

PHOTO ASSISTED MINERALIZATION OF AMARANTH BY IRON CONTAINING WELL-DAWSON HETEROPOLY ANION

DAKSHA SHARMA^A AND RAKSHIT AMETA^{*B}

^aDepartment of Chemistry, Vidya Bhawan Rural Institute, Udaipur (Raj.) India

^bDepartment of Chemistry, Shramjeevi College, J.R.N. Rajasthan Vidyapeeth University,
Udaipur (Raj.) India

ABSTRACT

Dyes, phenols, pesticides, fertilizers, detergents and many other chemical products are disposed off directly into the environment, without being treated and without an effective treatment strategy, which creates water pollution. This problem can be solved by photocatalytic degradation. Photoassisted mineralization of Amaranth was carried out using iron containing Well-Dawson Heteropoly anion with visible light. In the present investigation, the effect of various operational parameters like effect of pH, concentration of dye, amount of semiconductor and light intensity were studied. Kinetic studies reveal that the photocatalytic degradation follows pseudo-first order kinetics. A tentative mechanism for the photocatalytic degradation of Amaranth has been proposed.

Keywords:- Water pollution, Photoassisted Mineralization, Photocatalytic degradation, Amaranth, Well-Dawson Heteropoly anion

1. INTRODUCTION

Photocatalysis is a promising technology for waste water treatment, particularly for the mineralization of non-biodegradable, and toxic components in water. Kansal et al.[1] carried out photocatalytic degradation of methyl orange and rhodamine 6G employing heterogeneous photocatalytic process. Stasinakis[2] reviewed the use of titanium dioxide/UV light process, hydrogen peroxide/UV light process and Fenton's reaction in waste water treatment. Aluminium (III)-modified TiO₂ was prepared by sol-gel process and the degradation of dye pollutants under visible irradiation was examined by Zhao et al.[3] Photocatalytic activity of TiO₂-In₂O₃ powders for the degradation of 2-chlorophenol in water was reported by Shchukin et al.[4] Photocatalytic degradation of methyl orange and methylene blue by heterogeneous photocatalytic process using TiO₂ as semiconductor was carried out by Mehra and Sharma[5].

Abo-Farha[6] reported homogeneous photocatalytic degradation of two azo dyes acid orange 10 and acid red 114 in waste water. Bhardwaj et al.[7] used suspended TiO₂ nanoparticles and sunlight irradiation for photocatalytic treatment of giemsa dye at optimum pH. Mahyar et al.[8] reported the degradation of basic violet 2 (New fuchsin) using TiO₂-SiO₂ nanoparticles by the sol-gel method using titanium tetraisopropoxide as a titanium source. Reeves et al.[9] carried out photocatalytic destruction of organic dyes using TiO₂ and natural solar energy. Qamar et al.[10] selected two dyes chromotrope 2B and amido black 10B for photocatalytic degradation in aqueous suspensions of TiO₂ in the presence of light and oxygen.

The photo catalytic activities of ZnO/Cu₂O compound were evaluated using a basic organic dye, methyl orange (MO) by Xu et al.[11] The photocatalytic bleaching of azure-B was carried out by Sharma et al.[12] in the presence of semiconductor bismuth oxide. The photocatalysed degradation of acridine orange dye has been investigated by Pare et al.[13] in aqueous suspension of BaCrO₄ under variety of conditions. The photocatalytic activity of the CdS/TiO₂ was investigated by Tristao et al.[14] using artificial UV light for degradation of the textile azo-dye drimaren red. Sharma et al.[15] used bismuth sulfide as photo catalyst for the degradation of rose bengal.

Kim et al.[16] used visible light illuminated aqueous solution of polyoxometalate as an electron transfer catalyst in the simultaneous conversion of dye and hexavalent chromium. They used rhodamine B, methylene blue and acid orange 7 as test dyes. Chen et al.[17] used microporous solid K₃PW₁₂O₄₀ as a photocatalyst for the degradation of a series of dye pollutants such as rhodamine B, malachite green, rhodamine 6 G, fuchsin basic and methyl violet in the presence of H₂O₂ under visible light irradiation. Fu et al.[18] synthesized one new polyoxometalate compound and three new polyoxometalate-based metal organic frameworks under ionothermal condition using an ionic liquid and their structures were determined by single X-ray diffraction. Photoreactive decatungstates Na₄W₁₀O₃₂ and (nBu₄N)₄W₁₀O₃₂ were heterogenized inside the silica network via a sol-gel technique by Guo et al.[19] Neutral red was subjected to two different advanced oxidative processes, namely the photo-Fenton process and the photocatalytic process by Alnuaimi et al.[20]

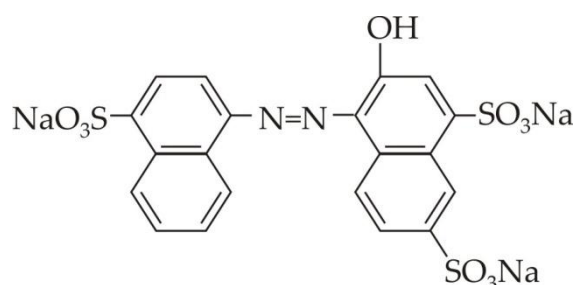
2. RESEARCH METHOD

Preparation of iron containing Well-Dawson Heteropoly anion $\text{Na}_{11}[\text{CuFeW}_{18}\text{O}_{62}]$ photocatalyst

Well-Dawson Heteropoly anion was prepared by the reaction between cupric chloride, ferric chloride and sodium metatungstate. The mixture of 40 mL cupric chloride dihydrate $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ solution (1.1 g, 6.45 mmol) and 40 mL ferric chloride FeCl_3 (1 g, 6 mmol) was added dropwise to 100 mL sodium metatungstate solution prepared by dissolving (36.6 g, 110.96 mmol) with continuous stirring till constant pH. 10 mL of glacial acetic acid was added to maintain the acidic conditions. After the addition of 68 mL of the above mixed solution to sodium metatungstate solution, the pH of the final mixture became constant at 4.0. The mixture was refluxed for 4-5 hrs. It was ice cooled, filtered and the filtrate was left overnight for crystallization. Blue crystals were separated out, which were washed with n-hexane and preserved for the analysis. In the present work, Well-Dawson Heteropoly anion $\text{Na}_{11}[\text{CuFeW}_{18}\text{O}_{62}]$ has been used as a photocatalyst for the degradation of dye amaranth.

Photocatalytic Degradation of Amaranth using $\text{Na}_{11}[\text{CuFeW}_{18}\text{O}_{62}]$

Molecular formula of Amaranth : $\text{C}_{20}\text{H}_{11}\text{N}_2\text{Na}_3\text{O}_{10}\text{S}_3$



Structure of Amaranth

A solution of 2.00×10^{-5} M amaranth was prepared in doubly distilled water and 0.10 g of Well-Dawson Heteropoly anion was added to it. The pH of the reaction mixture was adjusted to 7.5 and then this solution was exposed to a 200 W tungsten lamp at 50.0 mWcm^{-2} . The optical density of amaranth solution was determined with the help of a spectrophotometer at $\lambda_{\text{max}} = 520 \text{ nm}$.

The light intensities at various distances from the lamp were measured with the help of a solarimeter (Suryamapi CEL 201). A water filter was used to cut thermal radiations. A digital pH meter (Systronics Model 335) was used to adjust the pH of the solutions by the addition of previously standardized 0.1 N sulfuric acid and 0.1 N sodium

hydroxide solutions. Controlled experiments were also carried out to confirm that reaction is photocatalytic in nature.

3. RESULTS AND ANALYSIS

The photocatalytic degradation of amaranth was observed at $\lambda_{\max} = 520$ nm. The plot of log O.D. v/s time was found to be a straight line. This indicates that the photocatalytic degradation of dye in presence of Well-Dawson Heteropoly anion follows pseudo-first order kinetics and the rate constant of this reaction was determined using the following expression:

$$k = 2.303 \times \text{slope}$$

The observations for typical run are given in Table 1 and graphically represented in Figure 1.

Table 1: A TYPICAL RUN

pH = 7.5

[Amaranth] = 2.00×10^{-5} M

Well-Dawson Heteropoly anion = 0.10 g

Light Intensity = 50.0 mWcm^{-2}

Time (min.)	Optical Density (O. D.)	1 + log O. D.
0	0.562	0.7497
10	0.501	0.6998
20	0.426	0.6294
30	0.380	0.5798
40	0.331	0.5198
50	0.285	0.4548
60	0.251	0.3997
70	0.223	0.3483
80	0.195	0.2900
90	0.170	0.2304
100	0.149	0.1732
110	0.132	0.1206

$$\text{Rate constant (k)} = 2.22 \times 10^{-4} \text{ sec}^{-1}$$

3.1 EFFECT OF pH

The pH of the solution may affect degradation rate of amaranth and hence, the effect of pH on photocatalytic degradation of amaranth was investigated in the pH range 5.0 - 10.5. The results are reported in Table 2 and graphically presented in Figure 2.

Table 2 : EFFECT OF pH

[Amaranth] = 2.00×10^{-5} M

Well-Dawson Heteropoly anion = 0.10 g

Light Intensity = 50.0 mWcm^{-2}

pH	$k \times 10^4 \text{ (sec}^{-1}\text{)}$
5.0	1.09
5.5	1.41
6.0	1.53
6.5	1.80
7.0	2.01
7.5	2.22
8.0	1.84
8.5	1.27
9.0	1.17
9.5	1.02
10.0	0.76
10.5	0.53

It has been observed that the rate of photocatalytic degradation of amaranth increases with increase in pH upto 7.5. A further increase in pH above 7.5 results in a decrease in the rate of reaction. An increase in the rate of photocatalytic degradation of amaranth with increase in pH may be due to generation of more $\bullet\text{OH}$ radicals, which are produced from the reaction between OH^- ions and hole (h^+) of the semiconductor. On further increase in pH above 7.50, a decrease in the rate of photocatalytic degradation of the dye may be due to the fact that amaranth is present in its anionic form, which will experience a force of repulsion with negatively charged surface of the semiconductor due to adsorption of more OH^- ions on the surface of photocatalyst.

3.2 EFFECT OF DYE CONCENTRATION

Effect of variation of dye concentration was also observed by taking different concentrations of amaranth. The results are tabulated in Table 3 and graphically represented in Figure 3.

Table 3: EFFECT OF AMARANTH CONCENTRATION

pH = 7.5

Well-Dawson Heteropoly anion = 0.10 g

Light Intensity = 50.0 mWcm⁻²

[Amaranth] × 10 ⁵ M	k × 10 ⁴ (sec ⁻¹)
1.00	0.96
1.20	1.27
1.40	1.43
1.60	1.53
1.80	1.77
2.00	2.22
2.20	1.72
2.40	1.62
2.60	1.43

It is evident from the data that the rate of photocatalytic degradation of dye increases with an increase in concentration of the dye. It may be explained on the basis that as the concentration of the dye was increased, more dye molecules were available for excitation and consecutive energy transfer and hence, an increase in the rate of photocatalytic degradation of the dye was observed. The rate of photocatalytic degradation was found to decrease with an increase in the concentration of dye above 2.00 × 10⁻⁵ M. It may be due to the fact that the dye itself may start acting as an internal filter for the incident light and it will not permit the desired light intensity to reach the semiconductor particles and as a result, the degradation rate decreases.

3.3 EFFECT OF AMOUNT OF SEMICONDUCTOR

The amount of semiconductor may also affect the rate of degradation of dye and hence, different amounts of photocatalyst were used. The results are reported in Table 4 and graphically presented in Figure 4.

Table 4 : EFFECT OF AMOUNT OF SEMICONDUCTOR

pH = 7.5

[Amaranth] = 2.00×10^{-5} M

Light Intensity = 50.0 mWcm^{-2}

Amount (g)	$k \times 10^4 (\text{sec}^{-1})$
0.02	1.27
0.04	1.57
0.06	1.70
0.08	2.05
0.10	2.22
0.12	2.18
0.14	2.20
0.16	2.09
0.18	2.19

It has been observed that the rate of photocatalytic degradation of amaranth increases on increasing the amount of semiconductor Well-Dawson Heteropoly anion but it became virtually constant after a particular amount i.e. 0.10 g. It may be attributed to the fact that as the amount of semiconductor was increased, there was an increase in exposed surface area of the semiconductor, but after a certain limit (0.10 g), increase in the amount of semiconductor will not increase the exposed surface area.

It may be considered like a saturation point; above which there is negligible or no effect on the rate of photocatalytic degradation of dye, as an increase in the amount of semiconductor after this amount will only increase the thickness of the layer at the bottom of the reaction vessel and not the exposed surface area. This was confirmed by taking reaction vessels of different dimensions. The saturation point shifts to higher side for larger vessels, while reverse trend was observed for smaller vessels.

3.4 EFFECT OF LIGHT INTENSITY

The effect of light intensity on photocatalytic degradation of amaranth was observed by changing the distance between the light source and the exposed surface of semiconductor. The results are summarized in Table 5 and graphically presented in Figure 5.

Table 5 : EFFECT OF LIGHT INTENSITY

pH = 7.5

[Amaranth] = 2.00×10^{-5} M

Well-Dawson Heteropoly anion = 0.10 g

Intensity of light (mWcm^{-2})	$k \times 10^4$ (sec^{-1})
20.0	0.80
30.0	1.11
40.0	1.43
50.0	2.22
60.0	1.63
70.0	1.04

These results indicate that photocatalytic degradation of dye was accelerated as the intensity of light was increased, because an increase in the light intensity will increase the number of photons striking per unit area of semiconductor per unit time. On further increasing the intensity of light above 50.0 mWcm^{-2} there was a decrease in the rate of reaction. This may be due to some side reactions or thermal effect.

3.5 MECHANISM

On the basis of these observations, a tentative mechanism for photocatalytic degradation of amaranth may be proposed as –



Leuco AM \longrightarrow Products (6)

Amaranth (AM) dye absorbs radiations of suitable wavelength and gives rise to its first excited singlet state. Then it undergoes intersystem crossing (ISC) to give the triplet state. On the other hand, the semiconducting Well-Dawson Heteropoly anion (SC) also utilizes the radiant energy to excite its electron from valence band to the conduction band, thus, leaving behind a hole. This hole abstracts an electron from OH^- ions to generate $\bullet\text{OH}$ radicals. These radicals will oxidize the dye to its leuco form, which may ultimately degrade to products. The participation of $\bullet\text{OH}$ radicals as an active oxidizing species was confirmed by using hydroxyl radical scavengers (isopropanol), where the rate of degradation was drastically reduced.

4. CONCLUSION

Photoassisted mineralization of Amaranth dye was carried out successfully by using iron containing Well-Dawson Heteropoly anion. The optimum conditions for photocatalytic degradation were pH 7.5, concentration of dye $2.00 \times 10^{-5}\text{M}$, amount of semiconductor 0.10 g and light intensity 50.0mWcm^{-2} .

ACKNOWLEDGEMENT

The authors are grateful to the Professor Suresh C. Ameta, Director, Pacific College of Basic and Applied Sciences, PAHER University, Udaipur (Raj.) for providing necessary laboratory facilities and his valuable suggestions.

REFERENCES

- [1] Kansal S.K, Singh M. and Sud D., Studies on Photodegradation of Two Commercial Dyes in Aqueous Phase Using Different Photocatalysts, *J. Hazard. Mater.*, vol. **141** (3), pp. 581-590 , 2007.
- [2] Stasinakis A.S., Use of Selected Advanced Oxidation Processes (AOPs) for Wastewater Treatment - A Mini Review, *Global Nest J.*, vol. **10** (3), pp. 376-385 , 2008.
- [3] Zhao D., Chen C, Wang Y, Ma W, Zhao J, Rajh T and Zang L, Enhanced Photocatalytic Degradation of Dye Pollutants Under Visible Irradiation on Al (III)-modified TiO_2 : Structure, Interaction and Interfacial Electron Transfer, *Environ. Sci. Technol.*, vol. **42** (1), pp. 308-314 , 2008.

- [4] Shchukin D, Poznyak S, Kulak A and Pichat P, TiO₂-In₂O₃ Photocatalysts: Preparation, Characterisations and Activity for 2- Chlorophenol Degradation in Water, *J. Photochem. Photobiol. A: Chem.*, vol. **162** (2-3), pp. 423-430 ,2004.
- [5] Mehra M and Sharma T.R , Photocatalytic Degradation of Two Commercial Dyes in Aqueous Phase Using Photocatalyst TiO₂, *Adv. Appl. Sci. Res.*, vol. **3** (2), pp. 849-853, 2012.
- [6] Abo-Farha S.A , Photocatalytic Degradation of Monoazo and Diazo Dyes in Waste Water on Nanometer-Sized TiO₂, *J. Ameri. Sci.*, vol. **6** (2), pp. 130-142, 2010.
- [7] Bhardwaj L, Bhardwaj M and Sharma M.K, TiO₂ Mediated Photocatalysis of Giemsa Dye: An Approach Towards Biotechnology Laboratory Effluent Treatment, *J. Environ. Anal. Toxicol.*, vol. **1** (4), pp. 1-6, 2011.
- [8] Ali Mahyar, Behnajady M.A and Modirshahla N, Characterization and Photocatalytic Activity of SiO₂-TiO₂ Mixed Oxide Nanoparticles Prepared by the Sol-Gel Method, *Indian J. Chem.*, vol. **49 A**, pp. 1593-1600, 2010.
- [9] Reeves P, Ohlhausen R, Sloan D, Pamplin K and Scoggins T, Photocatalytic Destruction of Organic Dyes in Aqueous TiO₂ Suspensions Using Concentrated Simulated and Natural Solar Energy, *Solar Energy*, vol. **48**, pp. 413-420 , 1992 .
- [10] Qamar M, Saquib M and Muneer M, Photocatalytic Degradation of Two Selected Dyes Chromotrope 2B and Amido Black 10B in Suspensions of Titanium Dioxide, *Dyes Pigments*, vol. **65**, pp. 1-9, 2005.
- [11] Xu C, Cao L, Su G, Liu W, Liu H, Yu Y and Qu X, Preparation of ZnO/Cu₂O Compound Photocatalyst and Application in Treating Organic Dyes , *J. Hazard. Mater.*, vol. **176** (1-3), pp. 807-813, 2010.
- [12] Sharma D, Bansal A, Ameta R and Sharma H.S, Photocatalytic Degradation of Azure B Using Bismuth Oxide Semiconductor Powder, *Int. J. Chem. Tech. Res.*, vol. **3** (2), pp.1008-1014, 2011.
- [13] Pare B, Singh V, More P and Thapak T.R , Visible Light Induced Degradation of Acridine Orange Dye Over BaCrO₄ Photocatalyst, *Int. J. Chem. Sci.*, vol. **9** (2), pp. 537-549, 2011.

- [14] Tristao J.C, Magalhaes F, Corio P, Terezinha M and Sansiview C, Electronic Characterization and Photocatalytic Properties of CdS/TiO₂ Semiconductor Composite, *J. Photochem. Photobiol. A : Chem.*, vol. **181**, pp. 152-157 , 2006.
- [15] Sharma S, Ameta R, Malkani R.K and Ameta S.C, Use of Semi-Conducting Bismuth Sulfide as a Photocatalyst for Degradation of Rose Bengal, *Macedonian J. Chem. Chem. Eng.*, vol. **30** (2), pp. 229-234 , 2011.
- [16] Kim S, Yeo J and Choi W, Simultaneous Conversion of Dye and Hexavalent Chromium in Visible Light-Illuminated Aqueous Solution of Polyoxometalate as an Electron Transfer Catalyst, *Appl. Catal. B : Environ.*, vol. **84** (1-2), pp. 148-155 , 2008.
- [17] Chen C, Wang Q, Lei P. Song W, Ma W and Zhao J, Photodegradation of Dye Pollutants Catalyzed by Porous K₃PW₁₂O₄₀ Under Visible Irradiation, *Environ. Sci. Technol.*, vol. **40** (12), pp. 3965-3970 , 2006.
- [18] Fu H, Li Y, Lu Y, Chen W, Wu Q, Meng J, Wang X, Zhang Z and Wang E, Polyoxometalate-Based Metal-Organic Frameworks Assembled Under the Ionothermal Conditions, *Cryst. Growth. Des.*, vol. **11** (2), pp. 458-465 , 2011.
- [19] Guo Y, Hu C, Wang X, Wang E, Zou Y, Ding H and Feng S, Microporous Decatungstates : Synthesis and Photochemical Behaviour, *Chem. Mater.*, vol. **13** (11), pp. 4058-4064 , 2001.
- [20] Alnuaimi M.M , Rauf M.A and Ashraf S.S, A Comparative Study of Neutral Red Decoloration by Photo-Fenton and Photocatalytic Processes, *Dyes Pigments*, vol. **76** (2), pp. 332-337, 2008.

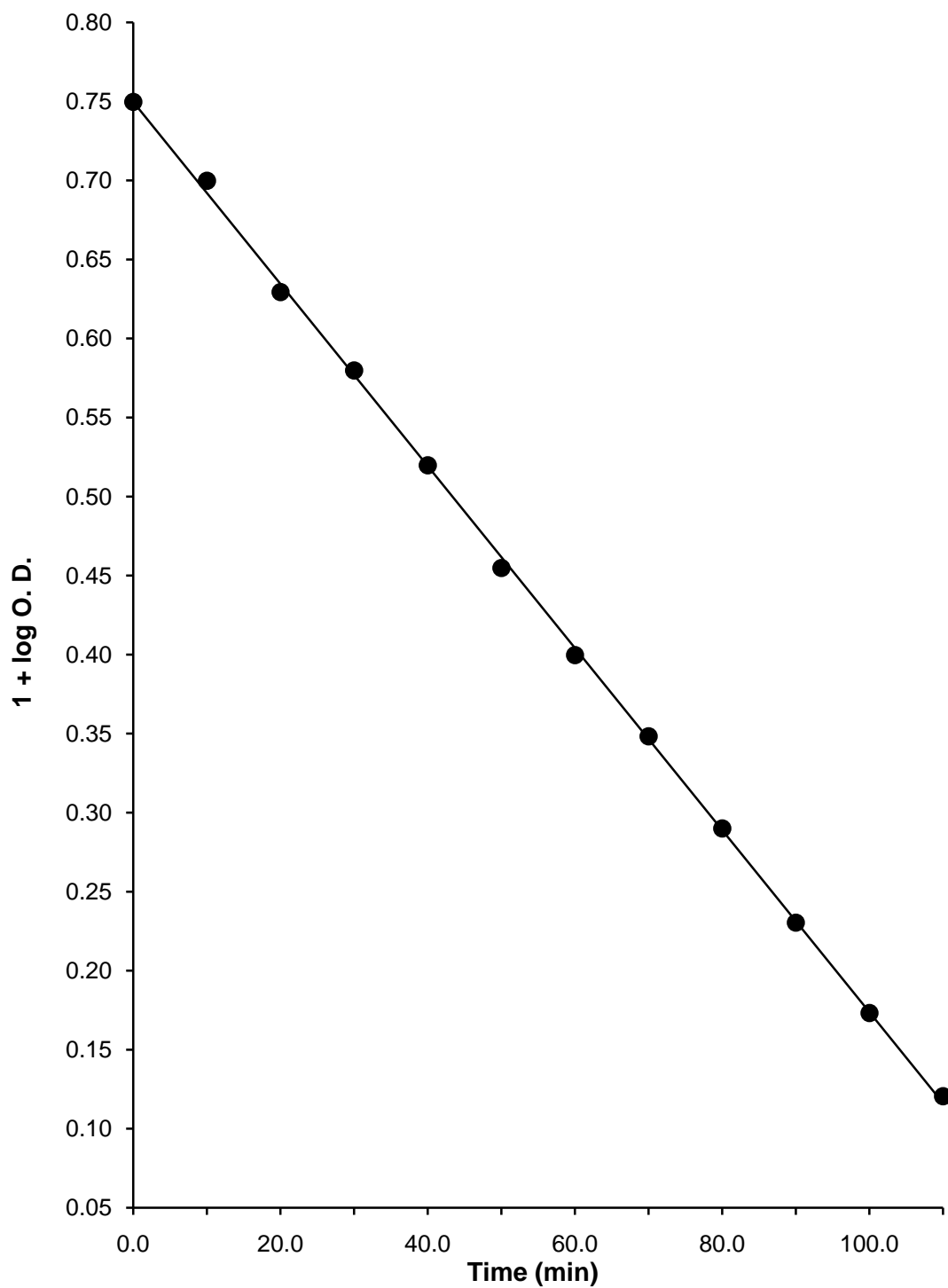


Fig. 1 : A TYPICAL RUN

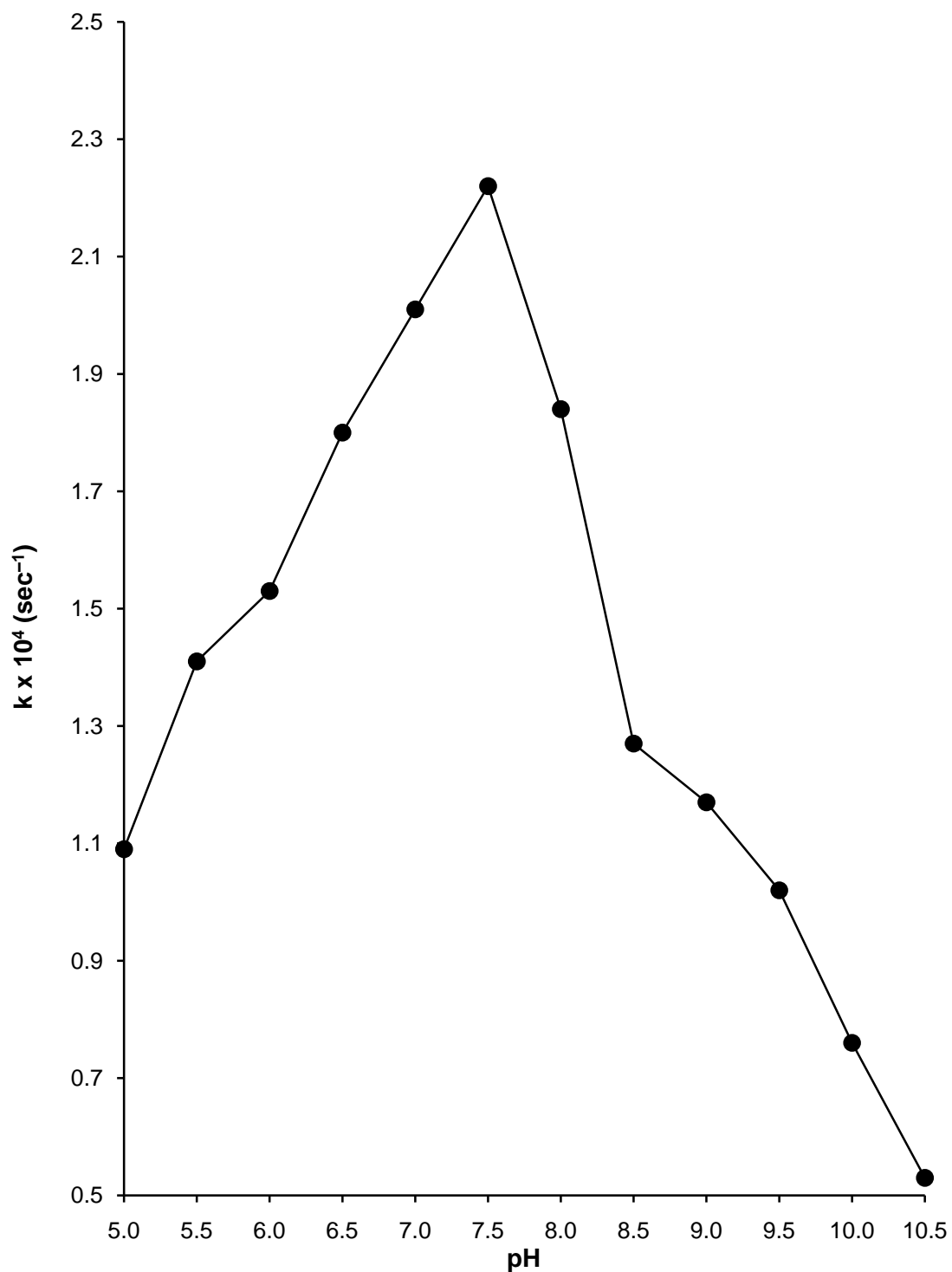


Fig.2 : EFFECT OF pH

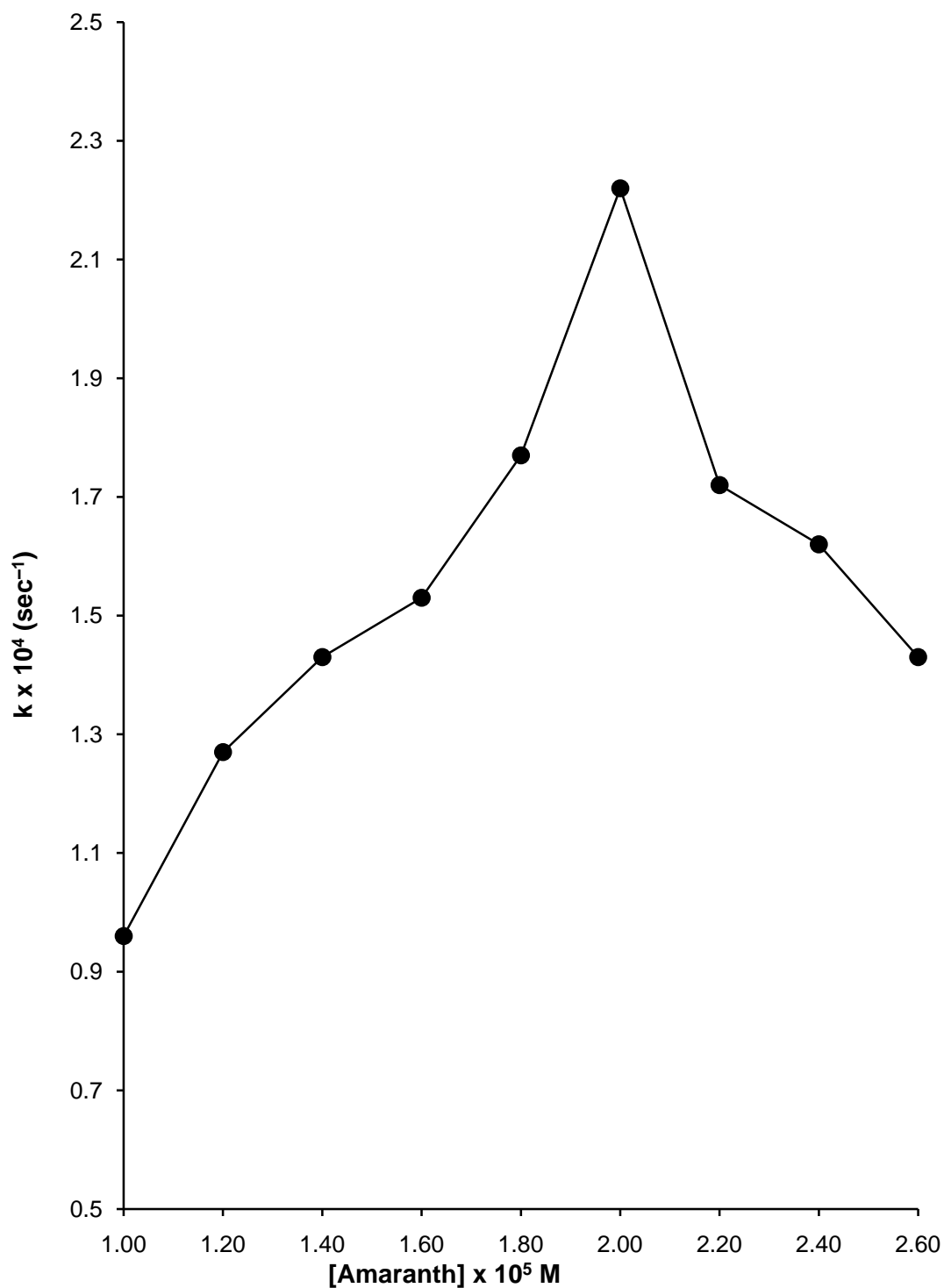


Fig. 3 : EFFECT OF DYE CONCENTRATION

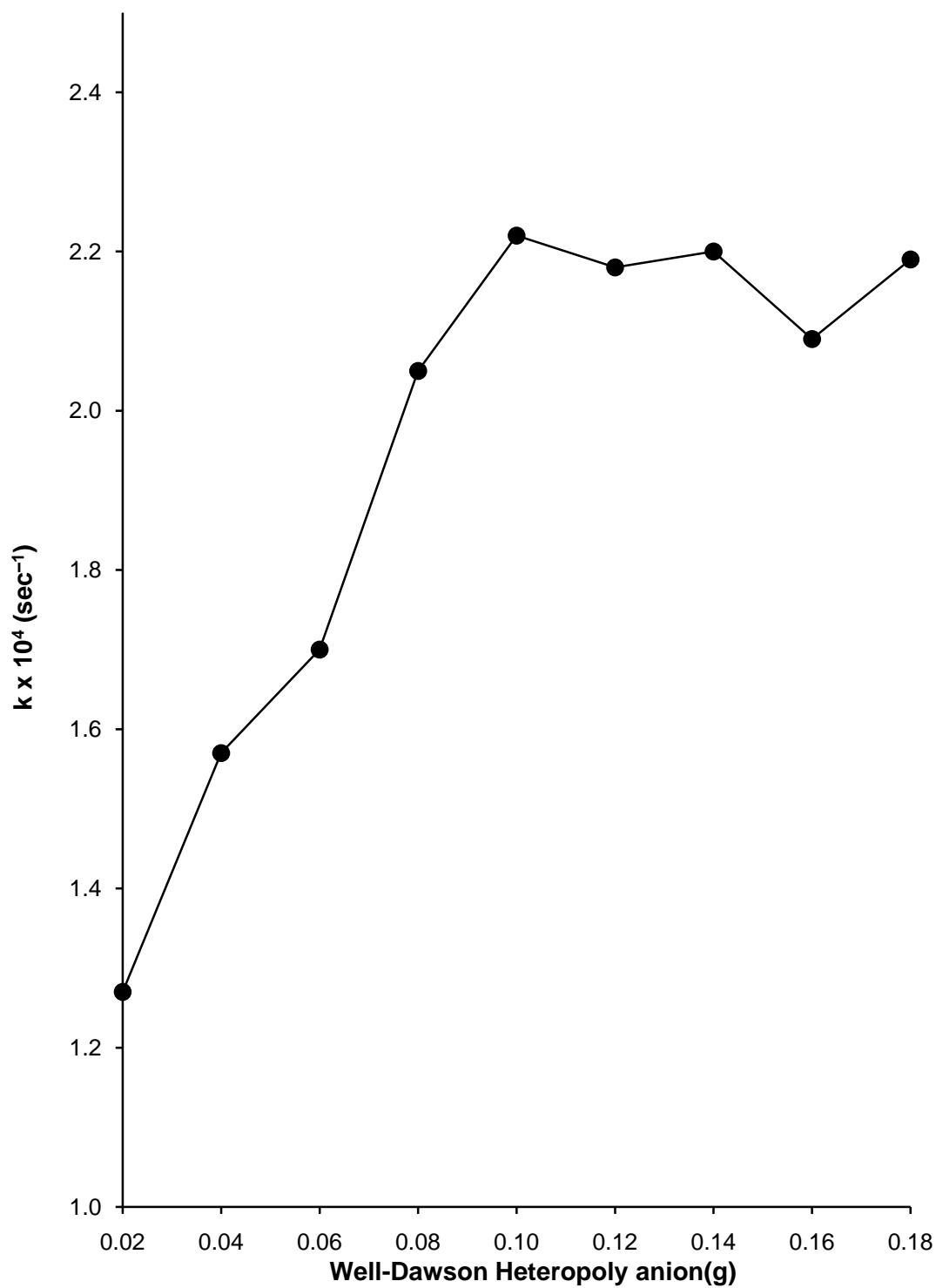


Fig. 4 : EFFECT OF AMOUNT OF SEMICONDUCTOR

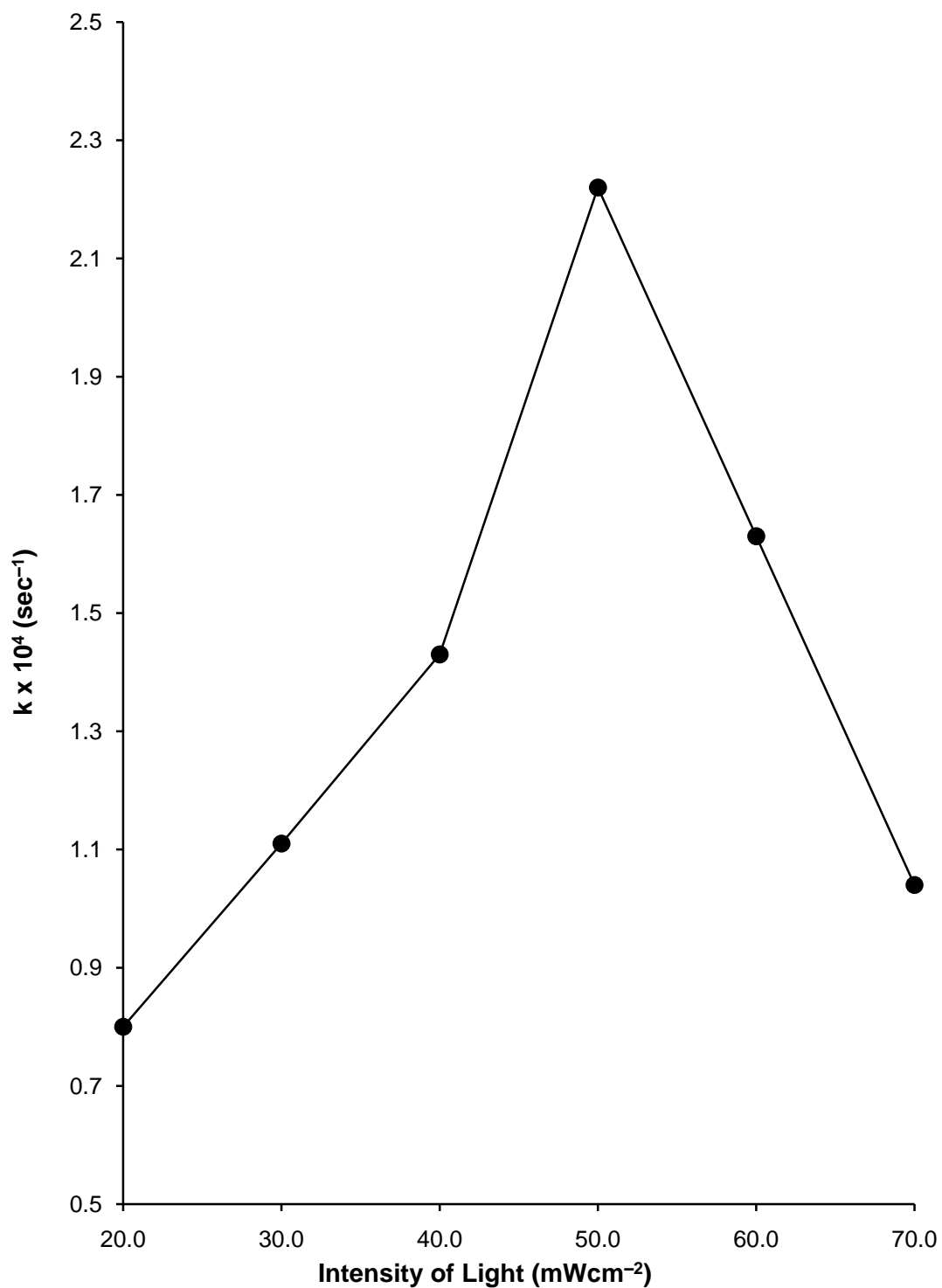


Fig. 5 : EFFECT OF LIGHT INTENSITY