



Na₁₁[CuFeW₁₈O₆₂] MEDIATED PHOTOCATALYTIC DEGRADATION OF METHYLENE BLUE

Rakshit Ameta¹

¹Department of Chemistry, Shramjeevi College, Vidhyapeeth University, Udaipur (Raj.) India

Mamta Ordia²

²Central Academy School, Sardarpura, Udaipur (Raj.) India

Daksha Sharma³

³Department of Chemistry, Vidya Bhawan Rural Institute, Udaipur (Raj.) India

ABSTRACT

Photocatalysis is an ecofriendly approach to degrade organic pollutants like dyes. In the present investigation, photocatalytic degradation of methylene blue has been carried out utilizing visible light and Na₁₁[CuFeW₁₈O₆₂] as a photocatalyst. The effect of various operational parameters such as variation of pH, dye concentration, amount of semiconductor and light intensity on the rate of degradation of dye has been studied. Kinetic studies reveal that the photocatalytic degradation follows pseudo-first order kinetics. A tentative mechanism for the photocatalytic degradation of methylene blue has also been proposed.

KEYWORDS : Methylene blue, Photocatalytic degradation, Na₁₁[CuFeW₁₈O₆₂]

INTRODUCTION

In photocatalysis, organic pollutants can be completely mineralized reacting with the oxidant to form CO₂, water and inorganic ions. Photocatalytic degradation of amaranth, an alimentary dye, was investigated by Karkmaz et al.¹ in an irradiated titanium dioxide aqueous suspension. Han et al.² used heterogeneous photocatalysis involving titanium dioxide for degradation of organic dyes. Bamba et al.³ studied the photocatalytic degradation of the pesticide diuron in aqueous solution in presence of two commercial TiO₂ catalysts, P₂₅ and PC 500. The photocatalytic degradation of the three pesticides acephate, dimethoate, and glyphosate in water has been investigated by Echavia et al.⁴, where they used TiO₂

immobilized on silica gel as photocatalyst in presence of UV light. Seven azo dyes orange G, acid orange 7, new Coccine, acid black 1, tartrazin, acid Yellow 17 and congo red were photocatalytically degraded in TiO₂ suspension by Tanaka et al.⁵ Photocatalytic reduction of azo dyes naphthol blue black and disperse blue 79 have been reported by Nasr et al.⁶ Sangchakr et al.⁷ studied photocatalytic degradation of sodium benzene sulfonate and its substituted compounds. The experiment was carried out under 500 W super high pressure mercury lamp in TiO₂ suspension.

The potential of a common semiconductor, ZnO, has been explored by Chakrabarti and Dutta⁸ as effective catalyst for the photodegradation of two model dyes, methylene blue and eosin Y. Ameta et al.⁹

also used semiconducting iron (III) oxide as a photocatalyst for bleaching of methylene blue, crystal violet and malachite green dyes.

Photocatalytic properties of Zn₂SnO₄ nanocrystals was investigated by Lou et al.¹⁰ ZnS-CdS catalysed photocatalytic bleaching of malachite green and brilliant green dyes has been investigated by Gandhi et al.¹¹ Sharma et al.¹² used nickel sulphide as photocatalyst for the production of desalinated water.

Martinez et al.¹³ used Sm₂FeTaO₇ as solar photocatalyst for the degradation of indigo carmine dye in aqueous solution. Estrada et al.¹⁴ carried out photo-Fenton degradation of diclofenac. Agustina et al.¹⁵ reviewed the field of integrated photocatalysis and ozonation for waste water treatment. The photofading mechanism of 16 commercial dyes was investigated by Batchelor et al.¹⁶

Israel et al.¹⁷ synthesized manganese (III) containing Well-Dawson sandwich type polyoxometalates and carried out comparison with their manganese (II) counterparts. Wang and Yang¹⁸ prepared silicotungstic acid and phosphotungstic acid and used these for photocatalytic degradation of organic dye methyl orange. Mylonas et al.¹⁹ reported mineralization of various aromatic derivatives and chlorinated acetic acids by using polyoxometalates. Liu and Xu²⁰ carried out photodegradation of textile dye X₃B and photoreduction of dichromate in the presence of a POM.

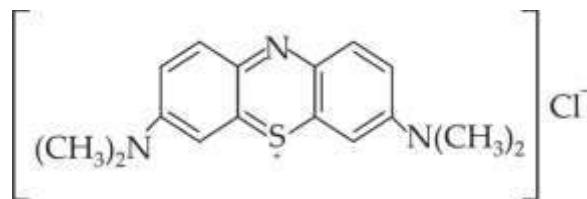
EXPERIMENTAL

Preparation of Well-Dawson Polyoxometalate Na₁₁[CuFeW₁₈O₆₂] photocatalyst

Well-Dawson polyoxometalate was prepared by the reaction between cupric chloride, ferric chloride and sodium metatungstate. The mixture of 40 mL cupric chloride dihydrate CuCl₂.2H₂O solution (1.1 g, 6.45 mmol) and 40 mL ferric chloride FeCl₃ (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 polyoxometalate Na₁₁[CuFeW₁₈O₆₂] has been used as a photocatalyst for the degradation of dye methylene blue.

Photocatalytic Degradation of Methylene Blue using Na₁₁[CuFeW₁₈O₆₂]

Molecular formula of Methylene Blue :
C₁₆H₁₈N₃SCl.3H₂O



Structure of Methylene blue

A solution of 1.0 × 10⁻⁵ M methylene blue was prepared in doubly distilled water and 0.10 g of Well-Dawson polyoxometalate was added to it. The pH of the reaction mixture was adjusted to 7.50 and then this solution was exposed to a 200 W tungsten lamp (visible light, Philips) at 50.0 mWcm⁻². The optical density of methylene blue solution was determined with the help of a spectrophotometer (Systronics Model 106) at λ_{max} = 664 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.

RESULTS AND DISCUSSION

The photocatalytic degradation of methylene blue was observed at λ_{max} = 664 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 polyoxometalate 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. (See Figures)

Table 1 : A TYPICAL RUN

pH = 7.5 [Methylene blue] = 1.00×10^{-5} M
 Well-Dawson polyoxometalate = 0.10 g Light Intensity = 50.0 mWcm^{-2}

Time (min.)	Optical Density (O.D.)	1 + log O. D.
0	0.871	0.9400
5	0.700	0.8451
10	0.589	0.7701
15	0.484	0.6848
20	0.398	0.5999
25	0.327	0.5145
30	0.269	0.4297
35	0.224	0.3502
40	0.186	0.2695

Rate constant (k) = $6.39 \times 10^{-4} \text{ sec}^{-1}$

EFFECT OF pH

The pH of the solution is likely to affect the degradation of methylene blue. The effect of pH on the rate of degradation of methylene blue was

investigated in the pH range 5.0-10.5. The results are reported in Table 2 and graphically presented in Figure 2. (See Figures)

Table 2 : EFFECT OF pH

[Methylene blue] = 1.00×10^{-5} M Well-Dawson polyoxometalate = 0.10 g
 Light Intensity = 50.0 mWcm^{-2}

pH	k × 10 ⁴ (sec ⁻¹)
5.0	2.55
5.5	3.85
6.0	4.11
6.5	5.31
7.0	5.50
7.5	6.39
8.0	5.93
8.5	4.72
9.0	4.42
9.5	3.43
10.0	2.20
10.5	1.34

It has been observed that the rate of photocatalytic degradation of methylene blue was increased as pH was increased and it got optimum value at pH 7.5. On further increasing pH, the rate of the reaction was decreased. This behavior may be explained on the basis that the rate of photocatalytic degradation increases as pH was increased as there was greater probability for the formation of hydroxyl radicals ($\cdot\text{OH}$), which are produced from the reaction between OH^- ions and hole

(h^+) of the semiconductor, which can act as an oxidant. Thus, the rate of photocatalytic degradation of the dye increases. Above pH 7.5, a decrease in the rate of photocatalytic degradation of the dye was observed, which may be due to the fact that cationic form of methylene blue converts in its neutral form, which faces no attraction towards the negatively charged semiconductor surface due to adsorption of OH^- ions.

EFFECT OF DYE CONCENTRATION

The effect of dye concentration was studied by taking different concentrations of methylene blue.

The results are tabulated in Table 3 and graphically represented in Figure 3. (See Figures)

Table 3 : EFFECT OF METHYLENE BLUE CONCENTRATION

pH = 7.5

Well-Dawson polyoxometalate = 0.10 g

Light Intensity = 50.0 mWcm⁻²

[Methylene blue] × 10⁶ M	k × 10⁴ (sec⁻¹)
5.00	1.72
5.50	2.27
6.00	3.11
6.50	3.26
7.00	3.54
7.50	3.83
8.00	4.79
8.50	5.23
9.00	5.54
9.50	5.96
10.00	6.39

The rate of photocatalytic degradation of dye was found to increase on increasing the concentration up to 10.0 × 10⁻⁶ M. It may be due to the fact that as the concentration of the dye was increased, more dye molecule was available for excitation and energy transfer and hence, an increase in the rate of degradation of the dye was observed.

EFFECT OF AMOUNT OF SEMICONDUCTOR

The amount of semiconductor is also likely to affect the degradation of dye and hence, different amounts of photocatalyst were used. The results are reported in Table 4 and graphically presented in Figure 4. (See Figures)

Table 4 : EFFECT OF AMOUNT OF SEMICONDUCTOR

pH = 7.5

[Methylene blue] = 1.00 × 10⁻⁵ M

Light Intensity = 50.0 mWcm⁻²

Amount (g)	k × 10⁴ (sec⁻¹)
0.02	1.34
0.04	2.14
0.06	2.65
0.08	3.83
0.10	6.39
0.12	6.22
0.14	6.30
0.16	6.34
0.18	6.36

It was observed that the rate of reaction increases with increase in the amount of semiconductor iron containing Well-Dawson polyoxometalate. The rate of

degradation was optimum at 0.10 g of the photocatalyst. Beyond 0.10 g, the rate of reaction become virtually constant. This may be due to fact that

as the amount of semiconductor was increased, the exposed surface area of the semiconductor was also increased. However, after this limiting value (0.10 g), an increase in the amount of semiconductor only increases the thickness of the semiconductor layer and not the exposed surface area. This was also confirmed by using reaction vessels of different dimensions. It was observed that the point of saturation was shifted to a higher value for vessels of larger capacities while it

was shifted to lower value for vessels of smaller capacities.

EFFECT OF LIGHT INTENSITY

To investigate the effect of light intensity on the photocatalytic degradation of methylene blue, the distance between the light source and the exposed surface area of semiconductor was varied. The results are summarized in Table 5 and graphically presented in Figure 5. (See Figures)

Table 5 : EFFECT OF LIGHT INTENSITY

pH = 7.5

[Methylene blue] = 1.00 × 10⁻⁵ M

Well-Dawson polyoxometalate = 0.10 g

Intensity of light (mWcm ⁻²)	k × 10 ⁴ (sec ⁻¹)
20.0	2.44
30.0	3.78
40.0	5.92
50.0	6.39
60.0	5.27
70.0	4.30

The results indicate that photocatalytic degradation of methylene blue 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 surface 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.

MECHANISM

On the basis of these observations, a tentative mechanism for photocatalytic degradation of methylene blue dye is proposed as follows –



Methylene blue dye (MB) absorbs radiations of suitable wavelength and gives rise to its excited singlet state. Then it undergoes intersystem crossing (ISC) to give the triplet state of the dye. On the other hand, the semiconducting iron containing Well-Dawson polyoxometalate (SC) also utilizes the radiant energy to excite its electron from valence band to the conduction band. This electron will be abstracted by oxygen molecule (dissolved oxygen) generating superoxide anion radical (O₂^{•-}). This anion radical will reduce the dye methylene blue to its leuco form, which may ultimately degrade to products. It was also

confirmed that this degradation proceeds through reduction and not oxidation. •OH radical does not participate as an active oxidizing species which was confirmed by using hydroxyl radical scavenger (2-propanol), where the rate of degradation was not affected appreciably.

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FIGURES

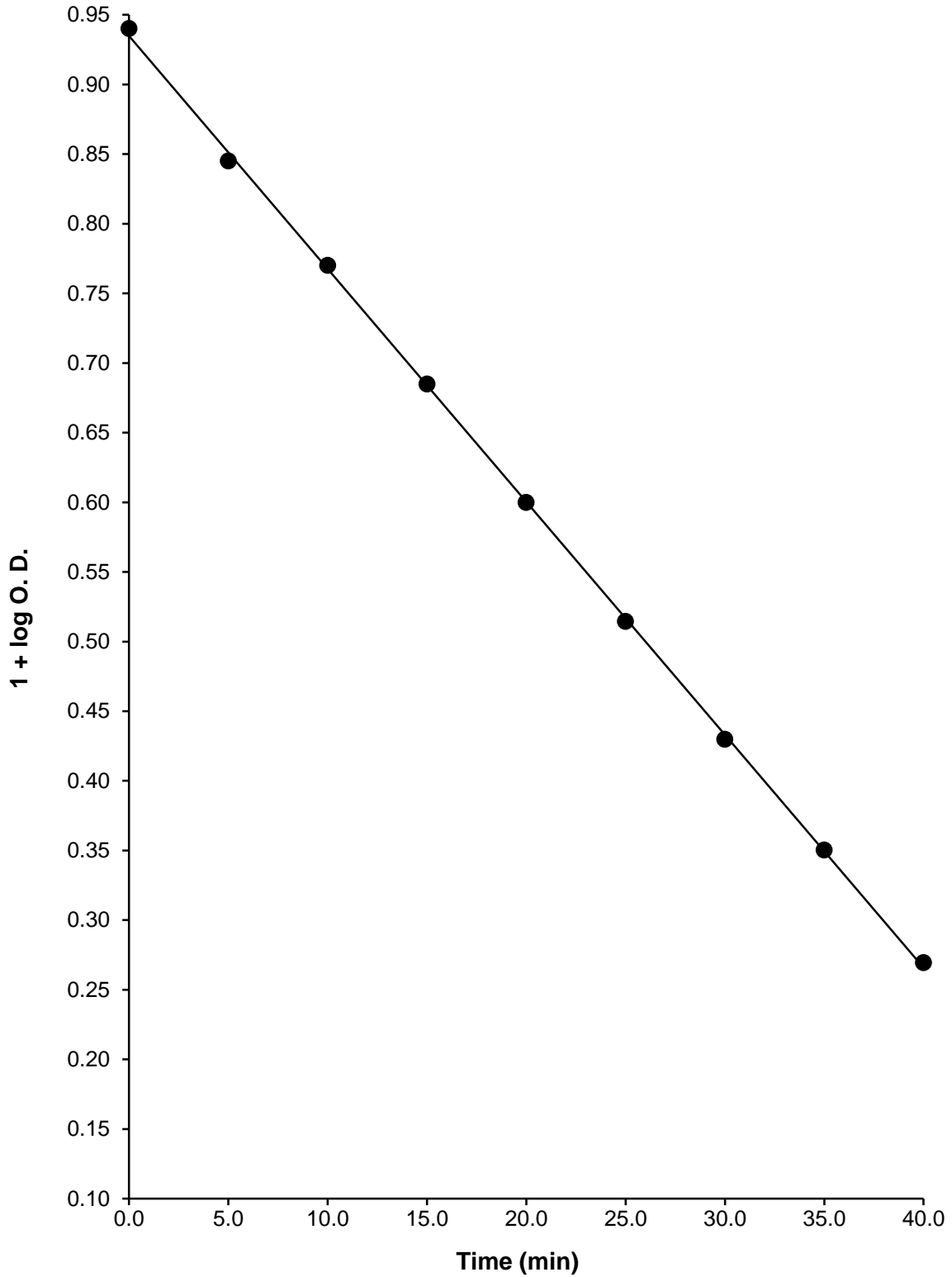


Fig. 1 : A TYPICAL RUN

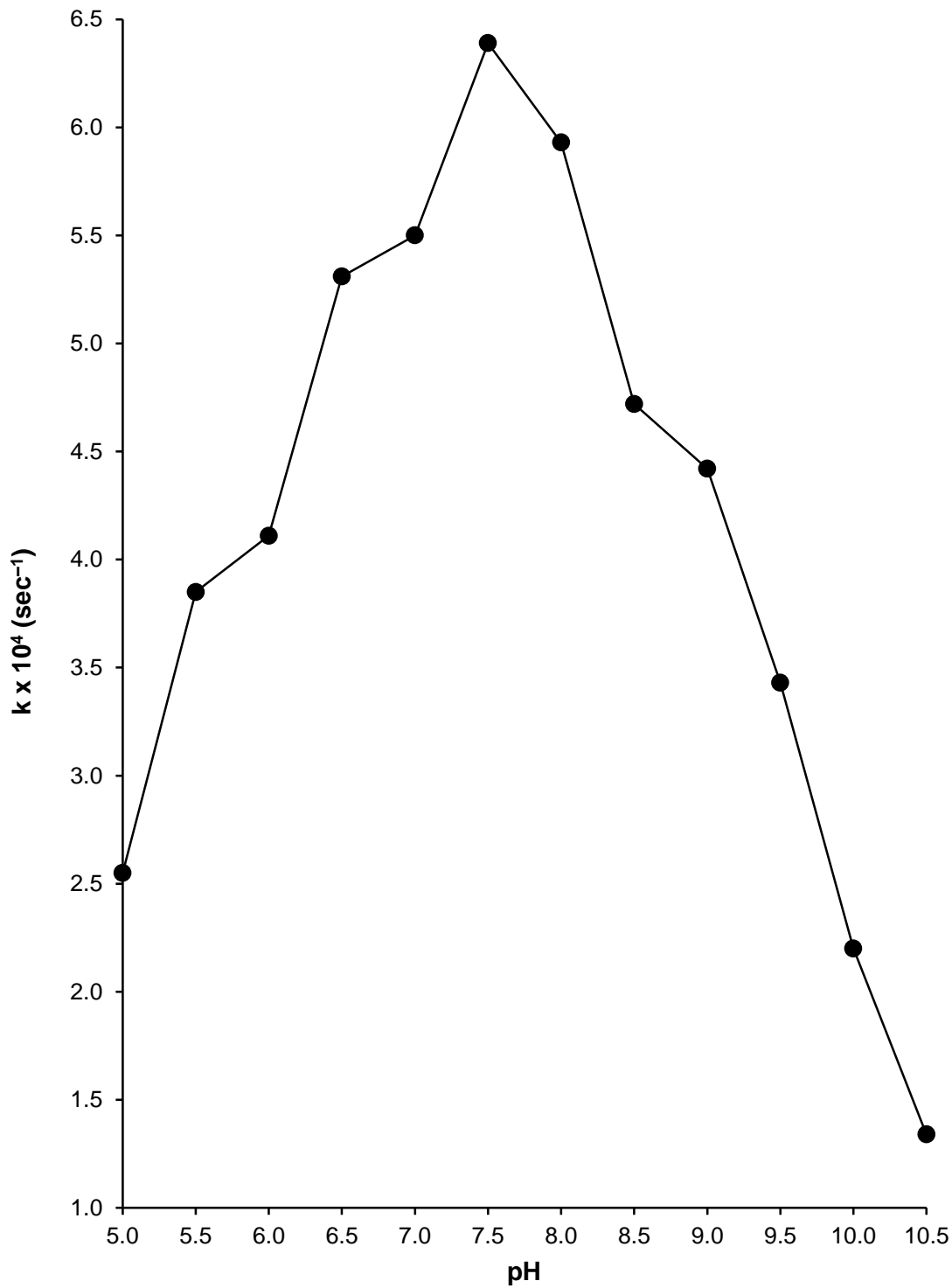


Fig. 2 : EFFECT OF pH

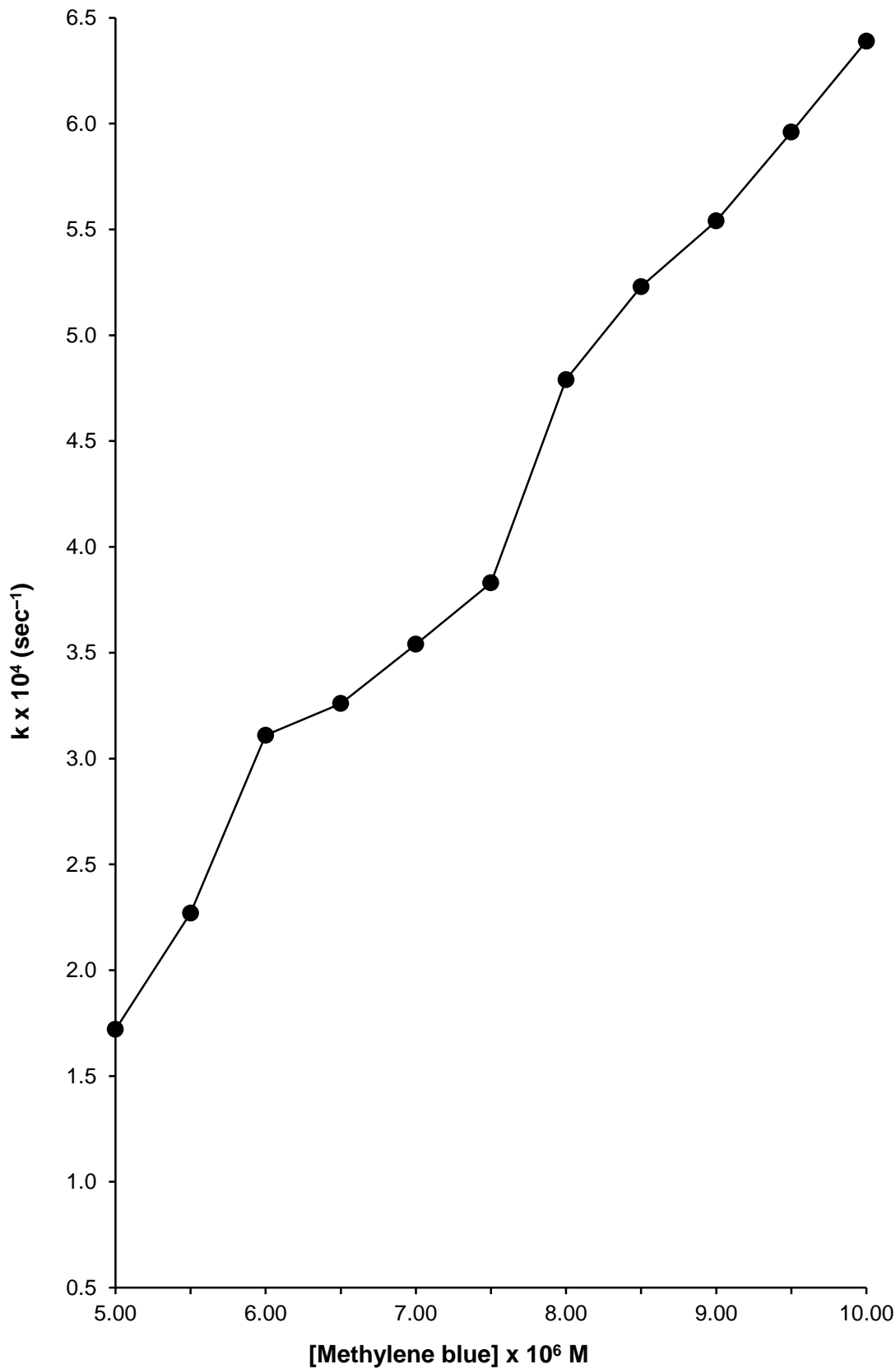


Fig. 3 : EFFECT OF DYE CONCENTRATION

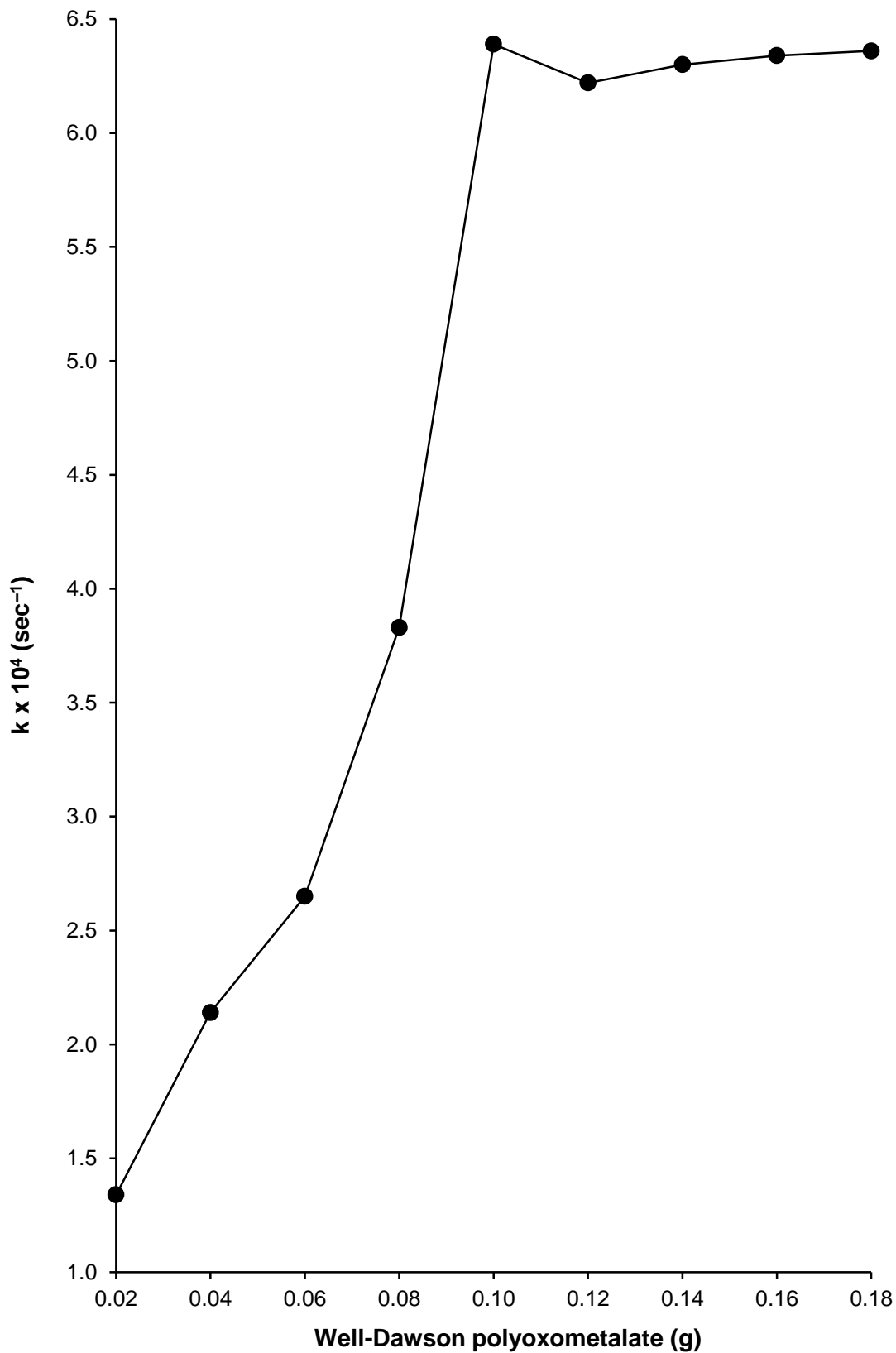


Fig. 4: EFFECT OF AMOUNT OF SEMICONDUCTOR

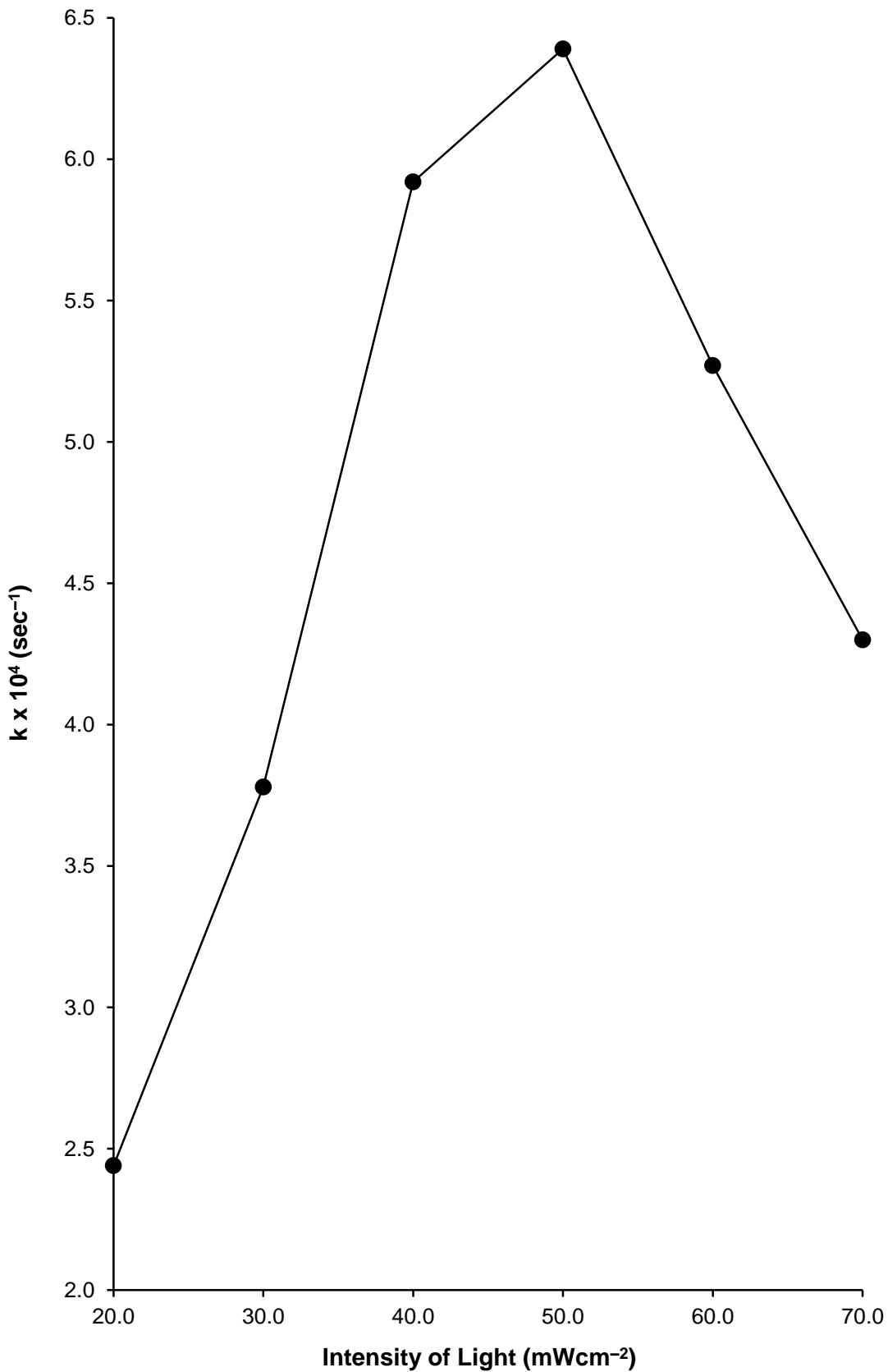


Fig. 5 : EFFECT OF LIGHT INTENSITY