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**Dr. Pratibha Rao**
Lecturer, Department of Chemistry, SMM Government Girls College, Bhilwara, Rajasthan, India

**Correspondence**
**Dr. Pratibha Rao**
Lecturer, Department of Chemistry, SMM Government Girls College, Bhilwara, Rajasthan, India

# Photocatalytic bleaching of malachite green on semiconducting zinc oxide powder

## Dr. Pratibha Rao

**Abstract**
Malachite green is used for direct dying silk, wool, jute, leather and cotton after mordanting. It is also used as a biological stain and as spot test reagent for detecting sulphurous acid and cerium. Photocatalytic degradation of malachite green over zinc oxide powder suspended in aqueous solution has been carried out. Photo catalytic bleaching of the dye was observed spectrophotometrically. The effect of variation of various parameters such as the concentration of malachite green, pH, amount and particles size of the semiconductor and light intensity on the rate of photocatalytic reaction were observed. A tentative mechanism for the photocatalytic bleaching of malachite green is proposed.

**Keywords:** Malachite green, photocatalytic bleaching, zinc oxide, semiconductor

## Introduction
Dyes are commercially important chemicals and are frequently used in dying, printing, textile, photography, food and cosmetic industries [1]. However the dyes are toxic and may be carcinogenic. Contamination of aquatic environment by these toxic chemicals is a serious problem as dyeing, printing and textile industries release their coloured effluent in nearby rivers, lakes, ponds etc [2]. Sharma and Dey used ozonation to remove die from aqueous solution. Photo catalytic bleaching may provide a low cost method to solve this problem. Cosa and Gsponer studied the photo ionization of malachite green leucocyanide. It has been suggested that the first singlet state is the precursor of this photo ionization and independent of light intensity and temperature. Porter and Spears studied the photo decomposition of basic green - 4 to 4-methyl amino benzophenone and 4-dimethyl amino benzophenone. To account for these observations, it was proposed that photodecomposition commences with the absorption of light by the leuco carbinol dye [3]. The excited carbinol dye in its triplet state is converted to the decomposition products.
A number of attempts have been made by Brown and Darwent. To degrade a few dyes photocatalytically. Reported photo catalytic degradation of crystal violet, a triphenylmethane dye over semiconductor zinc oxide powder suspended in aqueous solution. applied semiconductor photocatalysis for removal of dyes from aqueous solution.

## Experimental detail
Malachite green (s.d. fine) and zinc oxide (merck) were used. The photo catalytic bleaching of malachite green was observed by taking 100 ml of solution and 0.50 gram of zinc oxide powder. The irradiation was carried out with magnetic steering keeping the whole assembly exposed to light source. The desired pH of the solution was measured by a digital pH meter (systronics model 324). The pH of the solution was adjusted by HCl (for acidic range) and NaOH (for basic range) the solution was irradiated using 200 Watt tungsten lamp (Sylvania Laxman). The intensity of light was measured by surya mapi (CL model SM 201). A water filter was used to cut off thermal radiations.
The optical density was measured by a UV-visible spectrophotometer (Systronics model 108) the necessary condition for the correct measurement of the optical density is that the solution must be free from semiconductors particles and other impurities. Centrifuge (Remi1258) and Whatman filter paper were used to remove the species but proved to be unsuitable.

Thus a G-3 sintered glass crucible was used for filtration to obtain the desired accuracy in the measurement of the absorbance of the dye solutions and absorption maxima of dye was determined by a UV visible recording spectrophotometer [5].

## Results and discussion

The photo catalytic bleaching of malachite green was observed spectrophotometrically at absorption maxima 617 n. m. The results for typical run are given in Table 1

**Table 1:** A Typical Run [Malachite green] = 1.0 x $10^{-5}$ M Light Intensity = 40 mW $cm^{-2}$ Temperature = 303K pH = 7.0 Zinc oxide =0.50g

| Time (minutes) | Optical Density (O. D.) | 2+log O. D. |
|---|---|---|
| 0.0 | 1.091 | 2.038 |
| 30.0 | 0.700 | 1.8451 |
| 60.0 | 0.450 | 1.6532 |
| 90.0 | 0.315 | 1.4983 |
| 120.0 | 0.210 | 1.3222 |
| 150.0 | 0.135 | 1.1303 |
| 180.0 | 0.089 | 0.9500 |

It was observed that optical density decreases with time of irradiation indicating that malachite green is degraded on exposure to light. The rate constant for this reaction was determined using the expression,

Rate constant (k) = 2.303 × slop

### Effect of [malachite green] variation

Effect of variation of malachite green concentration on the rate of its photo catalytic bleaching was studied by taking different concentration of malachite green. The results obtained are represented in Table 2.

**Table 2:** Effect of [malachite green] variation Light Intensity = 40 mW $cm^{-2}$ pH = 7.0 Temperature = 303K Zinc oxide =0.50g

| [Malachite green] x $10^5$M | Rate constant k x $10^5$ ($sec^{-1}$) | 5 + log k ($sec^{-1}$) |
|---|---|---|
| 1.00 | 23.70 | 1.3750 |
| 1.25 | 18.80 | 1.2740 |
| 1.50 | 14.50 | 1.1613 |
| 1.75 | 11.00 | 1.0414 |
| 2.00 | 8.90 | 0.9494 |
| 2.25 | 6.65 | 0.8228 |
| 2.50 | 5.40 | 0.7324 |

It is evident from the Table 2 that as the concentration of malachite green increases, rate of photocatalytic bleaching of the dye decreases. It can be explained on the basis of results obtained that as the concentration of dye was increased it will start acting like a filter for the incident light and its larger concentration will not permit the desired light to reach the zinc oxide particles and the results into a decrease in the rate of photo catalytic bleaching of malachite green.

### Effect of variation of pH

The effect of pH on the rate of photo catalytic reaction was investigated in pH range 6.0 to 10.0. The value of pH was varied by the addition of HCl (for acidic range) and NaOH (for basic range) to the dye solution. Results are presented in Table 3.

**Table 3:** Effect of variation of pH [Malachite green] = 1.0 x $10^{-5}$ M Light Intensity = 40 mW $cm^{-2}$ Temperature = 303K Zinc oxide =0.50g

| pH | Rate constant k x $10^4$ ($sec^{-1}$) | 4 + log k ($sec^{-1}$) |
|---|---|---|
| 6.0 | 1.65 | 0.2175 |
| 6.5 | 1.97 | 0.2945 |
| 7.0 | 2.37 | 0.3747 |
| 7.5 | 2.82 | 0.4502 |
| 8.0 | 3.55 | 0.5502 |
| 8.5 | 4.17 | 0.6201 |
| 9.0 | 5.13 | 0.7101 |
| 9.5 | 6.32 | 0.8001 |
| 10.0 | 7.08 | 0.8500 |

It has been observed that rate of photo catalytic bleaching of malachite green increases on increasing pH above 6.0. This type of the behaviour can be explained on the basis of the fact that this dye is of cationic nature. The negative charge on the surface of the semiconductor will provide a site of attraction for the cationic dye thus increasing the rate of bleaching.

### Effect of variation of amount of semiconductor

Keeping all the other factors identical the effect of amount of semiconductor was observed. Results are tabulated in Table 4.

**Table 4:** Effect of variation of amount of semiconductor [Malachite green] = 1.0 x $10^{-5}$ M Light Intensity = 40 mW $cm^{-2}$ Temperature = 303K pH = 7.0

| Amount of semiconductor (g) | Rate constant k x $10^4$ ($sec^{-1}$) |
|---|---|
| 0.1 | 1.68 |
| 0.2 | 1.83 |
| 0.3 | 2.04 |
| 0.4 | 2.20 |
| 0.5 | 2.37 |
| 0.6 | 2.55 |
| 0.7 | 2.65 |
| 0.8 | 2.66 |
| 0.9 | 2.65 |

Rate of photo catalytic bleaching of malachite green increases with increase in the amount of semiconductor, but after a certain amount rate becomes almost constant, it may be considered like a saturation point. This may be attributed to the exposed surface area of the semiconductor initially the increase in the amount of semiconductor will increase the surface area but after saturation point any further addition will not increase surface area rather it will increase only the thickness of the layer of the semiconductor at the bottom of reaction vessel.

### Effect of variation of light intensity

To observe the effect of light intensity on the photo catalytic reaction of malachite green light sources of different wattage were used, and the distance between the light source and exposed surface was also varied. The results obtained are shown in Table 5.

**Table 5:** Effect of variation of light intensity [Malachite green] = 1.0 x $10^{-5}$ M pH = 7.0 Temperature = 303K Zinc oxide =0.50g

| Light Intensity (mW $cm^{-2}$) | Rate constant k x $10^4$ ($sec^{-1}$) |
|---|---|
| 10.0 | 0.625 |
| 20.0 | 1.300 |
| 30.0 | 1.875 |
| 40.0 | 2.370 |
| 50.0 | 2.825 |
| 60.0 | 3.050 |

The results indicate that bleaching action is accelerated as the intensity of light was increased. This maybe explain on the basis that more photons will be available for excitation on increasing the intensity of light and therefore more electron hole pairs will be generated in the semiconductor thus resulting into enhanced rate of reaction [6].

**Mechanism**

On the basis of observed data the following tentative mechanism may be proposed as follows.

In the initial step the semiconductor SC will be excited to give SC*, which will provide the electron –hole pair. The electron present in the conduction band will be utilised for reducing the dye to its leuco form. This luco form may further degrade to volatile or gaseous products.

SC----------→ SC*
SC* --------→ SC(h+) + e-
e- + Malachite green ----→ Leuco [MG]
Leuco [MG] ---→ Products

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