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Studies on photodegradation of malachite green using TiO_2/ZnO photocatalyst

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ABSTRACT

Wastewater containing dyes emanating from textile mills is strongly colored and is carcinogenic in nature. In order to reduce pollution load it is desirable to degrade the dye into non-toxic form before its discharge into the main stream. The present paper reports the photocatalytic degradation of malachite green (MG). MG is used to dye materials like silk, paper and leather. The batch experiments were carried out by irradiating the aqueous solution of dye in the presence of photocatalysts and UV light. The photocatalysts used for the study are titanium dioxide (TiO_2), zinc oxide (ZnO), and different ratios of ZnO and TiO_2. The rate of decolorization was estimated from residual concentration spectrophotometrically. The effect of process parameters viz. pH 2–9, initial concentration of dye 5–50 ppm and amount of catalyst 0.5–1.5 g/l on degradation of the dye has also been assessed. The experimental results indicated that ZnO efficiently compete with TiO_2 in terms of percentage degradation of MG. Maximum degradation of dye occurs in acidic range with TiO_2 and at neutral pH with ZnO. When photocatalysts are mixed in different ratios, best results were obtained with ZnO and TiO_2 in the ratio of 9:1.The high decolorizing efficiency was obtained with 1.0 g/l of catalyst dose.

Keywords: Decolorization; Photocatalytic degradation; ZnO; TiO_2; Malachite green

1. Introduction

Industrial effluents emanating from the textile processes, kraft mills, dye manufacturing units etc., are strongly colored. The conventional technologies currently used to degrade the color of the dye contaminated water includes primary (adsorption, flocculation), secondary (biological methods), and chemical processes (chlorination, ozonization) [1–4]. However, these techniques are non-destructive, since they only transfer the non-biodegradable matter into sludge, giving rise to a new type of pollution, which needs further treatment [5–7]. Advanced oxidation processes (AOP's) employing heterogeneous catalysis have emerged as a potential destructive technology leading to the total mineralization of most of organic pollutants [8–13]. Titanium dioxide (TiO_2) is found to be more efficient catalyst for photocatalytic degradation of pollutants due to faster electron transfer to molecular oxygen [14]. However, widespread use of TiO_2 is uneconomical for large-scale water treatment, thereby interest has been drawn towards the search for suitable alternatives to TiO_2. Many attempts have been made to study photocatalytic activity of different semiconductors such as SnO_2, ZrO_2, CdS and ZnO [15–19]. Daneshvar et al. [20] reported that zinc oxide (ZnO) is a suitable alternative to TiO_2 for the degradation of Acid Red 14, an azo dye, since its photodegradation mechanism has been proven

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to be similar to that of TiO_2. Efficiency of ZnO has been reported to be particularly noticeable in the photooxidation of pulp mill bleaching effluent [21] and textile mill wastewater [20].

Malachite green is used to dye materials like silk, leather, and paper. Malachite green is a powerful, though toxic medication with anti-protozoal and anti-microbial properties. However, malachite green has now become a highly controversial compound due to the risks it poses to the consumers of treated fishes [22,23], including its effects on the immune system and its carcinogenic properties [24]. Though the use of this dye has been banned in several countries and is not approved by US Food and Drug Administration, it is still being used in many parts of the world due to its low cost, ready availability, and efficacy [25]. A considerable amount of research is being devoted to the wide spectrum of biological effects it exerts on different animals and on mankind. The US Food and Drug Administration has nominated MG as a priority chemical for carcinogenicity testing. There is concern about the fate of MG in aquatic and terrestrial ecosystems because of its potential human health hazard [26]. Aqueous solution of malachite green is reasonably photostable if subjected to sunlight. Therefore, to assess the rate of degradation of malachite green using photocatalyst under UV/solar light appears to be quite promising. The photocatalytic degradation of methyl orange (MO) and rhodamine 6G (R6G) has been reported by using different photocatalysts [27].

In continuation with the earlier work [27], the present study reports the degradation of malachite green using TiO_2, ZnO and mixture of these photocatalysts in different ratios in presence of UV light. Subsequent experiments were conducted to investigate the effects of various process parameters (catalyst loading, pH, and initial dye concentration) on the process performance.

2. Experimental

2.1. Materials

Titania P-25 (surface area 50 m^2/g) was obtained from Degussa and ZnO (surface area 5 m^2/g) from Merck, and was used as received. Malachite green dye is a basic dye that was purchased from Merck and used without further purification. Potassium dichromate, sulfuric acid, silver sulphate, mercuric sulphate were purchased from S.D. Fine Chemical, India. Double distilled water was used for preparation of various solutions. pH of the solutions was adjusted with 1 M HCl or 1 M NaOH. HCl and NaOH were obtained from Merck, India.

2.2. Instruments

Photochemical degradation is carried out in specially designed double walled reaction vessels in the UV chamber equipped with 4 UV tubes each of 30 W (Philips) having wavelength 365 nm (Fig. 1). Constant stirring of solution was insured by using magnetic stirrers, and aeration was done with the help of aquarium aerator. The spectra were taken with UV-VIS Spectrophotometer (Systronics 119); pH meter (Thermo Orion 920A) was used to adjust the pH of the solution. COD analysis was carried with Thermo Orion Aqua Fast II AQ 2040 COD meter.

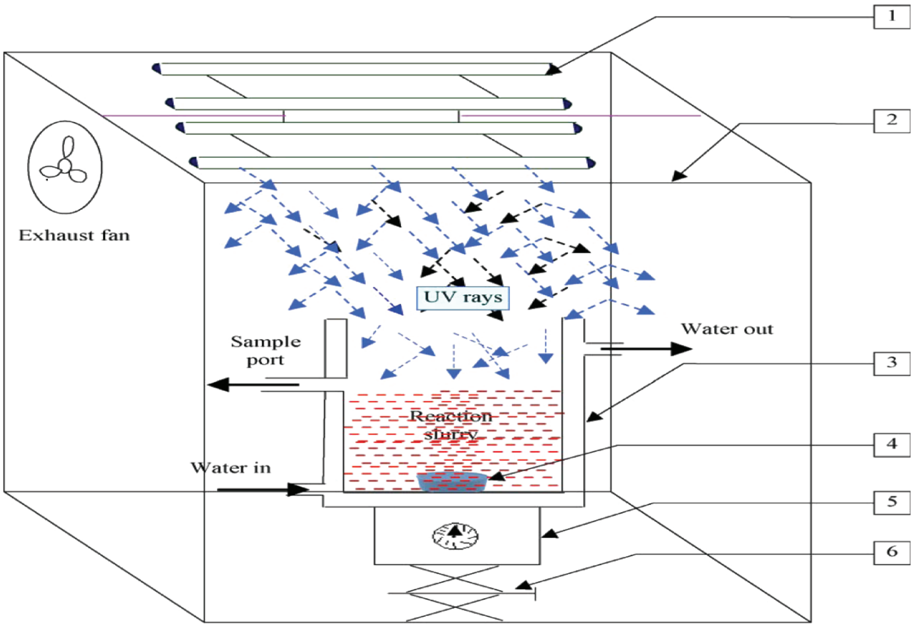


Fig. 1. Experimental setup for photocatalytic process. 1, UV lamps-5 (30 W); 2, chamber; 3, jacketed reactor; 4, magnetic bead; 5, magnetic stirrer; 6, lab jack.

2.3 Experimental procedure and analysis

For the degradation experiments, 1 g of photocatalyst TiO_2/ZnO or their mixtures was added to 100 ml of dye solution and suspension was subjected to irradiation under UV light. The aqueous suspension was magnetically stirred and aerated throughout the experiment. At different time intervals aliquot was taken out with the help of a syringe and then filtered through Millipore syringe filter of 0.45 µm. Then absorption spectra were recorded at λ_{max} = 614 nm. The rate of degradation was studied in terms of changes in the absorption spectra. The decolorization efficiency (%) was calculated as:

$$\text{Efficiency (\%)} = \frac{C_0 - C}{C_0} \times 100 \qquad (1)$$

where C_0 is the initial concentration of dye and C is the concentration of dye after photoirradiation. Similar experiments were carried out by varying the pH of the solution, concentration of dye and dose of photocatalysts.

For COD analysis 2 ml of test solution was pipette into the standard amount of potassium dichromate oxidizing mixture and digested at 150°C for 2 h. Then colored solution was measured against water blank.

3. Results and discussion

The molecular structure of malachite green is illustrated in Table 1. Malachite green, also called analine green, basic green 4, diamond green B, or Victoria green B having IUPAC name 4-[(4-dimethylaminophenyl)-phenyl-methyl]-N, N-dimethyl aniline is a toxic chemical primarily used as a dye. It is a green crystal powder with a metallic luster, very soluble in water, extremely soluble in ethanol, solutions are blue-green. It shows intense absorbance at 614 nm (Table 1). Malachite green shows characteristic absorption peaks at 243,313 nm in UV region and 427,614 nm in visible region. The rate of decolorization was recorded with respect to the change in intensity of absorption peaks at 614 nm. The absorption peaks corresponding to dye diminished during reaction, which indicated that the dye has been degraded.

3.1. Degradation of dye using TiO_2 and ZnO photocatlysts

Investigations were carried out with different semiconductors viz. TiO_2, ZnO and both mixed in different ratios as 9:1, 8:2, 7:3, 6:4, and 1:1 in order to select the most effective catalyst for degradation of dyes. Band positions of these semiconductors are listed in Table 2.

The photocatalysed degradation of dye in the solution is initiated by the photoexcitation of the semiconductor, followed by the formation of electron-hole pair on the surface of the catalyst [Eq. (2)]. The high oxidative potential of the hole (h^+_{VB}) in the catalyst permits the direct oxidation of the dye to reactive intermediates [Eq. (3)].

$$\underset{\text{Metal oxide}}{(\mathrm{MO/MO_2})} + h\nu \rightarrow (\mathrm{MO/MO_2})\left(e^-_{CB} + h^+_{VB}\right) \qquad (2)$$

$$h^+_{VB} + \text{dye} \rightarrow \text{dye}^{\bullet +} \rightarrow \text{Oxidation of the dye} \qquad (3)$$

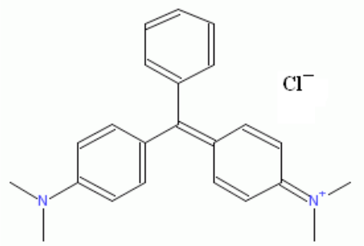
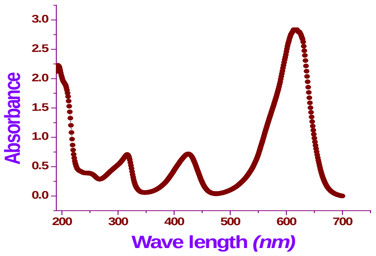
Besides the hole, hydroxyl radical ($OH^\bullet$) formed by the decomposition of water [Eq. (4)] or by reaction of the hole with OH^- [Eq. (5)] is also responsible for degradation. The hydroxyl radical is an extremely strong, non-selective oxidant (E_0 = +3.06 V) which leads to the partial or complete mineralization of several organic chemicals [20].

$$h^+_{VB} + \mathrm{H_2O} \rightarrow \mathrm{H^+} + {}^\bullet\mathrm{OH} \qquad (4)$$

Table 2
Band positions of semi conductor photocatalysts in aqueous solution

Semiconductor	TiO_2	ZnO
Valence band (V vs. NHE)	+3.1	+3.0
Conductance band (V vs. NHE)	−0.1	−0.2
Band gap (eV)	3.2	3.2
Band gap wavelength (nm)	387	387

Table 1
IUPAC name, molecular structure, molecular mass and absorption spectrum of MG

Name	IUPAC name	Molecular structure	Absorption spectrum of MG; λ_{max} = 614 nm
Malachite green	4-[(4 dimethylaminophenyl)-phenyl-methyl]-N,N-dimethyl-aniline	 364.911 g/mol (chloride)	

$$h^+_{VB} + OH^- \rightarrow {}^\bullet OH \tag{5}$$

Electrons in the conduction band are also responsible for the production of hydroxyl radicals and the species are the primary cause of organic matter mineralization [Eq. (6)].

$${}^\bullet OH + \text{dye} \rightarrow \text{ degradation of the dye} \tag{6}$$

Initially blank experiments were performed under UV irradiation without addition of any catalyst and negligible decolorization was observed. Photodegradation experiments were also performed by using fixed amount of dye (50 ppm) with catalyst dose, i.e. 1 g/l of various catalysts — TiO_2, ZnO and mixed in different ratios as 9:1, 8:2, 7:3, 6:4, and at natural pH. The percentage degradation of dye by using various catalysts is reported in Fig. 2.

Experimental studies show that the degradation occurs at same rate with TiO_2 as well as ZnO. The result is in confirmation with earlier findings of using ZnO as an alternative to TiO_2 for the photocatalytic degradation of azo dyes and the proposed mechanism of degradation for TiO_2 and ZnO is same [20,21]. However, when the photocatalyst were mixed, the degradation was comparatively high as compared with the individual catalyst. The maximum degradation (96.9%) has been observed when ZnO:TiO_2 were mixed in the ratio of 9:1. In earlier findings a higher rate of photocatalytic degradation of methyl blue was reported with TiO_2:ZnO mixed in the ratio of 9:1 [28].

3.2. *Effect of catalyst concentration*

The experiments were performed by varying catalyst concentration from 0.5 g/l to 1.5 g/l for dye solution of 50 ppm at natural pH (4.2). Maximum degradation is observed with 1 g/l of catalyst TiO_2 as well as ZnO and thereafter the rate of degradation decreases. This can be explained on the basis that the optimum catalyst loading is found to be dependent on the initial solute concentration because with the increase of the catalyst dosage, the total active surface area increases, hence availability of more active sites on the catalyst surface [29]. At the same time, due to an increase in turbidity of the suspension with a high dose of photocatalyst, there will be a decrease in penetration of UV light and hence the photoactivated volume of the suspension decreases [20]. Thus it can be concluded that a higher dose of the catalyst may not be useful both in view of aggregation as well as reduced irradiation field due to light scattering. Therefore the catalyst dose 1 g/l was fixed for further studies.

3.3. *Effect of pH*

Wastewater containing dyes is discharged at different pH; therefore it is important to study the role of pH on decolorization of dye. In the present study, the effect of pH of the solution on the percentage photodegradation was examined in the range 2–9 for constant dye concentration (50 mg/l) and 1 g/l catalyst loading. Fig. 3 shows the color removal efficiency of MG as a function of pH. It has been observed that the decolorization efficiency with TiO_2 increases with the increase in pH exhibiting maximum rate of degradation at pH 4 and after that it decreases. In the case of ZnO, the rate of photodecolorization reached maximum at pH 7. Thus it may be concluded that maximum degradation of dye occurs in acidic range with TiO_2 and at neutral pH with ZnO. Similar behavior has also been reported for the photocatalytic efficiency of ZnO and TiO_2 for decolorization of azo dye [30]. This can be explained on the basis that the pH influences at the same time both (i) surface state of catalyst and (ii) ionization state of ionisable organic molecules. The net effect is direct influence of pH of the solution on the heterogeneous photocatalytic process.

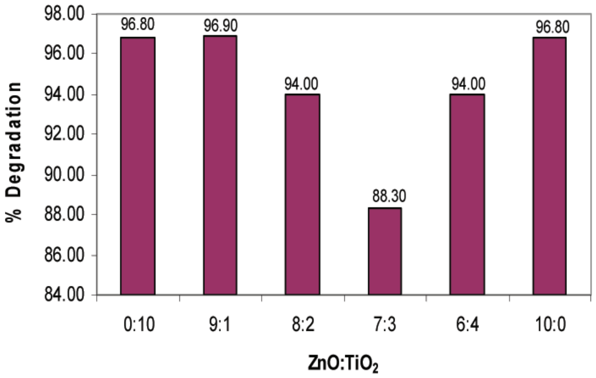


Fig. 2. Effect of variation of ratios of catalyst on degradation of malachite green (50 ppm MG; time of reaction 2 h).

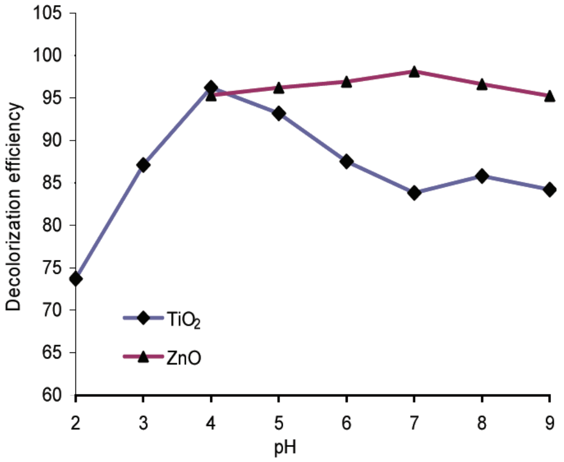


Fig. 3. Effect of pH on degradation of malachite green (50 ppm MG; 1 g/l catalyst; time 2.5 h).

3.4. *Effect of concentration of dye*

After optimizing the experimental conditions, pH 4, TiO_2 1 g/l (Table 3) the photocatalytic decolorization of

Table 3
Optimized conditions for various photocatalytic systems

	Catalyst dose (g/l)	Contact time (h)	pH
TiO_2/UV	1	4	4
ZnO/UV	1	2.5	neutral
9:1 ZnO/ TiO_2/UV	1	2	natural

MG was carried out by varying the initial concentrations of the dye from 5 to 50 ppm in order to assess the appropriate amount of the catalyst dose. As the concentration of the dye is increased, the rate of photodegradation decreases indicating either to increase the catalyst dose or time span. Fig. 4 clearly shows that for dye solutions of 5 ppm, 10 ppm, 100% degradation occurred, and in the case of 25 ppm, almost complete degradation was observed in 30 min. For 50 ppm of the dye solution degradation was 96.8% in 2 h and it decreased further with increasing the concentration of dye.

3.5. Kinetic study

The kinetics of disappearance of MG for an initial concentration of 50 mg/l with ZnO/TiO_2 (9:1) catalyst under optimized conditions (Table 3) was studied. Fig. 5 shows that the photocatalytic decolorization of the dye can be described by the first order kinetic model, $\ln (C_0/C) = kt$, where C_0 is the initial concentration and C is the concentration at any time, t. The semi-logarithmic plots of the concentration data gave a straight line. The correlation constant for the fitted line was calculated to be $R^2 = 0.822$. The rate constant was calculated to be 1×10^{-4} s^{-1}.

3.6. Mineralization studies of dyes

As the reduction of chemical oxygen demand (COD) reflects the extent of degradation or mineralization of an organic species, the percentage change in COD was studied for dye samples (initial concentration 50 mg/l) under optimized conditions (9:1 ZnO/TiO_2 catalyst dose 1 g/l, pH natural) as a function of irradiation time using UV light. The results are depicted in Table 4. It can be seen that under UV light, the percentage COD reduction was 72.30% in 3 h. The COD reduction is less than percentage decolorization which may be due to the formation of smaller uncolored products. Therefore, it seems that to achieve complete mineralization of dyes, longer irradiation time is required.

4. Conclusion

The results of degradation experiments show that photocatalytic method can effectively degrade the dye into nontoxic forms. The interesting results are obtained when the mixed photocatalyst systems containing TiO_2 and ZnO are employed. The possible reasons may be simultaneous photo excitation of the photocatalysts and quick passage of the electrons to the dye molecules

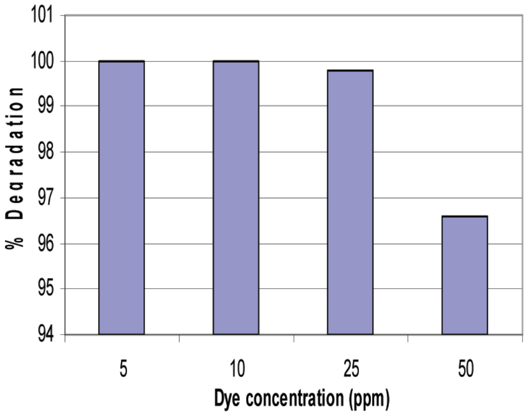


Fig. 4. Effect of MG concentration on degradation (1 g/l TiO_2; time 2 h).

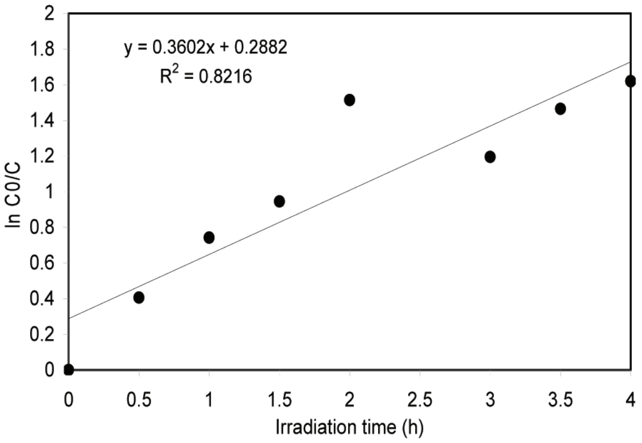


Fig. 5. Kinetic analysis of MG under optimized conditions.

Table 4
Percentage COD reduction studies of MG

Time of irradiation (min)	COD reduction under UV light (%)
0	0
30	36.92
60	47.69
90	58.46
120	66.15
150	67.69
180	72.30

thereby preventing the reunion of electrons and hole pair. This triggers the various reactions leading to the degradation of dye. The photocatalytic decolorization followed pseudo-first order kinetics. The COD analysis revealed that complete mineralization of dyes could be achieved in longer irradiation times. The optimum dose of the catalyst is required for the complete degradation of the known concentration of the dye solution because high as well as low catalyst dose reduces the percentage degradation of dye.

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