most of the thiazine dyes reacts with lipids, protein, and nucleic acid and have the highest level of antimalarial activity [1-2]. Environmental researchers have focused on different physical method such as activated carbon absorption [3], biological treatment, biodegradation, adsorption [4], reverse osmosis and chemical methods such as ozonations, chlorination and redox reactions [5-6] to remove these traces of dyes from industrial effluents. The stable nature of dye makes it difficult to remove, so its removal from waste water is difficult [7]. Methylene green is one member of thiazine dyes, which has excellent light fastness on acrylics. Several researches [8-11] have been carried out to degrade the dyes photochemically using heterogeneous catalyst as cyclic ketones, and Fenton’s reagent [12] and different techniques such as fluorescence [13], cyclic voltammetry [8] and stopped flow spectroscopy [14] were used to investigate the reduction of dyes.

The presence of electron withdrawing groups on the thiazine dyes slows down the bleaching rates and supports the photosensitizing oxidation process. This property makes thiazine dye act as a photosensitizers for conversion of solar energy and storage purpose [15, 16].

The photocatalytic degradation of textile dyes under ultraviolet light by Ag, Ag-TiO_2 and TiO_2 contributed for the removal of dye from industrial waste water [17-19]. The photocatalytic degradation of different dyes was also done in presence of nanoparticles of SnO_2, ZnO [20-21]. The photochemical oxidation process was also used to remove the dyes from industrial waste water [22-24]. The present work focused on the photochemical oxidation of ascorbic acid by methylene green in aqueous and aqueous alcohol such as aqueous methanol, aqueous ethanol, and aqueous isopropanol at in acidic medium. The effect of concentration of ascorbic acid, concentration of methylene green and temperature ranges from 303K to 318 K on quantum yield of reaction were studied and mechanism of reaction was proposed on the basis of kinetics data. Thermodynamic study was also carried to support results.

Experimental

Ascorbic acid (BDH), methylene green (Fluka with purity of 99.99%), methanol, ethanol and isoproponol (Merck) were purchased to prepare the solutions in aqueous, aqueous methanol, aqueous ethanol and aqueous isopropanol. These solutions were prepared by using double distilled water having conductivity 1.0×10^{-6} µS.cm^{-1}.

***To whom all correspondence should be addressed.**

The kinetics of oxidation of ascorbic acid with methylene green was studied as a function of dielectric constant and temperature by photochemical method. The photochemical reaction was performed using an optical processor having 250 watts high pressure mercury ME/D compact Mazda box type lamp as light source (S). A double walled cell (C) having capacity of 0.045 dm^3 with constant circulation of water to maintain constant temperature was used. A special optical bench arrangement with lenses (L_1, L_2, L_3) and filters (F_1 and F_2) was made to fulfill the requirements of the experiment as shown in Fig. 1.

The photochemical oxidation was performed by taking the known volume of reaction mixture in a double walled cell (C) connected to a thermostat water bath to maintain constant temperature. Photo cell responses (P_1 and P_2) were recorded on the galvanometer (G_1 and G_2) by passing monochromatic light of 657 nm through the reaction mixture up to 30 minutes. The initial intensity of light was measured by using an ammeter. The quantum yield for oxidation of ascorbic acid with methylene green was calculated as a function of concentration of ascorbic acid, concentration of methylene green, temperature, and percentage composition of alcohols such as aqueous methanol, aqueous ethanol and aqueous isopropanol at different temperatures ranging from 303 K to 318 K. The acidity of the reaction mixture was maintained at pH 3.

Results and Discussion

The photochemical oxidation of ascorbic acid by methylene green in aqueous and aqueous alcohol system was carried out as a function of dielectric constant and temperature. The rate of reaction in terms of quantum yield was determined by passing monochromatic light of 657 nm through the reaction mixture and the photo cell responses were recorded. The quantum yield (φ) is expressed as: [25]

$$\log\left(\frac{D_m - D_{nt}}{D_{nt}}\right) = \frac{\in \varphi L I_o (1-\alpha)}{V} t + \log\left(\frac{D_m - D_{ni}}{D_{ni}}\right) \qquad (1)$$

Where D_m , D_{nt} and D_{ni} are the photo cell responses with cell having solvent, reaction mixture at particular time and reaction mixture at time zero, V is the volume of the solution, I_o is the incident intensity of the beam, $(1 - \alpha)$ is the fraction of light transmitted through the window measured during the experiment, $\in$ is the molar absorptivity coefficient and L is the length of tube. The representative plot of $\log\left(\frac{D_m - D_{nt}}{D_{nt}}\right)$ with time is shown in Fig. 2 with the slope $\frac{I_o(1-\alpha)\in\varphi L}{V}$ and intercept log $\frac{D_m - D_{ni}}{D_{ni}}$. The values of quantum yield (φ) were calculated from the slope and are reported in Tables 1-3.

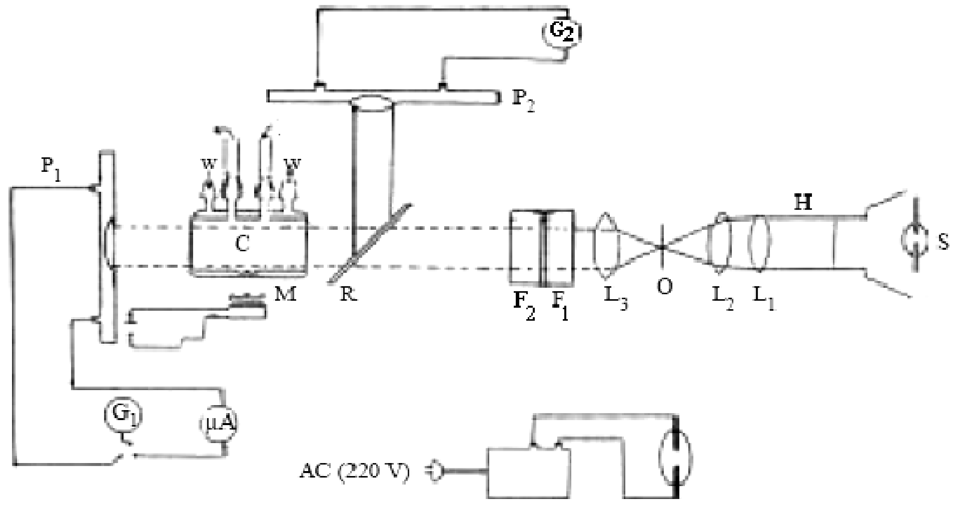

Fig. 1: Schematic of the Optical Bench Arrangement.

(S is light source,; L_1, L_2, L_3 are lenses; F_1 and F_2 are filters; R is reflector; M is magnetic stirrer; C is reaction cell; P_1 and P_2 are Photo cell responses; W connection to water bath; G_1 and G_2 are galvanometers)

Table-1: Effect of concentration of ascorbic acid on quantum yield for photochemical oxidation of ascorbic acid with methylene green in various solvent system.
[MG] = 7.78×10^{-6} mol.dm^{-3}
Temperature = 308 K

[AA] 10^4 (mol.dm^{-3})	Quantum Yield (φ)×10^2		
	Solvent (v/v)		
	0%	10%	20%
		Aqueous Methanol	
1.11	5.563	5.009	3.357
3.33	20.448	10.905	8.335
5.56	23.000	13.559	8.698
7.78	23.696	16.963	11.145
10.0	24.012	20.912	19.682
		Aqueous Ethanol	
1.11	5.563	3.102	2.573
3.33	20.448	5.910	3.804
5.56	23.000	9.832	6.303
7.78	23.696	12.464	7.824
10.0	24.012	14.610	8.374
		Aqueous Isopropanol	
1.11	5.563	2.098	1.784
3.33	20.448	5.066	3.753
5.56	23.000	6.142	5.347
7.78	23.696	9.084	6.624
10.0	24.012	11.972	8.220

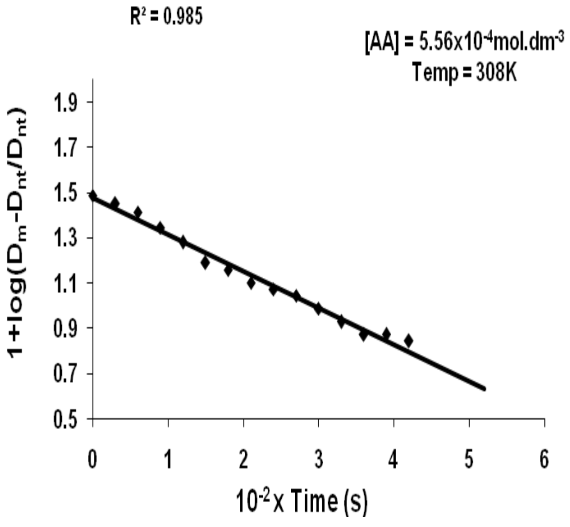

Fig. 2: Plot of log (D_m-D_{nt}/D_{nt}) versus time in aqueous medium.

Table-2: Effect of concentration of methylene green on quantum yield for oxidation of ascorbic acid.
[AA]= 5.56×10^{-4} mol. dm^{-3}
Solvent=Water
Temperature=308 K

[MG] 10^6 (mol.dm^{-3})	Quantum Yield (φ)×10^2
1.11	22.982
3.33	22.998
5.56	23.000
7.78	23.112
10.0	23.124
12.22	23.012

Table-3: Effect of temperature on quantum yield for photchemical oxidation of ascorbic acid with methylene green in different solvent system.
[MG] =7.78×10^{-6} mol.dm^{-3}

[AA] 10^4 (mol.dm^{-3})	Quantum Yield (φ) ×10^2 at Temperatures, K			
	303	308	313	318
		Aqueous		
1.11	5.289	5.563	7.986	13.270
3.33	11.254	20.448	23.245	24.284
5.56	13.592	23.000	24.017	27.541
7.78	15.487	23.696	24.604	29.874
10.0	20.773	24.012	27.314	35.912
		10% Aqueous Methanol		
1.11	2.887	5.009	7.465	7.591
3.33	6.361	10.905	13.270	14.828
5.56	12.123	13.559	23.245	24.604
7.78	13.103	16.963	24.824	27.314
10.0	15.239	20.912	29.329	31.548
		10% Aqueous Ethanol		
1.11	2.432	3.102	5.285	6.643
3.33	5.439	5.910	12.617	12.818
5.56	7.792	9.832	17.021	18.959
7.78	7.968	12.464	17.255	20.600
10.0	13.385	14.610	24.012	29.652
		10% Aqueous Isopropanol		
1.11	1.161	2.098	3.881	4.141
3.33	2.149	5.066	6.534	8.094
5.56	3.597	6.142	10.397	11.713
7.78	4.726	9.084	10.774	13.282
10.0	5.886	11.972	14.128	15.514

The influence of ascorbic acid on the quantum yield was studied in the concentration ranges from 1.11×10^{-4} to 10.0×10^{-4} mol. dm^{-3}. The results summarized in Table 1 showed that quantum yields increased with the increase in concentration of ascorbic acid. The induced excitation and released protons reduced the dye molecules to leuco dye with dehydroxy ascorbic acid. Thus, the increase in concentration of ascorbic acid, increase the liberated protons formed by photo oxidation process as shown by the Fig. 3 and reaction followed pseudo first order kinetics with respect to ascorbic acid as shown in Fig. 2.

The effect of the concentration of methylene green on the quantum yield was studied using various concentrations of methylene green ranging from 0.1×10^{-5} to 1.2×10^{-5} mol.dm^{-3} at fixed concentration of ascorbic acid and temperature. The results tabulated in Table 2 showed that the quantum yield was independent of the concentration of methylene green as there was no significant change in the values of quantum yield observed. It may be explained on the basis of the fact that at higher concentration of methylene green, interaction of the protons of ascorbic acid with methylene green molecules was minimized [25]. Thus the oxidation of ascorbic acid by methylene green followed pseudo first order kinetics.

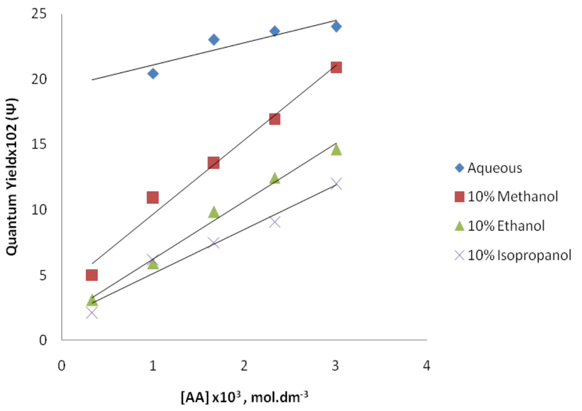

Fig. 3: Plot of quantum yield versus concentration of ascorbic acid in aqueous and aqueous alcoholic medium.

The effect of solvents regarding the polarity of medium on the quantum yield of reaction in aqueous and aqueous methanol, aqueous ethanol and aqueous isopropanol mixtures were studied using fixed concentration of ascorbic acid and methylene green. It was observed that the quantum yield decreased with the increase in the alcohol's content possessing low dielectric constant. The results tabulated in Table 1 showed that the reactants were more solvated than the activated complex in the low dielectric constant medium [26] and the following trend of quantum yield was observed.

Water > Aqueous methanol > Aqueous ethanol > Aqueous isopropanol

The effect of temperature on the quantum yield for photochemical reaction was studied at various temperatures ranging from 303 to 318 K at intervals of 5 K. The results summarized in Table 3 showed that quantum yield increased with the temperature show the rate of oxidation of ascorbic acid with methylene green increased. The increase in temperature accelerates the kinetic energy of reactant molecules which results in increasing the number of effective collisions and giving more products.

The effect of temperature on quantum yield was studied by Arrhenius relation [27].

$$\varphi = \mathrm{A.e}^{-\frac{\mathrm{E_a^*}}{\mathrm{RT}}} \qquad (2)$$

where R is gas constant, T is absolute temperature, A is frequency factor and E_a^* is the energy of activation. Energy of activation of the reaction was evaluated from the slope of the linear plot of ln φ versus 1/T shown in Fig 4. Results tabulated in Table 4 show that energy of activation increased with decrease of dielectric constant of the medium as the rate of reaction is high in aqueous medium and slow down as the alkyl chain of alcohol increased.

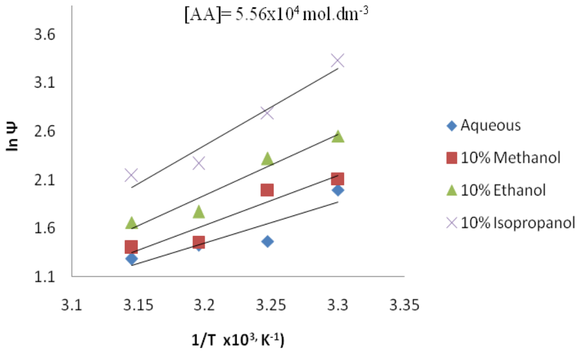

Fig. 4: Plot of ln Ψ versus 1/T.

The values of change in enthalpy of activation (ΔH^*), change in free energy of activation (ΔG^*) and change in entropy of activation (ΔS^*) were calculated using following relations and tabulated in Table 4.

$$\Delta \mathrm{H}^* = \mathrm{E}_a^* - \mathrm{RT} \qquad (3)$$

$$\Delta \mathrm{G}^* = \Delta \mathrm{H}^* - \mathrm{T}\,\Delta \mathrm{S}^* \qquad (4)$$

$$\Delta S^* = R \ln\left[\frac{Ah}{K_b T}\right] \qquad (5)$$

Where K_b is Boltzman constant, and h is Plank's constant.

Results showed that the change in enthalpy of activation (ΔH^*), change in free energy of activation (ΔG^*) and change in entropy of activation (ΔS^*) decreased with the increase in concentration of ascorbic acid and increased with decrease in dielectric constant. The decreasing values of change in free energy of activation with increase in concentration of ascorbic acid showed that the formation of activated state is spontaneous process. The negative values of entropy showed the decrease in randomness as a result of increase in charge on activated state as compare to individual ions. The activated state is less solvated than the reactants which restricts the motion of activated complex. The Gibbs free energy change of activation (ΔG^*) was found to be highest in aqueous isopropanol and lowest in water showed the formation of activated state is more favorable in water than in methanol, ethanol and isopropanol.

Table-4: Thermodynamic parameters for oxidation of ascorbic acid by methylene green at different concentrations of ascorbic acid
[MG] =7.78×10^{-6} mol.dm^{-3}
Temperature=308 K

[AA] .10^{4}, mol.dm^{-3}	**Energy of Activation (E_a^*) (kJ.mol^{-1})**	**Enthalpy change of Activation (ΔH^*) (kJ.mol^{-1})**	**Entropy change of Activation (ΔS^*) (J.mol^{-1}.K^{-1})**	**Free Energy change of Activation (ΔG^*) (kJ.mol^{-1})**
		Aqueous		
1.11	**49.753**	**47.192**	**-106.448**	**79.6592**
3.33	**39.301**	**36.740**	**-132.362**	**77.1109**
5.56	**34.834**	**32.273**	**-145.789**	**76.7391**
7.78	**32.297**	**29.736**	**-153.413**	**76.4853**
10.0	**28.306**	**25.745**	**-165.038**	**76.0817**
		10% Aqueous Methanol		
1.11	**53.129**	**50.568**	**-98.345**	**80.5649**
3.33	**44.042**	**41.481**	**-121.779**	**78.6235**
5.56	**42.677**	**40.116**	**-122.161**	**77.3749**
7.78	**41.484**	**38.923**	**-125.021**	**77.0135**
10.0	**40.512**	**37.952**	**-126.759**	**76.6131**
		10% Aqueous Ethanol		
1.11	**56.835**	**54.273**	**-88.755**	**81.3444**
3.33	**53.378**	**50.817**	**-93.702**	**79.3945**
5.56	**51.587**	**49.026**	**-96.229**	**78.3781**
7.78	**50.998**	**48.437**	**-97.394**	**78.1414**
10.0	**46.118**	**43.558**	**-110.255**	**77.1745**
		10% Aqueous Isopropanol		
1.11	**71.237**	**68.676**	**-46.329**	**82.8018**
3.33	**68.136**	**65.575**	**-50.735**	**81.0556**
5.56	**65.376**	**62.816**	**-56.422**	**80.0256**
7.78	**52.625**	**50.064**	**-95.781**	**79.2775**
10.0	**49.551**	**46.991**	**-103.771**	**78.6407**

Proposed Mechanism

On the basis of kinetic data the following reaction mechanism has been proposed for the oxidation of ascorbic acid with methylene green.

$$H_2A \xleftrightarrow{K_1} HA^- + H^+ \qquad (a)$$

$$HA^- \xleftrightarrow{K_2} A^{2-} + H^+ \qquad (b)$$

$$MG + H^+ \xleftrightarrow{K_3} MGH^+ \qquad (c)$$

$$MGH^+ + h\nu \rightarrow MGH_s^+ \qquad (d)$$

$$MGH_s^+ + H_2A \xrightarrow[slow]{k} MGH + HA^{\bullet} + H^+ \qquad (e)$$

$$MGH^+ + HA^{\bullet} \xrightarrow[fast]{} MGH + H^+ + A \qquad (f)$$

$$\text{Rate} = -\frac{d[MG]}{dt} = k[MGH^+][H_2A] \qquad (g)$$

$$K_3 = \frac{[MGH^+]}{[MG][H^+]} \qquad (h)$$

$$[MG] = \frac{[MGH^+]}{K_3[H^+]} \qquad (i)$$

$$[MGH^+] = K_3[MG][H^+] \qquad (j)$$

$$\text{Rate} = -\frac{d[MG]}{dt} = k[MGH^+][H_2A] \qquad (k)$$

$$\text{Rate} = -\frac{d[MG]}{dt} = kK_3[MG][H^+][H_2A] \qquad (l)$$

$$k' = kK_3[H^+] \qquad (m)$$

$$-\frac{d[MG]}{dt} = k'[MG][H_2A] \qquad (n)$$

$$-\frac{d[MG]}{dt} = k''[H_2A] \qquad (o)$$

$$k'' = k'[MG] \qquad (p)$$

where H_2A represents undissociated ascorbic acid, HA^- is the ascorbate monoanion, A^{-2} is the ascorbate dianion, [MG] is the total Methylene green, MGH^+ is the monoprotonated form of methylene green, MGH^+_s is the singlet excited state of monoprotonated form of methylene green, MGH is the reduced form of methylene green, A is the dehydroascorbic acid, K_1 and K_2 is the dissociation constants of ascorbic acid, K_3 is the formation constant for monoprotonated methylene green, and k is the rate constant for reduction of methylene green.

Conclusion

The rate of photochemical oxidation of ascorbic acid by methylene green was studied in terms of quantum yield of reaction. The quantum yield was found to be increased with the concentration of ascorbic acid, polarity of medium and temperature. It was concluded that the reaction followed pseudo first order kinetics. On the basis of Photokinetics data the reaction mechanism was proposed. Thermodynamic parameters were also evaluated and the decreasing value of change in free energy of activation with the concentration of ascorbic acid and polarity of medium showed the formation of activated complex is a spontaneous process.

Acknowledgement

The author (Sameera Razi Khan) gratefully acknowledges the financial support by Dean Science Research Grant by University of Karachi.

References

1. W. Azmi, R. K. Sani, U. C. Banerjee, Biodegradation of triphenylmethane dyes, *Enzyme Microb. Technol.*, **22,** 185 (1998).
2. K. M. Reza, A. Kurny, F. Gulshan, photocatalytic degradation of methylene blue by Magnetite+H_2O_2+UV process, *Int. J. Environ. Sci. Development*, **7**, 325 (2016).
3. M. Hema and S. Arivoli, Comparative study on the adsorption kinetics and thermodynamics of dyes onto acid activated low cost carbon, *Int. J. Phys. Sci*., **2**, 10 (2007).
4. O. Gulnaz, A. Kaya, F. Matyar, B. Arikan, Sorption of basic dyes from aqueous solution by activated sludge, *J. Hazard. Mater.*, **108**, 183 (2004).
5. M. Oelgemöller, N. Healy, L. Oliveira, C. Jung and J. Mattay, Green photochemistry: solar-chemical synthesis of Juglone with medium concentrated sunlight, *Green Chem..*, **8**, 831 (2006).
6. M. Oelgemöller, C. Jung, J. Ortner, J. Mattay, E. Zimmermann, Green photochemistry: solar photooxygenations with medium concentrated sunlight, *Green Chem.*, **7**, 35 (2005).
7. M. M. Nassar, Y. H. Magdy, Removal of different basic dyes from aqueous solutions by adsorption on palm-fruit bunch particles, *Chem. Eng. J*., **66**, 223 (1997).
8. R. P. Akermans, S. L. Roberts, R. G. Compton, Sono-electrosynthesis: electrode depassivation and trapping of insoluble redox products, *Chem. Commun.*, 1115 (1999).
9. S. R. Khan, R. Saeed, M. Ashfaq, S. Masood, Solvent effect on the oxidation of ascorbic acid, *Wulfenia,* **21**, 213 (2014).
10. Z. Khalid, R. Saeed, F. Uddin, M. Ashfaq, Kinetics of methylene green and ascorbic acid reaction in aqueous 2-propanol at different temperatures, *Amer. Chem. Sci. J.*, **4**, 229 (2014).
11. M. M. Rehman, M. A. Hasnat and K. Sawada, Degradation of commercial textile dye by fenton's reagent under xenon beam irradiation in aqueous medium, *J. Sci. Res.*, **1**, 108 (2009).
12. R. J. Ramirez, C. A. P. Arellano, A. A. A. Gallegos, A. E. J. Gonzalez and S. S. Martinez, H_2O_2-assisted TiO_2 generation during the photoelectrocatalytic process to decompose the acid green textile dye by Fenton reaction, *J. Photochem. Photobiol. A: Chem.*, **305**, 51 (2015).
13. T. Perez-Ruiz, C. Martinez-Lozano, V. Tomas and C. Sidrach, Flow injection Fluorimetric determination of ascorbic acid based on its photooxidation by thionine blue, *Analyst*, **122**, 115 (1997).
14. L. Venkatasubramanian, P. Maruthamuthu, Stopped-flow kinetic investigations of one-electron transfer reactions of phenothiazines and their radical cations in aqueous solution, *Bull. Chem. Soc. Jpn.*, 62, 3355 (1989).
15. A. Baffoun, A. El Ghali, I. Hachani, Decolorization kinetics of acid azo dye and basic thiazine dye in aqueous solution by UV/H_2O_2 and UV/Fenton: Effects of operational parameters, AUTEX *Res. J.*, **17**, 85 (2017).
16. K. R. Genwa, I. Prakasa, Photogalvanic effect: Comparative studies in three dyes Rhodamine B, Methylene blue and Safranine, *J. Indian Chem. Soc.*, **83**, 165 (2006).
17. V. K. Gupta, R. Jain, A. Mittal, M. Mathur and S. Sikarwar, Photochemical degradation of the hazardous dye Safranin-T using TiO_2 catalyst, *J. Colloid Interface Sci.*, **309**, 464 (2007).
18. M. El-Kemary, Y. Abdel-Moneam, M. Madkour, I. El-Mehasseb, Enhanced photocatalytic degradation of Safranin-O by heterogeneous nanoparticles for environmental applications, *J. Luminescence*, **131**, 570 (2011).
19. R. Chhajed, S. Sharma, R. Ameta, P. B. Punjabi, Silver(I) Catalyzed photochemical oxidation of methylene blue and safranine-O by peroxydisulphate: A green chemical approach, *Int. J. Photochem.*, **9**, 1 (2014).
20. G. Elango, S. M. Roopan, Efficacy of SnO_2 nanoparticles toward photocatalytic degradation of methylene blue dye, *J. Photochem. Photobiol. B: Biology*, **155**, 34 (2016).
21. M. Shanthi, V. Kuzhalosai, Photocatalytic degradation of an azo dye, Acid Red 27, in aqueous solution using nano ZnO, *Indian. J. Chem.*, **51A**, 428 (2012).
22. X. Ou, X. Quan, S. Chen, F. Zhang and Y. Zhao, Photocatalytic reaction by Fe(III)-citrate complex and its effect on the photodegradation of atrazine in aqueous solution, *J. Photochem. Photobiol. A: Chemistry*, **197**, 382 (2008).
23. A. Rezaee, M. T. Ghaneian, A. Khavanin, S. J. Hashemian, Gh. Moussavi, Gh. Ghanizadeh, E. Hajizadeh, Photochemical oxidation of reactive blue 19 dye in textile wastewater by UV/$K_2S_2O_8$ process, *Iran. J. Environ. Health. Sci. Eng.*, **5**, 95 (2008).
24. R. Azmat, N. Qamar and R. Naz, A new approach for reduction of methylene green with

ascorbic acid by de-oxygenation through carbondioxide, *Nat. Sci.*, **3**, 566 (2011).

25. R. Saeed and S. M. S. Nadeem, The kinetics of electron transfer reaction of methylene green and titanium trichloride in different solvents**,** *Russ. J. Phy. Chem.* A, **90**, 1143 (2016).
26. F. Uddin, Z. Khalid, Study of the rates of reaction between β-Monobromopropionate and thiosulphate ions in isodielectric media of aqueous n-propanol, *J. Isl. Acad. Sci*., **5**,4, 237 (1992**)**.
27. M. A. Tabbara, M. M. El Jamal, A kinetic study of discoloration of methylene blue by $Na_2S_2O_3$, comparison with NaOH, *J. Univ. Chem. Technol. Metall.*, **47**, 275 (2012).

.