CHAPTER – IIIA

AZURE A- GRAPHITIC CARBON NITRIDE SYSTEM

CONTENTS

3.1 AZURE A

3.2 EXPERIMENTAL

3.1 AZURE A

Azure A is light blue to dark blue dye. It is used for a monitoring test of mucopolysaccharides.

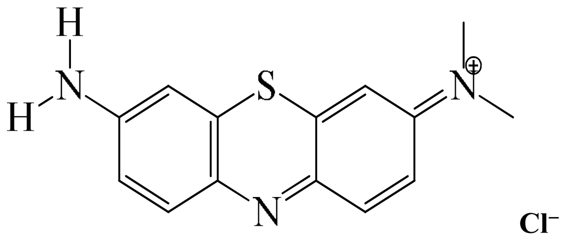

Fig. 3.1: Structure of Azure A

IUPAC Name : N’,N’-Dimethylphenothiazin-5-ium-3,7-diamine chloride

Molecular Formula : $C_{14}H_{14}ClN_3S$

Molecular Mass : 291.80 g mol^{-1}

λ max : 620 nm

Solubility : Water

3.2 EXPERIMENTAL

- Absorbance of dye solution was measured by UV-Visible spectrophotometer, (Systronics model 106)
- The pH was determined using a pH meter (Systronics model 335), and
- The light intensity was recorded by a Solarimeter Suryamapi (CEL Model SM 201).

A 1.0×10^{-4} M solution of azure-A (HIMEDIA) was prepared by dissolving 0.0292 g of azure-A in 100.0 mL of distilled water. This solution was used served as a stock solution. The absorbance (A) of azure-A dye solution was measured using a spectrophotometer (Systronics model 106) at a wavelength of λ max = 620 nm. The dye solution was divided into four portions.

- The first beaker containing dye solution was kept in dark,
- The second beaker containing dye solution was exposed to 200 W tungsten lamp,
- The third beaker containing dye solution and 0.08 g of graphitic carbon nitride was kept in dark, and
- The fourth beaker containing dye solution and 0.08 g photocatalyst graphitic carbon nitride was exposed to 200 W tungsten lamp.

It was observed that the absorbance of the first beaker remained almost same even after 3-4 h. while the second beaker had a slight decrease in initial value of its absorbance. The initial absorbance of the third beaker also showed a slight decrease. The absorbance of the fourth beaker had a significant reduction. These observations indicate that the reaction between azure-A and photocatalyst is a photocatalytic reaction only.

The 0.08 g of g-C_3N_4 was added to 1.00×10^{-4} M dye solution and pH was maintained at 7.0, Then it was exposed to a 200 W tungsten lamp at 70.0 m W cm^{-2}. The absorbance of azure A was found to decrease with increasing exposure time. A linear relationship was observed on plotting 1 + log A against time. The rate constant (k) of the reaction was calculated using the expression k = 2.303 × slope. The results are reported in Table 3.1: and represented in Fig. 3.2:

Table 3.1: A typical run

pH = 7.0 $g\text{-}C_3N_4 = 0.08$ g

[Azure-A] = 1.00×10^{-4} M Light intensity = 70.0 mW cm^{-2}

Time (min)	Absorbance (A)	1 + log A
0.00	0.476	0.6776
10.0	0.442	0.6454
20.0	0.342	0.5340
30.0	0.282	0.4502
40.0	0.258	0.4116
50.0	0.227	0.3560
60.0	0.203	0.3074
70.0	0.168	0.2253
80.0	0.148	0.1702
90.0	0.132	0.1205

Rate constant (k) = 2.54×10^{-4} s^{-1}

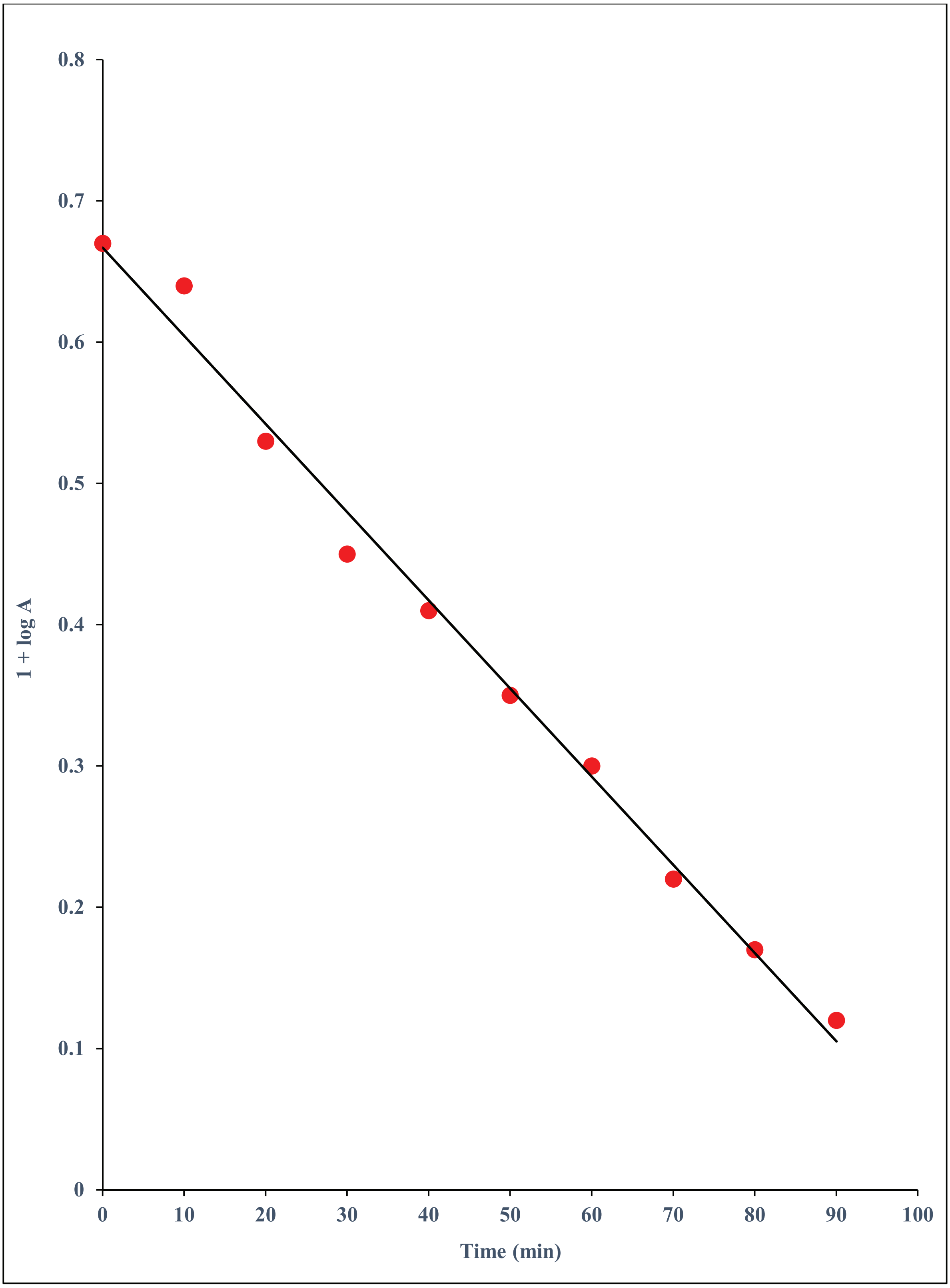

Fig. 3.2: A typical run

3.2.1 Effect of pH

The effect of pH on photocatalytic degradation was observed in the range of 5.0 to 9.0. The results are shown in Table 3.2: and Fig. 3.3:

Table 3.2: Effect of pH

[Azure A] = 1.00×10^{-4} M g-C_3N_4 = 0.08 g

Light Intensity = 70.0 mW cm^{-2}

pH	Rate constant (k) × 10^4 (s^{-1})
5.0	0.266
5.5	0.308
6.0	1.34
6.5	1.65
7.0	**2.54**
7.5	1.69
8.0	1.38
8.5	1.12
9.0	0.70

The rate of degradation of azure-A increases with increasing pH of solution up to 7.0, but above this value of pH, the rate of photodegradation of azure-A started decreasing.

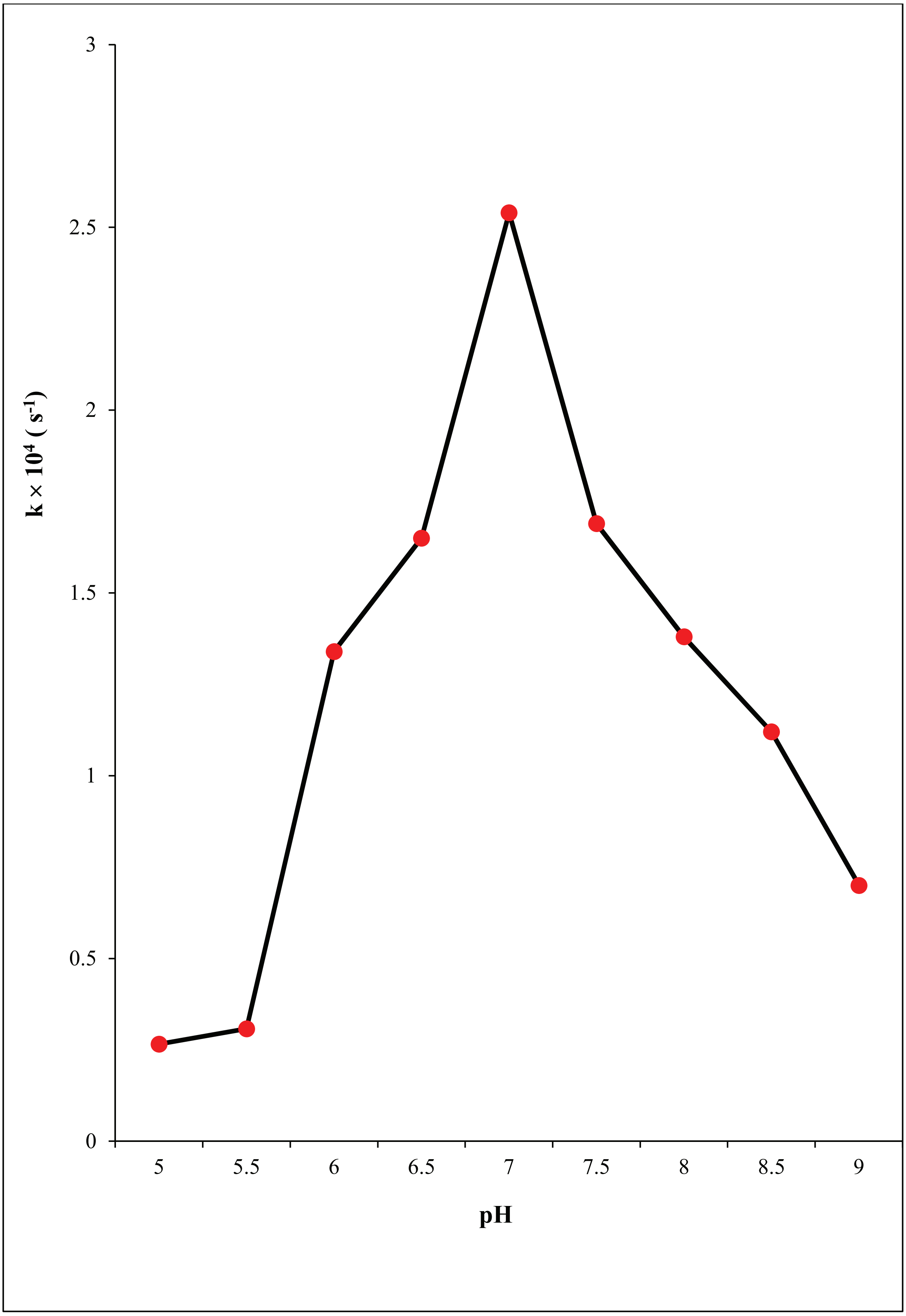

Fig. 3.3: Effect of pH

3.2.2 Effect of Dye Concentration

The effect of dye concentration on the rate of reaction was also observed using different concentrations of azure A solution in the range of 6.0 × 10^5 M to 2.6 × 10^4M. The results are tabulated in Table 3.3: and presented Fig. 3.4:

Table 3.3: Effect of dye concentration

pH = 7.0 Light intensity = 70.0 mW cm^{-2}

g-C_3N_4 = 0.08 g

[Azure A] × 10^4 M	**Rate constant (k)× 10^4 (s^{-1})**
0.6	2.24
0.8	2.43
1.0	**2.54**
1.2	1.78
1.4	1.39
1.6	1.27
1.8	1.25
2.2	1.09
2.4	0.95
2.6	0.94

It was noticed that the rate of photocatalytic degradation increases with dye concentration up to 1.00 × 10^4 M. but it started declining on increasing the dye concentration further.

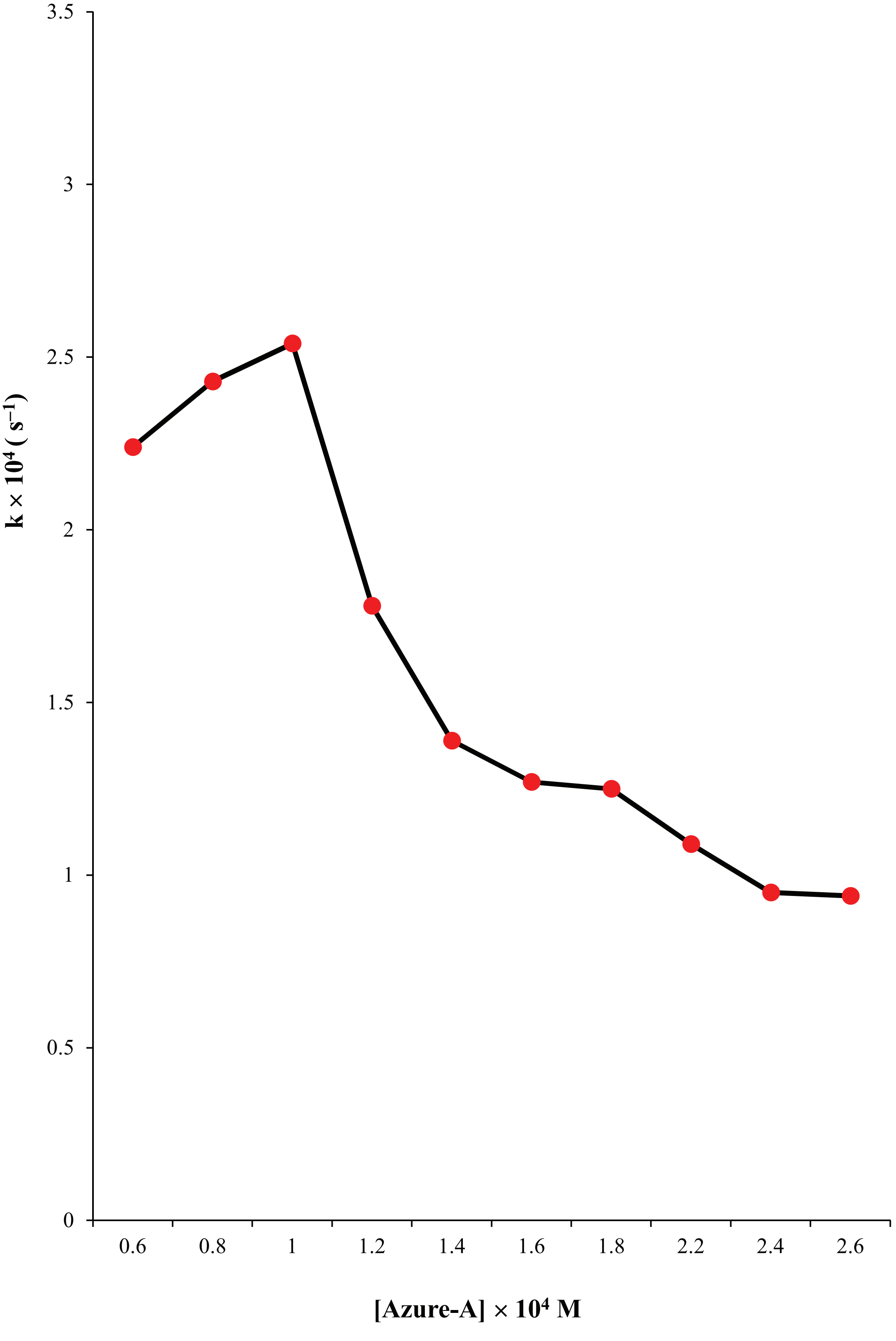

Fig. 3.4: Effect of dye concentration

3.2.3 Effect of Amount of Photocatalyst

The effect of amount of photocatalyst on the rate of photocatalytic degradation of azure-A was also observed between 0.02 to 0.14 g. The results are shown in Table 3.4: and Fig. 3.5:

Table 3.4: Effect of amount of photocatalyst

[Azure-A] = 1.00 × 10^4 M pH = 7.0

Light intensity = 70.0 mW cm^{-2}

g-C_3N_4 (g)	**Rate constant (k) × 10^4 (s^{-1})**
0.02	1.26
0.04	1.85
0.06	2.19
0.08	**2.54**
0.10	2.25
0.12	1.94
0.14	1.42

It was observed that reaction rate increases on increasing quantity of photocatalyst till 0.08 g, beyond which the rate of degradation exhibited a declining behaviour.

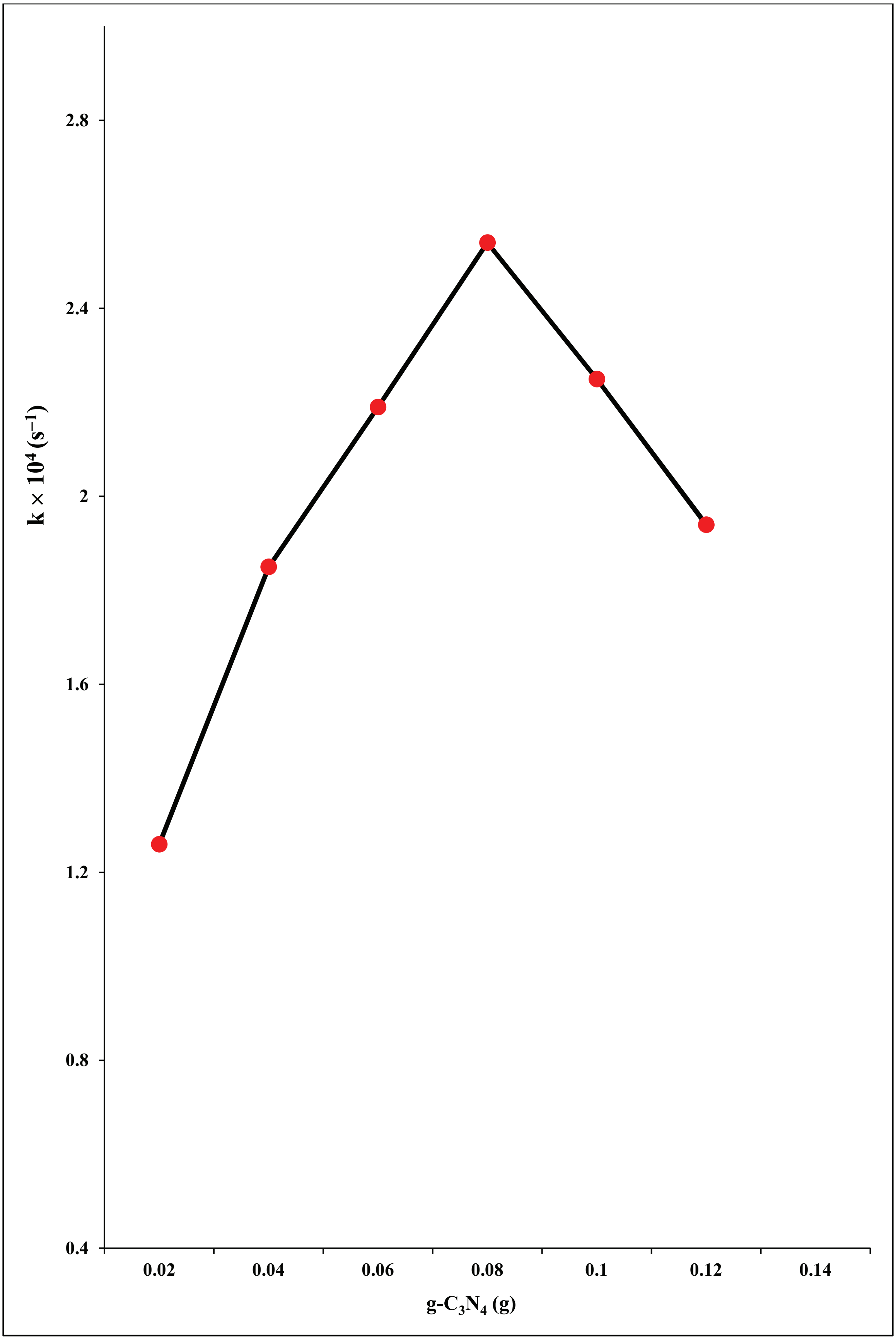

Fig. 3.1: Effect of amount of photocatalyst

3.2.4 Effect of Light Intensity

The effect of light intensity on the rate of degradation of azure-A was also observed from 20.0 to 70.0 mWcm^{-2}. The results are reported in Table 3.5: and Fig. 3.6:

Table 3.1: Effect of light intensity

[Azure-A] = 1.00×10^{-4} M pH = 7.0

g-C_3N_4 = 0.08 g

Light intensity (mW cm^{-2})	**Rate constant (k) × 10^4 (s^{-1})**
20.0	1.43
30.0	1.50
40.0	1.69
50.0	1.79
60.0	2.11
70.0	**2.54**

It was observed that rate of degradation of azure a increases as the light intensity was increased. There was an almost liner behaviour between rate and intensity of light.

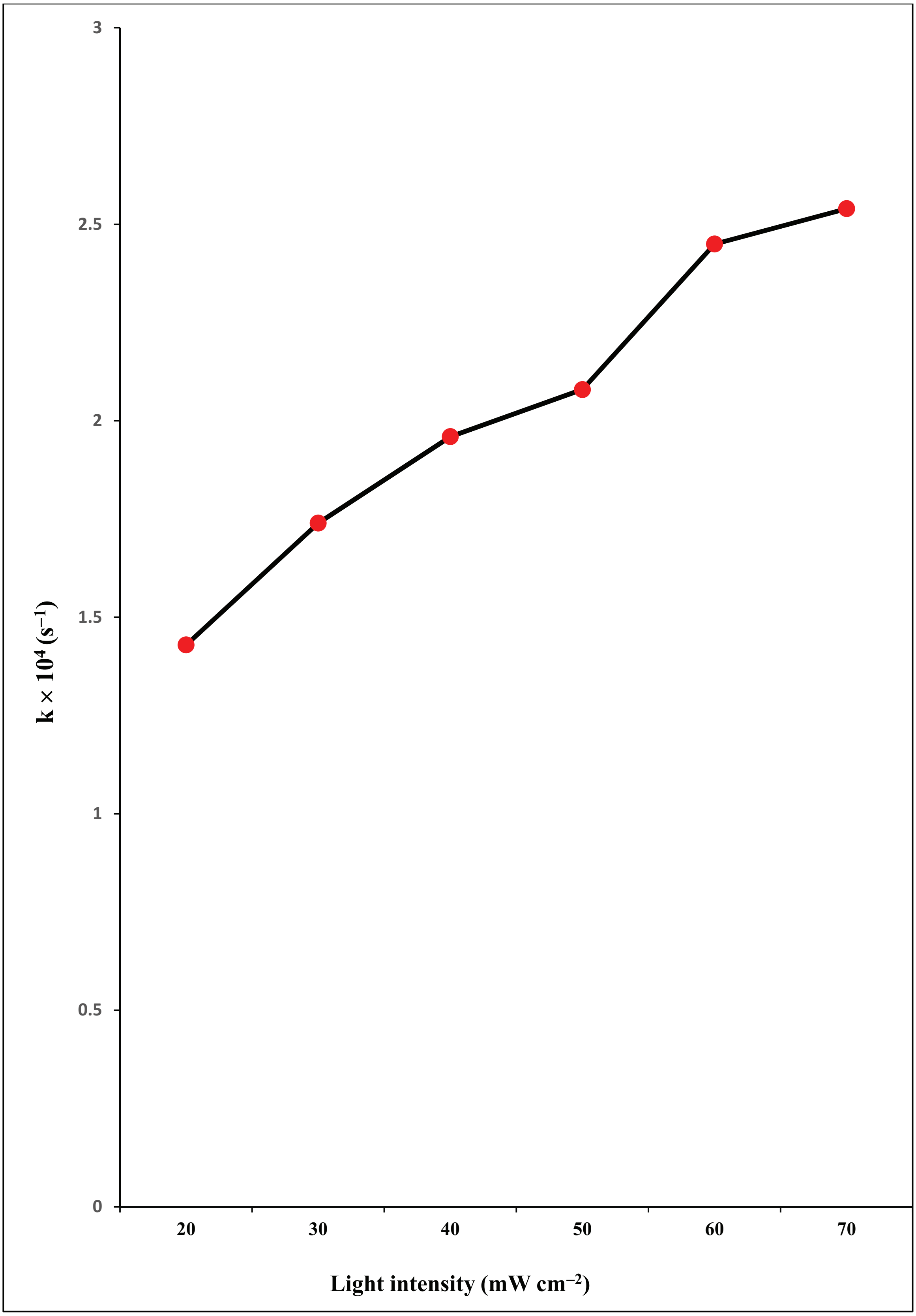

Fig. 3.6: Effect of light intensity

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CHAPTER – IIIB

EVANS BLUE- GRAPHITIC CARBON NITRIDE SYSTEM

CONTENTS

3.3 EVANS BLUE

3.4 EXPERIMENTAL

3.3 EVANS BLUE

Evans blue is a synthetic bis-azo dye, It is also named as T-1824 and Direct Blue 53. It is used for estimation of blood volume, detection of lymph nodes, and localization of tumours.

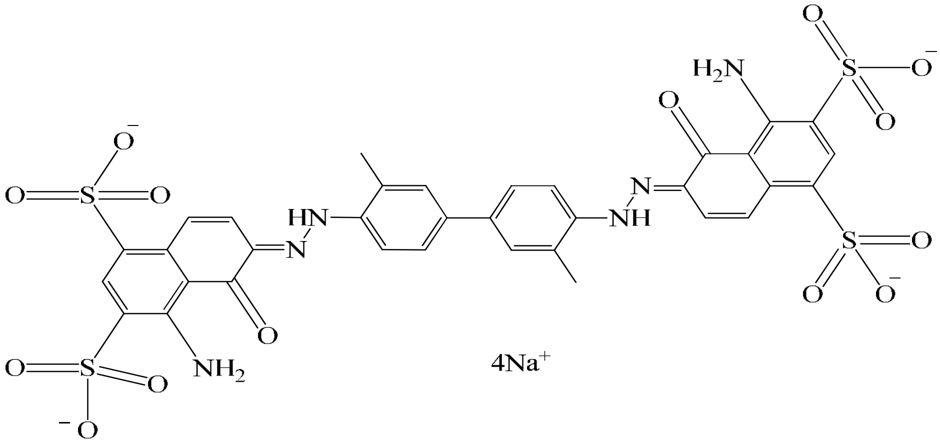

Fig. 3.7: Structure of Evans blue

IUPAC Name	:	Tetrasodium (6E,6'E)-6,6-[(3,3'-dimethylbiphenyl-4,4'-diyl) di(1E) hydrazin-2-yl-1-ylidene] bis (4-amino-5-oxo-5,6-dihydronaphthalene-1,3-disulfonate)
Molecular Formula	:	$C_{34}H_{24}N_6Na_4O_{14}S_4$
Molecular Mass	:	960.809 g mol^{-1}
λ max	:	608 nm
Solubility	:	Water

3.4 EXPERIMENTAL

A solution of Evans blue (HIMEDIA) 0.096 g was prepared by dissolving in 100.0 mL water to prepare 1.0×10^{-4} M and stored as a stock solution. The absorbance (A) of Evans blue dye solution was determined with the help of a spectrophotometer at λ max = 608 nm. The dye solution was placed in equal amounts in four beakers.

- The first beaker containing dye solution was kept in dark,

- The second beaker containing dye solution was exposed to 200 W tungsten lamp,
- The third beaker containing dye solution with 0.10 g photocatalyst graphitic carbon nitride was kept in dark, and
- The fourth beaker contain dye solution and 0.10 g photocatalyst graphitic carbon nitride was exposed to 200 W tungsten lamp.

The absorbance of dye solution was measured with the help of a spectrophotometer. It was observed that the absorbance of first beaker remained almost same after 3-4 h while the second beaker had a slight decrease in initial value of its absorbance. The initial absorbance value of the third beaker showed a slight difference. The initial absorbance value of the fourth beaker experienced a significant reduction. This observation confirmed that the reaction between Evans blue and photocatalyst is a photocatalytic reaction.

The photodegradation of Evans blue was monitored by taking absorbance of samples of dye solution 1.0×10^{-4}M containing 0.10 g photocatalyst (g-C_3N_4) and exposed to 200 W tungsten lamp (60.0 mW cm^{-2}) at pH = 9.5. The absorbance of Evans blue was found to decrease with increasing time of exposure. A plot of 1 + log A versus time was found to be linear. The rate constant of reaction was calculated with the following expression $k = 2.303 \times \text{slope}$. The data of typical run are presented in Table 3.6: and graphically in Fig. 3.8:

Table 3.6: A typical run

pH = 9.5 g-C_3N_4 = 0.10 g

[Evans blue] = 1.00×10^{-4} M Light Intensity = 60.0 mW cm^{-2}

Time (min)	**Absorbance (A)**	**1+ log A**
0	0.407	0.6095
10	0.381	0.5809
20	0.359	0.5550
30	0.310	0.4913
40	0.295	0.4698
50	0.282	0.4502
60	0.270	0.4313
70	0.260	0.4149
80	0.240	0.3802
90	0.226	0.3541
100	0.216	0.3344

Rate constant (k) = 1.50×10^{-4} sec^{-1}

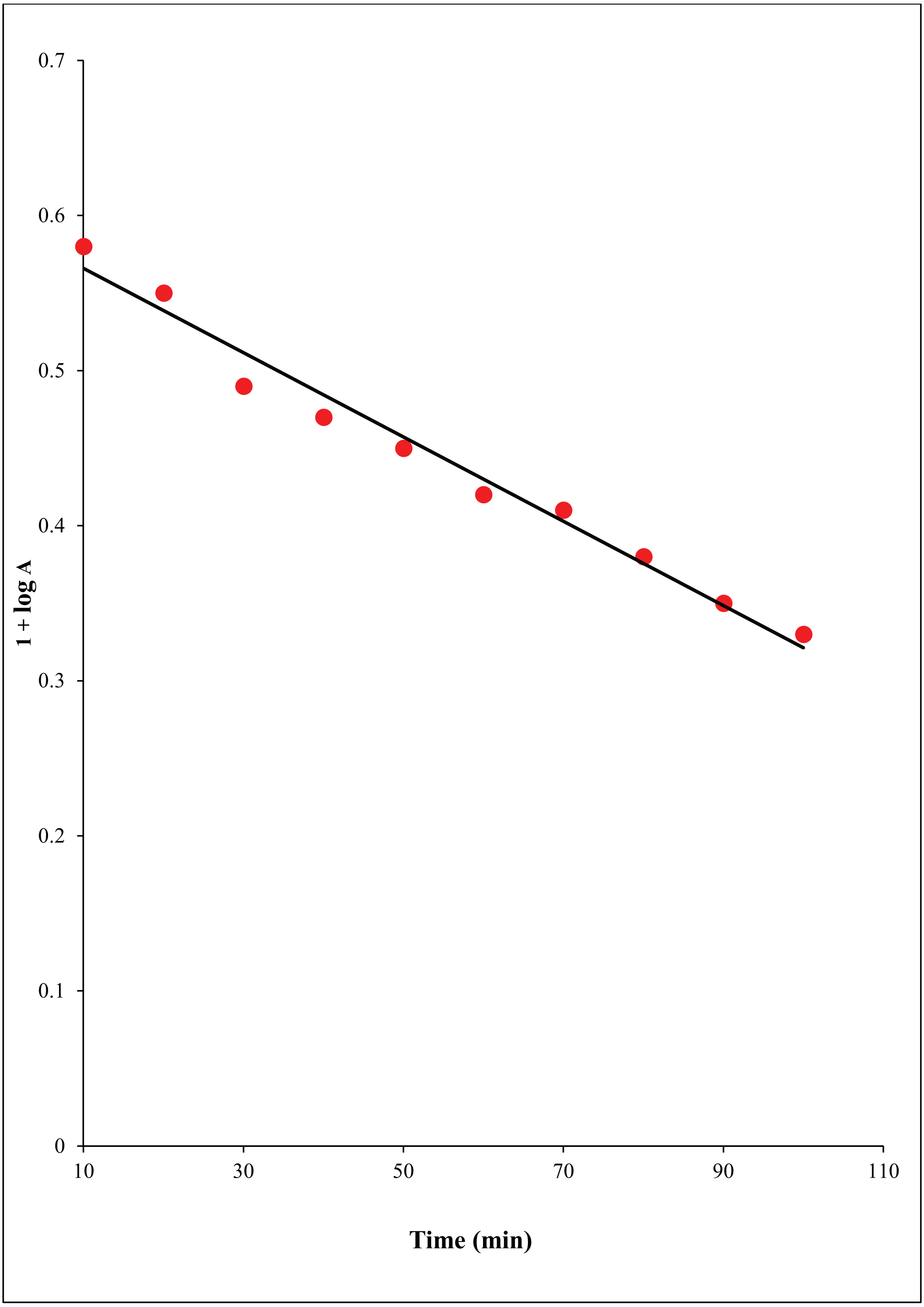

Fig. 3.8: A typical run

3.4.1 Effect of pH

The effect of pH on photocatalytic degradation was observed in the range of 6.0 to 10.5. The results are given in Table 3.7: and Fig. 3.9:

Table 3.7: Effect of pH

[Evans blue] = 1.00×10^{-4} M g-C_3N_4 = 0.10 g

Light Intensity = 60.0 mW cm^{-2}

pH	**Rate constant (k) × 10^4 (s^{-1})**
6.0	0.51
6.5	0.72
7.0	0.94
7.5	1.10
8.0	1.24
8.5	1.40
9.0	1.48
9.5	**1.50**
10.0	1.40
10.5	1.30

It was noticed that the degradation rate of Evans blue increases with increasing pH of solution up till 9.5, but above this value of pH, the rate of photodegradation of Evans blue started decreasing.

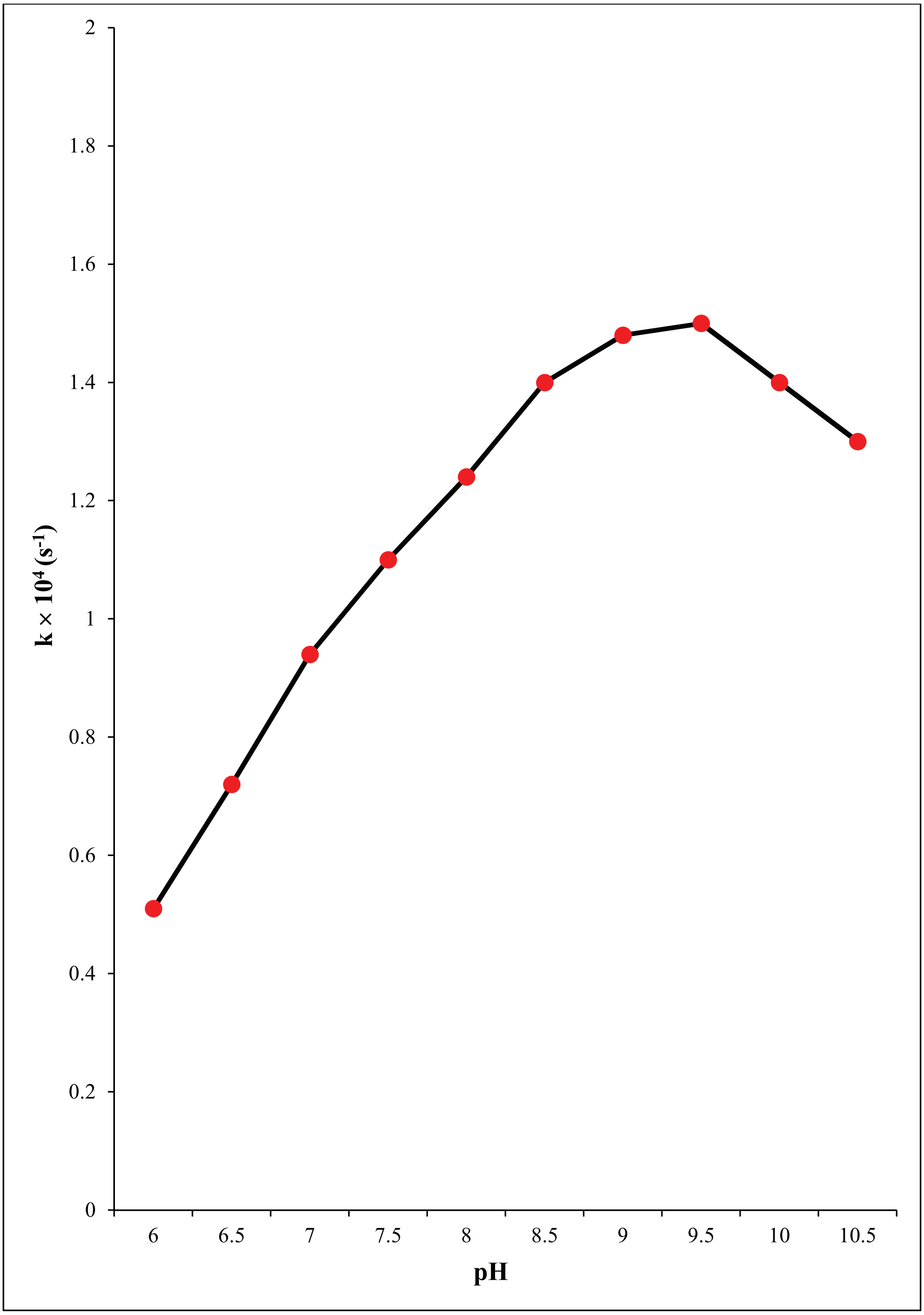

Fig. 3.9: Effect of pH

3.4.2 Effect of dye concentration

The effect of dye concentration on the rate of reaction was also observed using different concentrations of Evans blue solution (2.0×10^{-5}-1.8×10^{-4}M). The results are shown in Table 3.8: and Fig. 3.10:

Table 3.8: Effect of dye concentration

pH = 9.5 Light Intensity = 60.0 mW cm^{-2}

g-C_3N_4 = 0.10 g

[Evans blue] × 10^4 M	**Rate constant (k) × 10^4 (s^{-1})**
0.2	0.8
0.4	1.0
0.6	1.10
0.8	1.25
1.0	**1.50**
1.2	1.27
1.4	1.10
1.6	0.85
1.8	0.74

It was observed that the rate of photocatalytic degradation increases with increase in the concentration of the dye up to 1.0×10^{-4} M beyond which, it decreses.

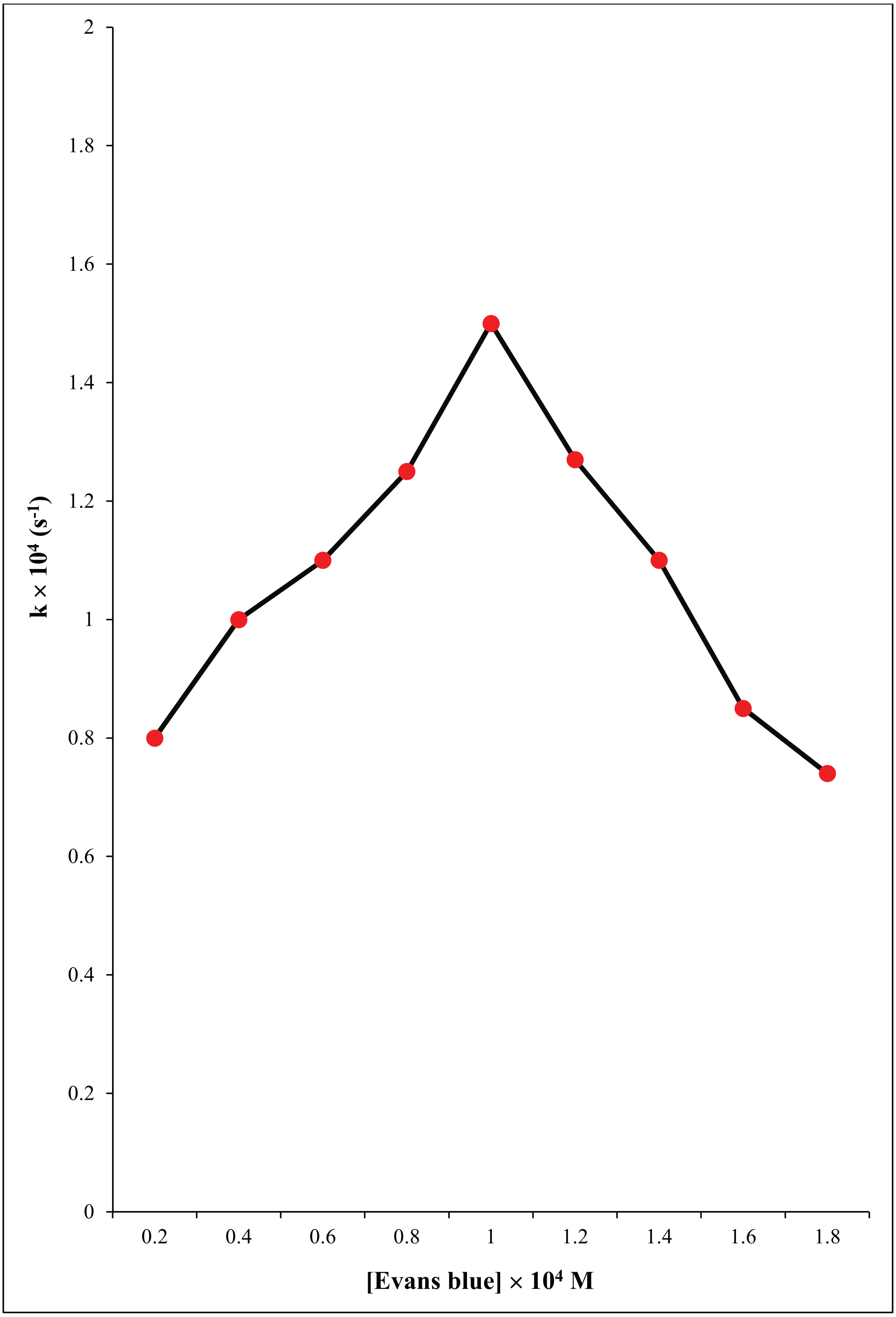

Fig. 3.10: Effect of dye concentration

3.4.3 Effect of amount of photocatalyst

The effect of amount of photocatalyst on the rate of photocatalytic degradation of Evans blue was also observed in the rang 0.02-0.16 g. The results are shown in Table 3.9: and Fig. 3.11:

Table 3.9: Effect of amount of photocatalyst

pH = 9.5 Light Intensity = 60.0 mW cm^{-2}

[Evans blue] = 1.00 × 10^{-4} M

g-C_3N_4 (g)	**Rate constant (k) × 10^4 (s^{-1})**
0.02	1.36
0.04	1.40
0.06	1.45
0.08	1.49
0.10	**1.50**
0.12	1.48
0.14	1.38
0.16	1.32

It was noticed that the rate of reaction increases with increase in the amount of photocatalyst up to 0.10 g, but above this value of photocatalyst, the rate of reaction decreased.

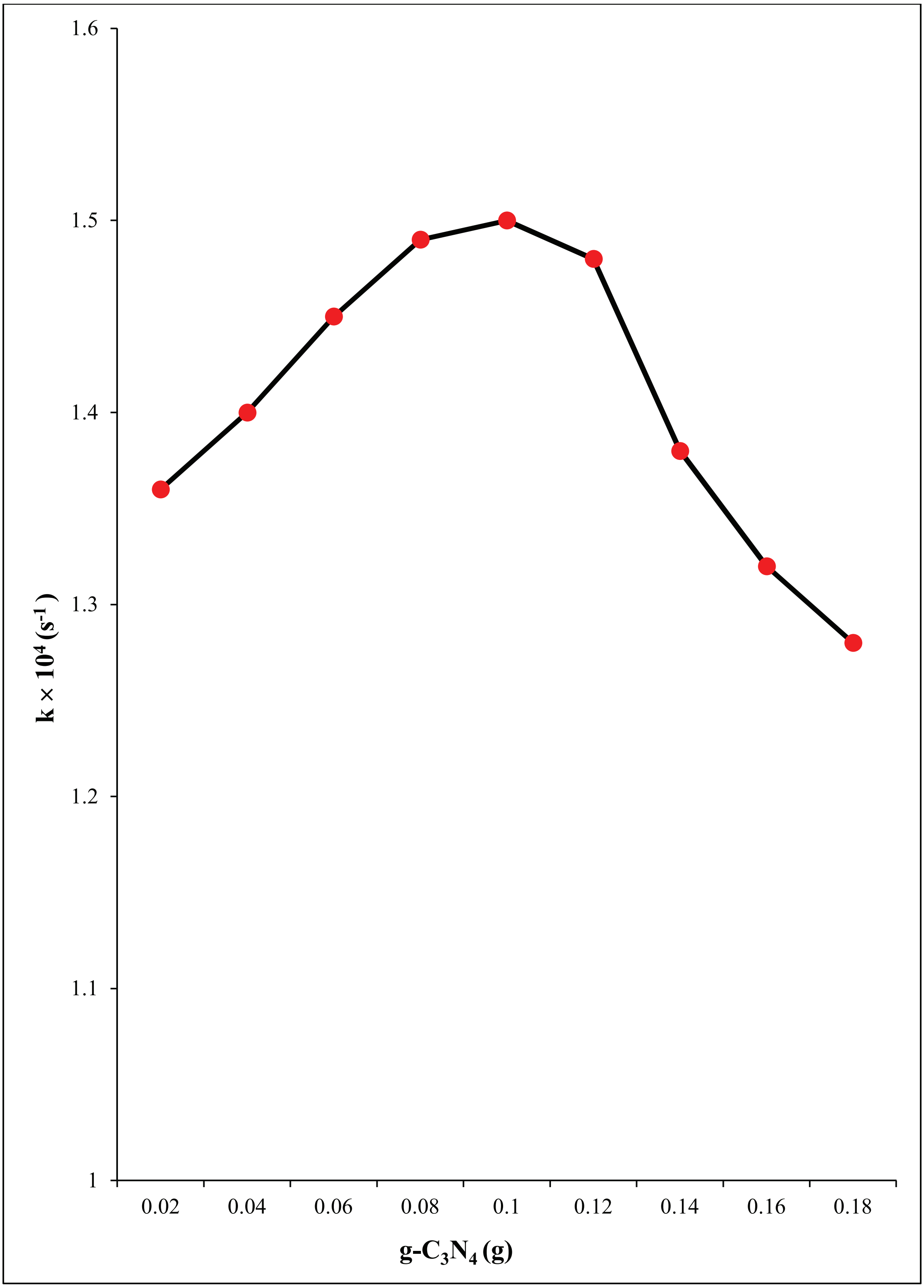

Fig. 3.11: Effect of amount of photocatalyst

3.4.4 Effect of light intensity

The effect of light intensity on the rate of Evans blue was also observed from 30.0 to 70.0 mW cm^{-2}. The results are reported in Table 3.10: and Fig. 3.12:

Table 3.10: Effect of light intensity

pH = 9.5 [Evans blue] = 1.0 ×10^{-4} M

g-C_3N_4 = 0.10 g

Light intensity (mW cm^{-2})	**Rate constant (k) × 10^4 (s^{-1})**
30.0	0.82
40.0	0.99
50.0	1.05
60.0	**1.50**
70.0	1.23

It was observed that the rate of degradation was increased on increasing light intensity, but there was a desrese above 60.0 mW cm^{-2}.

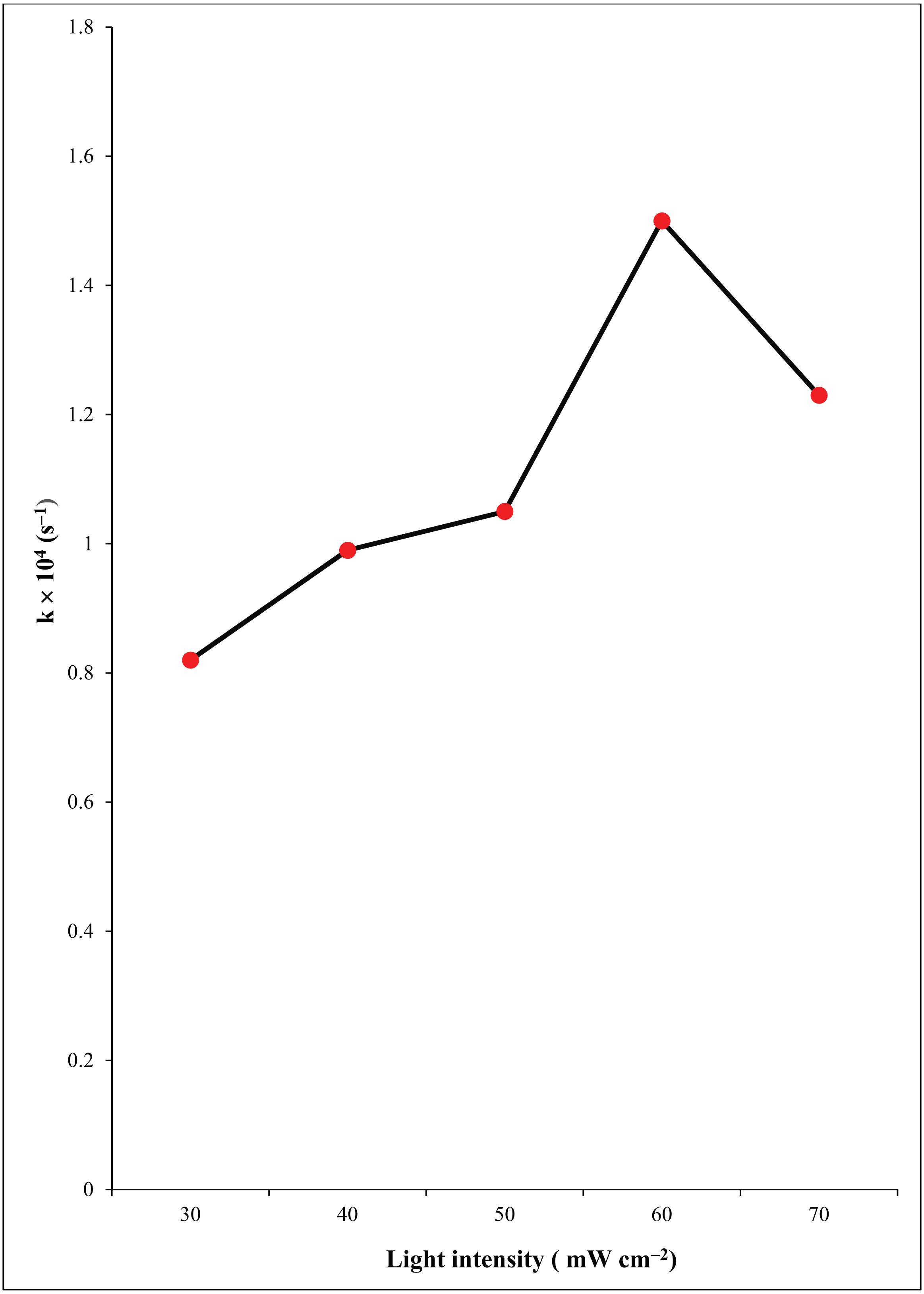

Fig. 3.12: Effect of light intensity

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CHAPTER – IIIC

ROSE BENGAL- GRAPHITIC CARBON NITRIDE SYSTEM

CONTENTS

3.5 ROSE BENGAL

3.6 EXPERIMENTAL

3.5 ROSE BENGAL

Rose Bengal belongs to the class of organic compounds called xanthenes. Its sodium salt is commonly used in eye drops to stain damaged conjunctival and corneal cells and thereby, identify damage to the eye.

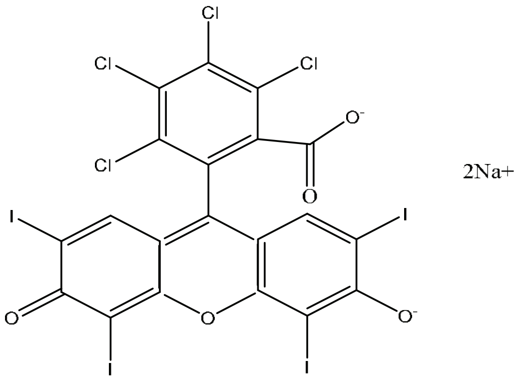

Fig. 3.13: Structure of Rose Bengal

IUPAC Name : 4,5,6,7-Tetrachloro-3′,6′-dihydroxy-2′,4′,5′,7′-tetraiodo-3H- spiro [[2] benzofuran-1,9′-xanthen]-3-one

Molecular Formula : $C_{14}H_{14}ClN_3S$

Molecular Mass : 973.67 g/ mol^{-1}

λ max : 527 nm

Solubility : Water

3.6 EXPERIMENTAL

Solution of Rose Bengal (HIMEDIA) was prepared by dissolving 0.254 g in 250.0 mL water to get 1.0×10^{-4} M solution as a stock solution. The absorbance (A) of Rose Bengal dye solution was determined with the help of a spectrophotometer at λ max = 527 nm. The dye solution was placed in equal amounts in four beakers.

- The first beaker containing dye solution was kept in dark,
- The second beaker containing dye solution was exposed to 200 W tungsten lamp,
- The third beaker containing dye solution with 0.08 g photocatalyst graphitic carbon nitride was kept in dark, and

- The fourth beaker contain dye solution and 0.08 g photocatalyst graphitic carbon nitride was exposed to 200 W tungsten lamp.

The absorbance of dye solution was measured with the help of a spectrophotometer. It was observed that the absorbance of first beaker remained almost same after 3-4 h while the second beaker had a decrease in initial value of its absorbance. The initial absorbance value of the third beaker showed a slight difference. The initial absorbance value of the fourth beaker experienced a significant reduction. This observation confirmed that the reaction between Rose Bengal and photocatalyst is a photocatalytic reaction.

The photodegradation of Rose Bengal was monitored by taking absorbance of samples of dye solution (8.0×10^{-5}M) containing 0.08 g photocatalyst (g-C_3N_4) and exposed to 200 W tungsten lamp (70.0 mW cm^{-2}) at pH = 8.5. The absorbance of Rose Bengal was found to decrease with increasing time of exposure. A plot of 1 + log A versus time was found to be linear. The rate constant of reaction was calculated with the following expression k = 2.303 × slope. The data of typical run are presented in Table 3.11: and Fig. 3.14:

Table 3.11: A typical run

pH = 8.5 $g\text{-}C_3N_4$ = 0.08 g

[Rose Bengal] = 8.0×10^{-5} M Light Intensity = 70.0 mW cm^{-2}

Time (min)	Absorbance (A)	1 + log A
0.00	0.685	0.8356
10.0	0.684	0.8350
20.0	0.672	0.8273
30.0	0.654	0.8155
40.0	0.637	0.8041
50.0	0.621	0.7930
60.0	0.613	0.7874
70.0	0.588	0.7694
80.0	0.576	0.7604
90.0	0.574	0.7589
100	0.557	0.7458
110	0.543	0.7347

Rate constant (k) = 3.83×10^{-5} s^{-1}

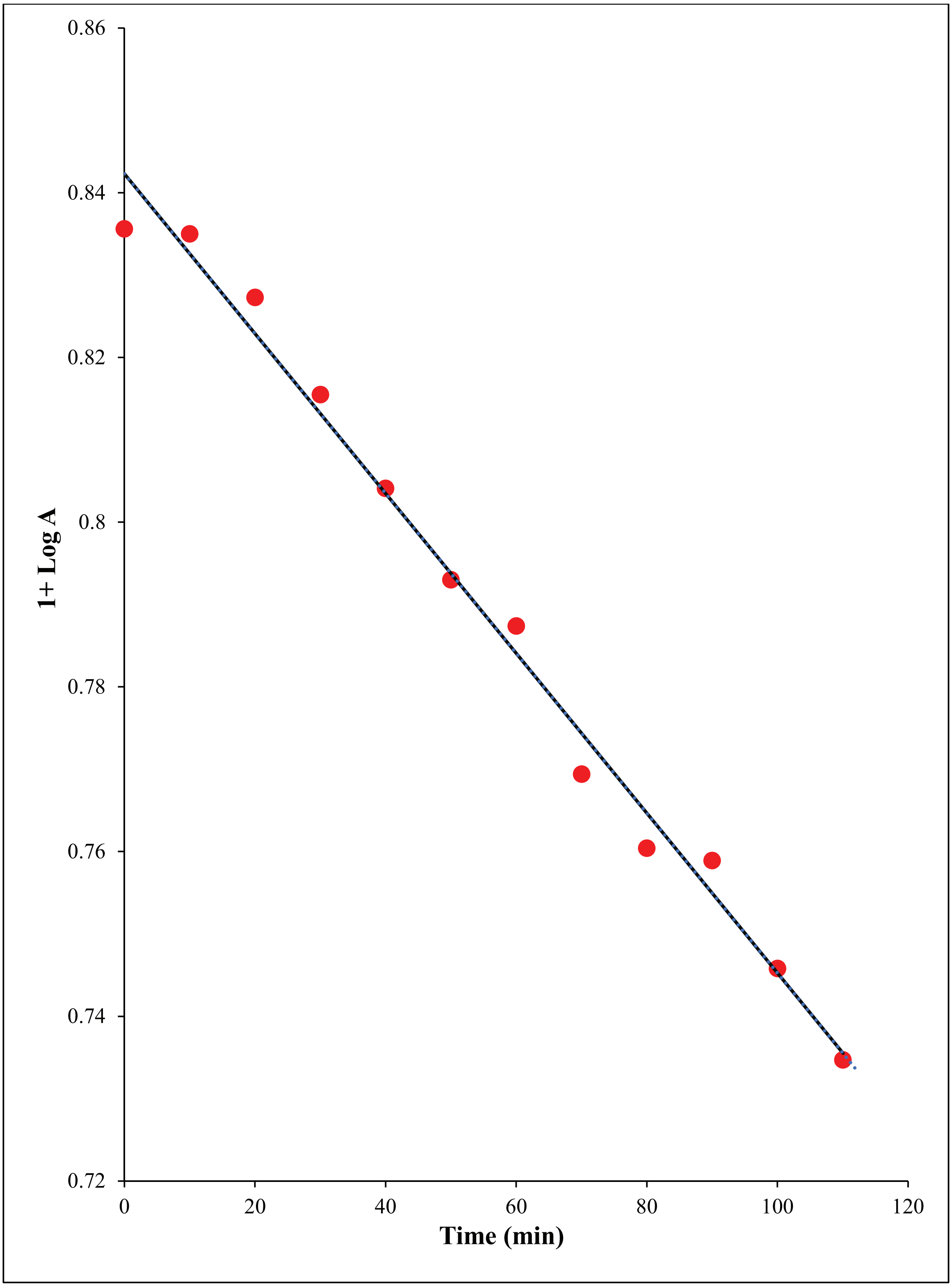

Fig. 3.14: A typical run

3.6.1 Effect of pH

The effect of pH on photocatalytic degradation was observed in the range of 6.5 to 10.0. The results are given in Table 3.12: and Fig. 3.15:

Table 3.12: Effect of pH

[Rose Bengal] = 8.0×10^{-5} M g-C_3N_4 = 0.08 g

Light Intensity = 70.0 mW cm^{-2}

pH	**Rate constant (k) × 10^5 (s^{-1})**
6.5	1.39
7.0	2.08
7.5	2.69
8.0	3.29
8.5	**3.83**
9.0	2.92
9.5	2.55
10	1.26

It was noticed that the degradation rate of Rose Bengal increases with increasing pH of solution up till 8.5, but above this value of pH, the rate of reaction of photodegradation of Rose Bengal started decreasing.

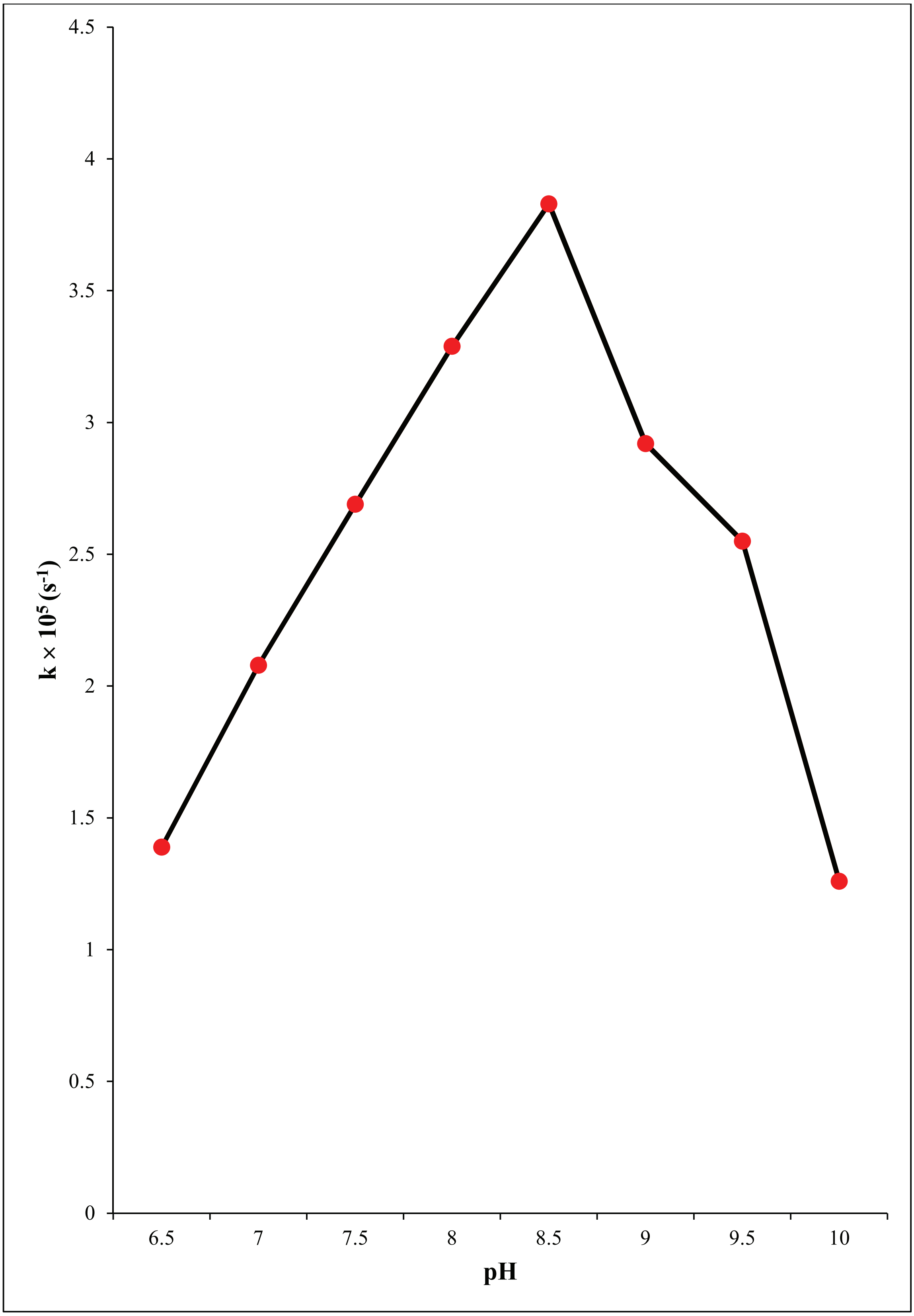

Fig. 3.15: Effect of pH

3.6.2 Effect of dye concentration

The effect of dye concentration on the rate of reaction was also observed using different concentrations of Rose Bengal solution (2.0×10^{-5}M-1.8×10^{-4}M) The results are shown in Table 3.13: and Fig. 3.16:

Table 3.13: Effect of dye concentration

pH = 8.5 Light Intensity = 70.0 mW cm^{-2}

g-C_3N_4 = 0.08 g

[Rose Bengal] × 10^4 M	**Rate constant (k) × 10^5 (s^{-1})**
0.2	1.58
0.4	2.02
0.6	2.54
0.8	**3.83**
1.2	3.01
1.4	2.63
1.6	2.18
1.8	1.69

It was observed that the rate of photocatalytic degradation increases with increase in the concentration of the dye up to 8.0×10^5 M, but therefore, it decreases.

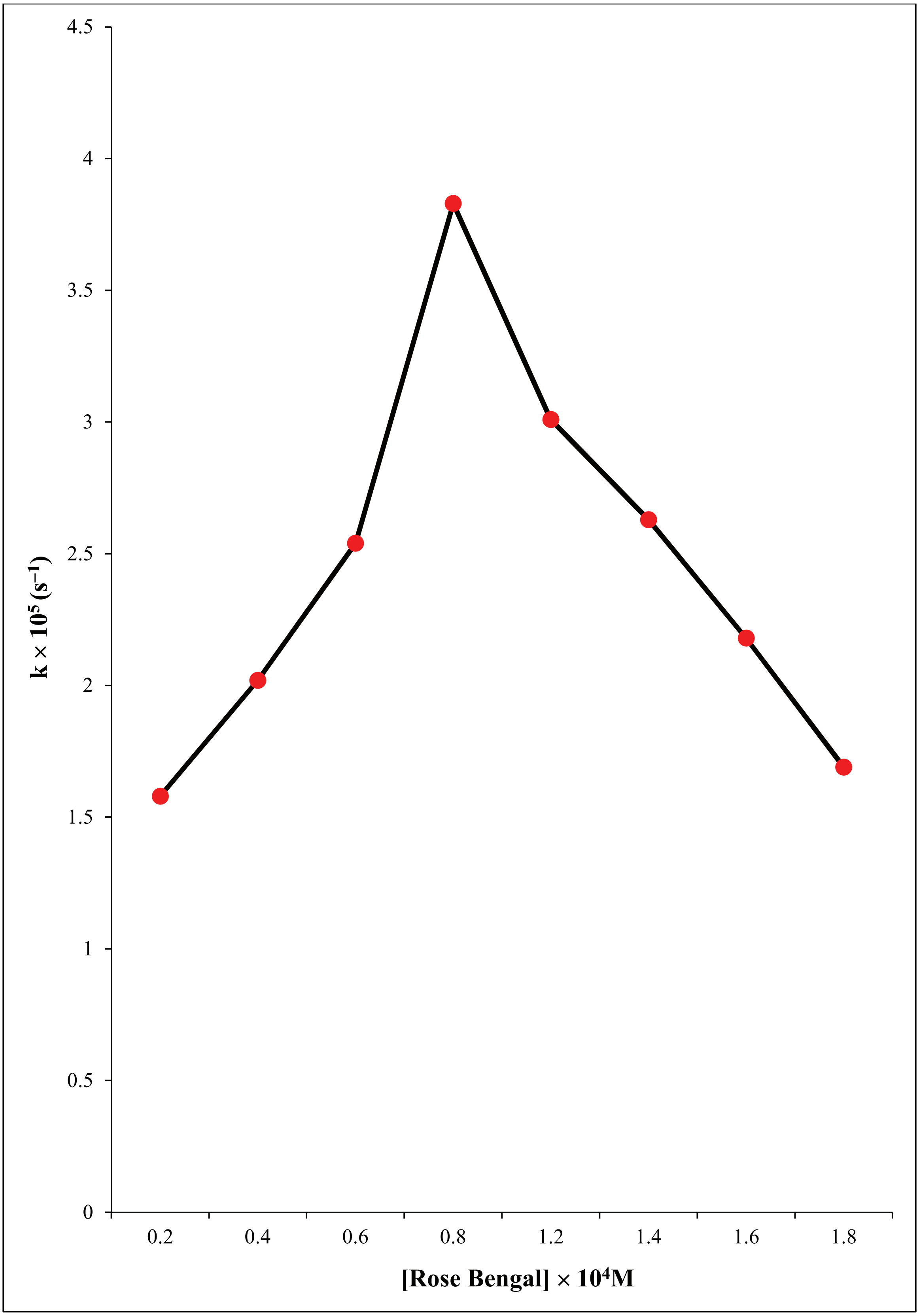

Fig. 3.16: Effect of dye concentration

3.6.3 Effect of amount of photocatalyst

The effect of amount of photocatalyst on the rate of photocatalytic degradation of Rose Bengal was also observed in the rang 0.02-0.18 g. The results are shown in Table 3.14: and Fig. 3.17:

Table 3.14: Effect of amount of photocatalyst

pH = 8.5 Light Intensity = 70.0 mW cm^{-2}

[Rose Bengal] = 8.0×10^{-5} M

$g\text{-}C_3N_4$ (g)	Rate constant (k) × 10^4 (s^{-1})
0.02	2.08
0.04	2.97
0.06	3.72
0.08	**3.83**
0.12	3.28
0.14	2.65
0.16	2.55
0.18	2.26

It was noticed that the rate of reaction increases with increase in the amount of photocatalyst up to 0.08 g, but above this value of photocatalyst, the rate of reaction decreased.

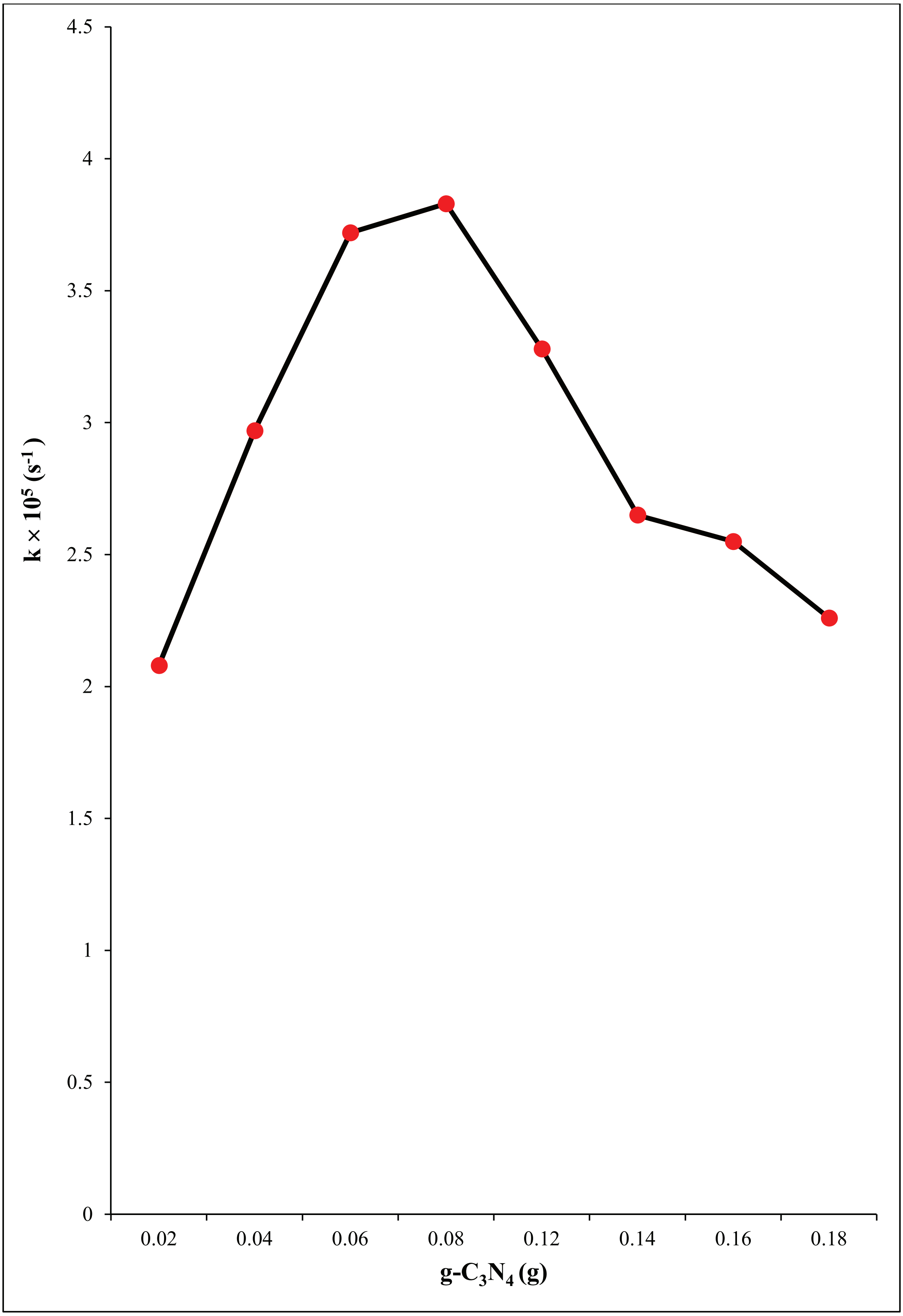

Fig. 3.17: Effect of amount of photocatalyst

3.6.4 Effect of light intensity

The effect of light intensity on the rate of Rose Bengal was also observed from 20.0 to 70.0 mW cm^{-2} The results are reported in Table 3.15: and Fig. 3.18:

Table 3.15: Effect of light intensity

pH = 8.5 [Rose Bengal] = 8.0 ×10^{-5} M

g-C_3N_4 = 0.08 g

Light intensity (mW cm^{-2})	**Rate constant (k) × 10^5 (s^{-1})**
30	0.35
40	1.78
50	3.10
60	3.59
70	**3.83**

It was observed that the rate of degradation increased on increasing light intensity.

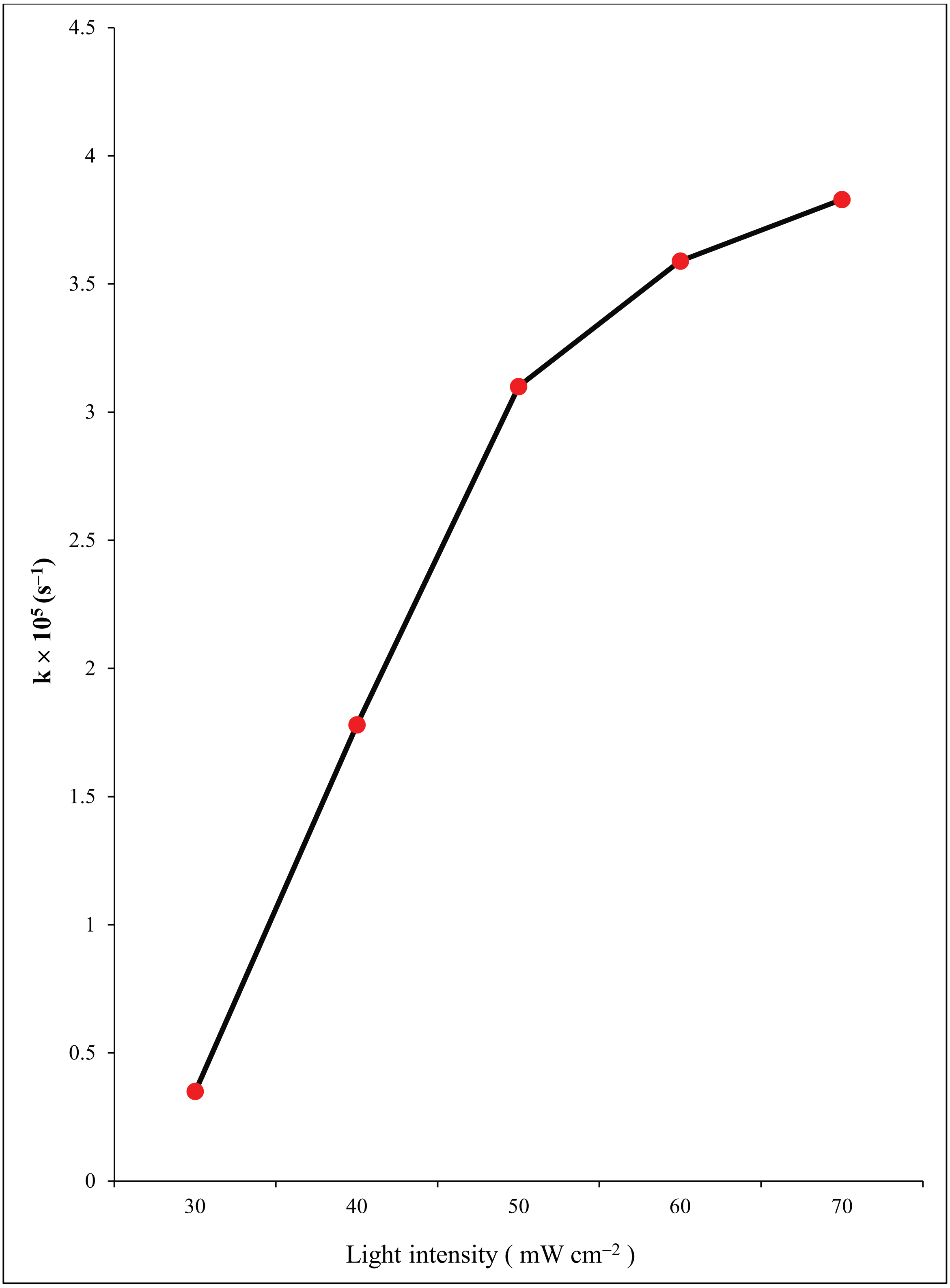

Fig. 3.18: Effect of light intensity

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CHAPTER – IIID

METHYLENE BLUE-GRAPHITIC CARBON NITRIDE SYSTEM

CONTENTS

3.7 METHYLENE BLUE

3.8 EXPERIMENTAL

3.7 METHYLENE BLUE

Methylthionine chloride is commonly called methylene blue. Its salt is used as a dye and for medication. It is mainly used to treat methemoglobinemia by chemically reducing the ferric iron in haemoglobin to ferrous iron

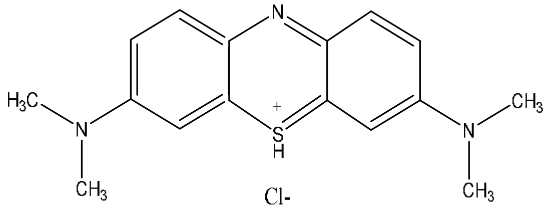

Fig. 3.19: Structure of Methylene Blue

IUPAC Name : 3,7-Bis(Dimethylamine)-phenothiazin-5-ium chloride

Molecular Formula : $C_{16}H_{18}ClN_3S$

Molecular Mass : 319.85 g mol^{-1}

λ max : 664 nm

Solubility : Water

3.8 EXPERIMENTAL

A 1.0×10^{-4} M solution of methylene blue (HIMEDIA) was prepared by dissolving 0.0934 g of methylene blue in 250.0 mL of distilled water. This solution served as a stock solution. The absorbance of methylene blue dye solution was measured using a spectrophotometer at a wavelength of λ max = 664 nm. The dye solution was divided into four portions.

- The first beaker containing dye solution was kept in dark,
- The second beaker containing dye solution was exposed to 200 W tungsten lamp,
- The third beaker containing dye solution and 0.16 g of graphitic carbon nitride was kept in dark, and

- The fourth beaker containing dye solution and 0.16 g photocatalyst graphitic carbon nitride was exposed to 200 W tungsten lamp.

It was observed that the absorbance of the first beaker remained almost same even after 3 h. while the second beaker had a slight decrease in initial value of its absorbance. The initial absorbance of the third beaker also showed a slight decrease. The absorbance of the fourth beaker experienced a significant reduction. These observations indicate that the reaction between methylene blue and photocatalyst is a photocatalytic reaction only.

The 0.16 g of g-C_3N_4 was added to 1.50×10^{-4} M dye solution and then exposed to a 200 W tungsten lamp at pH = 8.5 and 60.0 mW cm^{-2}. The absorbance of methylene blue was found to decrease with increasing exposure time. A linear relationship was observed on plotting 1 + log A against time. The rate constant (k) of the reaction was calculated using the expression k = 2.303 × slope. The results are reported in Table 3.16 and Fig. 3.20.

Table 3.16: A typical run

pH= 8.5 [Methylene blue] = 1.50×10^{-4} M

g-C_3N_4 = 0.16 g Light intensity = 60.0 mW cm^{-2}

Time (min)	Absorbance (A)	1 + log A
0.00	1.138	1.0561
10.0	1.105	1.0433
20.0	1.014	1.006
30.0	0.755	0.8779
40.0	0.743	0.8709
50.0	0.661	0.8202
60.0	0.637	0.8041
70.0	0.599	0.7774
80.0	0.563	0.7505
90.0	0.530	0.7242
100	0.497	0.6963
110	0.413	0.6159

Rate constant = $1.65 \times 10^{-4} s^{-1}$

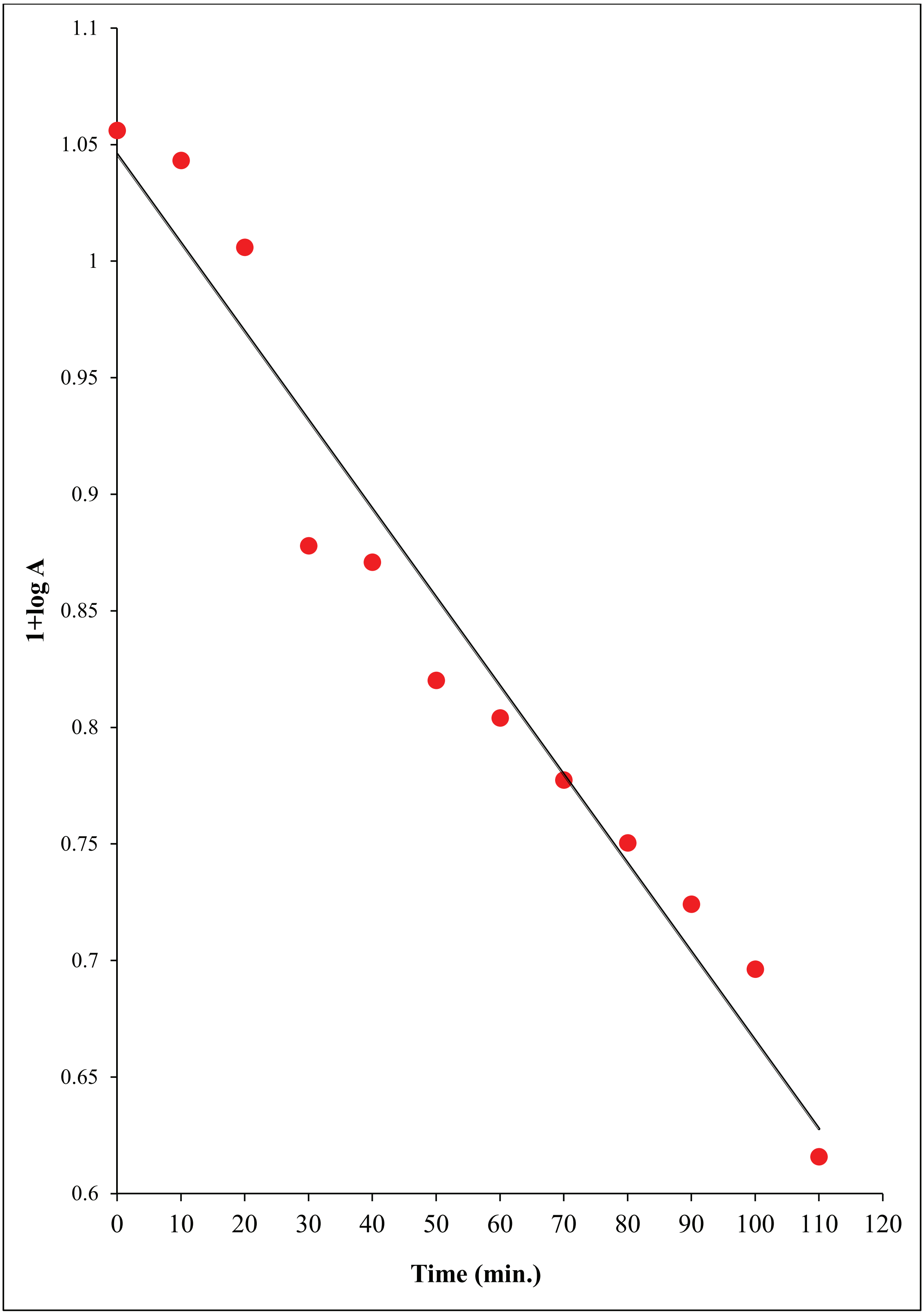

Fig. 3.20: A typical run

3.8.1 Effect of pH

The effect of pH on photocatalytic degradation was observed in the range of 5.5 to 9.5. The results are shown in Table 3.17: and Fig.3.21:

Table 3.17: Effect of pH

[Methylene blue] = 1.50×10^{-4} M g-C_3N_4 = 0.16 g

Light Intensity = 60.0 mW cm^{-2}

pH	Rate constant (k)× 10^4 (s^{-1})
5.5	0.47
6.0	0.88
6.5	1.19
7.0	1.32
7.5	1.59
8.0	1.76
8.5	**1.65**
9.0	1.29
9.5	1.02

The rate of degradation of methylene blue increases with increasing pH of solution up to 8.5, but above this value of pH, the rate of photodegradation of methylene blue started decreasing.

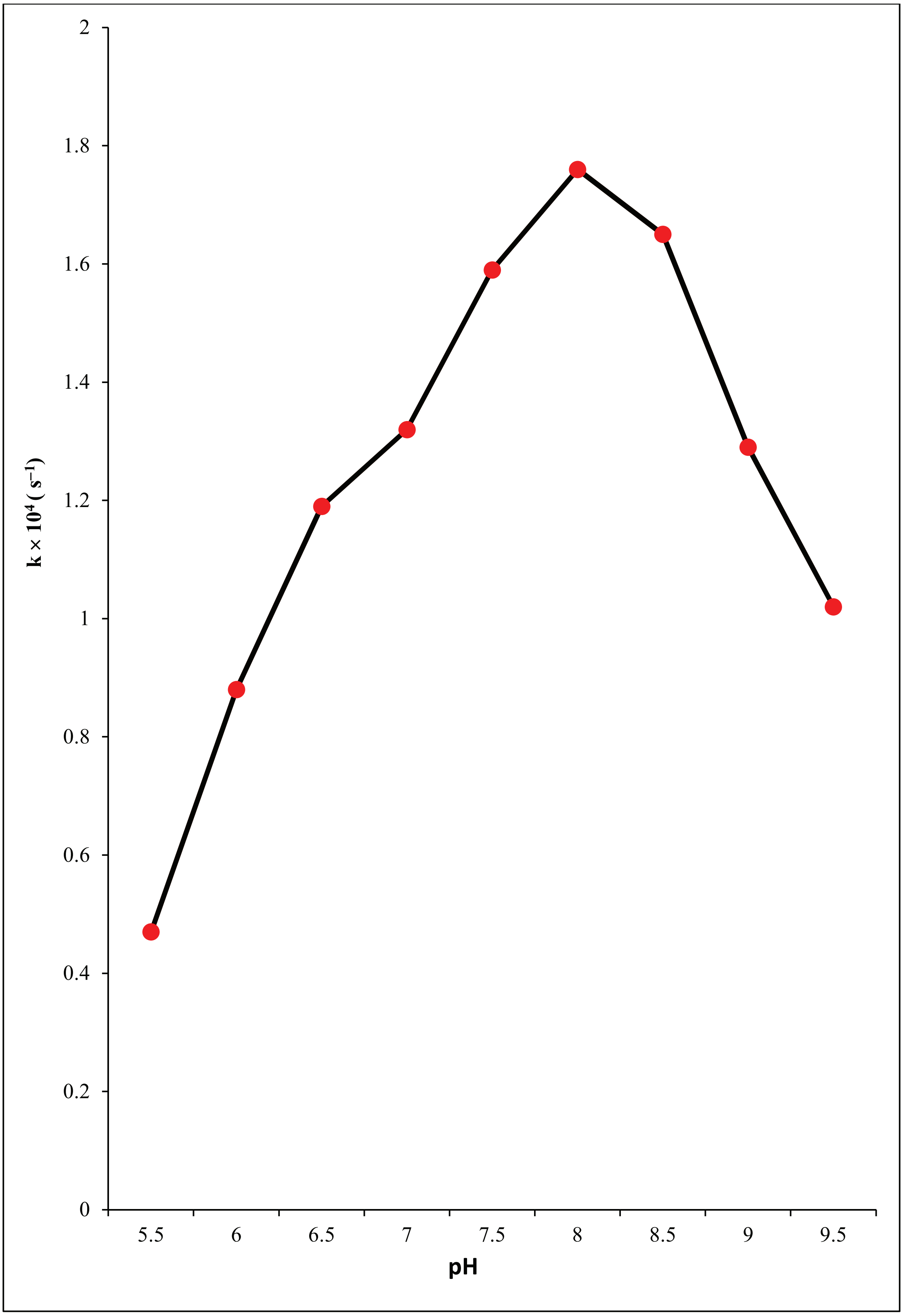

Fig. 3.21: Effect of pH

3.8.2 Effect of dye concentration

The effect of dye concentration of dye on the rate of reaction was also observed using different concentrations of methylene blue solution. The results are tabulated in Table 3.18: and presented in Fig. 3.22:

Table 3.18: Effect of dye concentration

pH = 8.5 Light intensity = 60.0 mW cm^{-2}

g-C_3N_4 = 0.16 g

[Methylene Blue] × 10^4 M	**Rate constant (k)× 10^4 (s^{-1})**
0.1	0.43
0.3	0.68
0.7	1.09
0.9	1.19
1.1	1.42
1.3	1.5
1.5	**1.65**
1.7	0.82
1.8	0.56

It was noticed that the rate of photocatalytic degradation increases with dye concentration up to 1.50 × 10^4 M, but it decreases on increasing the concentration of dye further.

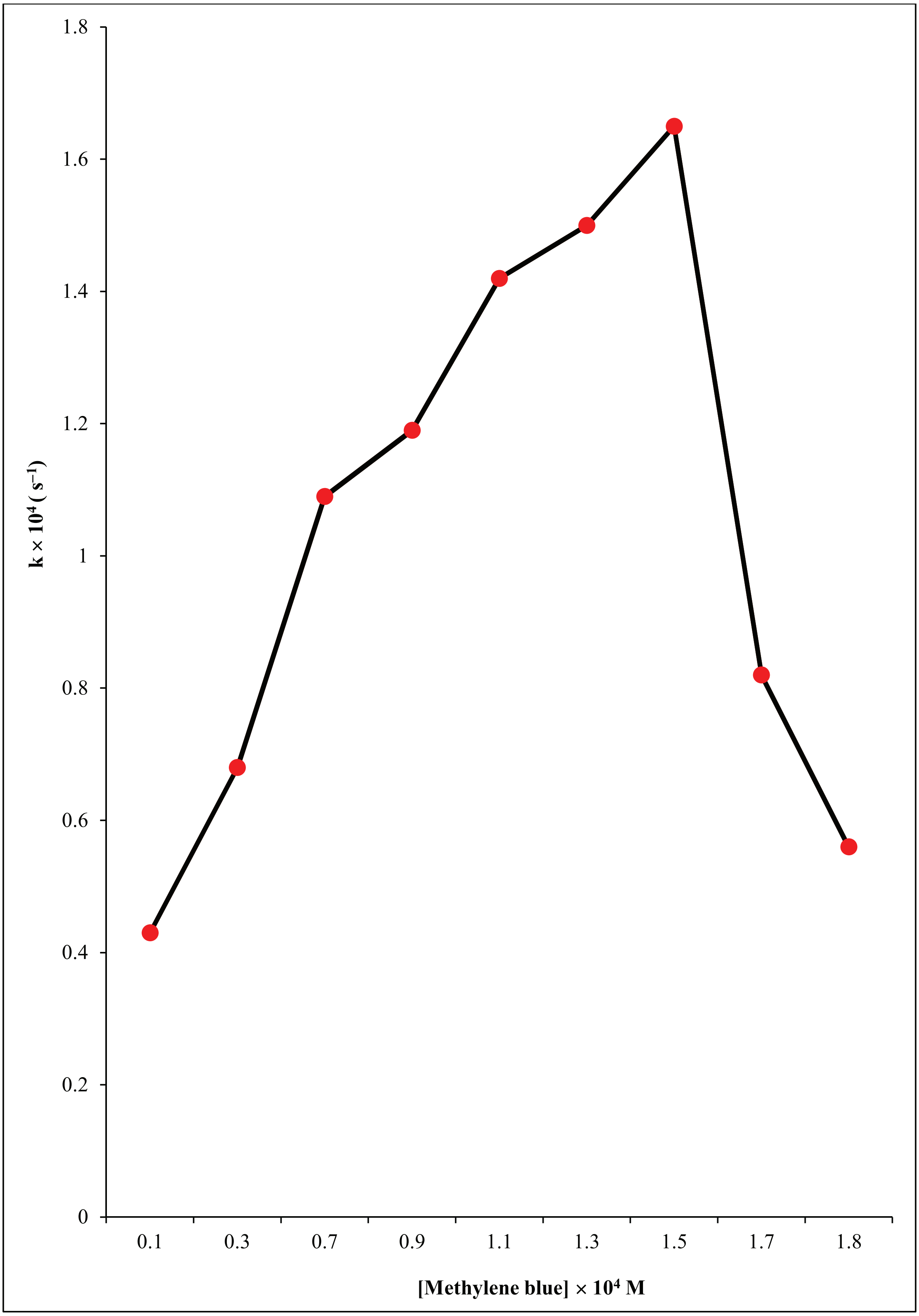

Fig. 3.22: Effect of dye concentration

3.8.3 Effect of amount of photocatalyst

The effect of amount of photocatalyst on the rate of photocatalytic degradation of methylene blue was also observed in the rang of 0.02-0.20 g. The results are shown in Table 3.19: and Fig. 3.23.

Table 3.19: Effect of amount of photocatalyst

[MB] = 1.50×10^{-4} M pH = 8.5

Light intensity = 60.0 mW cm^{-2}

g-C_3N_4 (g)	**Rate constant (k) × 10^4 (s^{-1})**
0.02	0.55
0.04	0.78
0.06	0.97
0.08	1.12
0.12	1.21
0.14	1.38
0.16	**1.65**
0.18	1.36
0.20	1.18

The reaction rate increased with increasing at larger quantity of photocatalyst till 0.16 g, beyond which, the rate started declining.

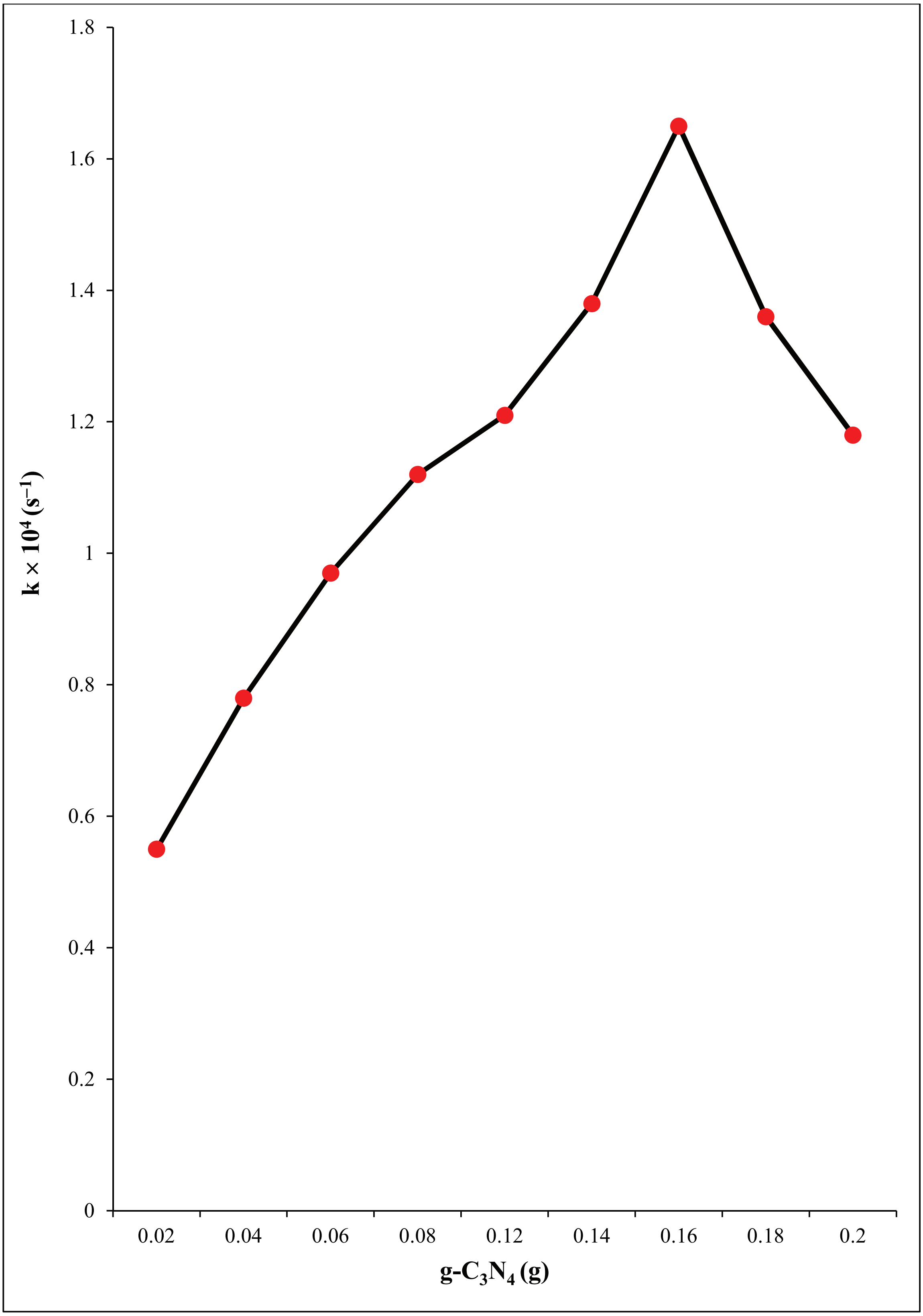

Fig. 3.23: Effect of amount of photocatalyst

3.8.4 Effect of light intensity

The effect of light intensity on the rate of degradation of methylene blue was also observed from 20.0-70.0 mW cm^{-2}. The results are reported in Table 3.20: and Fig. 3.24:

Table 3.20: Effect of light intensity

[MB] = 1.50×10^{-4} M pH = 8.5

g-C_3N_4 = 0.16 g

Light intensity (mW cm^{-2})	**Rate constant (k) × 10^4 (s^{-1})**
20.0	0.85
30.0	0.91
40.0	0.98
50.0	1.22
60.0	**1.65**
70.0	1.58

It was observed that the rate of degradation was increased on increasing light intensity up to 60.0 mWcm^{-2} but above this value, the rate of degradation again decreased.

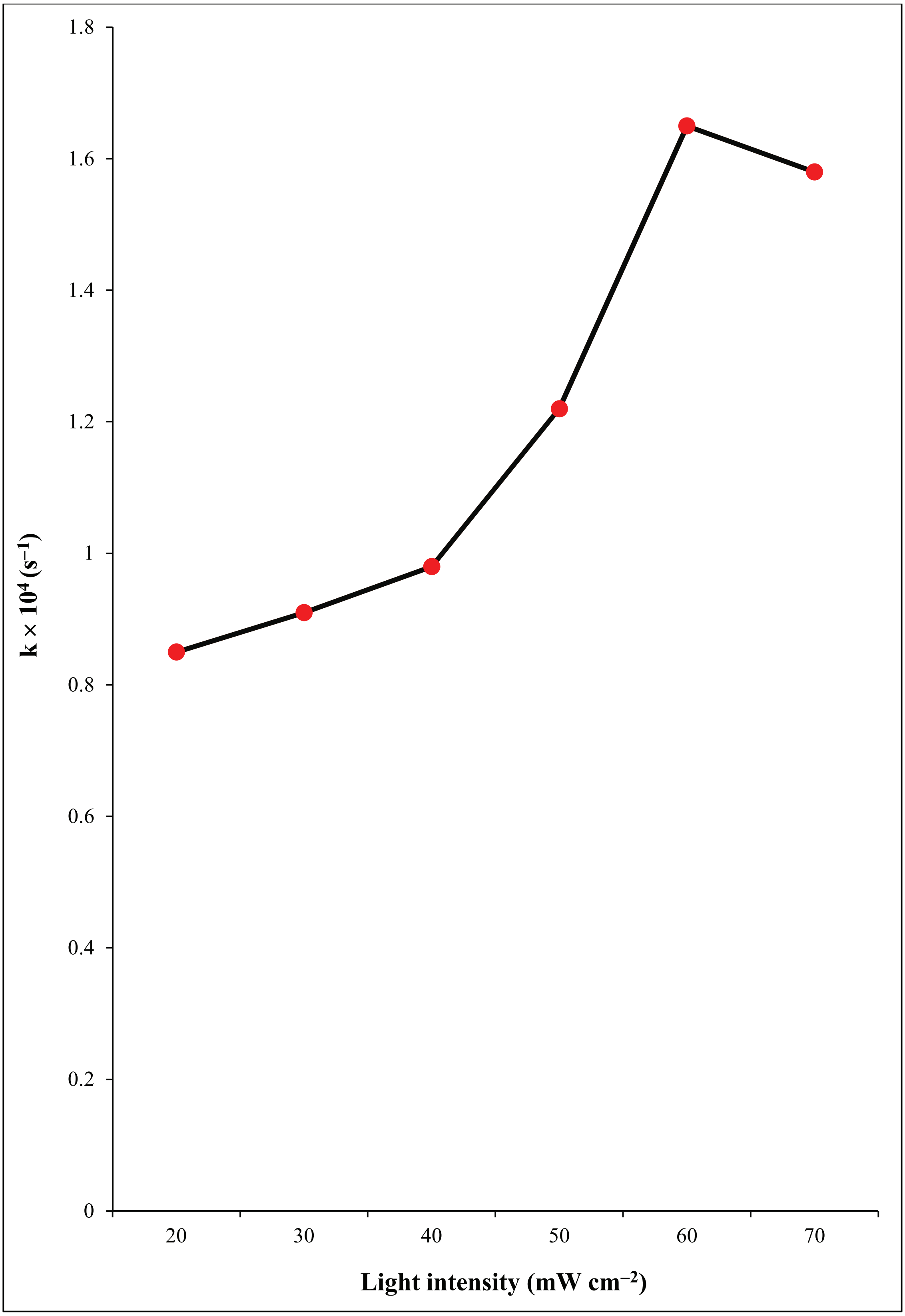

Fig. 3.24: Effect of light intensity

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CHAPTER – IIIE

RHODAMINE B- GRAPHITIC CARBON NITRIDE SYSTEM

CONTENTS

3.9 RHODAMINE B

3.10 EXPERIMENTAL

3.9 RHODAMINE B

Rhodamine B is a dye. It is often used as a tracer dye within water to determine the rate and direction of flow and transport. Rhodamine dye fluoresce and can be detected easily with fluorometer.

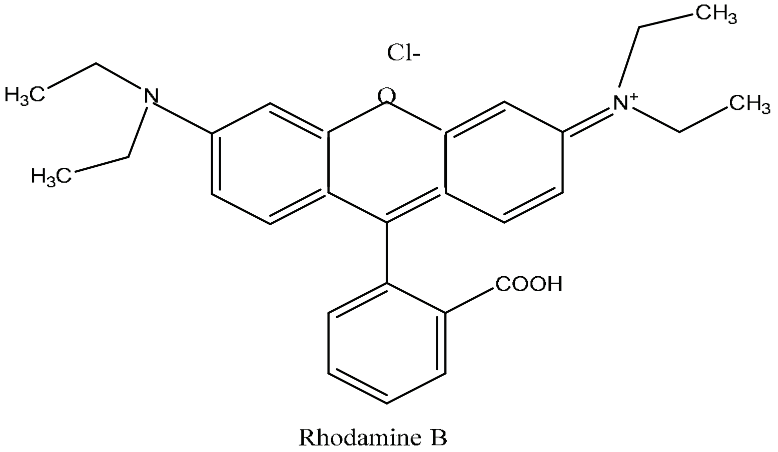

Fig. 3.25: Structure of Rhodamine B

IUPAC Name : 9-(2-Carboxyphenyl)-6-(diethylamino)-N,N-diethyl-3H-xanthen-3-iminium chloride

Molecular Formula : $C_{28}H_{31}N_2O_3Cl$

Molecular Mass : $479\ g\ mol^{-1}$

λ max : 556 nm

Solubility : Water

3.10 EXPERIMENTAL

A 1.0×10^{-3} M solution of rhodamine B (HIMEDIA) was prepared by dissolving 0.120 g of rhodamine B in 250.0 mL of distilled water. This solution served as a stock solution. The absorbance of rhodamine B dye solution was measured using a spectrophotometer at a wavelength of λ max = 556 nm. The dye solution was divided into four portions.

- The first beaker containing dye solution was kept in dark,
- The second beaker containing dye solution was exposed to 200 W tungsten lamp,
- The third beaker containing dye solution and 0.12 g of graphitic carbon nitride was kept in dark, and
- The fourth beaker containing dye solution and 0.12 g photocatalyst graphitic carbon nitride was exposed to 200 W tungsten lamp.

It was observed that the absorbance of the first beaker remained almost same even after 3 h. while the second beaker had a slight decrease in initial value of its absorbance. The initial absorbance of the third beaker also showed a slight decrease. The absorbance of the fourth beaker experienced a significant reduction. These observations indicates that the reaction between rhodamine B and photocatalyst is a photocatalytic reaction only.

The 0.12 g of g-C_3N_4 was added to 1.00×10^{-3} M dye solution and then exposed to a 200 W tungsten lamp at pH = 7.5 and 60.0 m W cm^{-2}. The absorbance of rhodamine B was found to decrease with increasing exposure time. A linear relationship was observed on plotting 1 + log A against time. The rate constant (k) of the reaction was calculated using the expression k = 2.303 × slope. The results are reported in Table 3.21 and Fig. 3.26.

Table 3.21: A typical run

[Rhodamine B] = 8.00×10^{-4} M pH = 7.5

g-C_3N_4 = 0.12 g Light intensity = 40.0 mW cm^{-2}

Time (min)	Absorbance (A)	1 + log A
0.00	0.735	0.8662
10.0	0.676	0.8299
20.0	0.631	0.8000
30.0	0.603	0.7803
40.0	0.586	0.7678
50.0	0.466	0.7438
60.0	0.531	0.7250
70.0	0.555	0.7212
80.0	0.525	0.7201
90.0	0.522	0.7176
100	0.510	0.7075

Rate constant (k) = $9.51 \times 10^{-5} s^{-1}$

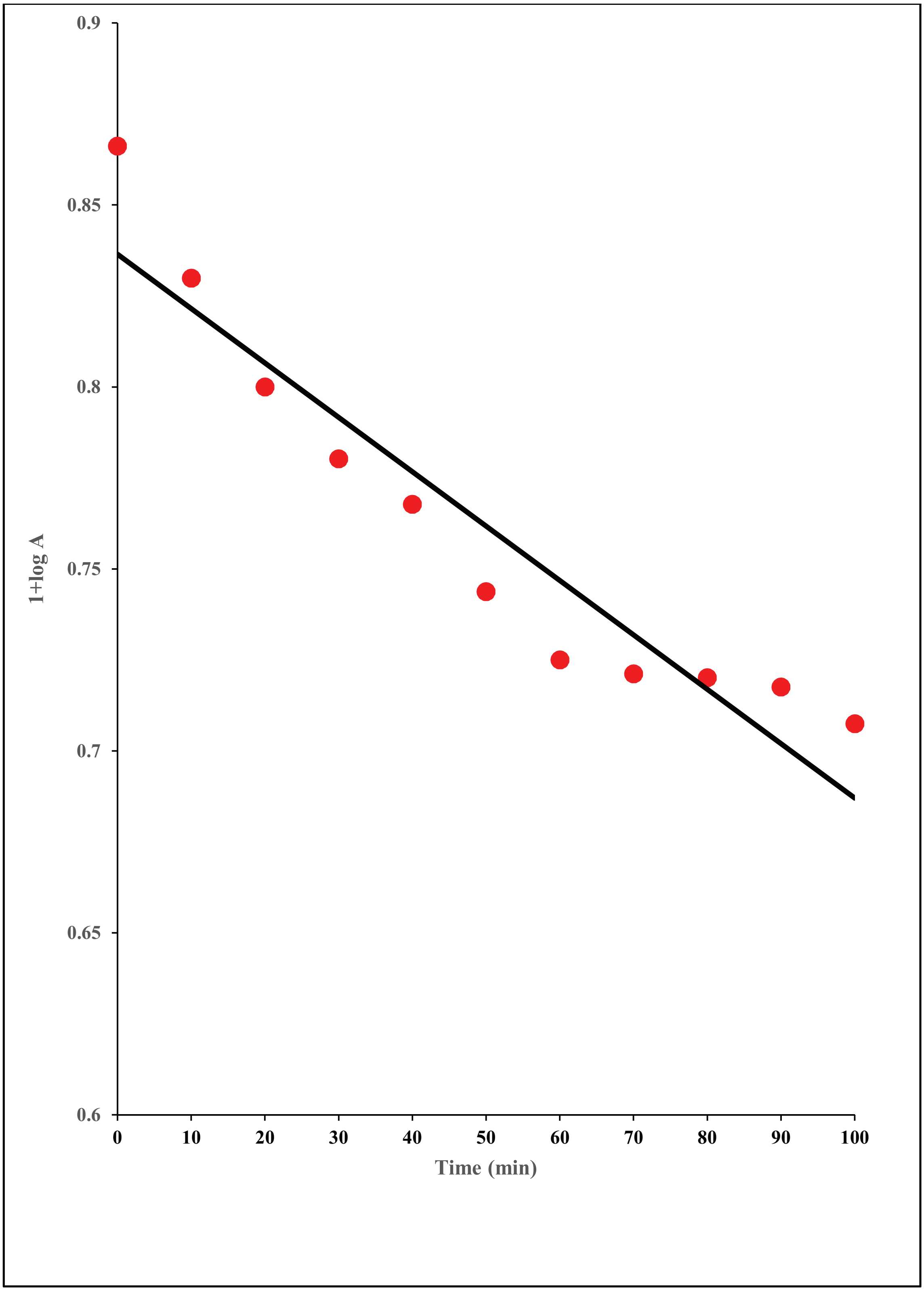

Fig. 3.26: A typical run

3.10.1 Effect of pH

The effect of pH on photocatalytic degradation was observed in the range of 5.5 to 9.0. The results are shown in Table 3.22: and Fig. 3.27:

Table 3.22: Effect of pH

[Rhodamine B] = 8.00×10^{-5} M g-C_3N_4 = 0.12 g

Light Intensity = 60.0 mW cm^{-2}

pH	**Rate constant (k) × 10^5 (s^{-1})**
5.5	3.00
6.0	3.34
6.5	4.01
7.0	5.72
7.5	**9.51**
8.0	7.11
8.5	4.74
9.0	3.36

The rate of degradation of Rhodamine B increases with increasing pH of solution up to 7.5, but above this value of pH, the rate of photodegradation of rhodamine B start decreasing.

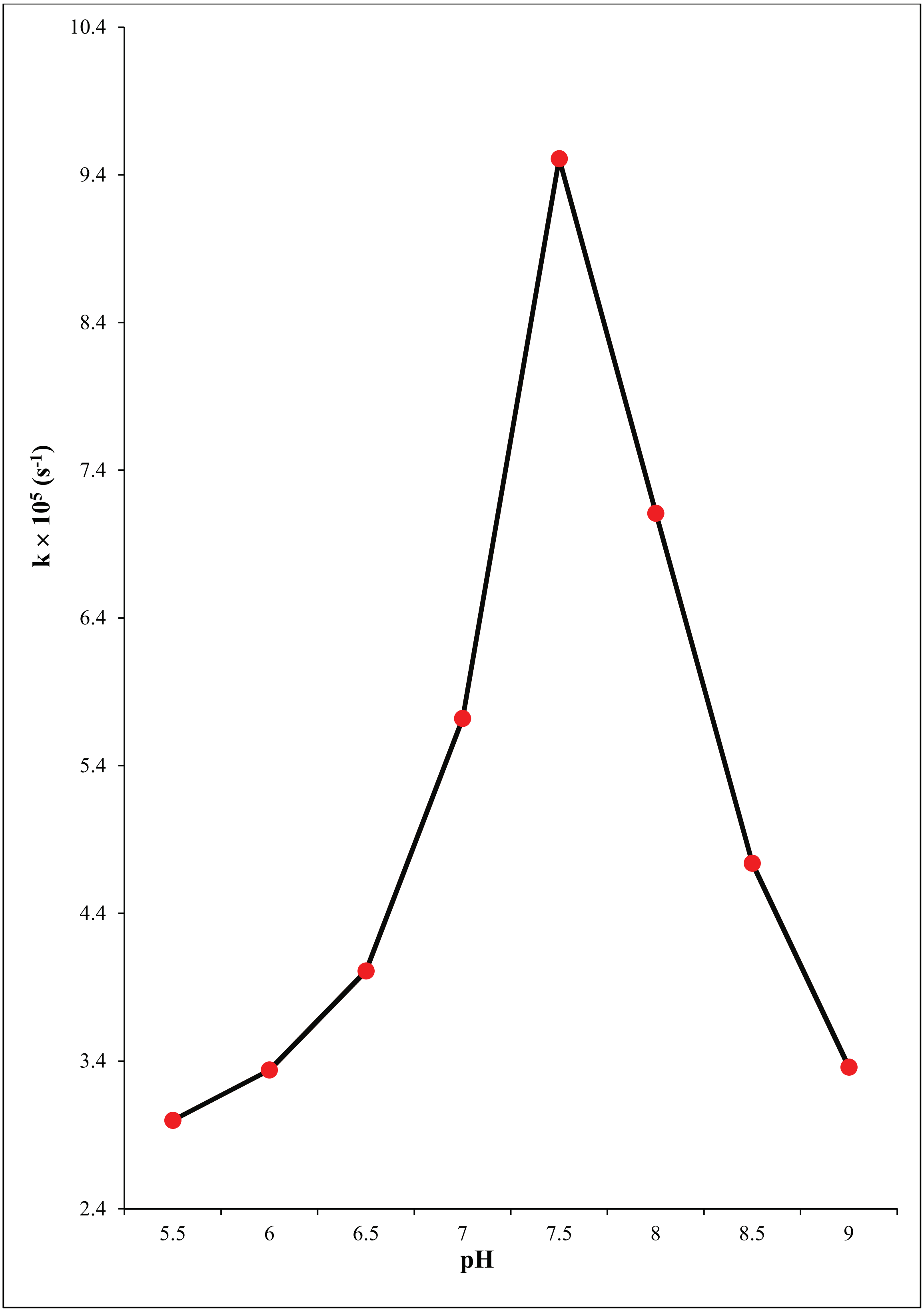

Fig. 3.27: Effect of pH

3.10.2 Effect of dye concentration

The effect of dye concentration on the rate of reaction was also observed using different concentrations of rhodamine B solution betweem 2.0×10^{-5} to 1.8×10^{-4}M. The results are tabulated in Table 3.23: and presented in Fig. 3.28:

Table 3.23: Effect of dye concentration

pH = 7.5 Light intensity = 60.0 mW cm^{-2}

g-C_3N_4 = 0.12 g

[Rhodamine B] × 10^4 M	**Rate constant (k)× 10^5 (s^{-1})**
0.2	3.24
0.4	3.94
0.6	6.75
0.8	**9.51**
1.0	8.43
1.2	6.64
1.4	5.71
1.6	3.99
1.8	2.12

It was noticed that the rate of photocatalytic degradation increases with dye concentration up to 8.0×10^{-5} M, but it started decreasing above this value.

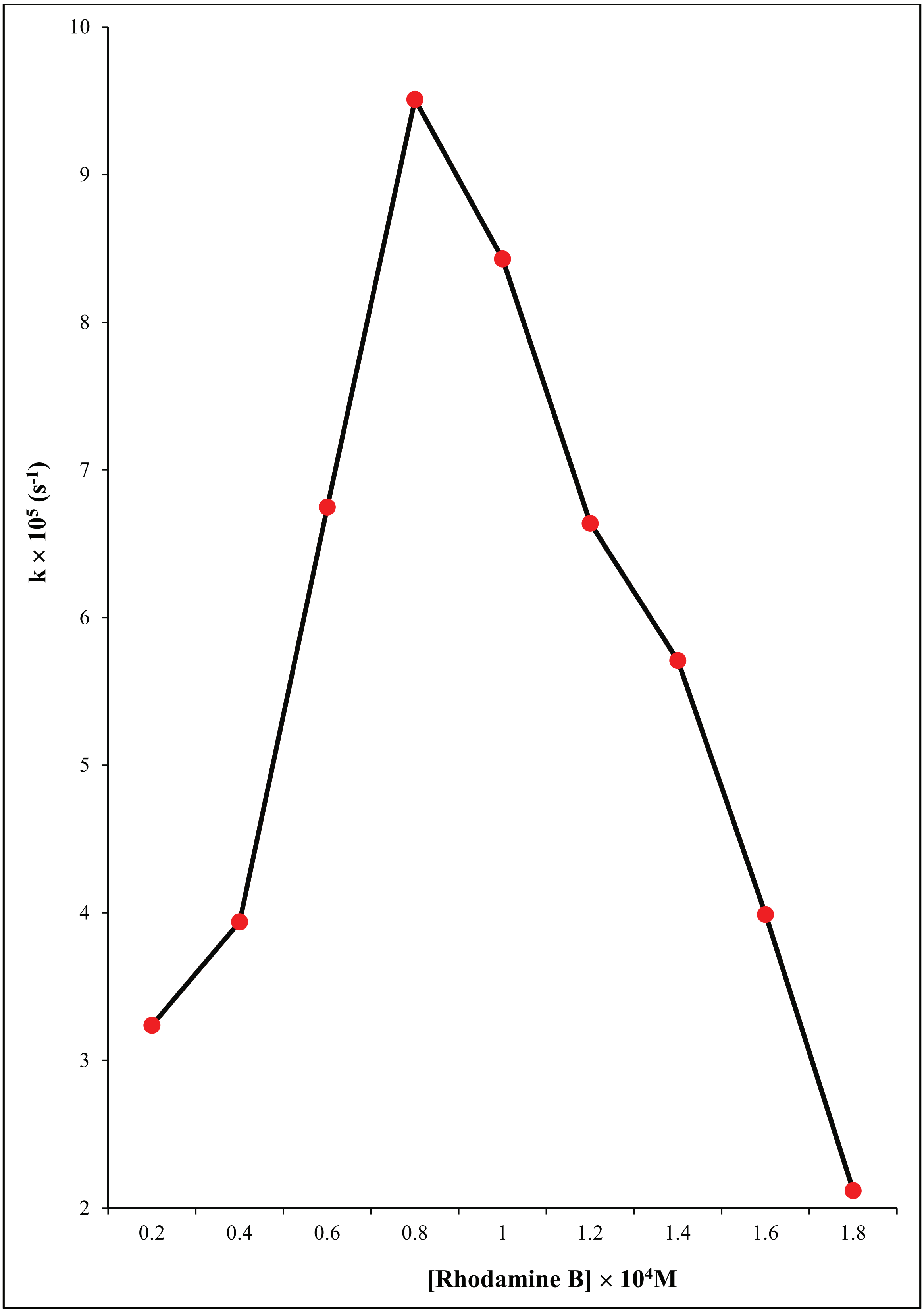

Fig. 3.28: Effect of dye concentration

3.10.3 Effect of amount of photocatalyst

The effect of amount of photocatalyst on the rate of photocatalytic degradation of Rhodamine B was also observed in the rang of 0.02-0.16 g. The results are shown in Table 3.24: and Fig. 3.29:

Table 3.24: Effect of amount of photocatalyst

[Rhodamine B] = 8.00 × 10^{-5} M pH = 7.5

Light intensity = 60.0 mW cm^{-2}

g-C_3N_4 (g)	**Rate constant (k) × 10^5 (s^{-1})**
0.02	4.24
0.04	4.67
0.06	5.21
0.08	6.86
0.10	8.18
0.12	**9.51**
0.14	8.03
0.16	6.99
0.18	5.83

The reaction rate was higher at larger quantity of photocatalyst till 0.12 g, beyond which, the rate started declining.

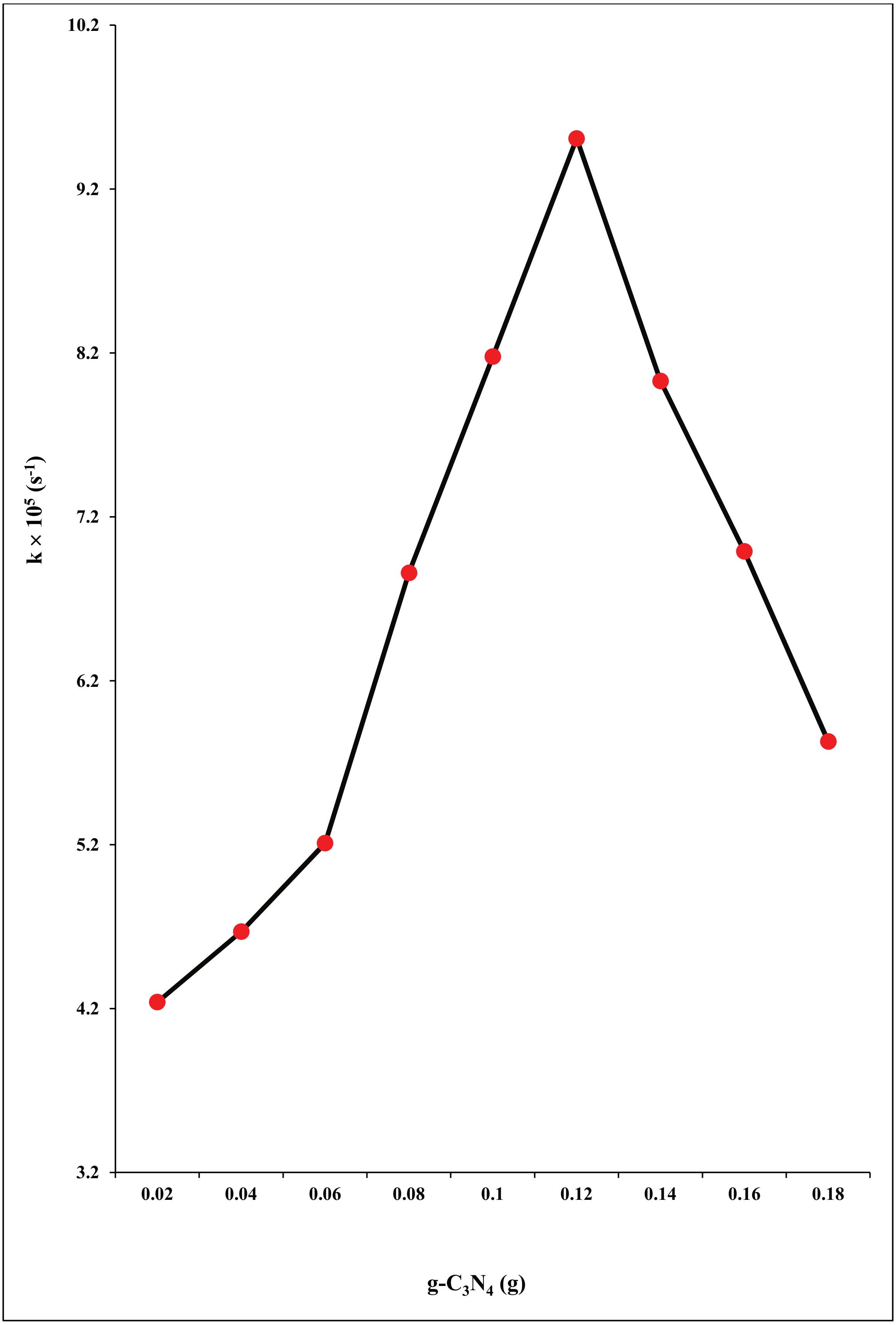

Fig. 3.29: Effect of amount of photocatalyst

3.10.4 Effect of light intensity

The effect of light intensity on the rate of degradation of Rhodamine B was also observed from 20.0 to 70.0 mW cm^{-2}. The results are reported in Table 3.25: and Fig. 3.30:

Table 3.25: Effect of light intensity

[Rh B] = 8.00×10^{-5} M pH = 7.5

g-C_3N_4 = 0.12 g

Light intensity (mW cm^{-2})	**Rate constant (k) × 10^5 (s^{-1})**
20.0	3.18
30.0	5.43
40.0	6.45
50.0	7.12
60.0	**9.51**
70.0	9.31

It was observed that the rate of degradation increased on increasing light intensity up to 60.0 mWcm^{-2}, but above this value, the rate of degradation again decreased.

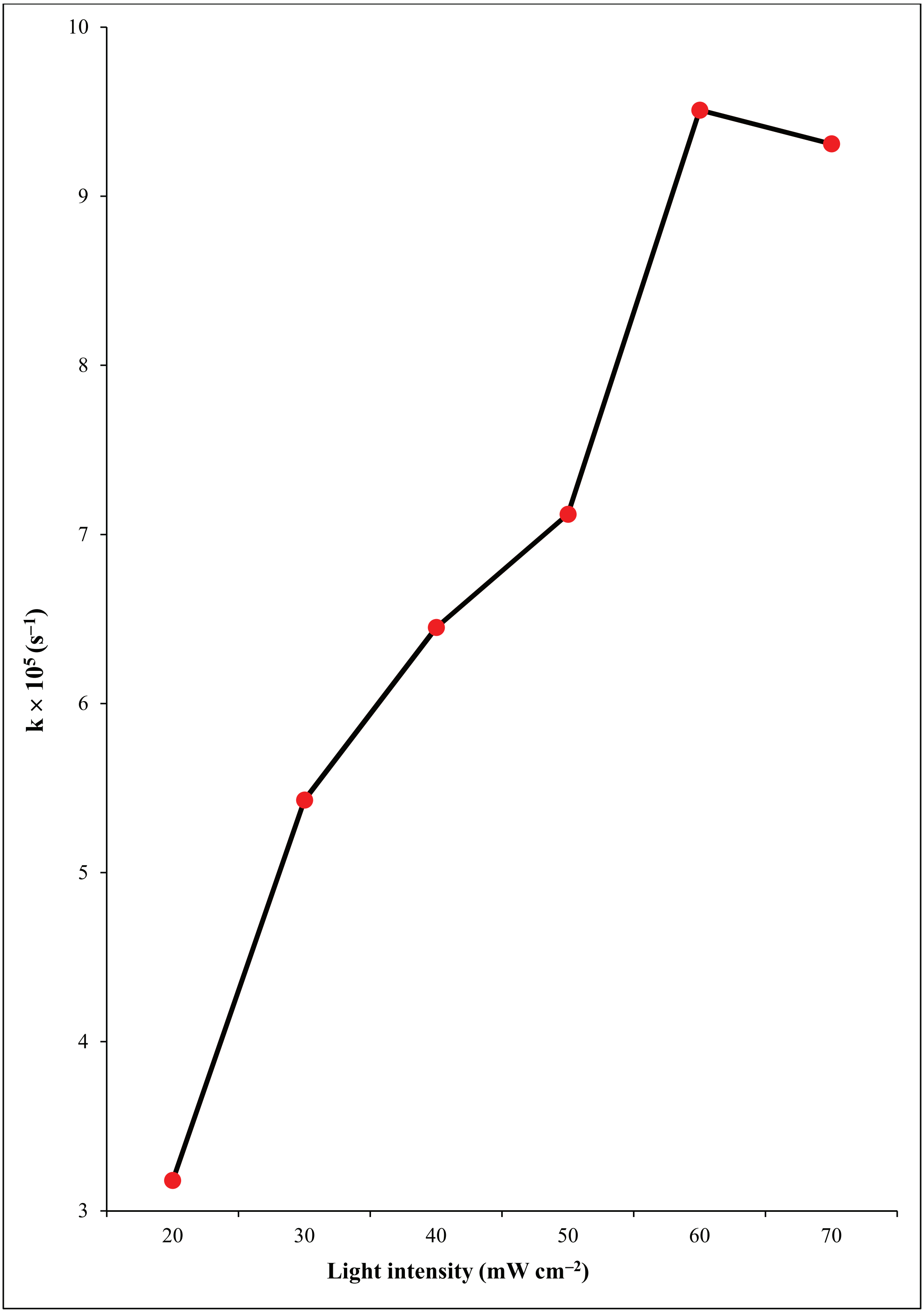

Fig. 3.30: Effect of light intensity

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CHAPTER – IIIF

ALIZARIN RED-S – GRAPHITIC CARBON NITRIDE SYSTEM

CONTENTS

3.11 ALIZARIN RED-S

3.12 EXPERIMENTAL

3.11 ALIZARIN RED-S

Alizarin red-S is also known as mordant red 3, or alizarin carmine. Alizarin red-S is used to stain calcium deposits in tissues in histology.

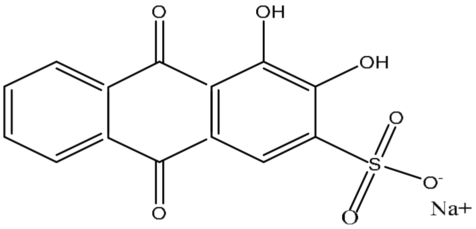

Fig. 3.31: Structure of Alizarin Red-S

IUPAC Name : 3,4-Dihydroxy-9,10-dioxo-9,10-dihydroanthracene-2-sulfonic acid
Molecular Formula : C14H7NaO7S
Molecular Mass : 342.2 g / mol–1
λ max : 527 nm
Solubility : Water

3.12 EXPERIMENTAL

Solution of alizarin red-S (HIMEDIA) was prepared by dissolving 0.0342 g in 100.0 mL water to get 1.0×10^{-3} M stock solution. The absorbance (A) of alizarin red-S dye solution was determined with the help of a spectrophotometer at λ max = 527 nm. The dye solution was placed in equal amounts in four beakers.

- The first beaker containing dye solution was kept in dark,
- The second beaker containing dye solution was exposed to 200 W tungsten lamp,
- The third beaker containing dye solution with 0.12 g photocatalyst graphitic carbon nitride was kept in dark, and
- The fourth beaker contain dye solution and 0.12 g photocatalyst graphitic carbon nitride was exposed to 200 W tungsten lamp.

The absorbance of dye solution was measured with the help of a spectrophotometer. It was observed that the absorbance of first beaker remained almost same after 3-4 h while the second beaker had a slight decrease in initial value of its absorbance. The initial absorbance value of the third beaker showed a slight difference. The initial absorbance value of the fourth beaker experienced a significant reduction. This observation confirmed that the reaction between Alizarin red-S and photocatalyst is a photocatalytic reaction.

The photodegradation of alizarin red-S was monitored by taking absorbance of samples of dye solution containing 0.12 g photocatalyst (g-C_3N_4) and exposed to 200 W tungsten lamp (70.0 mW cm^{-2}) at pH = 8.0. The absorbance of alizarin red-S was found to decrease with increasing time of exposure. A plot of 1 + log A versus time was found to be linear. The rate constant of reaction was calculated with the following expression k = 2.303 × slope. The data of typical run are presented in Table 3.26: and graphically Fig.3.32:

Table 3.26: A typical run

pH = 8.0 $g\text{-}C_3N_4$ = 0.12 g

[Alizarin red-S] = 3.20×10^{-4} M Light Intensity = 70.0 mW cm^{-2}

Time (min)	Absorbance (A)	1+ log A
0	0.642	0.8075
10	0.627	0.7972
20	0.567	0.7535
30	0.528	0.7226
40	0.510	0.7075
50	0.478	0.6794
60	0.525	0.7201
70	0.466	0.6683
80	0.430	0.6334
90	0.401	0.6031
100	0.375	0.5740
110	0.355	0.5502

Rate constant (k) = 8.72×10^{-5} s^{-1}

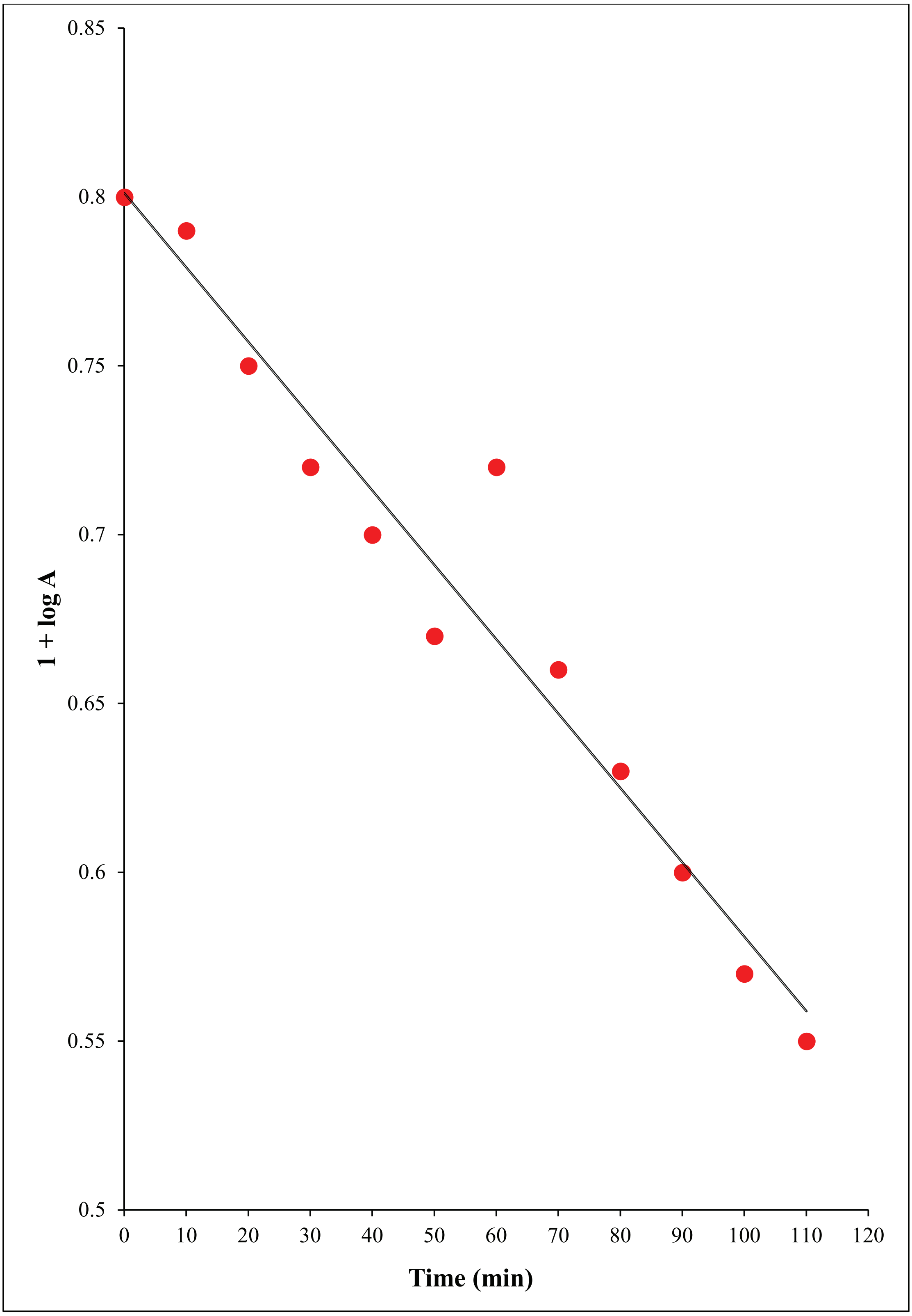

Fig. 3.32: A typical run

3.12.1 Effect of pH

The effect of pH on photocatalytic degradation was observed in the range of 6.5 to 10.0. The results are given in Table 3.27 and Fig. 3.33

Table 3.27: Effect of pH

[Alizarin red-s] = 3.20×10^{-4} M g-C_3N_4 = 0.12 g

Light Intensity = 70.0 mW cm^{-2}

pH	**Rate constant (k) × 10^5 (s^{-1})**
6.5	1.36
7.0	4.79
7.5	7.29
8.0	**8.72**
8.5	6.72
9.0	5.15
9.5	3.43
10.0	2.29

It was noticed that the degradation rate of Alizarin red-S increases with increasing pH of solution up till 8.0, but above this value of pH, the rate of photodegradation of Alizarin red-S started decreasing.

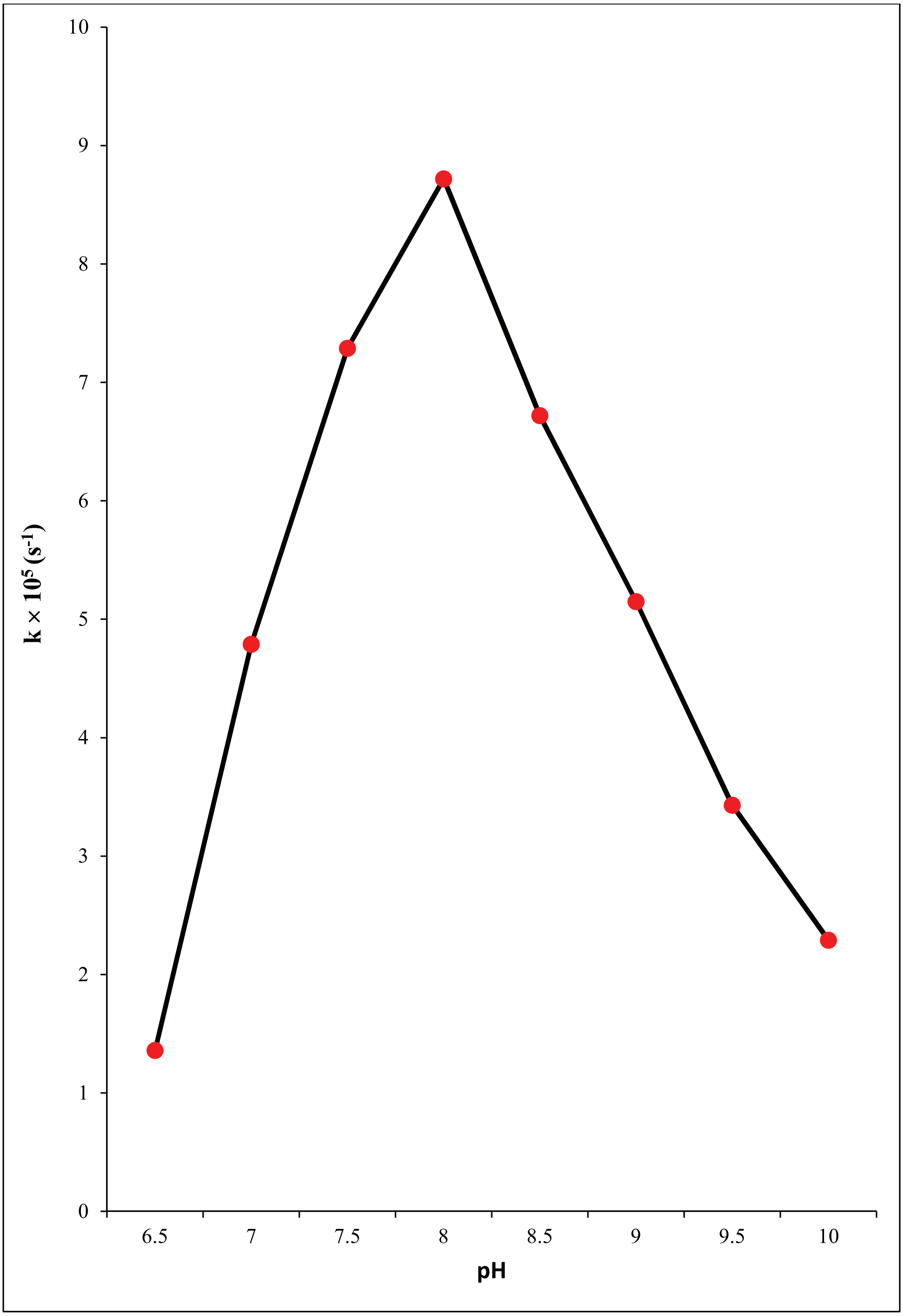

Fig. 3.33: Effect of pH

3.12.2 Effect of dye concentration

The effect of dye concentration on the rate of reaction was also observed using different concentrations of alizarin red-S solution. The results are shown in Table 3.28 and Fig. 3.34

Table 3.28: Effect of dye concentration

pH = 8.0, Light Intensity = 70.0 mW cm^{-2}

g-C_3N_4 = 0.12 g

[Alizarin red-S] × 10^4 M	**Rate constant (k) × 10^5 (s^{-1})**
2.6	4.33
2.8	4.67
3.0	5.30
3.2	**8.72**
3.4	5.72
3.6	5.41
3.8	4.79
4.0	4.50
4.2	3.53

It was observed that the rate of photocatalytic degradation increases with increase in the concentration of the dye up to 3.2 × 10^{-4} M, but it decreases on increasing concentration of dye further.

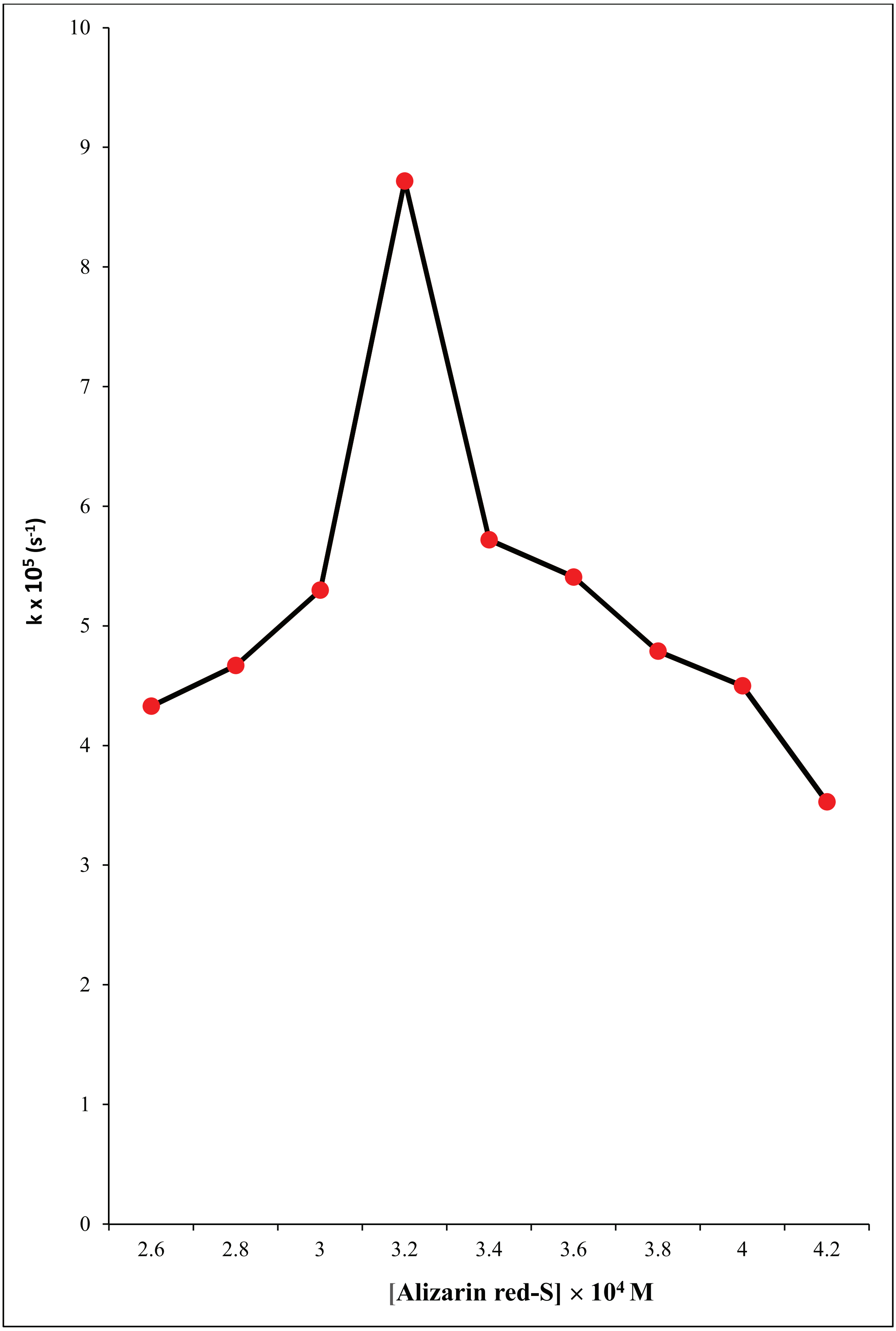

Fig. 3.34: Effect of dye concentration

3.12.3 Effect of amount of photocatalyst

The effect of amount of photocatalyst on the rate of photocatalytic degradation of alizarin red-s also observed in the rang of 0.02-0.18 g. The results are shown in Table 3.29 and Fig. 3.35

Table 3.29: Effect of amount of photocatalyst

pH = 8.0 Light Intensity = 70.0 mW cm^{-2}

[Alizarin red-S] = 3.2×10^{-3} M

g-C_3N_4 (g)	**Rate constant (k) × 10^5 (s^{-1})**
0.02	2.76
0.04	3.59
0.06	4.26
0.08	5.98
0.10	6.86
0.12	**8.72**
0.14	8.22
0.16	7.28
0.18	5.25

It was noticed that the rate of reaction increases with increase in the amount of photocatalyst up to 0.12 g, but above this value of photocatalyst, the rate of reaction decreased.

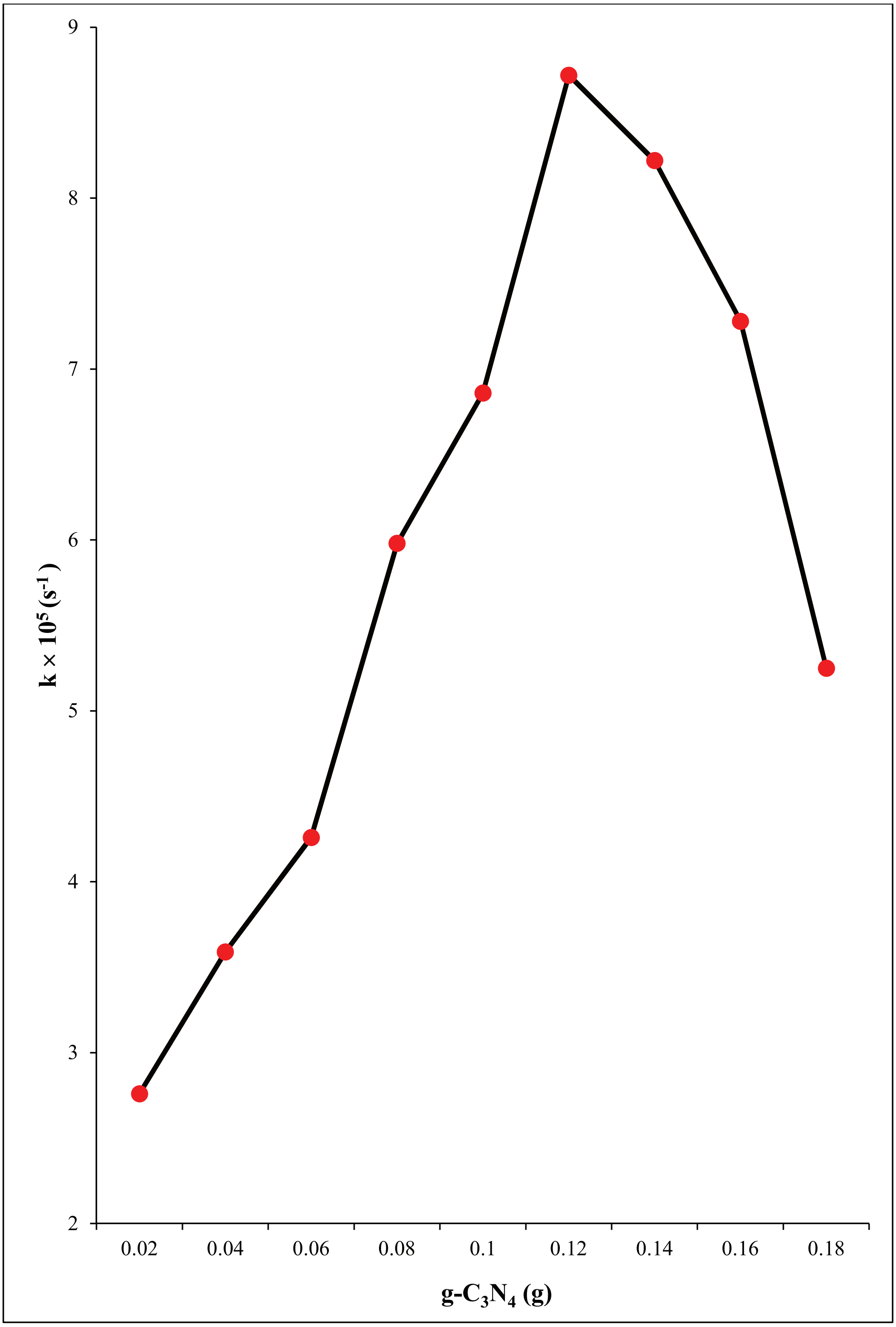

Fig. 3.35: Effect of amount of photocatalyst

3.12.4 Effect of light intensity

The effect of light intensity on the rate of Alizarin red-S was also observed from 20.0 to 70.0 m W cm^{-2}. The results are reported in Table 3.30: and Fig. 3.36:

Table 3.30: Effect of light intensity

pH = 8.0 [Alizarin red-S] = 3.2 x10^{-4} M

g-C_3N_4 = 0.12 g

Light intensity (m W cm^{-2})	**Rate constant (k) × 10^5 (s^{-1})**
30.0	7.54
40.0	7.96
50.0	8.23
60.0	8.38
70.0	**8.72**

It was observed that the rate of degradation was increased on increasing light intensity.

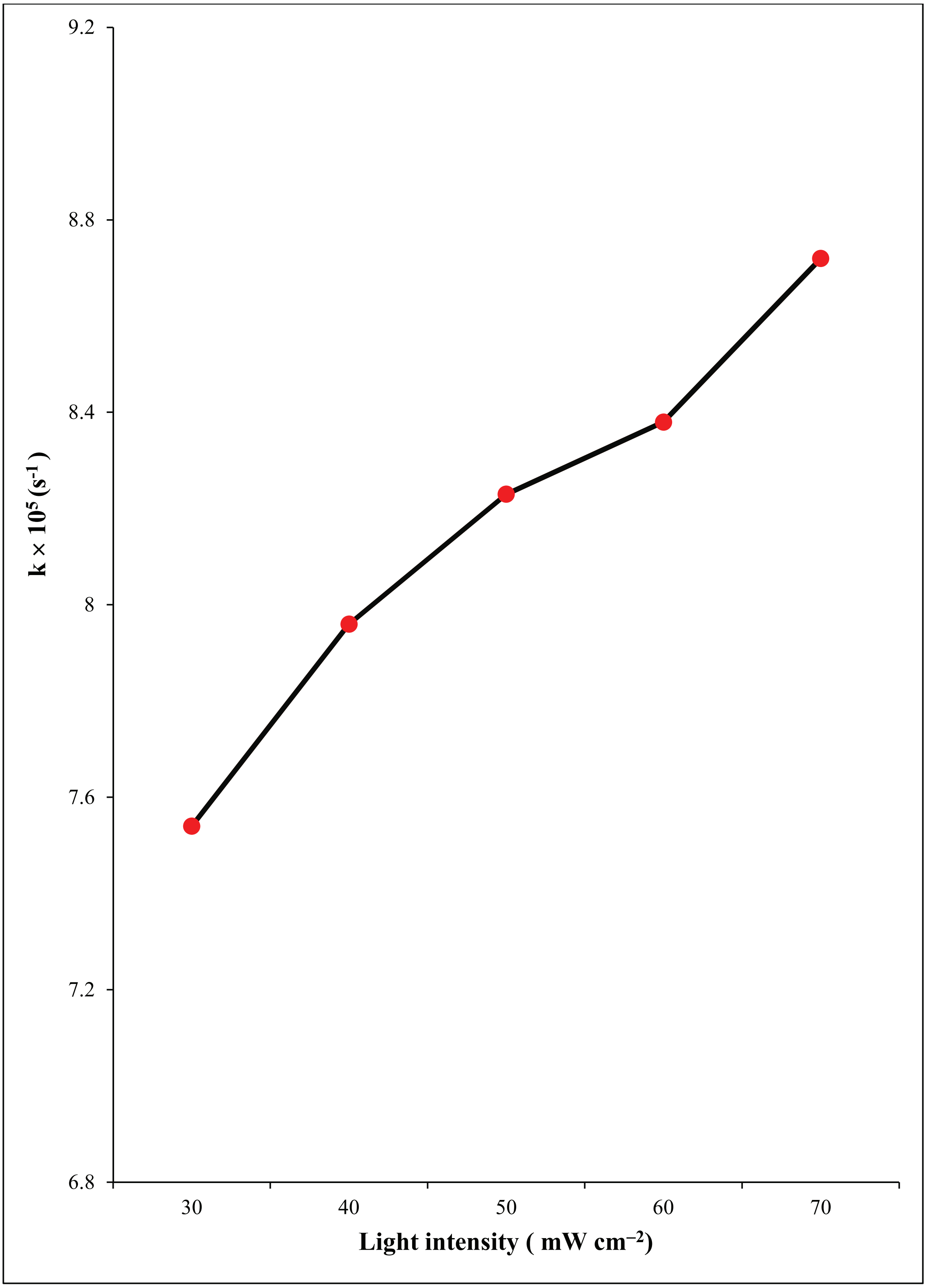

Fig. 3.36: Effect of light intensity

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