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PHOTOCATALYTIC DEGRADATION OF MALACHITE GREEN USING TiO_2 AS PHOTOCATALYST

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ABSTRACT

The photocatalytic action of the TiO_2 has been studied on malachite green dye. The degradation of dye was carried out using UV irradiations and monitored by UV-Vis. Spectrophotometer. The experimental results show that the degradation of the dye can be carried out conveniently and efficiently using TiO_2 semiconductor as photocatalyst.

Key words: Photocatalyst, Photodegradation, TiO_2, Semiconductor.

INTRODUCTION

The photocatalytic degradation of colored organic compounds especially pollutants on semiconductor surface has been proved to be a better process for waste water treatment[1-3]. Among various semiconductors used for photodegradation, TiO_2 has been recognized as an efficient photocatalyst for degradation of several organic contaminants[4,5], due to its low toxicity, high photoreactivity and chemical stability. Most studies related to the photodegradation reaction have been carried out in aqueous media using suspension of powdered TiO_2 in polluted aqueous solution[6,7]. Pozzo et al.[8] have studied the use of supported TiO_2 as photocatalyst on various contaminants. In the present investigation we described the useof TiO_2 for photodegradation of malachite green dye.

EXPERIMENTAL

A stock solution of malachite green 10^{-4} M was prepared by dissolving 0.0365 g of malacahite green in 100 mL double distilled water. 60.0 mL of dye solution was prepared from stock solution by diluting it. The pH of the solution was adjusted with the help of standardized H_2SO_4 and NaOH solutions. Naïve and treated TiO_2 was added to this solution

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and the reaction mixture was exposed to UV irradiations (200 W tungsten lamp). A water filter was used to cut off the thermal radiations. The progress of reaction was measured spectrophotometrically at λ_{max} = 617 nm.

RESULTS AND DISCUSSION

Photodegradation of malachite green catalyzed by TiO_2 under UV irradiation was carried out. The results show that the degradation of the dye under mentioned conditions is efficient and effective. The results are reported in the Table 1.

Table 1: A typical run

[Malachite green] = 5.00 x 10^{-5} M pH = 8.50

Light intensity = 60.00 mW cm^{-2} Titanium dioxide = 0.20 g

Time (min.)	Optical density (O.D.)	1 + log O.D.
0.00	0.562	0.7497
30.00	0.484	6848
60.00	0.426	6294
90.00	0.355	5502
120.00	0.305	4843
150.00	0.260	4149
180.00	0.226	3541
210.00	0.192	2833
240.00	0.142	1522
270.00	0.126	1004
		k = 8.35 x 10^{-5} (sec.$^{-1}$)

It was observed that the optical density decreases with increasing time of exposure. A plot of 1 + log OD verses time was linear showing that the reaction follows a pseudo first order kinetics. The rate of photodegradation of malachite green was observed 8.35 x 10^{-5} sec.$^{-1}$.

Effect of pH

The effect of pH on rate of degradation of dye was investigated in pH range 6.0-8.5. The results are tabulated in Table 2. From the data, it is evident that the rate of degradation increases with increase in pH, which may be due to the abundance of OH^- ions at higher pH value. OH^- ions will generate more $^{\bullet}OH$ radicals by combining with holes and are considered to be responsible for degradation.

Table 2: Effect of pH

Titanium dioxide = 0.20 g

[Malachite green] = 5.00×10^{-5} M Light intensity = 60.00 mW cm^{-2}

pH	k x 10^5 ($sec.^{-1}$)
6.00	2.75
6.50	3.32
7.00	3.85
7.50	5.23
8.00	6.27
8.20	7.14
8.50	8.35

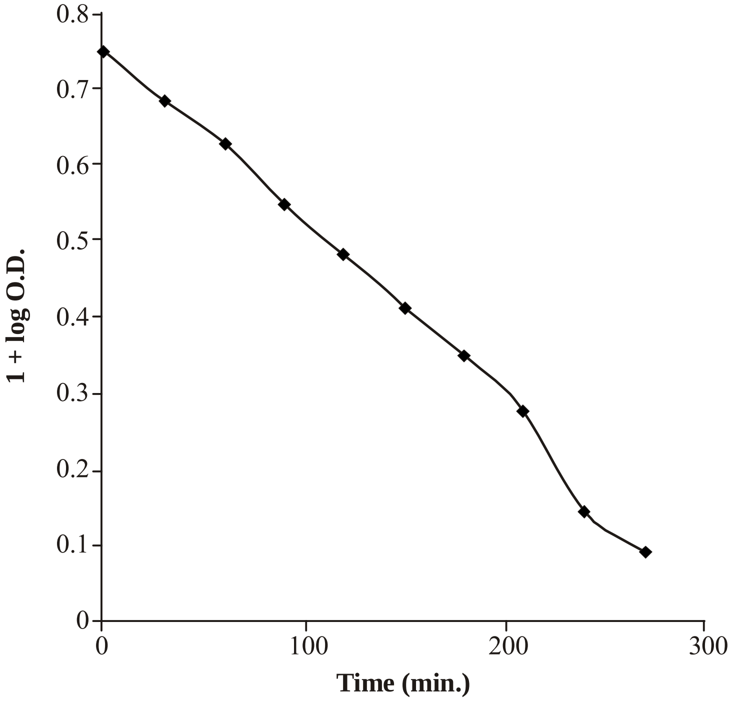

Fig. 1: A typical run

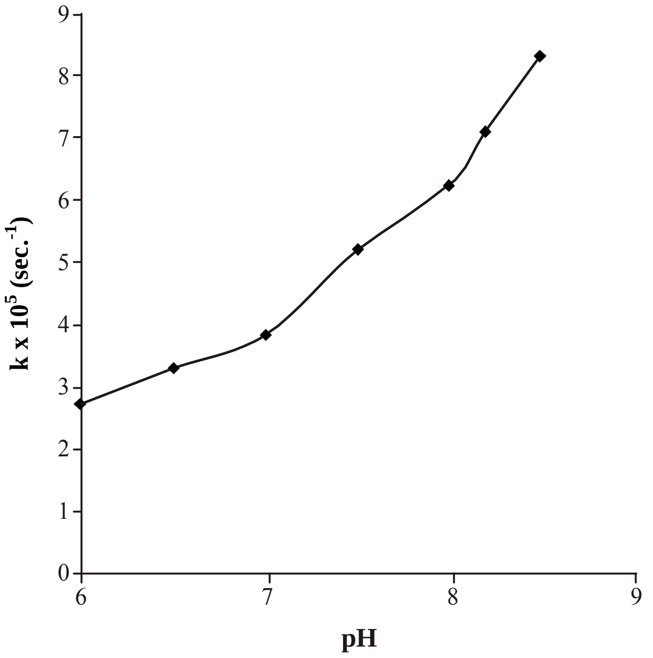

Fig. 2: Effect of pH

Effect of malachite green concentration

The results of variation in concentration of malachite green are tabulated in Table 3.

Table 3: Effect of malachite green concentration

Titanium dioxide = 0.20 g

pH = 8.50 Light intensity = 60.00 mW cm^{-2}

[Malachite green] x 10^{-5} M	k x 10^5 (sec.$^{-1}$)
1.25	4.28
2.00	4.54
3.33	5.93
5.00	8.35
7.25	6.20
9.00	4.18
10.00	2.84

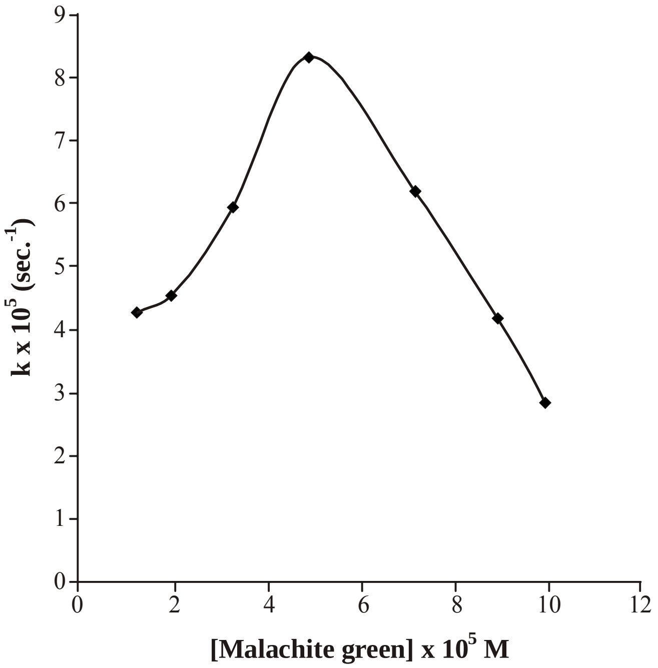

Fig. 3: Effect of malachite green concentration

It has been observed that the rate of photodegradation increases with increase in concentration of dye, as at higher concentration more molecules are available for excitation and energy transfer. The rate of photodegradation was found to decrease with further increase in the concentration of dye. This may be due to the fact that at higher concentration the dye itself starts acting as filter for incident light and does not permits the desired intensity to react with semiconductor.

Effect of concentration of semiconductor

The effect of variation in amount of semiconductor used has been observed. The results are tabulated in Table 4. It has been observed that the rate of photodegradation initially increases with increase in amount of semiconductor but after a certain amount it becomes constant. It may be due to the fact that as the amount of semiconductor was increased the exposed area of photocatalyst also increased. But after a saturation point there will be no further increase in the surface area. It may also be confirmed on the basis of the size and geometry of the reaction vessel used. The saturation point was shifted to a higher value when vessel of larger capacities are used. A reverse trend was observed when vessel of smaller capacity was used.

Table 4: Effect of the amount of semiconductor

pH = 8.50

[Malachite green] = 5.00×10^{-5} M Light intensity = 60.00 mW cm^{-2}

Amount of semiconductor TiO_2 (g)	Rate constant $k \times 10^5$ ($sec.^{-1}$)
0.04	2.22
0.08	3.98
0.12	4.95
0.16	6.20
0.18	7.17
0.20	8.35
0.22	8.38
0.24	8.36

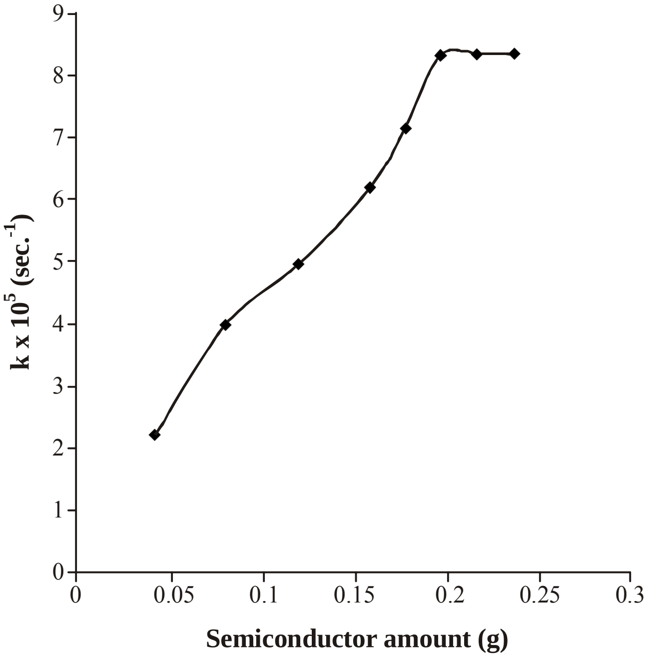

Fig. 4: Effect of amount of semiconductor

Effect of light intensity

The effect of light intensity on photo degradation of dye was studied by varying the distance between light source and exposed surface area. The results are tabulated in the Table 5.

Table 5: Effect of light intensity

Titanium dioxide = 0.20 g
[Malachite green] = 5.00×10^{-5} M pH = 8.50

Light intensity (mW cm^{-2})	**Rate constant k x 10^5 (sec.$^{-1}$)**
20.00	2.29
30.00	3.54
40.00	5.05
50.00	6.80
60.00	8.35
70.00	11.91

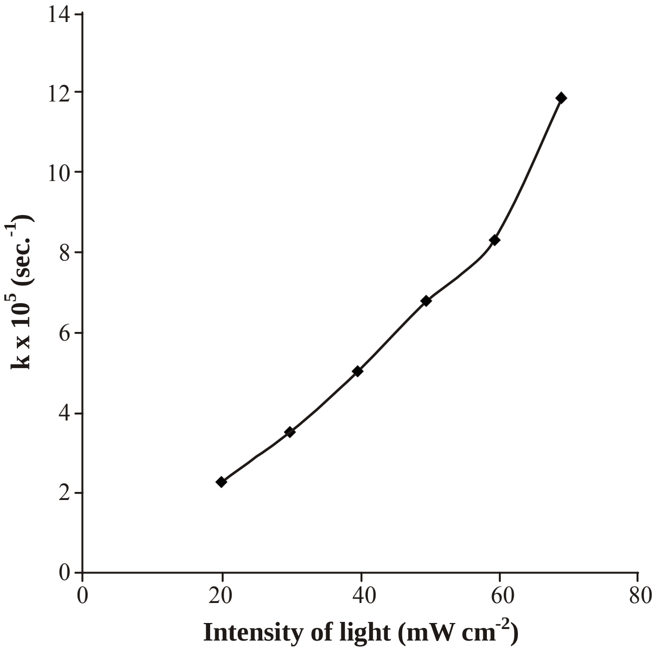

Fig. 5: Effect of light intensity

The data indicate that the photo degradation of the dye increases with increase in the light intensity as the number of photons striking per unit area of semiconductor increases. A linear behavior between light intensity and the rate of reaction has been observed.

Mechanism

On the basis of above observations a tentative mechanism for photocatalytic degradation of the malachite green may be proposed as follows -

$$\mathrm{MG} \xrightarrow{h\nu} \mathrm{MG}^{*}$$

$$\mathrm{SC} \xrightarrow{h\nu} e^{-}\,[\mathrm{CB}] + h^{+}\,[\mathrm{VB}] \text{ or } \mathrm{SC}^{*}$$

$$h^{+} + \mathrm{OH}^{-} \longrightarrow {}^{\bullet}\mathrm{OH}$$

$$\mathrm{MG}^{*} + {}^{\bullet}\mathrm{OH} \longrightarrow \text{Leuco [MG]}$$

$$\text{Leuco [MG]} \longrightarrow \text{Products}$$

Malachite green [MG] absorbs radiations of suitable wavelength and is excited to higher energy state. The semiconductor TiO_2 also utilizes the radiant energy to excite its electrons from valence band to conduction band, thus leaving behind a hole. This hole abstracts an electron from OH^{-} ion to generate ${}^{\bullet}OH$. radical which oxidizes the dye to its leuco form and finally degrades it to colorless product. The participation of ${}^{\bullet}OH$ radical as an active oxidizing species was confirmed by using ${}^{\bullet}OH$ radical scavenger when the rate of photo catalytic degradation was reduced drastically.

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