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**ORIGINAL ARTICLE** **OPEN ACCESS**

# Solar Light Induced Degradation of Triarylmethane Dye using Semiconductor Mediated Photocatalysis

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**ABSTRACT**
*In the present study, photocatalytic degradation of Malachite Green (MG), cationic triarylmethane dye in slurry mode has been carried out in a batch reactor using $TiO_2$ P-25 (surface area: 50 $m^2/g$) and ZnO (surface area: 50 $m^2/g$) as a photocatalyst under solar light irradiation. Decolourization rate was estimated from residual concentration using UV-Vis spectroscopy. To study the effect of various parameter, similar experiments were performed by varying pH (2-9), amount of catalyst (0.5-2.00 g), and concentration (5-100 ppm). The degradation rate of MG was found to be maximum at pH 4 and pH 8 with $TiO_2$ and ZnO respectively. An optimum dose of catalyst ($TiO_2$/ZnO) was found to be 1 $gl^{-1}$. Almost complete degradation of MG was achieved in only 0.5 h under solar irradiation with both the catalysts.*
**Keywords:** Triarylmethane dye; Malachite green; Titanium dioxide; Photodegradation; ZnO

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## INTRODUCTION

Water resources often get contaminated by the discharge of organic pollutants such as pesticides, phenols, detergents, pharmaceuticals, fertilizers, and dyes. Water pollution due to industrial dyes is a solemn reason of concern as some of the dyes may have an unfavorable effect on the ecosystem [1-3]. Xenobiotic dyes due to high thermal and photostability are recalcitrant towards biodegradation as a result they can persist in the environment for an ample period of time [4-5]. The presence of even a small quantity of dyes in water can be toxic, mutagenic, or carcinogenic [6-7]. Dyes besides being aesthetically intolerable they also prevent infiltration of light causing a decline in photosynthesis and affect the oxygen concentration in water hence disturb aquatic life [8-10]. Each class of dye includes a different chromophore which includes azobenzene, xanthene, triphenylmethane, etc. Malachite Green (MG) is a water-soluble cationic green colored crystalline triaryl methane dye (Three aryl groups attached to the central carbon atom).

MG is employed for dyeing paper, leather, elastics, and textiles (cotton, wool, silk, etc). MG is also used in pisciculture for the treatment of parasitic, fungal, and bacterial infections [11]. Although MG has a wide range of applications, its presence in water causes harmful/adverse effects to aquatic life and human health owing to its noxious characteristics as it damages organs (liver, spleen, kidney, and heart), causes abrasions (skin, eyes, lungs, and bones) besides producing teratogenic effects to the nervous system [11-12]. MG shows reasonable photo-stability and there is deep concern about its fate in the ecosystem encouraging researchers to design an eco-friendly and cost-effective technique for scientific and public interest to eradicate it from the environment. Properties of Malachite green are given in table 1. Various methods such as incineration, advanced oxidation, ozonation, adsorption on various solid phase, and microbiological treatment are extensively explored [13-16]. Amongst all of them, the advanced oxidation process (AOP) employing heterogeneous catalysis is the most effective technology for the treatment of effluents. $TiO_2$ involves fast electron transfer to molecular oxygen making it is the most extensively used effective heterogeneous catalyst employed in photo-catalytical degradation under UV light. Artificial UV irradiation is more consistent than natural sunlight and can speed up the removal of textile dyes from water. Solar light, on the other hand, is abundant and non-hazardous in nature and is predicted to emerge as a cost-effective energy source [17-18]. Although the study of photo-degradation of malachite green under UV-vis has been reported, its study in solar light is elusive to date

In the present work, photocatalytic degradation of MG a harmful dye was carried out with $TiO_2$/ZnO as photocatalyst under solar irradiation. The chemical structure of the dye is complex and molecular weight

is high. It is highly soluble in water and persists in the natural environment on discharge from industries. As a result, its degradation study under solar irradiation is fascinating not only as a probable pollutant of industrial effluents but cost-effective treatment technology can be developed for the destruction of other dyes on large scale.

## MATERIAL AND METHODS

### Materials

Titania P-25 (surface area 50 $m^2/g$) was obtained from Degussa. Malachite green and ZnO (surface area 5 $m^2/g$) was purchased from Merck and used as received without further purification. Various solutions were prepared by using double distilled water. 1M HCl or 1M NaOH was used to adjust the pH of the solutions.

### Instruments

For performing photochemical degradation experiments specially designed reaction vessels are used in the photoreactor equipped with 4 UV Philips tubes (each of 30W). Solutions were constantly stirred by using magnetic stirrers and aquarium aerators were used for the aeration of the solution. UV-Vis Spectrophotometer (Systronics 119) was employed to record the spectra; Thermo Orion 920A pH meter was used to adjust the pH of the solution.

### Procedure

Degradation experiments were performed by taking 100 ml of sample solution, a fixed amount of photocatalyst ($TiO_2$/ZnO) was added to it. Solar light was employed to irradiate the magnetically stirred aqueous suspensions. An aliquot was taken out with the help of a syringe at various time intervals, and Millipore syringe filter of 0.45 μm was used to filter the sample. The rate of decolourization was studied in terms of changes in absorption spectra recorded at $\lambda_{max}$ = 614 nm. The percentage of decolourization competence of catalyst has been calculated as follows:

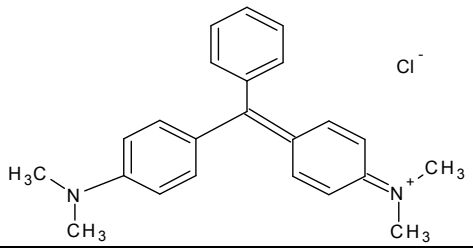
$$\text{Efficiency } (\%) = 100\times(C_0\text{-}C)/C_0$$

where $C_0$ = initial concentration of dye and C = concentration of dye after irradiation by solar light.
To study the process parameters similar experiments were performed by varying photocatalysts dose, pH of the experimental solution, and initial concentration of dye.

## RESULT AND DISCUSSION

Malachite green is 4-[(4-dimethylaminophenyl)-phenyl-methyl]-N, N-dimethyl aniline, is a poisonous chemical largely used as a dye. It is a triarylmethane dye. Malachite green is soluble in water, yielding a blue-green colloidal solution; solubility of it is better in ethanol and other organic solvents. Under solar light, the degradation experiments were using photocatalysts, $TiO_2$/ZnO. Variation in intensity of distinctive peak at 614 nm exhibits decolourization of the dye. The main features of MG are summarized in Table 1.

**Table 1 : Main characteristics of Malachite Green**

| Name of dye | Malachite Green |
|---|---|
| Synonym | AnilineGreen, Basic Green 4, Diamond Green B, Victoria Green B |
| IUPAC | 4-[(4-dimethylaminophenyl)-phenyl-methyl]-N, N-dimethyl aniline |
| Colour index number | C.I. 42000 |
| Molecular formula | $C_{23}H_{25}ClN_2$ |
| Molecular weight | 364.911 g/mol |
| $\lambda_{max}$ | 614 nm |
| pKa | 10.3 |
| Solubility in water | $6x10^4$ mg/$dm^3$ |
| Structure |  |

**UV-Vis Spectra**

A typical UV-Vis spectrum of Malachite solution is shown in Figure 1. The significant decrease in absorption peaks of MG in the visible as well as UV region during photodegradation using solar photo catalyst, specified degradation of dye with time. No new intermediate was formed during the degradation as there is no appearance of new absorbance peak in the visible or ultra-violet regions.

The present study involves the photocatalytic degradation of MG employing a heterogeneous photocatalytic process with $TiO_2$/ZnO. The present research work is an endeavor to study the effect of process parameters such as catalyst dose, and pH and concentration of MG solution. All the experiments were done by irradiating the aqueous suspension. A similar batch of experiments were performed by variation of pH (2-9), various amounts of catalyst dose (0.5-2.0 g/l) and concentration 5-100 mg/l.

**Effect of pH**

Wastewater containing dyes is realeased from the industry at different pH, as a result, it is significant to investigate the effect of pH on the decolourization of dye. In the present study, the effect of pH of the solution on the %age decolourization was studied in ranges 2-9. Figure 2 displays the colour removal of MG using fixed amount of catalyst. It was observed that degradation occurring in the basic medium was less as compared to the degradation of dye occurring in an acidic medium with $TiO_2$. At the same time, the pH influenced both (1) the surface state of semiconductors and (ii) the ionization state of ionizable organic molecules. The net consequence was the direct impact of pH of the dye solution on degradation of the dye [19]. Although the maximum degradation up to 99.44% took place at pH-4, after pH 4 significant decrease was observed. In basic medium maximum degradation (upto 92.78%) took place at pH 9 when $TiO_2$ is employed as photocatalyst. In the case of ZnO, the rate of photodecolourization reached the maximum at pH 8 (99.75%). The conclusion of the study is that that maximum degradation of dye took place in the acidic medium with $TiO_2$ whereas, in basic medium maximum degradation was observed with ZnO.

**Effect of Catalyst Dose**

There is both positive and negative impact of catalyst dose on the degradation efficiency during the heterogeneous photocatalytic process. Neppolian et al., 2002 reported that photodegradation rate increases with an increase in catalyst concentration due to the fact that more organic molecules get absorbed on the catalyst surface with the increase in the catalyst dose thereby enhancing the rate of decolourization [17].

The photodegradation experiments were performed under natural sun light employing a photocatalyst. The experiments were carried out by variation catalyst dose from 0.5g/l to 2.0g/l in order to optimize the catalyst dose. Figure 3 displays a graph between the amount of catalyst used and the percentage degradation showed that with an increase in catalyst dose (.5 to 1 g/l) decolourization efficiency increases. In the case of MG dye, the maximum decolourization was achieved with 1g/l of $TiO_2$/ZnO and thereafter decolourization rate decreases. Thus with the increase of catalyst amount, the total active surface area for the adsorption of dye increased, thereby enhancing the chances of collision of $TiO_2$ and dye resulting in efficient degradation. On the other hand, due to an increase in opacity of the suspension with the increase in the dose of catalyst, leading to a decrease in penetration of solar light in the suspension. Hence, the less photoactivated volume of suspension will decrease photo-catalytic performance. All these factors support our findings as the effective catalyst dose for decolourization of the MG was found to be 1 g/l.

**Effect of Dye Concentration**

After optimizing the experimental conditions i.e $TiO_2$/ZnO dose (0.5-2 g/l), pH-4 and pH-8 in case of $TiO_2$ and ZnO respectively, was investigated by altering the initial dye concentrations from 5-100 mg/l. It was observed that with the increase in the concentration of dye, the rate of photodecolourization decreases indicating that to have maximum decolourization either to increase the catalyst dose or time of irradiation for the complete removal.

**Comparison of Solar/UV Irradiation on Photocatalytic Degradation of MG under Optimized Conditions**

To compare the photocatalytic decolourization of MG under optimized conditions, the results obtained in the present work and the results from previous studies [20] by our research group are compared. The comparison of decolourization percentage of MG under UV/solar light is displayed in Figure 4. It was found that almost complete decolourization took place in half an hour under sun light with both the catalyst whereas, only 72.24% decolourization occurred with $TiO_2$ and 84.4% with ZnO under UV light for the same time period. Thus the decolourization of MG was achieved at a faster rate under natural sun light as compared to artificial light which is in agreement with literature reports [21]. Garcia et al., assessd $TiO_2$/$H_2O_2$/solar system for the photodegradation of real textile effluents through the advanced

oxidative process (AOP) employing and inferred that natural radiation (solar) is either comparable or more effective than artificial light.

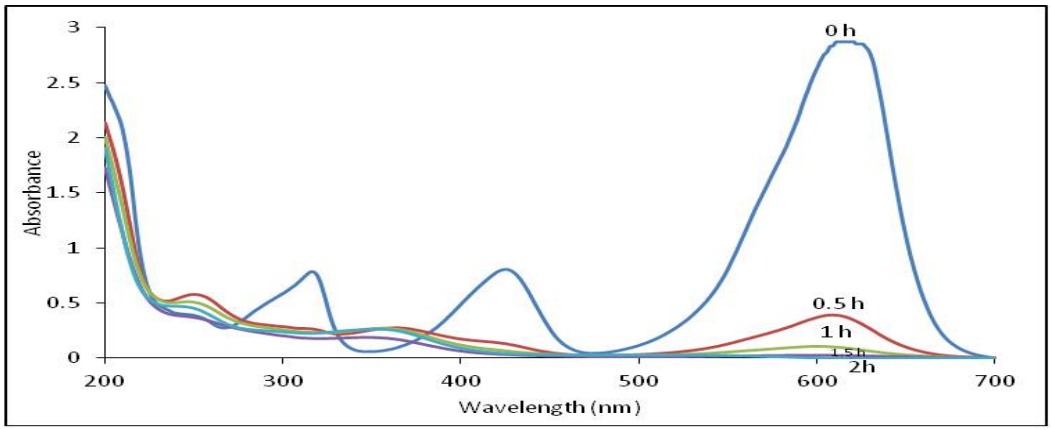



Figure1: Time dependent UV absorption spectra for degradation of MG using $TiO_2$ under Solar light.

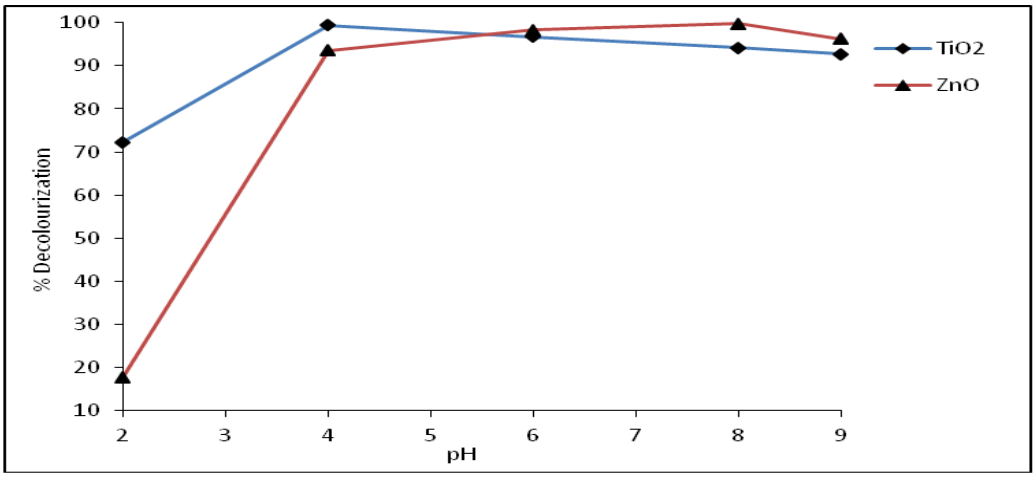



Figure 2: Effect of pH on decolourization of MG under solar light (Dye Initial Concentration—50 ppm, Catalyst Dose—1 g/L, Time: 0.5 h)

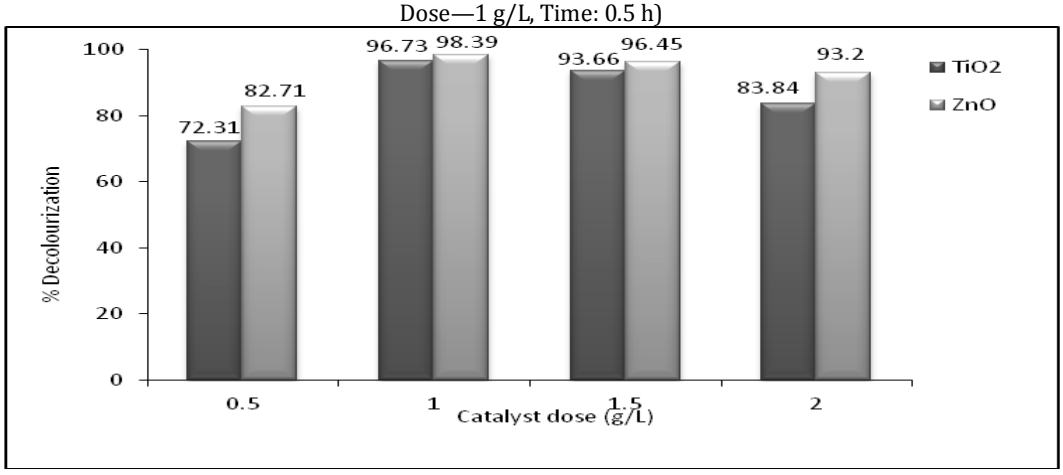



Figure 3: Effect of catalyst dose on decolourization of MG under solar light (Dye Initial Concentration—50 mg/L, pH— 4, Time: 0.5 h)

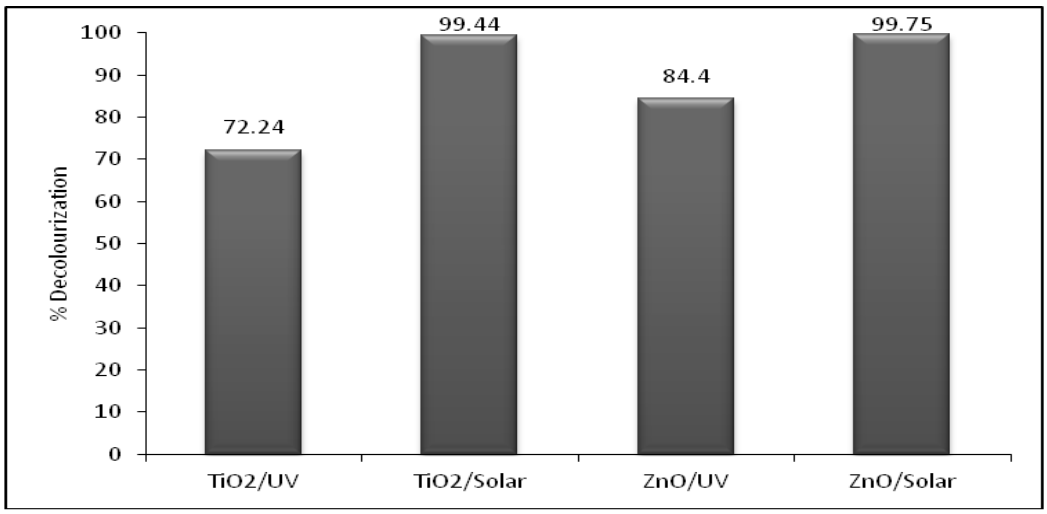



Figure 4: Comparison of Solar/UV Irradiation on Photocatalytic Decolourization of MG under Optimized Conditions (Dye Initial Concentration—50 ppm, Catalyst Dose—1 g/L, pH—4 for $TiO_2$, pH—8 for ZnO, Time: 0.5 h).

## CONCLUSION

Effective removal of dye (MG) is possible by using both the catalysts $TiO_2$ as well as ZnO. When the concentration of dye is more, then the catalyst dose should be increased but it should be optimum as in this study optimum concentration of catalyst was (1g/l). Further increase in catalytic dose has a negative impact on degradation efficiency. pH of the solution also affects decolourization of the dye for instance, comparison of photocatalytic activity of the catalysts has clearly specified that ZnO is more efficient photocatalyst for decolourization of MG at neutral as well as basic media, but $TiO_2$ shows better efficiency in acidic media. Under optimized conditions, decolourization of dye under solar light takes place more effectively than under UV light which may lead to the cost-effective treatment of the triarylmethane dyes.

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