Chemical Science Review and Letters ISSN 2278-6783

Research Article

$Na_{12}[CuNiW_{18}O_{62}].23H_2O$ Mediated Photocatalytic Degradation of Malachite Green G

Daksha Sharma*[1], Mamta Ordia[2] and Rakshit Ameta[3]

[1]Department of Chemistry, Vidya Bhawan Rural Institute, Udaipur, Rajasthan, India
[2]Central Academy School, Sardarpura, Udaipur, Rajasthan, India
[3]Department of Chemistry, Shramjeevi College, J.R.N. Rajasthan Vidyapeeth University, Udaipur, Rajasthan, India

Abstract

Photocatalysis is a promising technology for waste water treatment. Different oxides and sulphides semiconductor have been used as photocatalyst by researchers for degrading dyes. In the present paper, a quarternary oxide $Na_{12}[CuNiW_{18}O_{62}].23H_2O$ was used as a photocatalyst for the degradation of dye Malachite green G. The effect of various operational parameters such as effect of pH, concentration of dye, amount of semiconductor and light intensity were studied. Kinetic studies revealed that the photocatalytic degradation follows pseudo first order kinetics. A tentative mechanism for photocatalytic degradation of Malachite green G has been proposed.

Keywords:
$Na_{12}[CuNiW_{18}O_{62}].23H_2O$, photocatalyst, photocatalytic degradation, Malachite green G

***Correspondence**
Author: Daksha Sharma
Email: dakshasharma18@yahoo.in, rakshit_ameta@yahoo.in

Introduction

The most important aspect of photocatalysis is focus on metal oxide semiconductor for degradation of organic pollutants in water. Gouvea *et al.* [1] reported semiconductor assisted photochemical degradation of remazol brilliant blue R, remazol black B, reactive blue 221, reactive blue 222. The photocatalytic degradation of three commercial textile dyes i.e. reactive yellow (RY17), reactive red 2 (RR2), reactive blue 4 (RB4) has been investigated by Neppolian *et al.* [2] using TiO_2 photocatalyst in aqueous solution under solar irradiation. The potential of a common semiconductor, ZnO, has been explored by Chakrabarti and Dutta [3] as effective catalyst for the photodegradation of two model dyes: methylene blue and eosin Y. Akpan and Hameed [4] studied the effects of operating parameters on the photocatalytic degradation of textile dyes using TiO_2- based photocatalysts. The photocatalytic degradation of acid orange 7 (AO7), a non-biodegradable azo-dye, has been investigated over TiO_2 photocatalysts by Kiriakidou *et al.* [5].

Patterned ZnO films were used by Kaneva *et al.* [6] for photoinitiated decolorization of malachite green in aqueous solutions. Cheng *et al.* [7] studied visible light assisted degradation of dye pollutants over Fe (III) loaded resin in the presence of H_2O_2 at neutral pH values. Bhati *et al.* [8] prepared $CeCr_2O_5$ nanoparticles by microwave method and used it for the degradation of yellowish orange and fast green dyes. Sharma *et al.* [9] carried out the photocatalytic bleaching of xylidine ponceau in aqueous suspension of zinc oxide. Photocatalytic degradation of azo dye acid red 14 in water on ZnO as an alternative catalyst to TiO_2 was carried out by Daneshvar *et al.* [10]. Photocatalytic decolorization of remazol red R in aqueous ZnO suspensions was carried out by Akyol *et al.* [11]. The photochemical behaviour of CdS – suspended aerated aqueous solution of methylene blue and rhodamine-B was compared by Takizawa *et al.* [12].

Mills and Williams [13] used cadmium sulphide powder dispersions to sensitise the photoreduction of methyl orange at pH < 7 in aqueous solution. Yang *et al.* [14] used Keggin type $[X^{n+}W_{11}O_{39}]^{(12-n)-}$ and TiO_2 in macro porous hybrid materials $[X^{n+}W_{11}O_{39}]^{(12-n)}$ TiO_2 for the photocatalytic degradation of textile dyes. Xu *et al.* [15] investigated degradation of cationic red GTL by catalytic wet air oxidation over MO-Zn-Al-O catalyst under room temperature and atmospheric pressure. Kannan *et al.* [16] carried out degradation of methylene blue dye using MnO_2 supported polyoxometalate.

Aluminium (III)-modified TiO_2 was prepared by sol-gel process and the degradation of dye pollutants under visible irradiation was examined by Zhao *et al.* [17]. Phase pure layered perovskite $La_4Ni_3O_{10}$ powders were synthesized by Wu and Wen [18] and in the presence of $La_4Ni_3O_{10}$ powders, aqueous azo dyes were degraded. Photocatalytic properties of Zn_2SnO_4 nanocrystals were investigated by Lou *et al.* [19]. The layered compound BiOCl was the first oxyhalide to be used as a photocatalyst and for its photocatalytic activity, the methyl orange (MO) dye degradation was chosen by Zhang *et al.* [20]. Till now, much of the work has been done by using binary and ternary oxides as semiconductor. In the present work, nickel containing Well-Dawson Polyoxometalate (a quarternary oxide) was used for the degradation of Malachite Green G.

Experimental

Preparation of nickel containing polytungstometalate, $Na_{12}[CuNiW_{18}O_{62}].23H_2O$

Sodium tungstate solution was prepared by dissolving 34.8 g (105.5 mmol) in 150 mL distilled water and cupric chloride solution was prepared by dissolving 1.0 g (5.86 mmol) in 25 mL distilled water. These solutions were mixed. 40 mL of nickel chloride solution prepared by dissolving 1.4 g (5.89 mmol) was added drop wise with continuous stirring till constant pH. 10 mL of glacial acetic acid was added. The mixture was refluxed for 4 hrs and left overnight for slow cooling. The shining blue crystals obtained were washed with n-hexane and preserved for analysis. Nickel containing polytungstometalate, $Na_{12}[CuNiW_{18}O_{62}].23H_2O$, has been used as a photocatalyst for the degradation of Malachite green G.

Characterization of nickel containing polytungstometalate, $Na_{12}[CuNiW_{18}O_{62}].23H_2O$

FT-IR Spectroscopy (Fourier transform – infrared)

Fourier transform-infrared (FT-IR) spectrum of $Na_{12}[CuNiW_{18}O_{62}].23H_2O$ was taken by Shimadzu, IR Affinity, using KBr disk method and it is shown in **Figure 1**.

FT-IR spectrum of $Na_{12}[CuNiW_{18}O_{62}].23H_2O$ nano-particles shows the characteristic absorption bands of tungstate group located at 810, 822, 850, 925, 1670, 3310 cm^{-1} and it also confirms bonding between tungsten and oxygen.

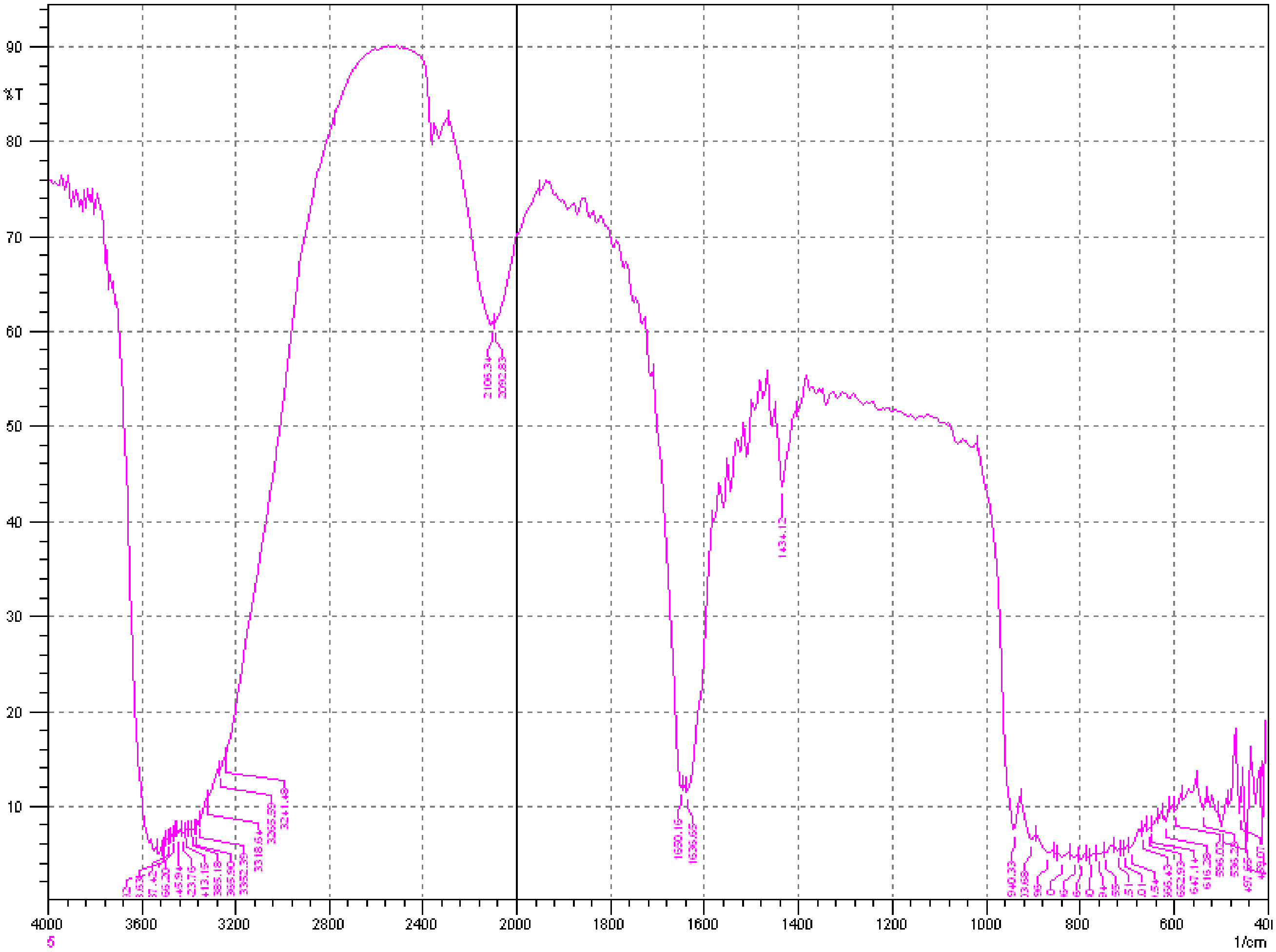


Figure 1 FT-IR spectrum of $Na_{12}[CuNiW_{18}O_{62}].23H_2O$

The IR spectra of $Na_{12}[CuNiW_{18}O_{62}].23H_2O$ show different characteristic W–O vibrations of polyoxometalates between 400-1000 cm-1 (Figure 1). A peak in the region 809cm^{-1} is due to metal oxygen vibrations.

TEM (Transmission electron microscopy)

The morphology and size of the particles were observed with a JEM 100CX-II transmission electron microscopy (TEM, JEM Company, Japan). Samples for TEM analysis were prepared by dispersing the particles in ethanol using ultrasonic agitation. A drop of the suspension was placed on a copper TEM grid and allowed to evaporate. The crystal structure of the final product was examined by a Bluker D8-Advance X-ray diffractometer (XRD, Germany) with Cu K radiation. The voltage was operated at 40 kV, and the current was set at 40 mA.

Transmission electron microscopy (TEM) image as shown in **Figure 2** showed the presence of uniform nanoparticles in the prepared sample. The sizes of most particles in the product were found to be about 200 nm.

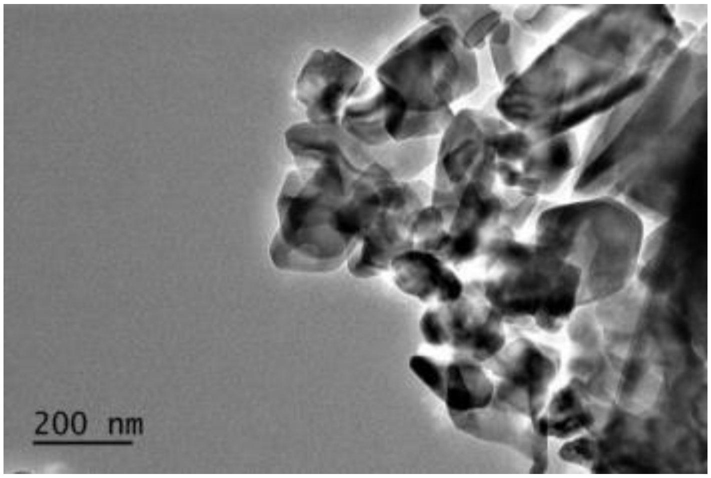
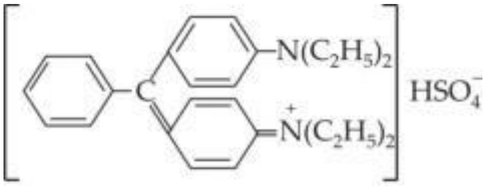


Figure 2 TEM image of $Na_{12}[CuNiW_{18}O_{62}].23H_2O$

Photocatalytic degradation of Malachite green G using $Na_{12}[CuNiW_{18}O_{62}].23H_2O$

Molecular formula of Malachite green G: $C_{27}H_{34}N_2O_4S$



Structure of Malachite green G

A solution of 5.00×10^{-5} M of malachite green G was prepared in doubly distilled water and 0.10 g of nickel containing polytungstometalate 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. The optical density of malachite green G solution was determined with the help of a spectrophotometer at $\lambda_{max} = 630$ nm.

The light intensities were measured at various distances from the lamp with the help of a solarimeter (Suryamapi CEL 201). A water filter was used to cut thermal radiations. A digital pH meter (Systronics Model 335) was used to adjust the pH of the solutions by the addition of previously standardized 0.1 N sulfuric acid and 0.1 N sodium hydroxide solutions. Controlled experiments were also carried out to confirm that reaction is photocatalytic in nature.

Results and Discussion

A decrease was observed in the optical density of malachite green G solution with increasing time of exposure. The photocatalytic degradation of the dye was studied at $\lambda_{max} = 630$ nm. The plot of 1 + log O.D. versus time was found linear, which indicates that the photocatalytic degradation of malachite green G follows pseudo-first order kinetics. The rate constant for this reaction was determined using equation:

$$\text{Rate constant (k)} = 2.303 \times \text{slope}$$

A typical run has been presented in **Table 1** and graphically represented in **Figure 3**.

Table 1 A typical run

Time (min.)	Optical Density (O. D.)	1+ log O. D.
0	0.422	0.6253
20	0.359	0.5551
40	0.335	0.5250
60	0.292	0.4654
80	0.247	0.3926
100	0.216	0.3345
120	0.185	0.2672
140	0.173	0.2380
160	0.140	0.1461

pH = 7.5, [Malachite green G] = 5.00×10^{-5} M,
Semiconductor = 0.10 g, Light Intensity = 50.0 $mWcm^{-2}$
k = 1.15×10^{-4} sec^{-1}

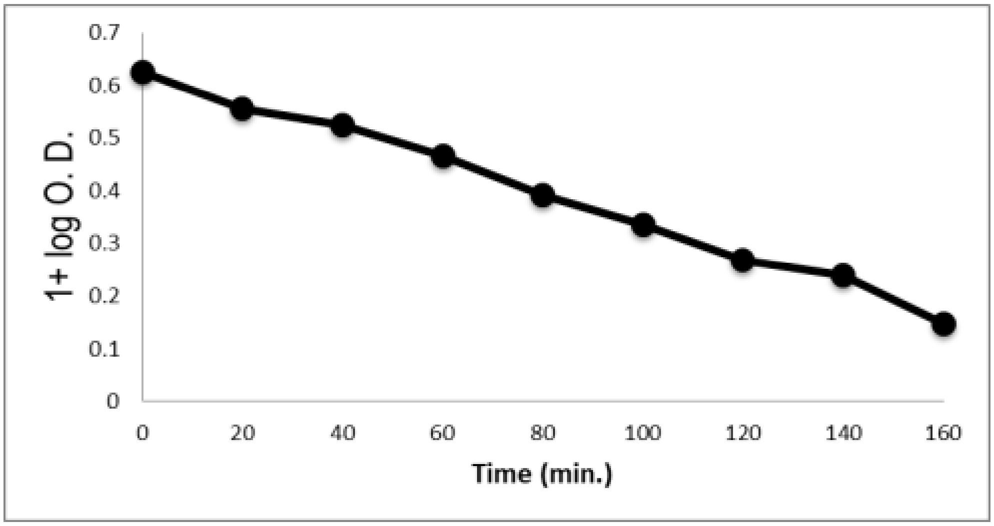


Figure 3 A typical run

Effect of pH

The pH of the solution is likely to affect the degradation of the malachite green G. The effect of pH on the rate of degradation of the dye was investigated in the pH range 5.0 - 10.0. The results are reported in **Table 2** and graphically presented in **Figure 4**.

Table 2 Effect of pH

pH	k × 10^4 (sec^{-1})
5.0	0.52
5.5	0.63
6.0	0.76
6.5	0.89
7.0	0.97
7.5	1.15
8.0	0.96
8.5	0.86
9.0	0.74
9.5	0.61
10.0	0.50

[Malachite green G] = 5.00×10^{-5} M
Semiconductor = 0.10 g
Light Intensity = 50.0 $mWcm^{-2}$

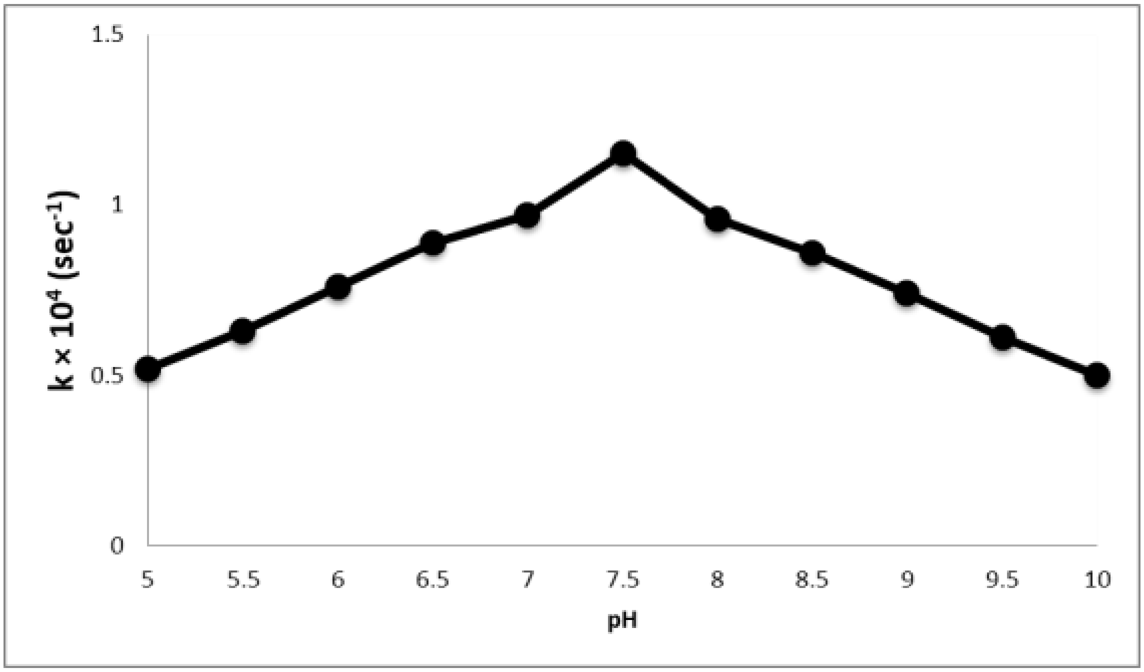


Figure 4 Effect of pH

It has been observed that the rate of photodegradation of malachite green G was increased with increase in pH upto 7.5. A further increase in pH above 7.5 results in a decrease in the rate of reaction. An increase in the rate of photodegradation of malachite green G with increase in pH may be due to generation of more $^{\bullet}OH$ radicals, which are produced from the reaction between ^{-}OH ions and hole (h^+) of the semiconductor. Above pH 7.5, a decrease in the rate of photodegradation of the dye was observed, which may be due to the fact that cationic form of malachite green G converts in its neutral form, which feels relatively less (negligibly small) attraction towards the negatively charged semiconductor surface due to adsorption of ^{-}OH ions.

Effect of dye concentration

The effect of dye concentration was also observed by taking different concentrations of the dye. The results are tabulated in **Table 3** and graphically represented in **Figure 5**.

The rate of photocatalytic degradation of dye was found to increase on increasing the concentration up to 5.00×10^{-5} M. It may be due to the fact that as the concentration of the dye was increased, more dye molecule was available for excitation and energy transfer and hence, an increase in the degradation rate of the dye was observed. The rate of photocatalytic degradation was found to decrease with increase in the concentration of the dye further as the dye itself will start acting as a filter for the incident irradiation.

Table 3 Effect of malachite green g concentration

[Malachite green G] × 10^5 M	**k × 10^4 (sec^{-1})**
3.00	0.62
3.50	0.76
4.00	0.84
4.50	0.97
5.00	1.15
5.50	0.96
6.00	0.86
6.50	0.82
7.00	0.74
7.50	0.63
8.00	0.31

pH = 7.5, Semiconductor = 0.10 g
Light Intensity = 50.0 $mWcm^{-2}$

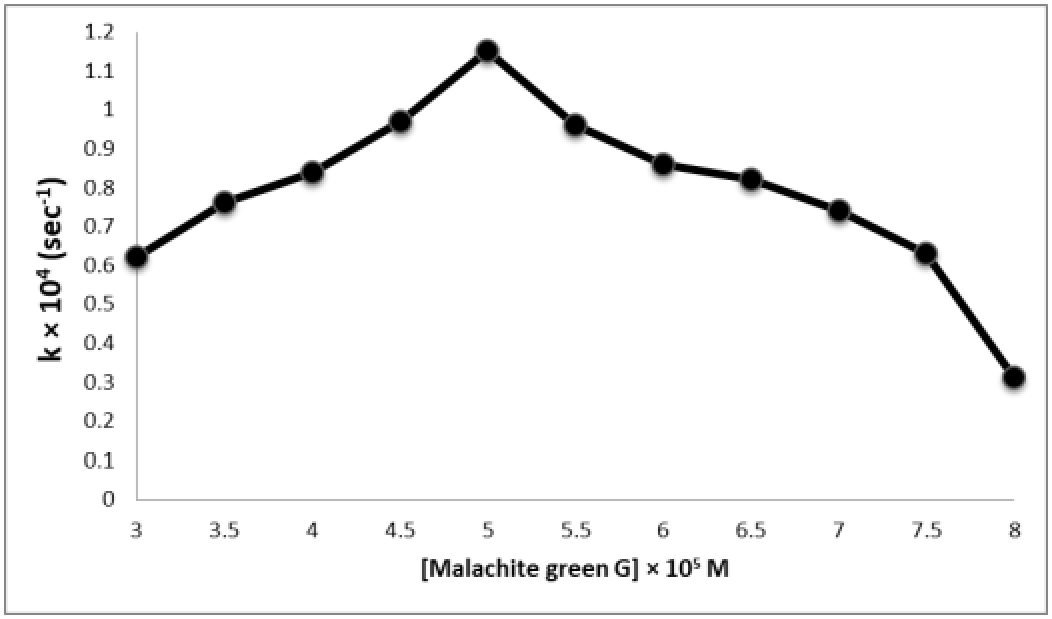


Figure 5 Effect of dye concentration

Effect of amount of semiconductor

The effect of amount of semiconductor was observed by taking different amount of semiconductor. The results are reported in **Table 4** and graphically presented in **Figure 6**.

Table 4 Effect of amount of semiconductor

Semiconductor Amount (g)	$k \times 10^4$ (sec^{-1})
0.02	0.44
0.04	0.63
0.06	0.82
0.08	0.96
0.10	1.15
0.12	1.13
0.14	1.15
0.16	1.14
0.18	1.13

pH = 7.5, [Malachite green G] = 5.00×10^{-5} M
Light Intensity = 50.0 $mWcm^{-2}$

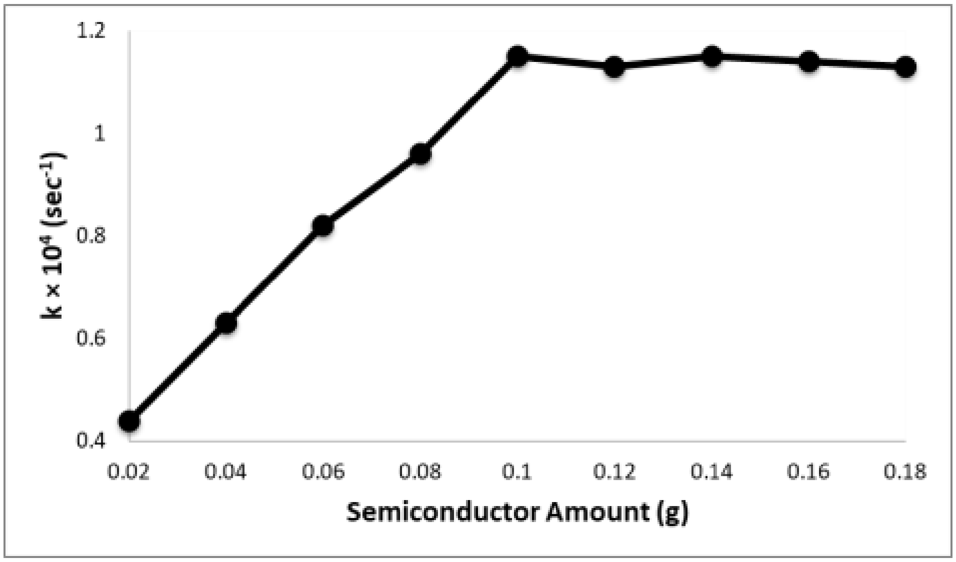


Figure 6 Effect of amount of semiconductor

It was observed that the rate of degradation was increased with increase in the amount of semiconductor nickel containing polytungstometalate. The rate of degradation was highest at 0.10 g of the photocatalyst $Na_{12}[CuNiW_{18}O_{62}].23H_2O$. Beyond 0.10 g, the rates of degradation become virtually constant. This was mainly due to the fact that as the amount of semiconductor was increased, the exposed surface area of the semiconductor was also increased. However, after this limiting value (0.10 g), on increasing the amount of semiconductor it only increases the thickness of the semiconductor layer and not the exposed surface area.

This was also confirmed by using reaction vessels of different dimensions. It was found that the point of saturation shifted to a higher value for vessels of larger capacities while it shifted to lower value for vessels of smaller capacities.

Effect of light intensity

To investigate the effect of light intensity on the photocatalytic degradation of malachite green G, the distance between the light source and the exposed surface area was varied. The results are summarized in **Table 5** and graphically presented in **Figure 7**.

Table 5 Effect of light intensity

Intensity of Light ($mWcm^{-2}$)	k × 10^4 (sec^{-1})
20.0	0.64
30.0	0.89
40.0	0.98
50.0	1.15
60.0	1.05
70.0	0.96
pH = 7.5, [Malachite green G] = 5.00 × 10^{-5} M Semiconductor = 0.10 g	

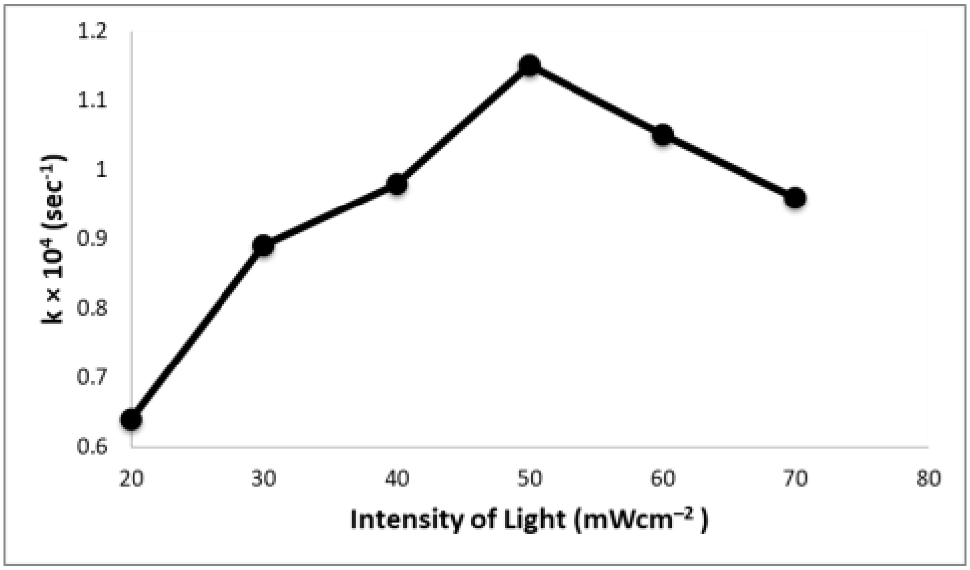


Figure 7 Effect of light intensity

The results indicate that there was an increase in the rate of photocatalytic degradation of malachite green G as the light intensity was increased, because an increase in the light intensity increases the number of photons which strike per unit area of semiconductor surface per unit time. When the light intensity was increased above 50.0 $mWcm^{-2}$, a decrease in the rate of degradation was observed. This may be due to some side reactions or thermal effect.

Mechanism

On the basis of these observations, a tentative mechanism for photocatalytic degradation of malachite green G may be proposed as –

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

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

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

$$ e^{-} + O_{2} \longrightarrow O_{2}^{-\bullet} \qquad (4)$$

$$ {}^{3}\mathrm{MGG}_{1} + O_{2}^{-\bullet} \longrightarrow \text{Leuco MGG} \qquad (5)$$

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

Malachite green G (MGG) absorbs radiations of suitable wavelength and gives rise to its excited singlet state. Then it undergoes intersystem crossing (ISC) to give the triplet state of the dye. The semiconducting nickel containing polytungstometalate (SC) also absorbs the radiant energy to promote its electron from valence band to the conduction band. Oxygen molecule (dissolved oxygen) abstracts this electron generating superoxide anion radical ($O_2^{-\bullet}$). This anion radical will reduce the dye malachite green G to its leuco form, which may ultimately degrade to products. It was also confirmed that this degradation proceeds through reduction and not oxidation.${}^{\bullet}$OH radicals do not participate as an active oxidizing species which was confirmed by using hydroxyl radical scavenger (2-propanol), where the degradation rate was not affected appreciably.

Conclusion

Photocatalytic degradation of Malachite Green G was carried out efficiently by using $Na_{12}[CuNiW_{18}O_{62}].23H_2O$ as a photocatalyst. The optimum conditions for photocatalytic degradation were pH 7.5, concentration of dye 5.00 x 10^{-5} M, amount of semiconductor 0.10 g and light intensity 50.0 $mWcm^{-2}$. It was an eco-friendly approach to degrade organic pollutants like dyes.

Acknowledgement

The authors are grateful to the Professor Suresh C. Ameta, Director, Pacific College of Basic and Applied Sciences, PAHER University, Udaipur (Raj.) for providing necessary laboratory facilities and his valuable suggestions.

References

[1] A. K. Gouvea, F. Wypych, S. G. Moraes, N. Duran, N. Nagata and P. Peralta-Zamora. 2000. Semiconductor-assisted photocatalytic degradation of reactive dyes in aqueous solution. Chemosphere. 40(4):433-440.
[2] B. Neppolian, H. C. Choi, S. Sakthivel, B. Arabindoo and V. Murugesan. 2002. Solar/UV-induced photocatalytic degradation of three commercial textile dyes. Journal of Hazardous Materials. 89(2-3):303-317.
[3] S. Chakrabarti and B. K. Dutta. 2007. Photocatalytic degradation of model textile dyes in waste water using ZnO as semiconductor catalyst. Journal of Hazardous Materials. 112(3):269-278.
[4] U. G. Akpan and B. H. Hameed. 2009. Parameters affecting the photocatalytic degradation of dyes using TiO2-based photocatalysts: A review. Journal of Hazardous Materials. 170(2-3):520-529.
[5] F. Kiriakidou, D. I. Kondarides and X. E. Verykios. 1999. The effect of operational parameters and TiO2-doping on the photocatalytic degradation of azo dyes. Catalysis Today. 54(1):119-130.
[6] N. V. Kaneva, G. G. Yordanov and C. D. Dushkin. 2010. Manufacturing of patterned ZnO films with application for photoinitiated decolorization of malachite green in aqueous solutions. Bulletin of Materials Science. 33:111-118.
[7] M. Cheng, W. Ma, J. Li, Y. Huang, J. Znao, Y. X. Wen and Y. Xu. 2004. Visible light assisted degradation of dye pollutants over Fe (III) loaded resin in the presence of H2O2 at neutral pH values. Environmental Science & Technology. 38(5):1569-1575.
[8] I. Bhati, J. Sharma, A. Ameta and S. C. Ameta. 2011. Synthesis and characterization of nanosized $CeCr_2O_5$ and its use as a photocatalyst. International Journal of Chemical Science. 9(4):1787-1796.
[9] A. Sharma, P. Rao, R. P. Mathur and S. C. Ameta. 1995. Photocatalytic reactions of xylidine ponceau on semiconducting zinc oxide powder. Journal of Photochemistry and Photobiology. 86A:197-200.
[10] N. Daneshvar, D. Salari and A. R. Khataee. 2004. Photocatalytic degradation of azo dye acid red 14 in water on ZnO as an alternative catalyst to TiO2. Journal of Photochemistry and Photobiology. 162A:317-322.
[11] A. Akyol, H. C. Yatmaz and M. Bayramoglu. 2004. Photocatalytic decolorization of remazol red RR in aqueous ZnO suspensions. Applied Catalysis B: Environmental. 54:19-24.

[12] T. Takizawa, T. Watanabe and K. Honda. 1978. Photocatalysis through excitation of adsorbates. 2. A comparative study of Rhodamine B and methylene blue on cadmium sulfide. Journal of Physical Chemistry. 82:1391-1396.

[13] A. Mills and G. Williams. 1987. Methyl orange as a probe of the semiconductor–electrolyte interfaces in CdS suspensions. Journal of the Chemical Society, Faraday Transactions I. 83:2647-2661.

[14] Y. Yang, Y. Guo, C. Hu, C. Jiang and E. Wang. 2003. Synergistic effect of Keggin type [Xn+W11O39](12-n)- and TiO2 in macro porous hybrid materials [Xn+W11O39](12-n)—TiO2 for the photocatalytic degradation of textile dyes. Journal of Materials Chemistry. 1686-1694.

[15] Y. Xu, X. Li, X. Cheng, D. Sun and X. Wang. 2012. Degradation of cationic red GTL by catalytic wet air oxidation oven MO-Zn-Al-O catalyst under room temperature & atmospheric pressure. Environmental Science & Technology. 46(5):2856-2863.

[16] R. Kannan, S. G. Peera, A. Obadiah and S. Vasanthkumar. 2011. MnO_2 supported POM– A novel nanocomposite for dye degradation. Digest Journal of Nanomaterials and Biostructures. 6 (2):829-835.

[17] D. Zhao, C. Chen, Y. Wang, W. Ma, J. Zhao, T. Rajh and L. Zang. 2008. Enhanced photocatalytic degradation of dye pollutants under visible irradiation on Al (III) - modified TiO2: Structure, interaction and interfacial electron transfer. Environmental Science & Technology. 42(1):308-314.

[18] J. M. Wu and W. Wen. 2010. Catalyzed degradation of azo dyes under ambient conditions. Environmental Science & Technology. 44(23):9123-9127.

[19] X. Lou, X. Jia, J. Xu, S. Liu and Q. Gao. 2006. Hydrothermal synthesis, characterization and photocatalytic properties of Zn2SnO4 nanocrystal. Material Science and Engineering: A. 432(1-2):221-225.

[20] K. L. Zhang, C. M. Liu, F. Q. Huang, C. Zheng and W. D. Wang. 2006. Study of the electronic structure and photocatalytic activity of the BiOCl photocatalyst. Applied Catalysis B: Environmental. 68(3-4):125-129.

Publication History

Received	24.05.2020
Revised	08.06.2020
Accepted	16.06.2020
Online	30.06.2020