



## Photocatalytic Degradation of Malachite Green over CuO/Al<sub>2</sub>O<sub>3</sub> Composite

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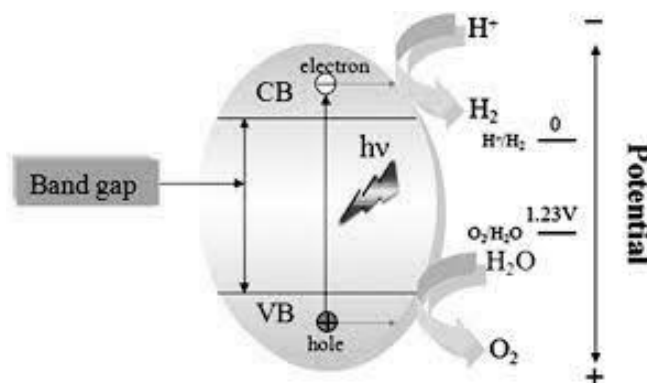
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### ABSTRACT

Waste water containing dyes emanating from textile mills is strongly coloured and it is carcinogenic in nature. In order to reduce pollution load, it is desirable to degrade the dye into nontoxic form before it is discharged into the main stream. Malachite green is used as dye material like silk, paper and leather industries. Degradation of malachite green was investigated using CuO/Al<sub>2</sub>O<sub>3</sub> composite as a semiconductor. Decolourization assay was performed by monitoring the programs of the reaction spectrophotometrically. The optimum conditions were obtained as; pH = 9, dye concentration = 1.0 × 10<sup>-5</sup> M, amount of composite (CuO/Al<sub>2</sub>O<sub>3</sub>) = 0.1g and light intensity = 60.0 mWcm<sup>-2</sup> where the rate constant was found as 2.43 × 10<sup>-4</sup> sec<sup>-1</sup>.

### Graphical Abstract:



**Keywords:** Photocatalysis, Malachite green, CuO/Al<sub>2</sub>O<sub>3</sub> composite.

## INTRODUCTION

Malachite green is an organic compound that is used as dyestuff and as an antimicrobial in aquaculture. It is traditionally used as a dye for material such as silk, leather and paper. It is a basic dye. It is brilliant and most fluorescent. Malachite green is also used as a pH indicator. Rathore et al. [1] degraded malachite green by using nickel vanadate powder and observed the effect of various parameters. Shanthi et al. [2] studied the photocatalytic degradation of malachite green dye by using solar light and TiO<sub>2</sub>, ZnO as semiconductor. Gandhi et al. [3] studied the ZnS-CdS catalyzed photocatalytic bleaching of malachite green and brilliant green dyes. Santhi and Sundari [4] degraded malachite green by using *Pseudomonas aeruginos* (MTCC 424). It showed maximum decolorization upon incubation for 18 hours at 37<sup>0</sup>C at pH 7. Panchal and Vyas [5] degraded malachite green by using undoped and iron doped zirconium dioxide. Asilturk et al. [6] synthesized Fe<sup>3+</sup> ion-doped TiO<sub>2</sub> particles by the hydrothermal process at 225 °C. Undoped and doped TiO<sub>2</sub> particles were used to coat glass surface. It was observed that doping of Fe<sup>3+</sup> ion improved the photodegradation performance of TiO<sub>2</sub> coated surfaces. Degradation performance of Fe<sup>3+</sup> doped TiO<sub>2</sub> coated surfaces was found to be higher than the undoped TiO<sub>2</sub> coated surface. Ameta et al. [7] also degraded malachite green in aqueous solution by using lead chromate powder. Afsharet al. [8] prepared TiO<sub>2</sub>/SiO<sub>2</sub>, Pt/TiO<sub>2</sub> and Pt-TiO<sub>2</sub>/SiO<sub>2</sub> nano-photocatalysts and degradation of malachite green was studied in presence of as-prepared catalysts.

Hu and Meng [9] used MoS<sub>2</sub>/TiO<sub>2</sub> nanocomposite for degradation of malachite green. It has been suggested that the MoS<sub>2</sub>/TiO<sub>2</sub> nanocomposite was a promising catalyst for the degradation of malachite green. Ameta et al. [10] prepared nano-sized cerium iron oxide nanoparticles and used as a photocatalyst for the degradation of malachite green. Chen et al. [11] degraded cationic triphenylmethane dye malachite green. About 99.9% of dye was degraded with 0.5 g L<sup>-1</sup> TiO<sub>2</sub> in a solution containing 50 mg L<sup>-1</sup> of the dye. Khizami et al. [12] investigated degradation of malachite green (MG) dye in aqueous medium using vanadium doped zinc oxide (ZnO:V<sub>3%</sub>) nanopowder. Result showed ZnO:3% nanopowder was particularly effective for the removal of MG and the data were found to comply with pseudo-first-order kinetic model. Bansal et al. [13] used different ratio of ZnO and TiO<sub>2</sub> composite for degradation of malachite green. Best result was obtained on with ZnO and TiO<sub>2</sub> in the ratio of 9:1. Spectrophotometrically the rate of decolorization was determined. Baeissa [14] degraded malachite green using nanoparticles of Au/NaNbO<sub>3</sub>. The sodium niobate nanocubes were doped with gold by impregnation with an aqueous solution of HAuCl<sub>4</sub>. It was observed that band gap decreases from 3.4 eV to 2.45 eV due to dropping of gold. Malachite green degradation was studied by using this gold-doped sodium niobate as a photocatalyst. Joshi et al. [15] used Li<sub>2</sub>CuMo<sub>2</sub>O<sub>8</sub> nanoparticles for photocatalytic mineralization of azure A while Ryali and Sanasi studied the effect of graphene oxide on nano titania particle for photocatalytic degradation of Congo red [16]. The photodegradation efficiency of the catalyst for the azure A was found to be 72.08 %. In the present investigation, an attempt has been made where CuO/Al<sub>2</sub>O<sub>3</sub> composite was used for photocatalytic degradation of malachite green and the performance of the as-prepared composite was compared with CuO and Al<sub>2</sub>O<sub>3</sub>.

## MATERIALS AND METHODS

Malachite green, CuO and Al<sub>2</sub>O<sub>3</sub> were purchased from Himedia and used as received. The pH of the solutions was measured by a digital pH meter (Systronics Model 335). The desired pH of solution was adjusted by addition of previously standardized sulphuric acid and sodium hydroxide solutions. Visible spectrophotometer (Systronics Model 106) was used for measuring absorbance at different time intervals. A 200 W tungsten lamp (Phillips) was used for irradiating the solution in the visible range. The intensity of light was measured with the help of Solarimeter (Surya Mapi Model CEL 201) in units of mWcm<sup>-2</sup>. The chemical structure of malachite green is given below in Fig. 1.

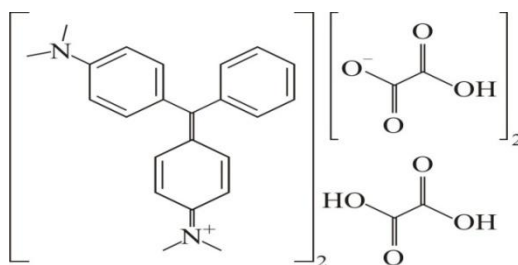


Fig 1. Structure of Malachite green

$1.0 \times 10^{-3}$  M stock solution was prepared by dissolving 0.0927 g of malachite green in 100.0 mL of doubly distilled water. Absorbance of malachite green was determined with the help of spectrophotometer at  $\lambda_{\max} = 630$  nm.

## RESULTS AND DISCUSSION

A solution of  $1.0 \times 10^{-5}$  M malachite green was prepared from its stock solution and 0.10 g of CuO/Al<sub>2</sub>O<sub>3</sub> composite was added to it. The pH of solution was kept 9.0 and then this solution was exposed to a 200 W tungsten lamp at  $60 \text{ mWcm}^{-2}$ . A decrease in absorbance of malachite green solution was observed with increasing time of exposure. A plot of  $1 + \log A$  against time was found to be linear (Fig. 2), which indicates that the photocatalytic degradation of malachite green follows pseudo-first order kinetics. The rate constant was measured with the help of expression  $k = 2.303 \times \text{slope}$ . The observations are shown in the typical run (Table 1).

Table 1. A typical run

pH = 9.0, [Malachite green] =  $1.00 \times 10^{-5}$  M, CuO/Al<sub>2</sub>O<sub>3</sub> = 0.10 g, Light intensity =  $60.0 \text{ mWcm}^{-2}$

Time (min)	CuO		Al <sub>2</sub> O <sub>3</sub>		CuO/Al <sub>2</sub> O <sub>3</sub>	
	A	1 + log A	A	1 + log A	A	1 + log A
0	0.375	0.5740	0.375	0.5740	0.375	0.5740
10	0.330	0.5185	0.366	0.5635	0.320	0.5051
20	0.299	0.4757	0.357	0.5527	0.282	0.4502
30	0.268	0.4281	0.355	0.5502	0.243	0.3856
40	0.237	0.3747	0.347	0.5403	0.219	0.3404
50	0.209	0.3201	0.339	0.5302	0.181	0.2577
60	0.188	0.2742	0.335	0.5250	0.158	0.1987
70	0.165	0.2175	0.325	0.5119	0.135	0.1303
80	0.150	0.1761	0.320	0.5051	0.114	0.0569
90	0.133	0.1238	0.315	0.4983	0.101	0.0043

Rate constant (k) for CuO =  $1.92 \times 10^{-4} \text{ sec}^{-1}$ ; Rate constant (k) for Al<sub>2</sub>O<sub>3</sub> =  $3.25 \times 10^{-5} \text{ sec}^{-1}$ ; Rate constant (k) for CuO/Al<sub>2</sub>O<sub>3</sub> =  $2.43 \times 10^{-4} \text{ sec}^{-1}$

**Effect of pH:** The rate of degradation of malachite green was investigated in the pH range 5.0 to 10. The results are reported in table 2. It has been seen that rate of degradation of malachite green increases as the pH was increased and optimum value was found at pH = 9.0. On further increasing pH, the rate of the reaction was found to decrease. This may be due to the formation of oxygen anion radical (O<sub>2</sub><sup>•-</sup>) which is formed by the reaction of O<sub>2</sub> (dissolved oxygen) and electron from conduction band of semiconductor. As a result, rate of reaction was increased. At pH 9.0 the maximum rate of reaction was achieved thereafter rate of reaction decreases. It may be attributed to the fact that formation of cationic form of malachite green is converted to its neutral form, which faces no attraction towards the negatively charged semiconductor surface due to the absorption of OH<sup>-</sup> ions.

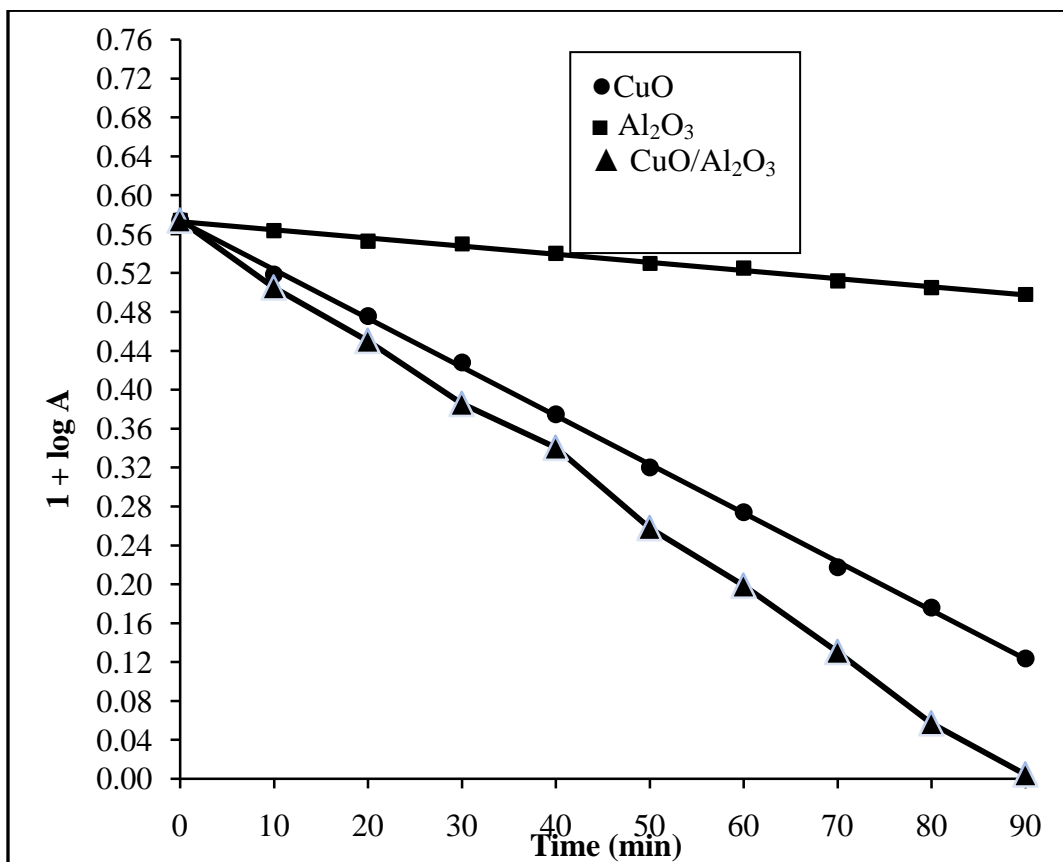


Fig 2. Typical run

Table 2. Effect of pH

[Malachite green] =  $1.00 \times 10^{-5}$  M, CuO/Al<sub>2</sub>O<sub>3</sub> = 0.10 g, Light intensity =  $60.0 \text{ mWcm}^{-2}$

pH	Rate constant (k) $\times 10^4$ (sec <sup>-1</sup> )
5.0	0.80
5.5	0.91
6.0	0.94
6.5	1.05
7.0	1.07
7.5	1.39
8.0	1.90
8.5	1.99
<b>9.0</b>	<b>2.43</b>
9.5	2.14
10.0	1.45

**Effect of malachite green concentration:** The effect of malachite green concentration was studied by taking different concentrations of the dye. The results are tabulated in table 3. As the concentration of malachite green was increased rate of reaction also increased up to  $1.0 \times 10^{-5}$  M concentration, and then rate of reaction decreases on increasing the concentration of dye further. It is because as concentration of dye was increased number of dye molecules also increased resulting in is higher rate of reaction. Increasing it above a particular limit ( $1.0 \times 10^{-5}$  M), it will start acting as an internal filter and as a consequence, proper light intensity will not reach semiconductor particles, which are present on the bottom of the surface.

**Table 3:** Effect of malachite green concentration  
pH = 9.0, Light intensity =  $60.0 \text{ mWcm}^{-2}$ , CuO/Al<sub>2</sub>O<sub>3</sub> = 0.10 g

[Malachite green] $\times 10^{-5}$ M	Rate constant (k) $\times 10^4$ (sec <sup>-1</sup> )
0.6	1.02
0.7	1.24
0.8	1.55
0.9	1.63
<b>1.0</b>	<b>2.43</b>
1.1	1.97
1.2	1.69
1.3	1.55
1.4	1.52
1.5	1.40

**Effect of amount of CuO/Al<sub>2</sub>O<sub>3</sub>:** The amount of semiconductor is also likely to affect the degradation of dye and hence, different amounts of CuO/Al<sub>2</sub>O<sub>3</sub> composite were used. Results are summarized in Table 4. The observations show that as the amount of composite was increased, the rate constant was also increased. After its optimum value at 0.10 g, the rate constant was decreased when the amount of composite was further increased. Such a behavior may be due to multilayer formation, which causes recombination of electron-hole pair. As a result, the rate of degradation is retarded.

**Table 4.** Effect of amount of CuO/Al<sub>2</sub>O<sub>3</sub> composite  
pH = 9.0, [Malachite green] =  $1.00 \times 10^{-5}$  M, Light intensity =  $60.0 \text{ mWcm}^{-2}$

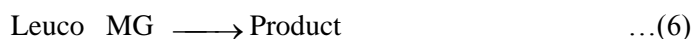
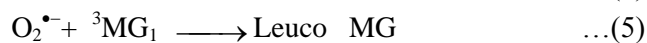
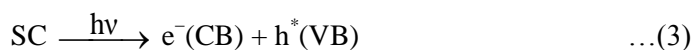
Amount of CuO/Al <sub>2</sub> O <sub>3</sub>	Rate constant (k) $\times 10^4$ (sec <sup>-1</sup> )
0.02	1.65
0.04	1.73
0.06	1.84
0.08	2.21
<b>0.10</b>	<b>2.43</b>
0.12	1.55
0.14	1.12

**Effect of light intensity:** The distance between the light source and exposed surface area of photocatalyst was varied to find out effect of light intensity. Results are tabulated in Table 5. It was observed that as the intensity of light was increased, the rate of degradation also increased. It may be due to increase in the number of photons striking per unit area of semiconductor powder per unit time on increasing light intensity. Above  $60.0 \text{ mWcm}^{-2}$  rate of reaction decreases lightly due to some side reactions.

**Table 5.** Effect of light intensity  
pH = 9.0, [Malachite green] =  $1.00 \times 10^{-5}$  M, CuO/Al<sub>2</sub>O<sub>3</sub> = 0.10 g

Light intensity (mWcm <sup>-2</sup> )	Rate constant (k) × 10 <sup>4</sup> (sec <sup>-1</sup> )
20.0	1.20
30.0	1.71
40.0	2.01
50.0	2.37
<b>60.0</b>	<b>2.43</b>
70.0	2.14

**Mechanism:** Based on the observations of malachite green degradation, a tentative mechanism may be proposed as:



After complete degradation of dye, the following results were obtained for physico-chemical parameters of the dye.

**Table 6.** Physico-chemical parameters of malachite green solution (Before and after treatment)

Parameters	Before degradation	After degradation
DO (ppm)	7.6	11.90
Hardness (ppm)	400	283
pH	9.0	7.5
Conductance (S)	1.89	2.00
TDS (ppm)	406	517

**Dissolved Oxygen:** Dissolved oxygen refers to the level of free, non-compound oxygen present in water or other liquids. It is an important parameter in assessing water quality because of its influence on the organisms living within a body of water. The dissolved oxygen is 5ppm in normal potable water. Value of malachite green dye was increased from 7.6ppm to 11.90ppm.

**Hardness:** Hardness is the amount of dissolved calcium and magnesium in the water. Hard water is high in dissolved minerals like calcium and magnesium. Malachite green hardness decreases from 400ppm to 283ppm.

**pH: Catalytic advanced oxidation** reactions developed for the discoloration of the dye wastewater results in very effective oxidative degradation of a variety of dyes from food and textile industry effluents. Malachite green dye has been degraded in present work. The pH value of the dye decreases from 9.0 to 7.5 and reached towards neutral pH.

**Conductance:** Conductivity is directly proportional to dissolved minerals in the solution. Conductance of malachite green dye solution was 1.89 S before degradation, and after degradation, it was increased to 2.00 S, which shows the mineralization of the dye.

**Total dissolved solid (TDS):** The total dissolved solids concentration is the sum of the cations (positively charged) and anions (negatively charged) in the water. Therefore, the total dissolved solids provides a qualitative measure of the amount of dissolved ions. TDS value of malachite green increased from 406 to 517ppm due to mineralization of dye molecules.

### APPLICATIONS

CuO and Al<sub>2</sub>O<sub>3</sub> semiconductors can be used as photocatalyst for removal of different pollutants. In the present investigation, it was observed that the composite of CuO and Al<sub>2</sub>O<sub>3</sub> performed better for photocatalytic degradation of malachite green. The use of CuO/Al<sub>2</sub>O<sub>3</sub> composite will explore its use in various fields in years to come.

### CONCLUSIONS

The use of semiconductors as photocatalysts is increasing day by day for removal of pollutants and researchers are attempting to achieve best performance of the photocatalysts by different modifications. In this context, combination of different semiconductors used as composite is also found good in performance. In the present investigation, it has been observed that the composite CuO/Al<sub>2</sub>O<sub>3</sub> has shown better performance in compare to its components i.e. CuO and Al<sub>2</sub>O<sub>3</sub>.

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