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PHOTOCATALYTIC DEGRADATION OF MALACHITE GREEN OVER NICKEL VANADATE POWDER

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ABSTRACT

In the present work, nickel vanadate has been used as a photocatalyst to degrade malachite green. Superoxide anion radical has been proposed responsible species for reduction of the dye molecules. The optimum parameters obtained for this degradation were pH = 9.5, [Malachite green] = 1.00×10^{-5} M, nickel vanadate = 0.10 g and light intensity = 50.0 mWcm^{-2}. The rate constant of photocatalytic degradation of malachite green at optimum conditions was 4.29×10^{-5} sec^{-1}.

Key words: Photocatalytic degradation, Malachite green, Nickel vanadate.

INTRODUCTION

Malachite green is a basic dye. Basic dyes are salts of the colored organic bases containing amino and imino groups and also combined with a colorless acid, such as hydrochloric or sulfuric acid. They are brilliant and most fluorescent among all synthetic dyes. Basic dyes are cationic, which has positive electrical charge and are used for anionic fabrics bearing negative-charge, such as wool, silk, nylon, and acrylics where bright dyeing is the prime consideration. Malachite green does not contain the mineral malachite; the name comes from the similarity of color. This chemical dye is primarily designed to be used as a dye for silk, leather, and paper. Malachite green in dilute solution is widely used medicinally as a local antiseptic. It is effective against parasites, fungal infections and gram-positive bacteria. In combination with formalin as a synergist, malachite green is a common antiseptic agent against the fungus *Saprolegnia*, a typical water mold that kills fish eggs and young fry. But its use has been banned in many countries due to its suspect of carcinogenicity. Malachite green is used as a biological stain as a counterstain against fuchsin, which stains gram-positive and gram-negative bacteria reddish colors and safranin, which stains nuclei red. Malachite green stains background to the surrounding tissue blue-green. Malachite green is used as a pH indicator between pH 0.2 (green) - 1.8 (blue-green).

Pawar and Khajone[1] synthesized nanocrystalline α-Fe_2O_3 by sol-gel method. α-Fe_2O_3 samples were prepared at different temperatures; 450º, 550º and 650ºC. The effects of heat treatment on the crystallite sizes, crystal pattern, surface composition, and optical property of the catalysts were investigated by means of techniques such as X-Ray diffraction (XRD), Transmission Electron Microscopy (TEM) and Brunauer-Emmett-Teller (BET). The photocatalytic activity was observed with malachite green dye is a modal system over the synthesized α-Fe_2O_3 nanoparticles, where it was observed spectrophotometrically. The effects of

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various operating variables such as calcination temperature, pH, light intensity, concentration of dye and catalyst etc. was also observed on the efficiency of catalyst. The 200 mg of the catalyst sample showed high photoactivity at 100 ppm dye concentration in alkaline medium at pH 10. The tentative reaction mechanism in photodegradation of malachite green dye has been proposed.

Panwar et al.[2] used zirconium phosphate as photocatalyst in photodegradation of some dyes (Eriochrome black-T, methylene blue and malachite green). The progress of the reaction was observed spectrophotometrically. The effects of various operating variables like pH, concentration of dyes, amount of semiconductor and light intensity on the rate of degradation was observed.

Tayade et al.[3] synthesized the nanocrystalline TiO_2 by controlled hydrolysis of titanium tetraisopropoxide. The anatase phase was converted to rutile phase by thermal treatment at 1023 K for 11 h. The catalysts were characterized by X-ray diffraction (XRD), diffuse reflectance spectroscopy (DRS), Fourier-transform infrared absorption spectrophotometry (FT-IR) and N_2 adsorption (BET) at 77 K. They compared the photocatalytic activity of the anatase and rutile phases of nanocrystalline TiO_2 for the degradation of acetophenone, nitrobenzene, methylene blue and malachite green in aqueous solutions. The initial rate of degradation was calculated to compare the photocatalytic activity of anatase and rutile nanocrystalline TiO_2 for the degradation of different substances under ultraviolet light irradiation. The higher photocatalytic activity was obtained in anatase phase TiO_2 for the degradation of all substances as compared to rutile phase. It was concluded that the higher photocatalytic activity in anatase TiO_2 is due to parameters like band gap, number of hydroxyl groups, surface area and porosity of the catalyst.

Gandhi et al.[4] studied the ZnS-CdS catalysed photocatalytic bleaching of malachite green and brilliant green dyes. The effect of various parameters, such as the pH, concentration of dyes, amount of semiconductor, light intensity etc. were observed and discussed. The progress of the photochemical oxidation was monitored spectrophotometrically. The optimum reaction conditions were experimentally determined. The photochemical oxidation of dyes follows pseudo-first kinetics. The final products of degradation were characterized.

Chen et al.[5] studied the photodegradation of malachite green (MG), a cationic triphenylmethane dye under different pH values and amounts of TiO_2. After irradiation with 15 WUV-365 nm for 4 hrs, 99.9% of MG was degraded with addition of 0.5 g L^{-1} TiO_2 to solutions containing 50 mg L^{-1} MG dye. The HPLC–PDA–ESI-MS technique was used to obtain a better understanding on the mechanistic details of this TiO_2-assisted photodegradation of the MG dye with UV irradiation. Five intermediates of the process were separated, identified, and characterized. The results indicated that the *N*-demethylation degradation of MG dye took place in a stepwise manner to yield mono-, di-, tri-, and tetra- *N*-demethylated MG species generated during the process. Under acidic conditions, the results indicated that the photodegradation mechanism is favorable for cleavage of the whole conjugated chromophore structure of the MG dye. Under basic conditions, the results showed that the photodegradation mechanism was favorable for the formation of a series of *N*-demethylated intermediates of the MG dye.

Tolia et al.[6] prepared ZnS nanoparticles using mechanochemical method. The ZnS nanoparticles prepared were doped with different concentrations of manganese using manganese acetate by mechanochemical method. The as-prepared particles were characterized using X-ray diffraction (XRD) and transmission electron microscopy (TEM). The photocatalytic activity of the prepared nanoparticles samples in the photocatalytic degradation of malachite green has been investigated. The nanoparticles were photoinduced to generate holes for photocatalytic activity. The photodegradation of malachite green was observed at different pH (2-5) values, dye concentrations (10-100 mg/L) and amount of ZnS nanoparticles (1-2.5 $g^{-1}L$). About 95% degradation of dye was observed on the addition of 2 $g^{-1}L$ ZnS in 50 $mg^{-1}L$ dye solution in 90 min illumination at 125 W. Degradation has been increased up to 99% using UV/nanoparticles/H_2O_2 (50 mL^{-1}L) combined process. The degradation efficiency was also compared using Mn doped ZnS nanoparticles (Zn_{1-x} Mn_xS, where x = 0.01, 0.22 and 0.3). Maximum of 97% degradation was observed with 0.01% concentration of Mn. Kinetics study and performance of UV/ZnS, UV/ZnS/H_2O_2 and UV/doped ZnS processes were evaluated to compare the efficiency of different processes.

Panchal and Vyas[7] used undoped and iron doped zirconium dioxide for photocatalytic degradation of malachite green. They carried out the photocatalytic degradation of malachite green by undoped and iron doped semiconductor zirconium dioxide and the progress of the reaction was observed spectrophotometrically at 616 nm. The effect of various operating variables like pH, concentration of dye, amount of semiconductor and light intensity on the rate of degradation was observed. A tentative mechanism has been proposed for the photocatalytic degradation of dye, involving hydroxyl radical as an active oxidizing species.

Bojinova et al.[8] discussed the sources of malachite green contamination and the wide range of its toxic effects. The photodegradation of this cationic triphenylmethane dye by TiO_2 and TiO_2/WO_3 composite was examined under different experimental conditions. Two types of salts-oxalate and hydrochloride were studied and unexpectedly different kinetics of degradation was observed in the presence of TiO_2 or TiO_2/WO_3 as photocatalysts. The behavior of the hydrochloride dye was almost identical in the presence of both catalysts; TiO_2 or TiO_2/WO_3, showing equal rates of degradation. However for the oxalate form, the TiO_2/WO_3 composite was significantly more efficient than pure TiO_2. Even more, the apparent rate constant of degradation for oxalate was higher than that obtained for hydrochloride with the same composite TiO_2/WO_3. It is suggested that initial adsorption of the dye on the surface of the catalyst plays an important role and it explains different photocatalytic performance of TiO_2/WO_3 composite powder. Most probably the sorption of malachite green oxalate is favored by the $C_2O_4^{2-}$ ions and in this way, it provides direct photooxidation of the dye. It was also established by UV-VIS comparative analysis that during the proposed photo-purification of the pollutants, the formation of the colorless carcinogenic leuco malachite green is negligible.

Kothari et al.[9] have carried out the photoreduction of malachite green in presence of CdS as photocatalyst and ascorbic acid/EDTA as reductants. The effect of different parameters like pH, concentration of malachite green, reductants, amount of semiconductor and light intensity on the rate of photocatalytic reaction has been studied. On the basis of observed data, a tentative mechanism for the photoreduction of malachite green has been proposed.

EXPERIMENTAL

0.0927 g of malachite green was dissolved in 100.0 mL of doubly distilled water so that the concentration of dye solution was 1.0 x 10^{-3} M. It was used as a stock solution. This stock solution was further diluted. The absorbance of malachite green solution was determined with the help of spectrophotometer at λ_{max} = 620 nm. The dye solution was placed in equal amounts 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 nickel vanadate was kept in dark.
- The fourth beaker containing malachite green solution and 0.10 g nickel vanadate was exposed to light.

After keeping these beakers for 3-4 hrs, the absorbance of the solution in each beaker was measured with the help of a spectrophotometer. It was found that the absorbance of solution of first three beakers remained almost constant, while the solution of fourth beaker had a decrease in initial value of absorbance. From this observation, it is clear that this reaction requires presence of both; the light as well as semiconductor nickel vanadate. Hence, this reaction is a photocatalytic reaction in nature.

A solution of 1.0 × 10^{-3} M malachite green was prepared in doubly distilled water and 0.10 g of nickel vanadate was added to it. The pH of the reaction mixture was adjusted to 9.5 and then this solution was exposed to a 200 W tungsten lamp at 50.0 mW cm^{-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, 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 x slope.

A typical run has been presented in Table 1.

Table 1: A typical run

pH = 9.5 Nickel vanadate = 0.10 g
[Malachite green] = 1.00 × 10^{-5} M Light intensity = 50.0 $mWcm^{-2}$

Time (min.)	Absorbance (A)	1 + log A
0.0	0.773	0.8881
10.0	0.753	0.8767
20.0	0.738	0.8680
30.0	0.713	0.8590
40.0	0.702	0.8463
50.0	0.679	0.8318
60.0	0.664	0.8221
70.0	0.646	0.8102
80.0	0.629	0.7986
90.0	0.615	0.7888
100.0	0.597	0.7759

Rate constant (k) = 4.29 × 10^{-5} sec^{-1}

Effect of pH

The pH of the solution is likely to affect the degradation of malachite green. The effect of pH on the rate of degradation of malachite green was investigated in the pH range 5.0-10.5. The results are reported in Table 2.

It has been observed that rate of photocatalytic degradation of malachite green increases as pH was increased and it attained optimum value at pH 9.5. On further increasing pH, the rate of the reaction was decreased. This behavior may be explained on the basis that on increasing pH, there was greater probability for the formation of oxygen anion radical ($O_2^{-\bullet}$), which are produced from the reaction between O_2 molecule and electron (e^-) of the semiconductor. Thus, the rate of photocatalytic degradation of the dye increases. Above pH 9.5, a decrease in the rate of the photocatalytic degradation of the dye 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 the absorption of OH^- ions.

Table 2: Effect of pH

[Malachite green] = 1.00 × 10^{-5} M Light intensity = 50.0 $mWcm^{-2}$
Nickel vanadate = 0.10 g

pH	Rate constant (k) × 10^5 (sec^{-1})
5.0	0.84
5.5	1.03
6.0	1.45
6.5	1.86
7.0	2.07
7.5	2.81
8.0	3.12
8.5	3.72
9.0	4.04
9.5	**4.29**
10.0	4.11
10.5	3.65

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.

Table 3: Effect of malachite green concentration

pH = 9.5 Light intensity = 50.0 $mWCm^{-2}$
Nickel vanadate = 0.10 g

[Malachite green] × 10^5 M	Rate constant (k) × 10^5 (sec^{-1})
0.6	2.65
0.7	3.12
0.9	3.74
0.9	4.07
1.0	**4.29**
1.1	4.16
1.2	3.87
1.3	3.10
1.4	2.44
1.5	2.05

The rate of photocatalytic degradation of dye was found to increase on increasing the concentration of malachite green upto 1.0×10^{-5} M. It may be due to the fact that as the concentration of dye was increased, more dye molecules were available for excitation and energy transfer and hence, an increase in the rate of degradation of dye was observed. A decrease in rate was observed on increasing the concentration of dye above 1.0×10^{-5} M because now, dye will start acting as an internal filter and it will not permit the desired light intensity to reach the surface of the semiconductor present at the bottom of the reaction vessel.

Effect of amount of nickel vanadate

The amount of semiconductor is also likely to affect the degradation of dye and hence, different amounts of nickel vanadate were used. The results are reported in Table 4.

Table 4: effect of amount of nickel vanadate

pH = 9.5 Light intensity = 50.0 mWcm^{-2}

[Malachite green] = 1.00×10^{-5} M

Nickel vanadate (g)	Rate constant (k) × 10^5 (sec^{-1})
0.02	1.98
0.04	2.48
0.06	3.12
0.08	4.04
0.10	**4.29**
0.12	4.27
0.14	4.32
0.16	4.28

It was observed that the rate of reaction increases with increase in the amount of semiconductor nickel vanadate. The rate of degradation was optimum at 0.10 g of the photocatalyst. Beyond 0.10 g, the rate constant was virtually constant. This may be due to the fact that as the amount of semiconductor was increased, the exposed surface area of semiconductor also increases. However, after this limiting value (0.10 g), an increase in the amount of semiconductor only increases the thickness of the semiconductor layer and not the exposed surface area. This was confirmed by taking reaction vessels of different dimensions. The saturation point shifts to higher side for larger vessels, while reverse trends was observed for the smaller vessels.

Effect of light intensity

To investigate the effect of light intensity on photocatalytic degradation of malachite green, the distance between the light source and exposed surface area of photocatalyst was varied. The result are summarized in Table 5.

The results indicate that degradation was accelerated as the intensity of light was increased, because any increase in the light intensity will increase the number of photons striking per unit area of semiconductor powder per unit time. However, on increasing the intensity above 50.0 mWcm^{-2}, there was a slight decrease in the rate. This may be due to some side reactions.

Table 5: Effect of light intensity

pH = 9.5 Nickel vanadate = 0.10 g

[Malachite green] = 1.00×10^{-5} M

Light intensity ($\mathrm{mWcm^{-2}}$)	Rate constant (k) × 10^5 ($\mathrm{sec^{-1}}$)
20.0	1.39
30.0	2.46
40.0	3.48
50.0	**4.29**
60.0	4.11
70.0	4.07

Mechanism

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

$$^{1}\mathrm{MG}_{0} \xrightarrow{h\nu} {}^{1}\mathrm{MG}_{1} \qquad ...(1)$$

$$^{1}\mathrm{MG}_{1} \xrightarrow{\mathrm{ISC}} {}^{3}\mathrm{MG}_{1} \qquad ...(2)$$

$$\mathrm{SC} \xrightarrow{h\nu} e^{-}(\mathrm{CB}) + h^{+}(\mathrm{VB}) \qquad ...(3)$$

$$e^{-} + O_2 \longrightarrow O_2^{-\bullet} \qquad ...(4)$$

$$O_2^{-\bullet} + {}^{3}\mathrm{MG}_{1} \longrightarrow \text{Leuco MG} \qquad ...(5)$$

$$\text{Leuco MG} \longrightarrow \text{Products} \qquad ...(6)$$

Malachite green (MG) dye absorbs radiations of suitable wavelength and gives rise to its first excited singlet state. Then it undergoes intersystem crossing (ISC) to give the triplet state of the dye. On the other hand, the semiconducting nickel vanadate also utilizes the radiant energy to excite its electron from valence band to the conduction band. This electron will be abstracted by oxygen molecule (dissolved oxygen) generating superoxide anion radical ($O_2^{-\bullet}$). This anion radical will reduce the dye malachite green to its leuco form, which may ultimately degrade to products. $^{\bullet}$OH radical does not participate as an active oxidizing species in this degradation. It was also confirmed that this degradation proceeds through reduction and not oxidation as the rate of degradation was not affected appreciably in presence of hydroxyl radical scavenger (2-propanol).

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