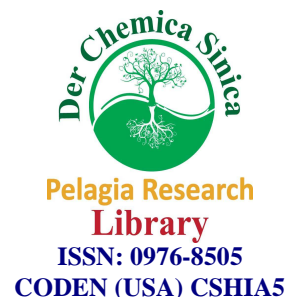




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Kinetic monitoring of photocatalytic activity of bismuth sulphide for degradation of malachite green

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ABSTRACT

The use of colored semiconductor like bismuth sulphide (Bi_2S_3) as photocatalysts in photocatalytic degradation of malachite green was investigated in detail. In order to harness solar energy, the effective wavelength of the photocatalyst is to be expanded into the visible region and that increases the rate of photocatalytic degradation of the dye. Progress of the reaction was recorded spectrophotometrically. The effects of various parameters like concentration of dye, pH, amount of semiconductor, light intensity etc. were studied. A tentative mechanism for the photocatalytic degradation of malachite green has also been proposed.

Key words: Photocatalysts, Photocatalytic degradation, Malachite green, Bismuth Sulphide, Photocatalytic activity.

INTRODUCTION

In recent years, the use of chalcogenides as photocatalyst for degradation of pollutants has attracted the attention of scientific community all over the world. Water is one of the fundamental requirements of life and any undesired addition of chemical substances leads to its contamination and makes it unfit for human utility.

Generally, various dyes found in industrial effluents, ultimately, enter the aquatic ecosystem and can create environmental hazards. These effluents have very adverse and sometimes irreversible effects on other animals and plants as well. The main purpose of waste water treatment is the removal of these toxic substances and color, and to make the water usable for industrial and domestic use. There are various methods like adsorption, osmosis, flocculation etc, which have been used traditionally to remove these dyes from the water bodies, but these methods suffer from some drawbacks. In recent years, Advanced Oxidation Processes (AOP's) like photocatalysis, photo-Fenton reaction, ozonation, sonolysis etc, have emerged as successful techniques in combating against the problem of environmental pollution. Research work and applications based on AOP's in treatment of water has increased considerably during last twenty five years. The photocatalytic degradation was found to be the most promising and efficient process in controlling the environmental pollution, waste water treatment etc, in which semiconductor particles act as photocatalysts or short-circuited microelectrodes on excitation. On excitation, semiconductor generates electron-hole pair which may be used either for reduction or oxidation of the dye.

The field of photocatalysis has been excellently reviewed by Sahasi *et al.* [1] Photocatalytic degradation of cetylpyridinium chloride over TiO₂ has been reported by Singhal *et al.* [2] Similar photocatalytic reaction of xylidine ponceau and orange-G dyes by ZnO powder has been reported by Sharma *et al.* [3] Yoneyama *et al.* [4] studied the photocatalytic reduction of dichromate ions using WO₃ powder in acidic range. Costa *et al.* [5] proposed the mechanism of gas phase degradation of cyclohexanol and methylcyclohexanol catalyzed by niobium pentoxide and phosphite. Shyama and Arakawa [6] have used zirconium dioxide as photocatalyst. A composite system of polycrystalline ZnO/TiO₂ and its photocatalytic activity was studied by Marci *et al.* [7] TiO₂ sol-gel deposited over glass and its application as an effect of TiO₂ acidic pretreatment on the photocatalytic phenol degradation was reported by Colon *et al.* [8] whereas photodegradation of lignin from black liquor using a UV/TiO₂ system was investigated by Ksibi *et al.* [9] Enhanced efficiency of unsymmetrical versus symmetrical squaraine dyes sensitized nanocrystalline TiO₂ was reported by Alex *et al.* [10] Morwetz and Selli [11] investigated the effect of iron species in photocatalytic degradation of azo dye in TiO₂ suspension. Photocatalyst for water decontamination has been reported by Gelover *et al.* [12] Kako *et al.* [13] suggested some preventive methods against catalytic poisoning of TiO₂ photocatalyst by H₂S. The Kim *et al.* [14] used ZnO coated TiO₂ nanoparticles for the flexible dye-sensitized solar cells. Photocatalytic degradation of brilliant red dye and textile waste water has been suggested by Martins *et al.* [15] Photocatalytic degradation of acid blue-62 over CuO-SnO₂ nanocomposite photocatalyst under simulated sunlight has been reported by Xia *et al.* [16] Degradation of some dyes using zirconium phosphate photocatalyst have been studied by Panwar *et al.* [17] Use of semiconducting iron (II) oxide in photocatalytic degradation of some dyes (malachite green, crystal violet and methylene blue) has been reported by Ameta *et al.* [18] Photoreduction of Congo red by ascorbic acid and EDTA over cadmium sulphide as photocatalyst was carried out by Kothari *et al.* [19] Photocatalytic activity of antimony (III) sulphide in degradation of Azure-B was carried out by Ameta *et al.* [20]

MATERIALS AND METHODS

In the present investigation, malachite green and bismuth sulphide of SDH and Himedia, respectively were used. All the solutions were prepared in doubly distilled water. UV-Visible spectrophotometer (Systronics - 104) was used for measuring optical density at different times. A 200 W tungsten lamp (Phillips) was used for irradiating the solution in the visible range. The pH of solution was measured by a digital pH Meter (Systronics digital pH Meter - 802). The desired pH of the solution was adjusted by previously standardized sulphuric acid (Rankem) and sodium hydroxide (Rankem) solutions. To confirm the photocatalytic nature of the reaction; solution of the malachite green was placed in equal amounts in four beakers; the first beaker containing the dye solution was kept in dark, second beaker containing dye solution was exposed to light, third beaker containing dye solution and 0.10 g bismuth sulphide was kept in dark and fourth beaker containing dye solution and 0.10 g bismuth sulphide was exposed to light.

These beakers were kept under these conditions for 3 to 4 hours and then, the optical density of the solution in each beaker was measured with the help of a spectrophotometer (Systronics - 104) at $\lambda_{\text{max}} = 615\text{nm}$.

The optical density was found to be almost same in case of solution of first three beakers, while a decrease in initial value of optical density was observed in fourth beaker. It was confirmed that this reaction required both; the light as well as the semiconductor bismuth sulphide and therefore, this reaction is photocatalytic reaction in nature and not chemical/thermal or photochemical. 0.3649 g of malachite green was dissolved in 100.0 mL of doubly distilled water, so that the concentration of dye solution was 1.0×10^{-3} M. It was used as a stock solution. The progress of reaction was observed by measuring optical density of the reaction mixture containing dye and the semiconductor bismuth sulphide at different time intervals during exposure.

RESULTS AND DISCUSSION

A solution of 1.75×10^{-5} M of malachite green was prepared in doubly distilled water and 0.10 g of bismuth sulphide was added to it. The pH of the reaction mixture was adjusted to 8.0 and then this solution was exposed to a 200W tungsten lamp. A decrease was observed in the optical density of malachite green solution with increasing time of exposure. A plot of $2 + \log \text{O.D.}$ against time was found to be linear. The rate constant was measured with the expression –

$$k = 2.303 \times \text{slope} \quad \dots (1)$$

A typical run has been presented in Table 1 and graphically represented in Figure 1

Table 1: A TYPICAL RUN

Time (min.)	2 + log O.D.
0.0	1.6830
10.0	1.6212
20.0	1.5729
30.0	1.5302
40.0	1.4914
50.0	1.4425
60.0	1.3927
70.0	1.3424
80.0	1.2900
90.0	1.2430
100.0	1.2014
110.0	1.1523
120.0	1.1004
130.0	1.0569
140.0	1.000
150.0	0.9542
160.0	0.9031
170.0	0.8513
180.0	0.8129
190.0	0.7634
200.0	0.7160
210.0	0.6721
220.0	0.6335
230.0	0.5798
240.0	0.5315

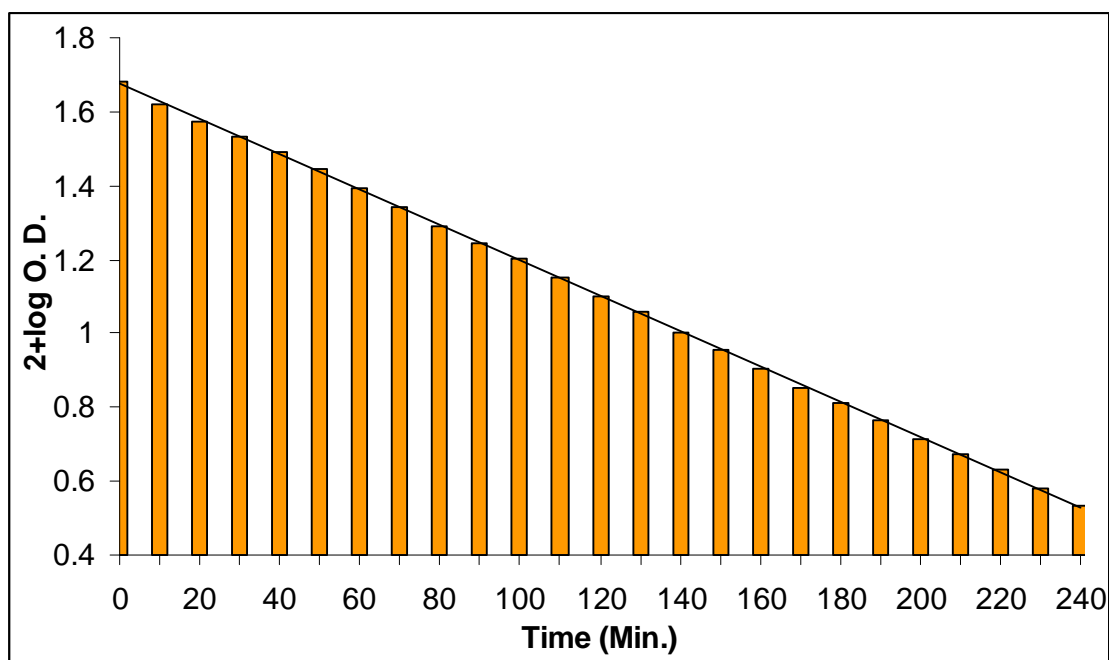


Figure: - 1. A Typical Run ($\text{Bi}_2\text{S}_3 = 0.10\text{g}$, $[\text{Malachite green}] = 1.75 \times 10^{-5}\text{M}$, $\text{pH} = 8.00$, Light intensity = 50 mWcm^{-2}); Rate Constant ($k = 1.88 \times 10^{-4} \text{ s}^{-1}$)

EFFECT OF pH

The pH of the solution may affect the rate of photocatalytic degradation of the malachite green and therefore, the effect of pH on the rate of photocatalytic degradation of malachite green was investigated in the pH range 5.0 - 9.0.

The results are reported in Table 2. It has been observed that the rate of degradation of malachite green increases with increase in pH upto 8.0. A further increase in pH above 8.0 results in a decrease in the rate of reaction. An increase in the rate of degradation of malachite green with increase in pH may be due to generation of more $\cdot\text{OH}$ radicals, which were produced from the reaction between OH^- ions and hole (h^+) of the semiconductor. Above pH 8.0, a decrease in the rate of degradation of the dye was observed, which may be due to the fact that malachite green is a cationic dye, and at higher pH, OH^- may interact with dye molecules to convert it into its neutral form and the attraction between neutral dye molecules and negatively charged semiconductor surface is reduced relatively.

Table 2: EFFECT OF pH
 [Malachite green] = 1.75×10^{-5} M
 Light Intensity = 50.0 mWcm^{-2}
 $\text{Bi}_2\text{S}_3 = 0.10 \text{ g}$

pH	$k \times 10^5 \text{ (sec}^{-1}\text{)}$
5.00	2.39
5.50	3.07
6.00	3.48
6.50	4.04
7.00	5.48
7.50	9.59
8.00	18.76
8.50	15.99
9.00	14.99

EFFECT OF DYE CONCENTRATION

Effect of variation of malachite green concentration was also observed by taking different concentrations of malachite green. The results are given Table 3.

It is evident from the data that the rate of degradation was increased with an increase in concentration of the malachite green. It may be explained on the basis that as the concentration of malachite green was increased, more dye molecules were available for excitation and consecutive energy transfer and hence, an increase in the rate of degradation of the dye was observed. The rate of degradation was found to decrease with an increase in the concentration of malachite green above 1.75×10^{-5} M. It may be due to the fact that the dye itself will start acting as an internal filter for the incident light and it will not permit the desired light intensity to reach the semiconductor particles; thus, a corresponding decrease in the rate of degradation of malachite green was observed.

Table 3: EFFECT OF DYE CONCENTRATION
 Light Intensity = 50.0 mWcm^{-2}
 $\text{Bi}_2\text{S}_3 = 0.10 \text{ g}$
 pH = 8.00

[malachite green] $\times 10^5$ M	$k \times 10^4 \text{ (sec}^{-1}\text{)}$
1.00	1.40
1.25	1.47
1.50	1.58
1.75	1.88
2.00	1.84
2.25	1.81
2.50	1.77
2.75	1.73

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. It has been observed that the rate of degradation of malachite green was increased on increasing the amount of semiconductor but ultimately, 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), if the amount of semiconductor was increased further, then the exposed surface area of the photocatalyst will not increase.

It may be considered like a saturation point; above which there is negligible or no effect on the rate of degradation of malachite green. Any 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.

Table 4: EFFECT OF AMOUNT OF SEMICONDUCTOR

[Malachite green] = 1.75×10^{-5} M

Light Intensity = 50.0 mWcm^{-2}

pH = 8.00

Bismuth Sulphide (g)	k x 10 ⁴ (sec ⁻¹)
0.02	1.41
0.04	1.51
0.06	1.62
0.08	1.80
0.10	1.88
0.12	1.85
0.14	1.84

EFFECT OF LIGHT INTENSITY

The effect of light intensity on degradation of malachite green was observed by changing the distance between the light source and the exposed surface of semiconductor.

The results are reported in Table 5.

These results indicates that degradation of malachite green 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.

Table 5: EFFECT OF LIGHT INTENSITY

[Malachite green] = 1.75×10^{-5} M

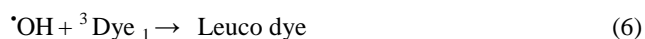
Bi₂S₃ = 0.10 g

pH = 8.00

Intensity of Light (mW cm ⁻²)	k x 10 ⁴ (sec ⁻¹)
10.0	1.60
20.0	1.76
30.0	1.79
40.0	1.81
50.0	1.88

CONCLUSION

On the basis of above observations, a tentative mechanism for photocatalytic degradation of malachite green in presence of bismuth sulphide may be proposed as follows –



Malachite green dye 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 dyes. The involvement of triplet state was confirmed by using triplet state scavengers, where the reaction rate was almost negligible. On the other hand, the semi-conducting bismuth sulphide (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 $\cdot\text{OH}$

radicals. These radicals will oxidize the dye to its leuco form, which may ultimately degrade to harmless products. The participation of $\cdot\text{OH}$ radicals as an active oxidizing species was confirmed by using hydroxyl radical scavenger isopropanol, where the rate of degradation was drastically reduced.

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