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AUTHORS: Japinder Kaur, S. Bansal and Sonal Singhal

CORRESPONDING AUTHOR: Sol

Sonal Singhal

Assistant Professor, Department of Chemistry, Panjab University, Chandigarh, India - 160 014 Ph. No. +91-172-2534421(o) +91-09872118810(m) Fax No. +91-172-2545074 **E-mail:** sonal1174@gmail.com

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Photocatalytic degradation of Methyl Orange using ZnO nanopowders synthesized via thermal decomposition of oxalate precursor method

Japinder Kaur¹, S. Bansal² and Sonal Singhal¹*

¹Department of Chemistry, Panjab University, Chandigarh-160 014

²Dept. Sci. Tech., New Delhi

*sonal1174@gmail.com

Abstract

ZnO nanoparticles were synthesized by thermal decomposition of oxalate precursor method. The nanopowders were characterized using Powder X-Ray Diffraction Technique and Scanning Electron Microscopy and sample was found to have hexagonal wurtzite structure of ZnO. Average crystallite size of ZnO was found to be ~ 27 nm. The photocatalytic activity of ZnO was evaluated by using Methyl Orange (MO) as probe molecule. It was inferred from control experiments that presence of both ZnO and UV light is necessary for photodegradation. From photocatalytic experiment it was observed that MO is completely degraded in 80 min when the amount of catalyst is 1g/L and initial concentration of MO is 0.03 mM. The effect of dye concentration, catalyst loading and solution pH on photodegradation rate was also investigated. It was found that optimal conditions for photodegradation of MO are 1g/L catalyst at a solution pH 9. Photodegradation of MO was found to follow pseudo-first order kinetics. Langmuir-Hinshelwood Model was also used to describe the photodegradation process.

Key Words: Photocatalytic degradation, Zinc oxide, Methyl Orange, Oxalate Precursor method

1. Introduction

Methyl Orange (MO) is an important example of azo dye and is widely used as a coloring agent in textile, food, leather and pharmaceutical industries. MO can also be used as coloring agent for the detection of hydrogen gas and for the determination of Itopride hydrochloride [1, 2]. But discharge of MO from dye industries into water bodies is causing many health hazards. MO is toxic, mutagenic and carcinogenic [3-5]. MO is not readily biodegradable and thus special methods are required for its degradation. Some of the methods are Physical Methods (coagulation, reverse osmosis, membrane filtration), chemical methods (reduction, oxidation, ion exchange, complexometric methods) and biological methods (aerobic, anaerobic) [6]. Recently, Advanced Oxidation Processes (AOP) is gaining attention for the removal of organic pollutants from water [7-10]. These processes involve the treatment of wastewater through the generation of hydroxyl radicals [11]. These radicals are strong oxidizing agents and thus oxidize pollutant to CO₂ and H₂O. This is an extremely fast process and no solid waste is generated. Generally, these are carried out in the presence of ozone (O₃), hydrogen peroxide (H₂O₂) and/or UV light. In these, semiconductor metal oxides, such as ZnO act as catalyst for the degradation of pollutant.

ZnO is an n-type semiconductor with a wide band gap of 3.37 eV and a large exciton binding energy of 60 meV [12]. Due to these properties, it has found applications in many fields, such as in solar cells, gas sensors, photoelectrochemical cells, antibacterial activity and photocatalysis [13-18]. ZnO can be synthesized with wide range of morphologies like nanorods, nanobelts, nanowires, nanotubes, and whiskers using different methods such as ball-milling, solgel process, hydrothermal, spray pyrolysis, chemical vapor deposition, etc [19-24].

A large number of reports are there on the photocatalytic degradation of Methyl Orange using ZnO as a catalyst in the presence of UV light [25-33]. Zhu et al. [29] synthesized ZnO rod-

assembled microspheres using microwave-assisted hydrothermal method and observed that complete degradation of MO takes place in 9 h. ZnO powders with various size scale were synthesized by Wang et al. [30] via thermal evaporation method and chemical deposition method. It was observed that 50 nm ZnO powder degraded 80% MO in 2 h. Hong et al. [31] prepared Fe_3O_4/ZnO core/shell magnetic nanoparticles by co-precipitation method and noticed 83% degradation of MO after 6 h. Cu-doped ZnO nanoparticles were prepared by Fu et al. [32] and 88% degradation of Methyl Orange was observed in 4h. ZnO nanorods on indium-tin oxide substrate were synthesized by Zheng et al. [33] via thermal evaporation method and 71% degradation of MO was observed after 2.5 h.

Although ZnO nanoparticles have been investigated for photodegradation of MO, but the time period required for the degradation of MO is very high. The present work is an attempt to reduce the time required for the degradation of MO. This work deals with the synthesis of ZnO nanopowders by thermal decomposition of oxalate precursor, which is an economical, facile and low temperature solution route. Then photocatalytic activity of synthesized ZnO is evaluated by studying the photodegradation of MO. Also a systematic investigation has been carried out to find the optimum conditions for MO degradation by varying the dye concentration, catalyst loading and solution pH.

2. Experimental

2.1 Synthesis

Nanocrystalline powders of ZnO were synthesized by thermal decomposition of oxalate precursor. This method is an economical and eco-friendly method without the involvement of solvents. Oxalate precursor was prepared by mixing aqueous solutions of zinc chloride and oxalic acid. The mixture was then stirred for 2 h. This resulted in the formation of zinc oxalate

precipitates which were filtered and washed thoroughly with distilled water and then dried. The zinc oxalate was used as precursor for the synthesis of ZnO. Fig. 1 shows the flow chart depicting the synthesis of ZnO nanopowders.

2.2 Physical Characterization

To determine the temperature at which zinc oxalate decomposes to zinc oxide, the oxalate precursor was subjected to Thermogravimetric Analysis upto 1000 °C at the heating rate of 10 °C/min using TA, SDT Q600. X-Ray Diffraction (XRD) patterns were recorded using PANalytical's X'Pert PRO spectrophotometer equipped with Cu-K α radiation (λ = 1.5404 Å) in 20 range from 10° to 100°. The crystallite size was calculated by employing Debye-Scherrer equation. The Scanning electron micrographs were taken on JEOL, JSM-6610LV. The UV-Vis spectra were recorded on JASCO, V-530 spectrophotometer.

2.3 Photocatalytic Measurements

The photocatalytic activity of zinc oxide powder was evaluated by measuring photocatalytic degradation of MO in water under the illumination of UV light. The molecular structure of MO is shown in Fig. 2. The experiment was carried out by dispersing 100 mg of photocatalyst in 100 mL MO aqueous solution having concentration of 0.03 mM, after which, it was magnetically stirred in dark for 30 min to ensure the establishment of adsorption/desorption equilibrium between MO molecules and the surface of the photocatalyst. Subsequently, the suspension was irradiated with UV light. 4 mL samples were withdrawn from the above suspension at different time intervals and it was filtered through a syringe filter to completely remove the catalyst particles. The obtained samples were then analyzed using UV-Vis spectroscopy by recording variations in absorbance at wavelength of 463 nm. The percentage of degradation was calculated using the following equation (eq. 1) [34]:

$$Degradation(\%) = \frac{C_o - C_t}{C_o} \times 100$$
⁽¹⁾

where C_0 is the initial dye concentration and C_t is the dye concentration at certain reaction time t (min). Unless otherwise specified, all the experiments were carried out at natural pH of MO (8.06). Effect of variation of initial dye concentration (0.01-0.09 mM), catalyst loading (0.25-2.00 g/L) and pH of the solution (pH 5-11) on rate of photocatalytic degradation was also studied. The pH of solution was adjusted to desired level by adding NaOH and HNO₃ before the addition of photocatalyst. For comparison, blank experiment was carried out in the absence of UV light and in presence of the photocatalyst. Another experiment was performed in the presence of UV light and in the absence of photocatalyst.

3. Results and Discussion

3.1 Thermogravimetric Studies

The TGA curve for the precursor is presented in Fig. 3 and it exhibits two discernible stages of weight loss. The first weight loss of 20% between 90 and 100 °C corresponds to the elimination of two molecules of water from zinc oxalate dihydrate (theoretical value of 19%) to form anhydrous zinc oxalate. The second weight loss of 40% between 370 and 400 °C is due to decomposition of anhydrous zinc oxalate to zinc oxide with the elimination of CO₂ and CO (theoretical value of 38%) followed by formation of clear plateau between 400 and 1000 °C. Since there was no appreciable weight loss above 400 °C, the oxalate precursor was annealed at 450 °C to obtain ZnO powders. The decomposition of zinc oxalate dihydrate can be expressed as the following reaction:

$$ZnC_2O_4.2H_2O \rightarrow ZnC_2O_4 + 2H_2O$$
⁽²⁾

$$ZnC_2O_4 \rightarrow ZnO + CO + CO_2 \tag{3}$$

3.2 Powder X-Ray Diffraction Studies

Fig. 4 shows XRD pattern of annealed sample. All the diffraction peaks can be indexed to the hexagonal wurtzite structure of zinc oxide with lattice constants a = 3.2459 Å and c = 5.215 Å. The sharp and intense peaks indicate that sample is highly crystalline. The average crystallite size was found to be ~ 27 nm by applying Debye Scherrer equation (eq. 4) [35]:

$$d = \frac{0.9\lambda}{\beta\cos\theta} \tag{4}$$

where d is the average crystallite size, $\lambda = 1.541$ Å (wavelength of radiation used), θ is the Bragg angle and β is the angular width of the diffraction peak at the half maximum (FWHM) on the 2 θ scale.

3.3 Scanning Electron Microscopy

The surface morphology of synthesized ZnO powders was investigated using SEM (Fig. 5). It can be seen that ZnO powder is nanocrystalline and exist in the form of bundles. The bundles are composed of aggregates of nanoparticles. This aggregation of nanoparticles is due to large surface area to volume ratio and high surface energy.

3.4 Photocatalytic Activity

3.4.1 UV-Vis spectra study

The photocatalytic activity of ZnO powder was examined by degradation of MO. Fig. 6 shows the UV-Vis spectra of aq. solution of MO (0.03 mM) in presence of ZnO (1 g/L) at different irradiation times (inset shows the photograph of MO solution). It can be seen from the graph that the maximum absorbance at 463 nm decreased gradually and finally disappeared after 80 min indicating the complete degradation of dye. However when the same experiment was

carried out in the absence of ZnO nanoparticles, only 9% degradation was observed even after irradiation for 5 hr. In the presence of ZnO, but in the absence of UV light, 21% degradation was observed after 5 hr, which could be due to the adsorption of dye on the surface of ZnO. This observation indicated that presence of both catalyst and UV light are required for an effective degradation of dye.

3.4.2 Mechanism

When ZnO is irradiated by light with energy greater than or equal to its band gap, an electron in the valence band can be excited to the conduction band, with the simultaneous generation of hole in the valence band (eq. 5). These photogenerated electron-hole pair can either recombine (eq. 6) or interact separately with other molecules. The holes in the valence band can react with water on the surface of ZnO or hydroxide ions to form highly reactive hydroxyl radicals ('OH) (eq. 7 and 8) while electrons are accepted by adsorbed oxygen to form superoxide radical anion (O_2^{--}) (eq. 9). This radical may form organic peroxides or H_2O_2 in the presence of organic scavenger (eq. 10 and 11). The hydroxyl radical is a powerful oxidizing agent and attacks the dye molecule to give the oxidized product (eq. 12). The reactions are summarized as below [36]:

$$ZnO + hv \rightarrow h^{+} + e^{-}$$
(5)

$$h^+ + e^- \rightarrow heat$$
 (6)

$$H_2O + h^+ \rightarrow H^+ + OH$$
(7)

$$h^+ + OH^- \rightarrow OH$$
 (8)

$$e^{-} + O_2 \rightarrow O_2^{-}$$
⁽⁹⁾

$$O_2^{\cdot-} + HO_2^{\cdot} + H^+ \rightarrow H_2O_2 + O_2$$

$$\tag{10}$$

$$O_2^{\cdot-} + \text{ organic species } \rightarrow \text{ organic species } OO^{\cdot}$$
 (11)

 $OH + \text{organic species} \rightarrow \text{oxidized product}$ (12)

3.4.3 Effect of initial dye concentration

The effect of initial MO concentration on the photocatalytic degradation was studied by varying the concentration of MO from 0.01 to 0.09 mM, at a constant catalyst loading of 1 g/L for 45 min. It was found that degradation percentage is strongly influenced by the initial dye concentration and decreased from 98.1% to 50% with increase in concentration of dye from 0.01 to 0.09 mM (Fig. 7). The rate of degradation is related to the available catalyst surface for the generation of electron-hole pair, which in turn generates hydroxyl radicals. In this case, the amount of catalyst is kept constant and thus number of hydroxyl radicals generated remains same, while dye concentration is increased. Thus the number of hydroxyl radical which attack dye molecule decreases and thus rate of degradation decreases.

The kinetics of photocatalytic degradation of MO can be depicted by first-order equation (eq. 13) [37]:

$$In\left(\frac{C_o}{C_t}\right) = K_{app} t$$
(13)

where K_{app} is the pseudo-first order rate constant (min⁻¹), C_o is initial concentration, C_t is the concentration of MO at time t (min). Fig. 8 shows the plot of $\ln(C_o/C_t)$ vs. time at different initial concentration of dye at fixed catalyst loading of 1 g/L. Linear plots were observed (with R² values higher than 0.9) which attested that photodegradation of MO obeys pseudo-first order kinetics. The calculated pseudo-first order rate constant and corresponding R² values are presented in Table 1. It can be seen that with increase in dye concentration from 0.01 mM to 0.09

mM, degradation rate constant decreases from 0.0877 to 0.017 min⁻¹. Many researchers have used Langmuir-Hinshelwood model to scrutinize the heterogeneous photocatalytic reaction of organic compounds in aqueous solutions. The experimental data was restructured in terms of the Langmuir-Hinshelwood model to accommodate reactions taking place at solid-liquid interface (eq. 14 and 15) [37].

$$r_{o} = -\frac{dC}{dt} = \frac{K_{1}K_{2}C}{(1+K_{2}C_{o})} = K_{app}C$$
(14)
$$\frac{1}{K_{app}} = \frac{1}{K_{1}K_{2}} + \frac{C_{o}}{K_{1}}$$
(15)

where r_o is the rate of disappearance of dye, K_1 is the surface reaction rate constant (mol L⁻¹ min⁻¹), K_2 is the Langmuir-Hinshelwood adsorption equilibrium constant (L mol⁻¹). A plot of $1/K_{app}$ vs. C_o for the photocatalytic degradation of MO is shown in Fig. 9. A linear relationship between $1/K_{app}$ and C_o was observed ($R^2 = 0.9811$), which established the validity of Langmuir-Hinshelwood model for photocatalytic degradation of MO by ZnO photocatalyst. The values of K_1 and K_2 were found to be 1.637×10^{-6} mol L⁻¹ min⁻¹ and 3.092×10^5 L mol⁻¹ respectively.

3.4.4 Effect of Catalyst Loading

To study the effect of catalyst loading on the photodegradation of MO, experiments were carried out by varying the amount of ZnO from 0.25–2.00 g/L at a fixed dye concentration of 0.03 mM for 40 min. It was observed that percentage of MO degraded after 40 min increased from 58.9 to 95.3% with increase in catalyst loading from 0.25–2.00 g/L (Table 2). Fig. 10 shows the plot of $\ln(C_o/C_t)$ vs. time for different amount of ZnO. The change of rate constant with change in catalyst loading is shown in Fig. 11. It can be seen that rate constant increases with increase in catalyst loading. However two regions of increase are there. First region from 0.25–1.00 g/L where slope of curve is very steep, and second region from 1.25–2.00 g/L where

increase in rate constant is relatively less. The increase in rate constant with increase in amount of ZnO is due to an increase in number of active sites on photocatalyst surface. This result in an increase in generation of hydroxyl radicals and thus leads to an increase in the number of dye molecules degraded. However, increase in catalyst dosage also increases the turbidity of solution, and results in decrease in UV light penetration due to increased light scattering. This factor comes into existence at higher catalyst dosage (above 1 g/L) and thus results in relatively smaller increase in rate constant with increase in catalyst dosage. Keeping these observations in mind, other experiments were carried out with 1.00 g/L ZnO so as to avoid the excessive usage of catalyst.

3.4.5 Effect of pH

To study the role of pH on photodegradation of MO, experiment was carried out in the pH range of 5 - 11 at 0.03 mM MO concentration and 1 g/L catalyst loading for 40 min. Fig. 12 shows the effect of pH on the percentage of dye degraded after 40 min. Fig. 13 shows the plot of ln (C_o/C_t) vs. time for different values of pH. Calculated rate constants are presented in Table 3. It can be seen that degradation rate increases with increase in pH, exhibiting maximum at pH 9. Further increase in pH resulted in decrease in degradation rate. So, maximum degradation rate was observed in alkaline region. Alkaline medium facilitate the formation of OH⁻ ions which are responsible for the generation of OH⁻ radicals, which leads to an increase in rate of photodegradation [38]. The decrease in degradation rate at pH 11 may be due to dissolution of ZnO. So the optimum pH for photodegradation of MO is 9.

4. Conclusions

ZnO nanoparticles, synthesized by thermal decomposition of oxalate precursor, were found to be efficient catalyst for the photodegradation of MO dye under UV irradiation. Control experiments revealed that presence of both ZnO and UV light is necessary for the degradation of dye. The reaction was found to follow pseudo-first order kinetics and Langmuir-Hinshelwood Model described it well. The surface reaction rate constant and Langmuir-Hinshelwood adsorption equilibrium constant were found to be 1.637×10^{-6} mol L⁻¹ min⁻¹ and 3.092×10^{5} L mol⁻¹ respectively. It was observed that degradation of MO is dependent upon operational parameters, such as, concentration of dye, catalyst loading and pH. The optimal conditions for photodegradation of MO were found to be 1g/L catalyst at a solution pH 9.

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Initial dye		K	
concentration	Degradation (%)	Kapp	R^2
(mM)		(min ⁻¹)	
0.01	98.09	0.0876	0.9975
0.03	90.67	0.057	0.9976
0.05	77.86	0.0334	0.9967
0.07	60.19	0.0223	0.9423
0.09	50.01	0.017	0.9116
	cepted		
	5		

Table 1 Effect of initial dye concentration on photocatalytic degradation of MO.

Catalyst Loading	Decise detient (0/)	K _{app}	p ²
(g/L)	Degradation (%)	(min ⁻¹)	K
0.25	58.92	0.022	0.9953
0.50	74.41	0.0358	0.9896
0.75	86.24	0.0512	0.9847
1.00	90.10	0.057	0.9976
1.25	93.26	0.065	0.992
1.50	93.64	0.0678	0.9911
1.75	94.80	0.0707	0.9922
2.00	95.29	0.0726	0.9911

Table 2 Effect of catalyst loading on photocatalytic degradation of MO.

 [39]

рН	Degradation (%)	K _{app} (min ⁻¹)	R^2				
5	79.72	0.0411	0.9885				
7	83.06	0.0449	0.9903				
Natural	90.10	0.057	0.9976				
9	95.72	0.0761	0.995				
11	79.54	0.0382	0.9931				
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Table 3 Effect of solution pH on photocatalytic degradation of MO.



Fig. 1. Flowchart depicting the synthesis of ZnO powders

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Fig. 2. Molecular Structure of Methyl Orange

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Fig.6. UV-Vis spectra of photodegradation of MO with ZnO as a function of time (inset shows the photographs of MO solution).







Fig. 8. Effect of initial dye concentration on the photocatalytic degradation of MO using ZnO.



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Fig. 10. Effect of catalyst loading on the photocatalytic degradation of MO using ZnO.



Fig. 11. Variation of rate constant with catalyst loading



Fig. 12. Comparison of percent degradation at different solution pH.



Fig. 13. Effect of pH on the photocatalytic degradation of MO using ZnO.

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