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USE OF UNDOPED AND IRON DOPED ZIRCONIUM DIOXIDE IN PHOTOCATALYTIC DEGRADATION OF MALACHITE GREEN

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ABSTRACT

The present study involves 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.

Key words: Photocatalytic degradation, Malachite green, Undoped and iron doped zirconium dioxide.

INTRODUCTION

Dye pollutants from textile, printing, production etc. industries play a vital role to damage the environment. These effluents enter in water ecosystem and create various environmental and health hazards. Several methods like adsorption, osmosis, flocculation and others have been used for dye removal from water, but each one has its own advantages and limitations. Photocatalytic treatment provides a promising, eco friendly and relatively low cost method to solve this problem.

In last few decades TiO_2 has been most commonly used for degradation of various organic pollutants[1-3]. Photoelectrochemical behavior of SnO_2/TiO_2 composite systems and its role in photocatalytic degradation of a textile azo dye was studied by K. Vinodgopal et al.[4] Lin et al.[5] investigated photocatalytic activities of $InVO_4$ and $NiO/InVO_4$ for water splitting under visible light irradiation. Semiconductor iron (III) oxide was used in photocatalytic bleaching of some dyes by Ameta et al.[6] Hwang et al.[7] fabricated novel SnO_2/TiO_2 nanofibers by a simple electrospinning method. The SnO_2 nanoparticles embedded TiO_2 nanofibers had enhanced contact interface between TiO_2 and SnO_2. The SnO_2/TiO_2 nanofibers with SnO_2 contents of 10 wt.% showed the highest photocatalytic activity for rhodamine B decomposition.

Stodolny and Laniecki[8] prepared two series of Ta_2O_5–TiO_2 photocatalysts (Ta:Ti = 4:1, 1:1 and 1:4) by sol-gel technique applying triblock copolymer of Pluronic P123 and were tested in platinized form (0.3 wt.%) in photodecomposition of water under ultraviolet and visible light ($\lambda > 300$ nm). The mixed oxides of Ta_2O_5–TiO_2 system showed much lower band-gap than pure Ta_2O_5 and relatively high activity in

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platinized state in photocatalytic hydrogen generation under visible. Jing and Guo[9] synthesized Fe-doped mesoporous (Fe-m-Ta_2O_5) and non-porous bulk Ta_2O_5 (Fe-s-Ta_2O_5) with sol–gel and solid reaction methods. They investigated the photocatalytic hydrogen production over two kinds of photocatalysts from an aqueous methanol solution. The effects of Fe doping on the photocatalytic properties of the materials depended heavily on the morphology and crystallinity of the photocatalyst.

A new composite photocatalyst (Fe_2O_3 and ZrO_2/Al_2O_3) combining the properties of both semiconductor and Fenton like catalyst was prepared by Liu et al.[10] The catalyst shows high catalytic activity in phenol photodegradation reaction with the phenol conversion efficiency higher than 93% at experimental conditions (catalyst dose, 1.0 g L^{-1}; H_2O_2 dose, 50 mM; solution pH, 6.0). After two runs of regeneration, the activity of the catalyst shows only a slight decrease. Farhadi and Zaidi[11] reported a polyoxometalate-zirconia (POM/ZrO_2) nanocomposite, prepared through entrapment of $H_3PW_{12}O_{40}$ polyoxometalate into zirconia matrix by sol–gel technique involving the hydrolysis of zirconium (IV) *n*-butoxide, Zr(*n*-OBu)$_4$, as the ZrO_2 source. Photoexcited POM/ZrO_2 nanocomposite oxidized various primary and secondary benzylic alcohols into the corresponding aldehydes and ketones in high yields under O_2 atmosphere. The photocatalyst has been reused several times, without observable loss of activity and selectivity. Alvarez et al.[12] studied different zirconium oxide materials doped with transition metals (Mn, Fe, Co, Ni and Cu). The photodegradation of 2,4-dichlorophenoxyacetic acid (2,4-D), a herbicide used in agricultural applications, was used as a test reaction to study the activity of the compounds synthesized.

EXPERIMENTAL

A stock solution of malachite green of concentration 1.00×10^{-3} M was prepared in doubly distilled water. This stock solution was further diluted as and when required. The optical density of malachite green solution was determined with the help of spectrophotometer at $\lambda_{max} = 616$ nm. The dye solution was divided into four parts and control experiments were performed.

- The first beaker containing malachite green solution was kept in the dark.
- The second beaker containing malachite green was exposed to the light of a 200 W tungsten lamp.
- The third beaker containing malachite green solution and 0.10 g zirconium dioxide was kept in dark.
- The fourth beaker containing malachite green solution and 0.10 g zirconium dioxide was exposed to the light of a 200 W tungsten lamp.

After keeping these beakers for three hours, the optical density of the solution in each beaker was measured with the help of a spectrophotometer. It was found that the solutions of the first three beakers had almost the same optical density in compare to their initial value while the solution of the fourth beaker had a decrease in it. From this observation, it becomes clear that this reaction required the presence of both light and the semiconductor zirconium dioxide. Hence, this reaction is photocatalytic in nature.

1.40×10^{-5} M solution of malachite green was prepared in doubly distilled water and 0.10 g of zirconium dioxide was added to it. The pH of the reaction mixture was kept to 8.0 and this solution was exposed to a 200 W tungsten lamp. A decrease in optical density of malachite green solution was observed with increasing time of exposure.

The typical run for the photocatalytic degradation of malachite green in the presence of ZrO_2 photocatalyst has been presented in Table 1 and graphically represented in Fig. 1.

Table 1: Typical run

[Malachite green] = 1.40×10^{-5} M ZrO$_2$ = 0.10 g

Light intensity = 50.0 mW cm^{-2} pH = 8.0

Time (min.)	Optical density (O.D.)	2 + log O.D.
0.0	0.331	1.5198
10.0	0.240	1.3802
20.0	0.181	1.2577
30.0	0.140	1.1461
40.0	0.104	1.017
50.0	0.080	0.9031
60.0	0.061	0.7853
70.0	0.045	0.6532
		k = 4.65×10^{-4} (s^{-1})

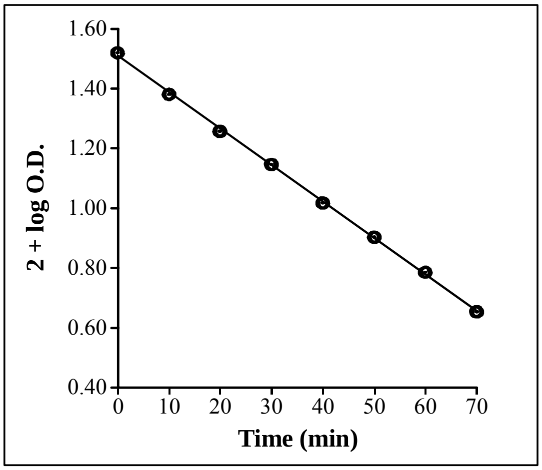

Fig. 1: Typical run

The plot of 1 + log O.D. v/s time was linear and hence, it may be concluded that this reaction follows pseudo-first order kinetics. The rate of this reaction was determined by the expression:

$$k = 2.303 \times \text{slope} \qquad ...(1)$$

Effect of pH

The effect of pH on the rate of degradation of dye solution was investigated in the pH range (6.0-9.0) (Table 2). The results are graphically presented in Fig. 2. It has been observed that the rate of degradation was increase with increase in pH upto 6.0 to 8.0, further increase in pH result 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 pH 8.0 the rate decreases because more OH$^-$ ions are available and these will be absorbed 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

[Malachite Green] = 1.40×10^{-5} M ZrO$_2$ = 0.10 g
Light intensity = 50.0 mW cm^{-2}

pH	k × 10^4 (s^{-1})
6.0	0.55
6.5	0.89
7.0	2.0
7.5	3.82
8.0	**4.65**
8.5	4.37
9.0	3.42

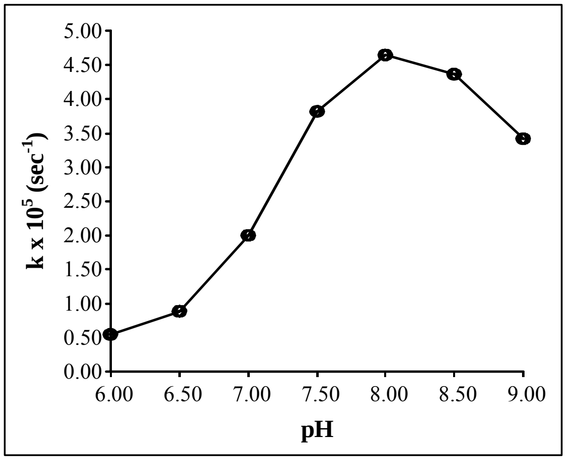

Fig. 2: Effect of pH

Effect of malachite green concentration

The effect of malachite green dye concentration on the rate of its degradation was also investigated. The results are reported in Table 3 and graphically represented in Fig. 3.

Table 3: Effect of malachite green concentration

pH = 8.0 Light intensity = 50.0 mW cm^{-2}
ZrO$_2$ = 0.10 g

[Malachite green] × 10^5 M	k × 10^4 (s^{-1})
0.60	2.61
0.80	3.19
1.00	3.71
1.20	4.36
1.40	**4.65**
1.60	4.61
1.80	4.47

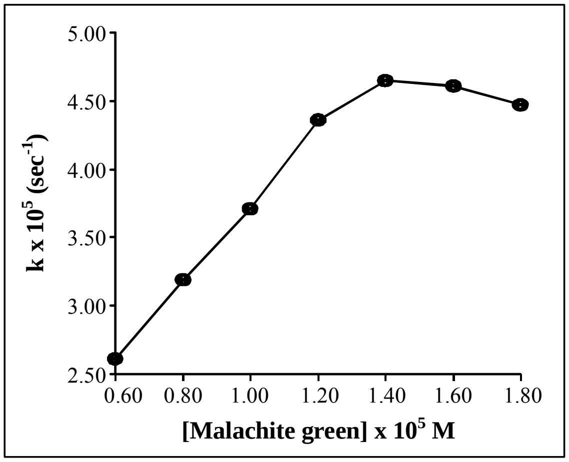

Fig. 3: Effect of dye concentration

It has been observed that the rate of photocatalytic degradation increases with increase in concentration of dye upto 1.40 × 10^{-5} M. 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 followed by inter system crossing 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.

Effect of amount of photocatalyst

The rate of degradation of dye was also affected by the amount of semiconductor and therefore different amounts of semiconductor were used. The result are tabulated in Table 4 and graphically represented in Fig. 4.

Table 4: Effect of amount of photocatalyst

[Malachite Green] = 1.40 × 10^{-5} M Light intensity = 50.0 mW cm^{-2}

pH = 8.0

ZrO_2 (g)	k × 10^4 (s^{-1})
0.04	4.46
0.06	4.54
0.08	4.60
0.10	**4.65**
0.12	4.60
0.14	4.55
0.16	4.53

Here the data indicate that as the amount of photocatalyst was increased, the rate of degradation also increased but after the amount 0.10 g of photocatalyst, it shows saturation like behavior. 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.

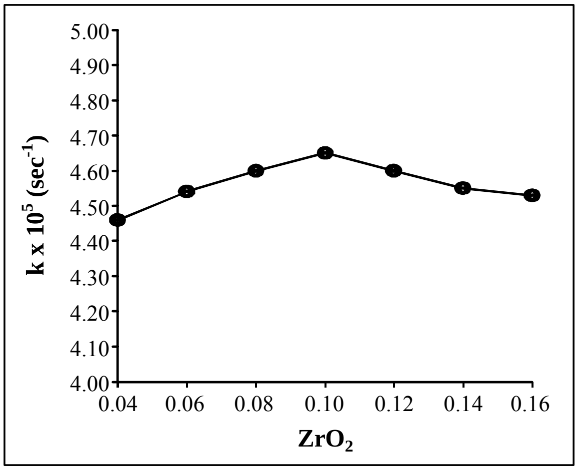

Fig. 4: Effect of amount of photocatalyst

Effect of light intensity

The effect of light intensity on the photocatalytic degradation of the dye was investigated. It was observed that degradation of dye was enhanced on increasing the intensity of light. The results are reported in Table 5 and graphically presented in Fig. 5.

Table 5: Effect of light intensity

[Malachite Green] = 1.40×10^{-5} M $ZrO_2 = 0.10$ g
pH = 8.0

Light intensity (mW cm^{-2})	k × 10^4 (s^{-1})
10.0	2.78
20.0	3.12
30.0	3.72
40.0	4.03
50.0	**4.65**
60.0	5.29

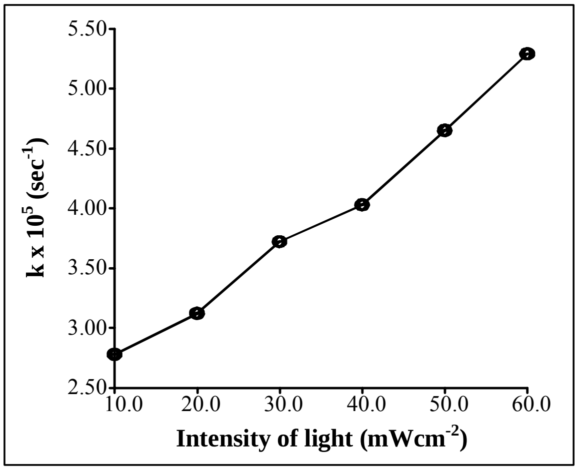

Fig. 5: Effect of light intensity

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 zirconium dioxide powder on increasing the intensity of light. However, higher intensities were avoided due to thermal effects.

Effect of doping

The typical run for the photocatalytic degradation of malachite green in the presence of iron doped ZrO_2 photocatalyst has also been studied and the results are presented in Table 6 and graphically represented in Fig. 6.

Table 6: A typical run

[Malachite green] = 1.40×10^{-5} M
Fe doped ZrO_2 = 0.10 g
Light intensity = 50.0 mW cm^{-2}
pH = 8.0

Time (min.)	Optical density (O.D.)	2 + log O.D.
0.0	0.891	1.9494
10.0	0.585	1.7672
20.0	0.439	1.6425
30.0	0.321	1.5065
40.0	0.213	1.3284
50.0	0.148	1.1703
60.0	0.102	1.0086
70.0	0.064	0.8062
		k = 6.12×10^{-4} (s^{-1})

The rate of degradation of malachite green was found 4.65×10^{-4} sec^{-1} and 6.12×10^{-4} sec^{-1} for undoped and iron doped zirconium dioxide, respectively. It gives about 31.61% rise in the rate, which means that iron doping enhances the photocatalytic activity of zirconium dioxide.

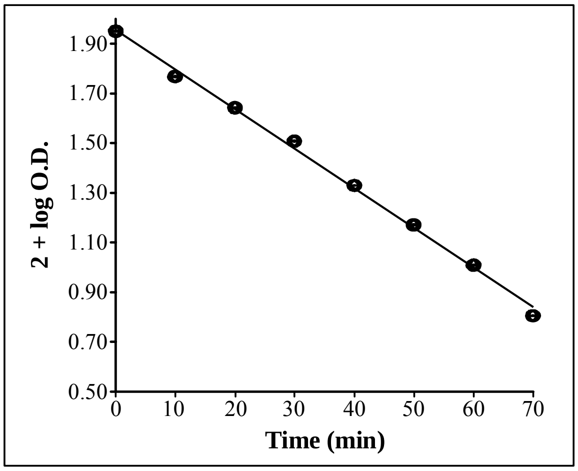

Fig. 6: A typical run

Mechanism

On the basis of the experimental observation a tentative mechanism of photocatalytic degradation of malachite green may be proposed as-

Malachite green (MG) absorbs radiation of suitable wavelength and it is excited to its first singlet state followed by intersystem crossing (ISC) to triplet state. On the other hand, the semiconducting zirconium dioxide also utilized the incident light energy to excite its electron from valence band to conducting band; thus, leaving behind a hole. 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 products.

$$^{1}MG_{0} \xrightarrow{h\nu} {}^{1}MG_{1} \quad \ldots (2)$$

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

$$SC \xrightarrow{h\nu} e^{-}(CB) + h^{+}(VB) \text{ or } SC^{*} \quad \ldots (4)$$

$$h^{+} + OH^{-} \longrightarrow {}^{\bullet}OH \quad \ldots (5)$$

$$^{3}MG_{1} + {}^{\bullet}OH \longrightarrow \text{Leuco MG} \longrightarrow \text{Product} \quad \ldots (6)$$

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.

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