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PHOTOCATALYTIC DEGRADATION OF NON-BIODEGRADABLE MALACHITE GREEN DYE BY Ni-DOPED TITANIUM DIOXIDE

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ABSTRACT

The removal of colour from textile dyeing waste water by using Ni (0.5, 1.0, 1.5 and 2.0% weight) doped semiconductor titanium dioxide was studied. Photocatalytic degradation studies were carried out for malachite green using Ni doped TiO_2 in aqueous solution and the progress of the reaction was observed spectrophotometrically at 616 nm. The effect of various operating parameters like pH, concentration of dye, dose of semiconductor and light intensity has been studied to optimise reaction conditions. A tentative mechanism has been proposed for the photocatalytic degradation of malachite green, involving hydroxyl radical as an active oxidizing species. It was observed that the pseudo-first order model was more favorable for the degradation of malachite green using Ni doped TiO_2. This was observed that the degradation is more effective and fast for 1.0% Ni-TiO_2. This photocatalytic degradation may prove to be an ecofriendly and cost effective process for the removal of hazardous and toxic dyes present in effluents of textile, printing and dyeing industries.

Key words: Photocatalytic degradation, Nickel doped TiO_2, Malachite green, Titanium dioxide.

INTRODUCTION

Contaminants from industrial effluents often pose a major environmental problem. Semiconductor photocatalysis is a technique with great potential to control aqueous organic contaminants or air pollutants. It holds several advantages over conventional oxidation processes[1-5], such as (i) Complete mineralization of the pollutants, (ii) Use of near-UV or solar light, (iii) No addition of other chemicals, and (iv) Operation at near room temperature. Preparation of photocatalysts with high photocatalytic activity, the immobilization of powder photocatalyst and the improvement of photocatalyst performance by doping with other mertal/non metal have been considered[5-8]. Among various oxide semiconductor photocatalysts so far, TiO_2 is an important photocatalyst due to its strong oxidizing power, non-toxicity and long-term photostability. Specific applications of TiO_2 crystalline particles were determined by their chemical, structural and physical properties. In particular, its surface state, the nature and concentration of surface active centers and defects are considered to play important roles. TiO_2 exists in four different mineral forms[9], rutile, anatase and brookite and TiO_2B, among which anatase is a most stable form[10]. It can be converted to rutile by heating to temperatures above 700°C. The photocatalytic activity of TiO_2 depends on its phase structure, crystallite size, specific surface areas, and pore structure[10-13]. Many studies have confirmed that the anatase phase of TiO_2 is a superior photocatalytic material for air purification, water disinfection, hazardous waste remediation and water purification. However, it is not yet well understood, which factors are responsible for the higher photocatalytic activity of anatase than rutile TiO_2[14].

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Ni-doped TiO_2 has been prepared with different percentages (0.5, 1.0, 1.5, 2.0%) of Ni and the photocatalytic activity of these four different catalysts have been determined towards the degradation of non- biodegradable malachite green dye.

EXPERIMENTAL

Materials and methods

Titanium(IV)oxide (Merck), Nickel(II)hexahydrate and malachite green (HiMEDIA) were used.

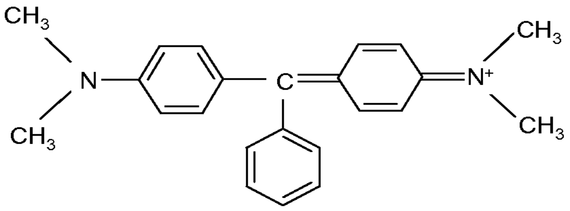

Fig. 1: Structure of malachite green

Preparation of Ni-doped TiO_2

10 g of commercially available TiO_2 was dissolved in 100 mL of double distilled water and 0.05 g of $NiCl_2$ was added to synthesize 0.5% Ni doped TiO_2. Then the mixture was stirred at room temperature for 4 hrs continuously. The powder was separated by decantation. The supernatant liquid was discarded. It was dried in oven at 100°C for 3 hrs and calcined for 4 hrs at 300°C. Then it was crushed manually in the form of very fine powder.

Similarly, 1.0, 1.5 and 2.0% Ni-TiO_2 were prepared only by changing the amount of $NiCl_2$ to 0.10 g, 0.15g, 0.20 g for obtaining samples of 1.0, 1.5 and 2.0% Ni-TiO_2, respectively.

Photocatalytic degradation

1.0×10^{-3} M stock solution of malachite green was prepared. The obsorbance of malachite green solution was determined at $\lambda_{max} = 616$ nm.

The dye solution was divided into parts in four beakers. The initial and final absorbance (A) was observed after 4 hrs solution of each beaker.

- Beaker 1 - Malachite green solution was kept in dark. Same initial and final absorbance was there even after 4 hrs.
- Beaker 2 - Malachite green solution was kept in light. Same initial and final absorbance was there even after 4 hrs.
- Beaker 3 - Malachite green solution + 0.10 g titanium dioxide was kept in dark. Same initial and final absorbance was there even after 4 hrs.
- Beaker 4 - Malachite green solution + 0.10 g titanium dioxide was kept in light. A significant decrease was there in the absorbance before and after exposure, which indicates degradation of dye.

Thus, it is revealed that this reaction requires the presence of both; the light and the semiconductor titanium dioxide. Hence, this reaction is photocatalytic in nature.

The photocatalytic efficiency of 0.5, 1.0, 1.5 and 2.0% Ni doped TiO_2 particles was investigated using degradation of malachite green solutions under visible light. The kinetic measurements were performed at room temperature (300 K). The concentration of dye in the form of absorbance before and after photocatalytic degradation was measured at 616 nm. A 200 W tungsten lamp was used as the visible light source. A cutoff filter was used to remove any thermal radiation just to ensure illumination by visible light only. The progress of the photocatalytic reaction was observed by taking absorbance at regular time intervals.

The change in absorbance at the λ_{max} value versus the irradiation time was measured. A typical run is presented in Table 1. It was observed that the absorbance of malachite green solution decreased in presence of the photocatalyst and light. The plot of 1 + log A versus time was linear and hence, this reaction followed pseudo-first order kinetics. The rate constant (k) for this reaction was determined from the expression $k = 2.303 \cdot \text{slope}$. A value of $k = 7.89 \times 10^{-4}\ s^{-1}$ was determined for this reaction in the optimum conditions

Table 1: A typical run

[Malachite green] = 5.6×10^{-5} M [1% Ni-TiO_2] = 0.10 g
Light intensity = 60.0 mW·cm^{-2} pH = 8.5

Time (min.)	Absorbance (A)	1 + log A
0.0	0.891	0.9500
5.0	0.708	0.8500
10.0	0.565	0.7520
15.0	0.447	0.6503
20.0	0.363	0.5599
25.0	0.272	0.4345
30.0	0.221	0.3443
35.0	0.174	0.2405
40.0	0.142	0.1522
45.0	0.023	-0.6382

Rate constant (k) = 7.89×10^{-4} sec^{-1}

RESULTS AND DISCUSSION

Kinetic studies

Effect of pH

The effect of pH on the rate of degradation of dye was investigated in the pH range (5.0-10.0). It has been observed that the rate of degradation increases with increase in pH upto certain pH, but a further increase in pH results in a decrease in the rate of reaction. The increase in the rate of photocatalytic degradation with increase in pH may be due to more generation of $^{\bullet}OH$ radicals, which are produced from the interaction of OH^- and hole (h^+) of the semiconductor. These $^{\bullet}OH$ radicals are responsible for the oxidative degradation of dye. After certain pH, the rate decreases because more OH^- ions are available and these will be adsorbed on the surface of the semiconductor making it negatively charged so that the approach of neutral form of malachite green towards semiconductor surface will be retarded. This will result into a decrease in the rate of degradation.

Table 2: Effect of pH of dye solution

pH	0.5% Ni-TiO_2	1.0% Ni-TiO_2	1.5% Ni-TiO_2	2.0% Ni-TiO_2
	Light intensity 60.0 mW cm^{-2}	**Light intensity 60.0 mW cm^{-2}**	**Light intensity 70.0 mW cm^{-2}**	**Light intensity 60.0 mW cm^{-2}**
	[Dye] = 3.8×10^{-5} M	**[Dye] = 5.6×10^{-5} M**	**[Dye] = 6.0×10^{-5} M**	**[Dye] = 5.5×10^{-5} M**
	$k \times 10^{-4}\ s^{-1}$	**$k \times 10^{-4}\ s^{-1}$**	**$k \times 10^{-4}\ s^{-1}$**	**$k \times 10^{-4}\ s^{-1}$**
5.0	0.57	0.63	0.38	0.64
6.0	0.68	0.71	0.58	0.93
6.5	0.93	0.84	1.22	1.20
7.0	1.24	2.98	1.37	1.90
7.5	2.94	4.64	1.60	2.92
8.0	3.15	6.78	1.99	3.82
8.5	4.05	**7.89**	2.77	3.99
9.0	4.60	7.37	4.32	**5.11**
9.5	**6.26**	6.23	**5.99**	4.08
10.0	3.98	5.88	3.66	3.93

Effect of concentration of malachite green

It has been observed that the rate of photocatalytic degradation increases with increase in concentration of dye upto a certain concentration. The rate of photocatalytic degradation was found to decrease with an increase in the concentration of dye further. This may be attributed to the fact that as the concentration of dye was increased, more dye molecules were available for excitation and hence, there was an increase in the rate. The rate of photocatalytic degradation was found to decrease with an increase in the concentration of dye further. Here, the dye starts acting as a filter for the incident light and it does not permit the desired light intensity to reach the semiconducting particles and thus, decreasing the rate of the photocatalytic degradation of dye.

Table 3: Effect of concentration of malachite green

[Dye] × 10^5 M	0.5% Ni-TiO_2	1.0% Ni-TiO_2	[Dye] × 10^5 M	1.5% Ni-TiO_2	2.0% Ni-TiO_2
	pH = 9.5	**pH = 8.5**		**pH = 9.5**	**pH = 9.0**
	Light intensity 60.0 mW cm^{-2}	**Light intensity 60.0 mW cm^{-2}**		**Light intensity 70.0 mW cm^{-2}**	**Light intensity 60.0 mW cm^{-2}**
	$k \times 10^{-4}\ s^{-1}$	**$k \times 10^{-4}\ s^{-1}$**		**$k \times 10^{-4}\ s^{-1}$**	**$k \times 10^{-4}\ s^{-1}$**
2.6	3.98	4.59	4.0	4.05	2.14
3.2	5.16	4.74	4.5	4.26	3.32
3.8	**6.26**	4.87	5.0	4.69	3.59

Cont…

[Dye] × 10^5 M	0.5% $Ni\text{-}TiO_2$	1.0% $Ni\text{-}TiO_2$	[Dye] × 10^5 M	1.5% $Ni\text{-}TiO_2$	2.0% $Ni\text{-}TiO_2$
	pH = 9.5	**pH = 8.5**		**pH = 9.5**	**pH = 9.0**
	Light intensity 60.0 mW cm^{-2}	**Light intensity 60.0 mW cm^{-2}**		**Light intensity 70.0 mW cm^{-2}**	**Light intensity 60.0 mW cm^{-2}**
	k × 10^{-4} s^{-1}	**k × 10^{-4} s^{-1}**		**k × 10^{-4} s^{-1}**	**k × 10^{-4} s^{-1}**
4.2	5.95	5.04	**5.5**	4.87	**5.11**
4.5	5.70	5.22	**6.0**	**5.99**	4.98
4.8	4.96	5.41	6.3	5.11	3.72
5.2	4.41	6.21	6.6	4.80	2.84
5.6	3.80	**7.89**	6.9	4.35	2.34
6.0	3.52	3.82	7.2	3.86	2.17

Effect of amount of catalyst

Here, the data indicate that as the amount of photocatalyst was increased, the rate of degradation also increased in all cases, but after a particular amount of photocatalyst, it shows saturation like behavior followed by some decrease in rate constant. It may be due to fact that the as the amount of semiconductor was increased, the exposed surface area of the semiconductor was also increased. After this, the rate of degradation decrease, as the catalyst amount was increased because it only increases the thickness of the layer of semiconductor, and not the exposed surface area.

Table 4: Effect of amount of catalyst

Catalyst loading (g)	0.5% $Ni\text{-}TiO_2$	1% $Ni\text{-}TiO_2$	1.5% $Ni\text{-}TiO_2$	2% $Ni\text{-}TiO_2$
	pH = 9.5	**pH = 8.5**	**pH = 9.5**	**pH = 9.0**
	[Dye] = 3.8 × 10^5 M	**[Dye] = 5.6 × 10^5 M**	**[Dye] = 6.0 × 10^5 M**	**[Dye] = 5.5 × 10^5 M**
	Light intensity 60.0 mW cm^{-2}	**Light intensity 60.0 mW cm^{-2}**	**Light intensity 70.0 mW cm^{-2}**	**Light intensity 60.0 mW cm^{-2}**
	k × 10^{-4} s^{-1}	**k × 10^{-4} s^{-1}**	**k × 10^{-4} s^{-1}**	**k × 10^{-4} s^{-1}**
0.02	2.93	2.03	5.04	4.38
0.04	3.16	2.98	5.12	4.26
0.06	5.27	4.28	5.75	4.64
0.08	5.90	6.40	**5.99**	**5.11**
0.10	**6.26**	**7.89**	5.62	5.07
0.11	4.58	6.98	4.04	4.23
0.12	4.58	5.98	3.98	4.12
0.13	4.53	3.19	4.13	4.29
0.14	4.56	2.96	3.49	4.23

Effect of light intensity

An almost linear relationship between light intensity and the rate of reaction was observed. It was observed that degradation of dye was enhanced on increasing the intensity of light. This may be due to an increase in the number of photon striking per unit area of titanium dioxide powder on increasing the intensity of light. However, higher intensities were avoided due to thermal effects.

Table 5: Effect of light intensity

Light intensity ($mWcm^{-2}$)	**0.5% Ni-TiO_2**	**1.0% Ni-TiO_2**	**1.5% Ni-TiO_2**	**2.0% Ni-TiO_2**
	pH = 9.5	**pH = 8.5**	**pH = 9.5**	**pH = 9.0**
	[Dye] = 3.8×10^5 M	**[Dye] = 5.6×10^5 M**	**[Dye] = 6.0×10^5 M**	**[Dye] = 5.5×10^5 M**
	$k \times 10^{-4}\ s^{-1}$	**$k \times 10^{-4}\ s^{-1}$**	**$k \times 10^{-4}\ s^{-1}$**	**$k \times 10^{-4}\ s^{-1}$**
20.0	2.76	2.75	2.88	2.60
30.0	3.95	3.12	3.43	3.47
40.0	5.26	4.42	3.69	3.68
50.0	5.85	5.59	4.26	4.53
60.0	**6.26**	**7.89**	5.20	**5.11**
70.0	5.42	6.27	**5.99**	5.09

Activity of undoped TiO_2

Table 6: Typical run for degradation of dye by undoped TiO_2

[Malachite green] = 5.6×10^{-5} M TiO_2 = 0.10 g
Light intensity = 60.0 $mWcm^{-2}$ pH = 8.5

Time (min.)	**Absorbance (A)**	**1 + log A**
0.0	0.495	0.6950
10.0	0.426	0.6294
20.0	0.354	0.5490
30.0	0.295	0.4698
40.0	0.251	0.3996
50.0	0.213	0.3283
60.0	0.177	0.2479
70.0	0.147	0.1673
80.0	0.125	0.0969

Rate constant (k) = $2.85 \times 10^{-4}\ s^{-1}$

Effect of change of anion

Table 7: Typical run

[Malachite green] = 4.20×10^{-5}M 1% Ni-TiO_2 = 0.06 g
pH = 8.5 Light intensity = 60.0 mWcm^{-2}

Time (min.)	Absorbance (A)	1 + log A
0.0	0.582	0.7650
5.0	0.446	0.6493
10.0	0.346	0.5390
15.0	0.263	0.4199
20.0	0.199	0.2988
25.0	0.147	0.1673
30.0	0.112	0.0492

Rate constant (k) = 9.09×10^{-4} sec^{-1}

Effect of pH

Table 8: Effect of pH

[Malachite green] = 4.2×10^{-5} M
1.0% Ni-TiO_2 = 0.06 g
Light intensity = 60.0 mW cm^{-2}

pH	Rate constant (k) × 10^4 (s^{-1})
6.0	0.71
6.5	1.53
7.0	2.20
7.5	3.98
8.0	7.90
8.5	**9.57**
9.0	9.57
10.0	6.40

Effect of malachite green concentration

Table 9: Effect of malachite green concentration

pH = 8.5
Light intensity = 60.0 mW cm^{-2}
1.0% Ni-TiO_2 = 0.06 g

[Malachite green] × 10^5 M	Rate constant(k) × 10^4 (s^{-1})
3.20	4.08

Cont…

[Malachite green] × 10^5 M	**Rate constant(k) × 10^4 (s^{-1})**
3.80	6.20
4.20	**9.57**
4.50	9.50
4.80	8.52
5.20	8.05
5.60	7.02

Effect of dose of photocatalyst

Table 10: Effect of amount of photocatalyst

[Malachite green] = 4.20 × 10^{-5} M
Light intensity = 60.0 mW cm^{-2}
pH = 8.5

1.0% Ni-TiO_2 (g)	**Rate constant (k) × 10^4 (s^{-1})**
0.02	6.16
0.04	7.86
0.06	**9.57**
0.08	7.57
0.10	7.47
0.12	7.26
0.14	7.22

Effect of light intensity

Table 11: Effect of light intensity

[Malachite green] = 4.2 × 10^{-5} M
1.0% Ni-TiO_2 = 0.06 g
pH = 8.5

Light intensity ($mWcm^{-2}$)	**Rate constant (k) × 10^4 (s^{-1})**
20.0	4.83
30.0	5.73
40.0	6.28
50.0	6.47
60.0	**9.57**
70.0	7.76

Mechanism

On the basis of our experimental observations, a tentative mechanism for photocatalytic degradation (mineralization) of malachite green may be proposed as:

$$^{1}MG_{0} \xrightarrow{h\nu} {}^{1}MG_{1} \quad \ldots(1)$$

$$^{1}MG_{1} \xrightarrow{ISC} {}^{3}MG_{1} \quad \ldots(2)$$

$$PC \xrightarrow{h\nu} PC\,[h^{+}\,(VB) + e^{-}\,(CB)] \quad \ldots(3)$$

$$h^{+} + OH^{-} \longrightarrow {}^{\bullet}OH \quad \ldots(4)$$

$$^{3}MG_{1} + {}^{\bullet}OH \longrightarrow \text{Leuco MG} \quad \ldots(5)$$

$$\text{Leuco MG} \longrightarrow \text{Product} \quad \ldots(6)$$

Malachite green (MG) molecules absorb radiations of suitable wavelength and give rise to the singlet excited state. Then it undergoes an intersystem crossing (ISC) process to yield the more stable triplet excited state of the dye. Photocatalyst (PC) also utilizes the radiant energy to excite its electron from the valence band (VB) to the conduction band (CB); thus, leaving behind a hole (h^+) in the VB. This hole may abstract an electron from hydroxyl ions to generate hydroxyl radicals. These hydroxyl radicals will then oxidize the dye to its leuco form, which may ultimately degrade to less toxic products. The participation of $^{\bullet}OH$ radicals as an active oxidizing species was confirmed by using hydroxyl radical scavengers (isopropanol), where the rate of degradation was drastically reduced.

- Doping with nickel enhanced the photocatalytic activity of TiO_2 significantly.
- Dopant concentration affects the efficiency of a photocatalyst.
- Among all the four different semiconductors (0.5, 1.0, 1.5, 2.0%) 1.0% Ni-TiO_2 gives most efficient photocatalytic degradation of malachite green.
- Rate constant increased from 2.85×10^{-4} sec^{-1} to 7.89×10^{-4} sec^{-1} (i.e. by 2.76 times or 176%) after doping with 1.0% Ni (by weight) in TiO_2 under same experimental conditions.
- Changing anion in nickel source also affect the efficiency of Ni-doped TiO_2.

REFERENCES

1. A. Syoufian and K. Nakashima, Degradation of Methylene Blue in Aqueous Dispersion of Hollow Titania Photocatalyst: Study of Reaction Enhancement by Various Electron Scavengers, J. Coll. Inter. Sci., **317**, 507-512 (2008).
2. L. Ge, M. Xu and H. Fang, Synthesis of Titanium Oxide Layers on Glass Substrates with Aqueous Refluxed Sols (RS) and Photocatalytic Activities, J. Mater. Sci., **42**, 4926-4934 (2007).
3. E. Forgacs, T. Cserhati and G. Oros, Removal of Synthetic Dyes from Wastewaters: A Review, Environ. Int., **30**, 953-971 (2004).
4. J. Madhavan, P. Maruthamuthu, S. Murugesan and S. Anandan, Kinetic Studies on Visible Light-Assisted Degradation of Acid Red 88 in Presence of Metal-Ion Coupled Oxone Reagent, Appl. Catal. B: Environ., **83**, 8-14 (2008).

5. P. Brijesh, S. Dawid, M. Prakash, Q. Themina and T. R. Thapak, Mineralization of Methyene Violet Dye using Titanium Dioxide in Presence of Visible Light, Int. J. Chem. Sci., **9(4)**, 1685-1697 (2011).
6. J. Sun, X. Wang, J. Sun, R. Sun, S. Sun and L. Qiao, Photocatalytic Degradation and Kinetics of Orange G using Nano-Sized Sn(IV)/TiO2/AC Photocatalyst, J. Mol. Catal. A: Chem., **260**, 241-246 (2006).
7. L.-C. Chen, C.-M. Huang and F.-R. Tsai, Characterization and Photocatalytic Activity of K^+-Doped TiO_2 Photo Catalysts, J. Mol. Catal. A: Chem., **265**, 133-140 (2007).
8. Y. Zhiyong, H. Keppner, D. Laub, E. Mielczarski, J. Mielczarski, L. Kiwi-Minsker, A. Renken and J. Kiwi, Photocatalytic Discoloration of Methyl Orange on Innovative Parylene–TiO_2 Flexible Thin Films Under Simulated Sunlight, Appl. Catal. B: Environ., **79**, 63-71 (2008).
9. L. P. Gianluca, A. Bono, D. Krishnaiah and J. G. Collin, Preparation of Titanium Dioxide Photocatalyst Loaded Onto Activated Carbon Support using Chemical Vapor Decomposition: A Review Paper, J. Hazard. Mater., **157(2-3)**, 209-219 (2008).
10. A. I. Kokorin and D. W. Bahnemann, Chemical Physics of Nanostructured Semiconductors, VSP: Boston, MA, USA (2003).
11. H. T. Chang, N. M. Wu and F. Zhu, A Kinetic Model for Photocatalytic Degradation of Organic Contaminants in a Thin-Film TiO_2 Catalyst, Water Res., **34**, 407-416 (2000).
12. X. Chen and S. S. Mao, Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications and Applications. Chem. Rev., **107**, 2891-2959 (2007).
13. H. Nakano, H. Hasuike, K. Kisoda, K. Nishio, T. Isshiki and H. Harima, Synthesis of TiO_2 Nanocrystals Controlled by Means of the Size of Magnetic Elements and the Level of Doping with them, J. Phys.: Condens. Matter., **21**, 064214 (2009).
14. D. C. Hurum, A. G. Agrios, K. A. Gray, T. Rajh and M. C. Thurnauer, Explaining the Enhanced Photocatalytic Activity of Degussa P25 Mixed-Phase TiO_2 Using EPR, J. Phys. Chem. B, **107**, 4545-4549 (2003).