



PHOTOCATALYTIC DECOMPOSITION OF MALACHITE GREEN OVER LEAD CHROMATE POWDER

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ABSTRACT

Lead chromate powder has been used as a photocatalyst for the decomposition of malachite green dye in aqueous solution. The rate of decomposition was affected by different parameters such as pH, amount of photocatalyst, concentration of malachite green and intensity of light. This reaction proceeds through oxidation by hydroxyl radical as confirmed by the radical scavenger, 2-propanol. A plausible mechanism has been proposed for this photocatalytic degradation.

Key words: Photocatalytic, Malachite green, Lead chromate.

INTRODUCTION

The world is facing the challenge of purification of water and air resources. The society is enjoying the comforts and benefits that chemistry has provided on one hand e.g. from drugs to dyes, from polymer, composites to computer chips, etc. But on the other hand, it is also facing the problem of proper disposal of various products and by products of various industries including dye industries. In spite of many uses, the dyes are quite toxic and sometimes even carcinogenic in nature also. Thus, environmental contamination by these toxic chemicals has emerged as a serious global problem. Coloured solution containing dyes from industrial effluents from textile, dyeing and printing industries may cause different diseases including skin cancer due to photosensitization and photodynamic damage. On the contrary, bleached dye after degradation of solution is relatively less toxic and almost harmless. Secondly, dye containing coloured water is of almost no practical use, but if this coloured solution is bleached to give colourless water, then it may be used for some useful purposes like washing, cooling, irrigation and cleaning. The photocatalytic bleaching or degradation seems to be quite promising as it can provide a low cost method to solve this problem.

Photocatalysis is a booming field of chemistry due to its numerous potential applications. Using light as an energy source to drive a reaction in a desired direction has resulted in chemistry, which is much more 'green'. It also helps to eliminate the need for harsh reactants, which are often toxic and unrecoverable. Photocatalysis has applications in the area of renewable energy also. A photocatalyst could be used to split water into hydrogen and oxygen for energy purposes.

Sn-doped and undoped nano-TiO₂ particles have been synthesized by hydrothermal process without acid catalyst at 225°C in one hr by Sayilkan et al.¹ They prepared nanostructure-TiO₂ based thin films on

glass surfaces by spin-coating technique. The photocatalytic performance of the films was tested for degradation of malachite green dye in solution under UV and visible lights. They showed that the hydrothermally synthesized nano-TiO₂ particles were fully in anatase crystalline form and these are easily dispersed in water. Mittal² utilized meticulously hen feather as potential adsorbent to remove the hazardous triphenylmethane dye, Malachite green from wastewater. The adsorption studies were carried out at different temperatures (30, 40 and 50°C) and the effect of pH, temperature, amount of adsorbent, contact time, concentration of adsorbate, etc. on the adsorption were observed. Langmuir and Freundlich adsorption isotherm models were also confirmed. The thermodynamic parameters like ΔT° , ΔH° and ΔS° were calculated.

Samira et al.³ investigated the photocatalytic oxidation of crystal violet, (a triphenyl methane dye) in aqueous solutions with nanoanatase TiO₂ containing anatase and rutile phases in the ratio of 3:1. They used UV light (125 W high pressure mercury vapor lamp) as the light source. The dye degradation using Ag⁺ doped TiO₂ and nanoanatase TiO₂ was compared with an optimum catalyst dose of 1 g/L⁻¹. It was found that nanoanatase TiO₂ had a higher efficiency than the Ag⁺ doped titanium dioxide. The degradation of the dye (with initial concentration: 5×10^{-5} mol/L⁻¹), using nanoanatase TiO₂ was greater than 99.5% on UV illumination for 45 min. while with Ag⁺ doped titanium dioxide, it was only 75% on 45 min. of illumination. The kinetics of degradation fit well to Langmuir-Hinshelwood rate law

Ong et al.⁴ observed the effects of adsorbability and number of sulfonate groups on solar photocatalytic degradation of monoazo methyl orange (MO) and diazo reactive green 19 (RG19) in single and binary dye solutions. The adsorption capacity of MO and RG19 onto the TiO₂ was 16.9 and 26.8 mg/g, respectively in single dye solution, which reduces to 5.0 and 23.1 mg/g, respectively in the binary dye solution. Evans blue (an azo dye) and its mixture with amaranth were degraded photocatalytically by Kothari et al.⁵ in presence of zinc oxide. The optimum conditions for photobleaching of these dyes, like concentration of dye, pH, amount of semiconductor, light intensity, etc., have been observed. The semiconductor remains unaffected during the photocatalytic degradation. These dyes are commonly used in dyeing, printing and textile industries and hence, this degradation will be helpful in the treatment of coloured effluents from these industries.

Liu et al.⁶ studied the influence of native defects on the adsorption and photocatalytic degradation of anionic and cationic dyes for different ZnO nanoparticles. It was found that there was no relationship between the dye adsorption onto ZnO nanoparticles and their photocatalytic activity. While the absorption of cationic dyes was not significantly affected by ZnO nanoparticle properties, dye adsorption of several anionic dyes was strongly affected by native defects in ZnO. The defects involved in the dye adsorption may be shallow donor centers resulting in positively charged sites at the surface. Sharma et al.⁷ used zinc sulphide semiconductor as a photocatalyst for the removal of rose Bengal dye. Effect of different parameters affecting the rate of reaction, such as pH, concentration of dye, amount of semiconductor and light intensity were studied. A mechanism has been proposed, where hydroxyl radicals act as the active oxidizing species.

Sharma et al.⁸ studied thioglycerol capped and uncapped ZnS nanoparticles for their photocatalytic activity and generation of electron-hole pairs. Bromophenol blue, crystal violet and reactive red dyes were successfully photoreduced using ZnS nanoparticles in 3.0 hours. The photocatalytic activity depends on the generation of electron-hole pairs and the existence of different phases.

Fe³⁺ ion-doped TiO₂ particles were synthesized by a hydrothermal process at 225°C using titanium isopropoxide as a precursor surfaces⁹. Both undoped and doped TiO₂ particles were used to coat glass surface. The coated surfaces were used for their photocatalytic performance for degrading malachite green (MG) dye in aqueous solution under UV and vis-light irradiation. They found that crystalline sizes of the

hydrothermally synthesized TiO₂ particles were in nanoscale. It was observed that the doping of Fe³⁺ ion improved the photodegradation performance of TiO₂ coated surface. The photodegradation rate of malachite green (2.5 mg L⁻¹) under UV-light irradiation catalyzed by Fe³⁺ doped TiO₂ followed pseudo-first order kinetics and the rate constant was 0.0202 min⁻¹.

Saha et al.¹⁰ used commercial TiO₂ impregnated with silver nanoparticles (at 1 and 2 mol% Ag) with a simple liquid impregnation method followed by heat treatment. The UV-induced photodegradation of malachite green in aqueous medium using these modified TiO₂ catalysts was studied to evaluate the effect of silver impregnation. It was observed that the presence of silver in TiO₂ enhances the photon induced mineralization of malachite green but reduces its decolorization efficiency. 1% silver impregnated commercial TiO₂ was found to give the best results. The dye (~ 25 mg/L) was bleached almost completely upon 1 h light irradiation under the experimental conditions.

Complete decolorization of Malachite green was reported under static anoxic condition within 5 h by bacteria *Kocuria rosea* MTCC 1532 by Parshetti et al.¹¹; however, decolorization was not observed in shaking condition. *K. rosea* have also shown decolorization of other dyes like azo, triphenylmethane and industrial dyes. Semi-synthetic media containing molasses, urea and sucrose have shown 100, 91 and 81% decolorization, respectively. Toxicity study revealed that the malachite green was degraded into non-toxic products by *K. rosea*. The microbial degradation of malachite green was investigated in presence of the *Bacterium klebsiella*¹². It was found that the best experimental conditions were: dye concentration (25 ppm), temperature (30°C), pH (-6), carbon source (Lactose) and nitrogen source (Ammonium nitrate). Habib et al.¹³ reported photocatalytic decolorization of brilliant golden yellow (BGY), an anionic dye, in TiO₂ and ZnO aqueous dispersions under UV-light irradiation. Adsorption is a prerequisite for the metal oxide-mediated photodegradation/ photodecolorization and the extent of decolorization has been discussed in terms of the Langmuir-Hinshelwood model. Complete decolorization was achieved in case of UV irradiation. The effects of various parameters, such as catalyst loading, pH and initial concentration of the dye on decolorization of BGY have been evaluated.

Hachem et al.¹⁴ investigated the photocatalytic degradation of various dyes (Orange II, orange G, congo red, indigo carmine, crystal violet, malachite green, remazol blue and methyl yellow) using P25 Degussa as catalyst. All dye solutions underwent decolourization. The kinetics of reaction have been studied and reactions were found to be zero or first order with respect to the dyes. The effect of the addition of hydrogen peroxide has also been studied. The order with respect to the additive was found to be almost zero.

Malachite green is 4-{[4-(dimethylamino)phenyl] (phenyl)methylidene}-N,N-dimethylcyclohexa-2,5-dien-1-iminium chloride. Its molecular formula and molar mass is C₂₃H₂₅ClN₂ and 364.91 g/mol, respectively. It is soluble in water. Malachite green is traditionally used as a dye. It is also active against the *oomycete saprolegnia*, which infects fish eggs in commercial aquaculture. It is a very popular treatment against *ichthyophthirius* in freshwater aquaria. Malachite green is also used as a parasiticide and antibacterial.

EXPERIMENTAL

0.0365 g of malachite green was dissolved in 100.0 mL of doubly distilled water so that the concentration of dye solution was 1.0 × 10⁻³ M. It was used as a stock solution. This stock solution was further diluted. The optical density of malachite green solution was determined with the help of a spectrophotometer at λ_{max} = 620 nm. The dye solution was divided in four beakers.

- The first beaker containing malachite green solution was kept in dark.

- The second beaker containing malachite green solution was exposed to light.
- The third beaker containing malachite green solution and 0.10 g lead chromate was kept in dark, and
- The fourth beaker containing malachite green solution and 0.10 g lead chromate was exposed to light.

These beakers were kept for 3-4 hours and then the absorbance of each solution was measured with the help of a spectrophotometer. It was observed that the absorbance of solutions of first three beakers remained virtually constant, while the solution of fourth beaker showed a decrease in its initial value. This observation suggests that this reaction requires both; the presence of light as well as semiconductor lead chromate. Therefore, this reaction is a photocatalytic reaction in nature and not chemical or photochemical.

A solution of 9.00×10^{-5} M malachite green was prepared in doubly distilled water and 0.12 g of lead chromate was added to it. The pH of the reaction mixture was adjusted to 7.5 and then this solution was exposed to a 200 W tungsten lamp at 60.0 mWcm^{-2} .

It was observed that there was a decrease in absorbance of malachite green solution with increasing time of exposure. A linear plot between $1 + \log A$ v/s time was obtained, which indicates that the photocatalytic degradation of malachite green follows pseudo-first order kinetics. The rate constant for this reaction was measured with the help of following equation-

$$k = 2.303 \times \text{slope} \quad \dots(1)$$

A typical run has been presented in Table 1.

Table 1: A typical run

pH = 7.5		Lead chromate = 0.12 g
[Malachite green] = 9.00×10^{-5} M		Light intensity = 60.0 mWcm^{-2}
Time (min.)	Absorbance (A)	$1 + \log A$
0.0	0.600	0.7782
5.0	0.511	0.7084
10.0	0.448	0.6513
15.0	0.376	0.5752
20.0	0.341	0.5328
25.0	0.291	0.4639
30.0	0.250	0.3980
35.0	0.215	0.3324
40.0	0.190	0.2787
45.0	0.160	0.2041
50.0	0.139	0.1430
55.0	0.119	0.0750
60.0	0.105	0.0210
Rate constant (k) = $4.83 \times 10^{-4} \text{ sec}^{-1}$		

Effect of pH

The pH of the solution may also affect the degradation of malachite green. The effect of pH on the rate of degradation of malachite green was investigated in the pH range 5.0-10.0. The results are reported in Table 2.

Table 2: Effect of pH

[Malachite green] = 9.00×10^{-5} M Light Intensity = 60.0 mWcm^{-2}
Lead Chromate = 0.12 g

pH	Rate constant (k) $\times 10^4$ (sec ⁻¹)
5.0	1.47
5.5	2.22
6.0	3.73
6.5	4.24
7.0	4.61
7.5	4.83
8.0	4.02
8.5	3.67
9.0	3.22
9.5	2.98
10.0	2.02

It has been observed that the rate of photocatalytic degradation of malachite green increases as pH was increased and it attained optimum value at pH 7.5. On further increasing pH, the rate of the reaction was decreased. This behavior may be explained on the basis that as pH was increased, there is greater probability for the formation of hydroxyl radicals, which are produced from the reaction between OH ions and hole (h^+) in valence band of the semiconductor. With the formation of more $\bullet\text{OH}$ radicals, the rate of photocatalytic degradation of the dye increases. Above pH 7.5, a decrease in the rate of photocatalytic degradation of the malachite green was observed, which may be due to the fact that cationic form of malachite green is converted to its neutral form, which faces no attraction towards the negatively charged semiconductor surface due to adsorption of OH^- ions.

Effect of dye concentration

The effect of dye concentration was observed by taking different concentrations of malachite green. The results are summarized in Table 3.

It was observed that the rate of photocatalytic degradation of dye increases on increasing the concentration of malachite green up to 9.00×10^{-5} M. It may be attributed to the fact that as the concentration of the malachite green was increased, more dye molecules were available for excitation and consecutive energy/electron transfer and hence, an increase in the rate of degradation of the dye. There was a decrease in degradation rate on increasing the concentration of dye above 9.00×10^{-5} M. This may be

because of the fact that after a particular concentration, the dye may start acting as an internal filter and it will not permit the sufficient light intensity to reach surface of the photocatalyst at the bottom of reaction vessel.

Table 3: Effect of malachite green concentration

pH = 7.5

Light intensity = 60.0 mWcm⁻²

Lead chromate = 0.12 g

[Malachite green] × 10 ⁴ M	Rate constant (k) × 10 ⁴ (sec ⁻¹)
0.60	2.77
0.70	3.26
0.80	4.08
0.90	4.83
1.00	4.22
1.10	3.89
1.20	3.41
1.30	2.97
1.40	2.00
1.50	1.61

Effect of amount of semiconductor

The amount of semiconductor may also affect the degradation of dye and hence, different amounts of lead chromate were used. The results are reported in Table 4.

Table 4: Effect of amount of lead chromate

pH = 7.5

Light Intensity = 60.0 mWcm⁻²

[Malachite green] = 9.00 × 10⁻⁵ M

Lead Chromate (g)	Rate constant (k) × 10 ⁴ (sec ⁻¹)
0.02	2.39
0.04	3.06
0.06	3.56
0.08	4.22
0.10	4.49
0.12	4.83
0.14	4.82
0.16	4.84

The rate of reaction was found to increase on increasing the amount of semiconductor, lead chromate. The rate of degradation reached to its optimum value at 0.12 g of the photocatalyst. Beyond 0.12 g, the rate of reaction becomes almost constant. This may be explained on the basis that as the amount of semiconductor was increased, the exposed surface area of the semiconductor was also increases. However, after a particular value (0.12 g), an increase in the amount of semiconductor will only increase the thickness of layer of the semiconductor and not its exposed surface area. This was confirmed by taking reaction vessels of different sizes. It was observed that this point of saturation was shifted to a higher value for vessels of larger volumes while a reverse trend was observed for vessels of smaller capacities.

Effect of light intensity

The effect of light intensity on the photocatalytic degradation of malachite green was also investigated. The light intensity was varied by changing the distance between the light source and the exposed surface area of semiconductor. The results are given in Table 5.

Table 5: Effect of light intensity

pH = 7.5		Lead chromate = 0.12 g
[Malachite green] = 9.00×10^{-5} M		
Light intensity (mWcm ⁻²)	Rate constant (k) × 10 ⁴ (sec ⁻¹)	
20.0	1.67	
30.0	2.87	
40.0	3.69	
50.0	4.29	
60.0	4.83	
70.0	4.80	

These data indicate that photocatalytic degradation of malachite green was enhanced with the increase in intensity of light, because an increase in the light intensity will increase the number of photons striking per unit area per unit time of photocatalyst surface. There was a slight decrease in the rate of reaction as the intensity of light was increased beyond 60.0 mWcm⁻². Therefore, light intensity of medium order was used throughout the experiments.

Mechanism

On the basis of these observations, a tentative mechanism for photocatalytic degradation of malachite green dye is proposed as follows:





Malachite green (MG) absorbs radiations of desired wavelength and it is excited giving its first excited singlet state. Further, it undergoes intersystem crossing (ISC) to give its more stable triplet state. Along with this, the semiconducting lead chromate (SC) also utilizes this energy to excite its electron from valence band to the conduction band. An electron can be abstracted from hydroxyl ion by hole (h^+) present in the valence band of semiconductor generating $\bullet\text{OH}$ radical. This hydroxyl radical will oxidize malachite green to its leuco form, which may ultimately degrade to products. It was confirmed that the $\bullet\text{OH}$ radical participates as an active oxidizing species in the degradation of malachite green as the rate of degradation was appreciably reduced in presence of hydroxyl radical scavenger (2-propanol).

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