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Contributed Paper

ZnO Catalyzed Degradation of Methyl Orange in Aqueous Medium

Muhammad Saeed* [a], Shahid Adeel [a], Hafiz Abdur-raoof [a], Muhammad Usman [a], Asim Mansha [a], Aziz Ahmad [b] and Muhammad Amjed [a]

[a] Department of Chemistry, Government College University Faisalabad, Allama Iqbal Road Faisalabad, Pakistan.

[b] National Center for Nanoscience & Technology, University of Chinese Academy of Sciences Beijing, China.

* Author for correspondence; e-mail: msaeed@gcuf.edu.pk

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ABSTRACT

Synthesis and characterization of zinc oxide nano particles (ZnO NPs) and investigation of their catalytic activity for the degradation of methyl orange in aqueous medium has been reported in this work. ZnO NPs were prepared by reaction of zinc acetate dihydrate and sodium hydroxide in distilled water. The prepared ZnO NPs were characterized by XRD, FTIR, SEM TGA and surface area analysis. ZnO NPs were employed as catalyst for oxidative degradation of methyl orange in aqueous medium. The effects of various parameters like time, temperature, initial concentration of dye and catalyst dose on degradation experiments were investigated. Oxidative degradation reaction followed Eley-Rideal mechanism. According to Eley-Rideal mechanism the gaseous reactant, oxygen adsorbs at the surface of catalyst while methyl orange reacts in fluid phase. Adsorbed oxygen transform to reactive radicals through the formation of electron-hole pair between conduction and valence band of zinc oxide catalyst. These active radicals mineralized the dye into water and carbon dioxide.

Keywords: methyl orange, zinc oxide, Eley-Rideal mechanism, activation energy, degradation

1. INTRODUCTION

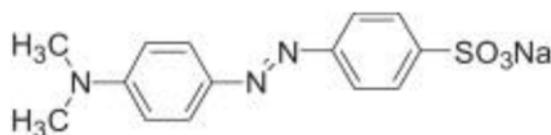
Textile industry is graded as highest contaminating among all industries as it releases about 15% of the total dye production to the environment as wastewater. Textile industrial effluents consist of huge chunk of azo dyes. These azo dyes are non-biodegradable, toxic and potential carcinogenic and persistent in nature causing serious problem threatening the environment [1]. Hence the removal of these dyes from aqueous system has gain much

attention. Hence some of the methods like sonolysis Fenton oxidation, electrochemical treatment and photochemical treatment method have been preferred. However, these techniques can succeed only to some extent, due to some limitations like generation of hardly oxidizable carboxylic acids, cost effectiveness etc. Heterogeneous catalysis especially photo catalysis using semiconductor particulate system, is found

to be the most suitable and efficient method for decomposition of toxic compounds to non-hazardous product. Semiconducting materials mediated photocatalytic decolorization is a successful and convenient method for the treatment of water contaminated with organic pollutants. As a significant p-type semiconductor, ZnO has various applications in heterogeneous catalysts, gas sensors, optical switch, magnetic, etc [2]. It has unique characteristics, such as direct and wide band gap in the near-UV spectral region, strong oxidation ability, good photocatalytic property, and a large free-excitation binding energy of 60 MeV. The greatest advantage of ZnO is the ability to absorb a wide range of solar spectrum and more light quanta than some semiconducting metal oxides [3, 4]. ZnO is an environmental friendly material as it is compatible with living organisms, which lending itself nicely to a broad range of daily applications that will not leave any risks to human health, and environmental impacts. ZnO has earned enough consideration in the degradation and complete mineralization of environmental

organic pollutants like dyes [5, 6]. Ko *et al.*, [7] have used ZnO nanowires as catalyst for degradation of methylene blue, rhodamine 6G, methyl orange and 4-nitrophenol under UV irradiation. Jyothi *et al.*, [8] have reported zinc oxide catalyzed removal of phenol from aqueous system under sono and phot irradiation in the presence of hydrogen peroxide. It was reported that formation of the formation and participation of reactive oxygen species is involve in removal of phenol. Similarly, Fenoll *et al.*, [9] and Ashar *et al.*, [10] have reported zinc oxide catalyzed degradation of different insecticides and surfactants in aqueous medium respectively.

In this work methyl orange was degraded with ZnO as catalyst. Methyl orange (MO, C.I. number 13025) is a typical water-soluble anionic dye with molecular weight of 327.3 g/mol. By use of MO as a model pollutant, the ZnO catalyzed degradation of methyl orange was studied. Moreover, the influence of various parameters like time, temperature, catalyst dose, initial concentration of dye on degradation of dye has been examined.



The structural formula of methylene orange (C₁₄H₁₄N₃O₃SNa)

2. MATERIAL AND METHODS

2.1 Chemicals

Analytical grade reagents were used without further purification. Zinc acetate and sodium hydroxide were obtained from Uni-CHEM. Methyl orange was purchased from local market of Faisalabad Pakistan.

2.2 Synthesis of Catalyst

For synthesise of zinc oxide nano particles

(ZnO NPs), 2 M solution of NaOH (100 mL) was added drop wise to 0.2 M solution of Zn(CH₃COO)₂·2H₂O (100 mL) until the pH of reaction mixture reached to 12. Reaction mixture was stirred continuously for 2 hours. Mixture was strain and zinc hydroxide was collected by filtration. Zinc hydroxide collected was washed with distilled water. The resultant solid was calcined at 623 K. The resulted white zinc oxide nano

particles were collected and stored for further process.

2.3 Characterization

XRD, SEM, FTIR and surface area measurement were used for characterization of ZnO NPs. The crystalline phases of ZnO NPs were identified by X-Ray diffraction (XRD) pattern using X-Ray Diffractometer (JEOL-JDX-3532 Japan) operated at 40kV and 20 mA with Cu-K α radiation of wavelength 1.54 Å. Scherer's equation (equation 1) was used for calculation of crystallite size of the particle.

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

Where D , λ , β and θ is crystallite size, wave length of Cu-K α radiation (1.54 Å), line broadening at half peak width in radian and Bragg angle (degree) respectively.

For FTIR analyses Bruker ALPHA FT-IR Spectrometers was used. Infra-red analysis was carried out in the range of 4000-400 cm^{-1} .

SEM analyses were carried out by Scanning Electron Microscope (JOEL-JSM 5910 Japan). For this purpose, the catalyst samples were mounted on the sample stubs and coated with gold foil using gold coating machine (JEOL-JSM-420, Japan).

2.4 Catalytic Experiment

ZnO catalyzed degradation experiments of methyl orange dye was carried out at three temperatures (303, 313 and 323 K) and four different initial concentrations (50, 100, 150 and 200 mgL^{-1}) of methyl orange. For a typical run, the reactor was charged with 50 mL solution of methyl orange. The temperature of the reaction mixture was kept constant at a desired value using hot plate while stirring the solution continuously. After stirring the solution for

30 minutes at desired temperature, 0.5 mL sample was taken to observe any variation in concentration of dye during heating and stirring period. Then 0.2 g ZnO was added to reaction mixture and stirred continuously under visible light. At appropriate time intervals, 0.5 mL samples were taken from reactor. UV-Visible spectrophotometer (Shimadzu UV-160A, Japan) was used for analyses of reaction mixture. The absorbance of the sample was measured by spectrophotometer at 483 nm which corresponds to the maximum absorbance of methyl orange dye. The absorbance was converted to concentration using standard curve of methyl orange dye. HPLC (Agilent Technologies) was used to determine inorganic products and the reaction intermediates.

The degradation of the dye was estimated by the following equation.

$$\text{Degradation} = \frac{A_0 - A_t}{A_0} \quad (2)$$

where A_0 and A_t are the initial and final absorbance of each dye in the mixture, which respectively relate to the initial (C_0) and final (C) concentrations according to the Beer-Lambert law.

3. RESULTS AND DISCUSSION

3.1 Characterization

Figure 1 shows the XRD pattern of zinc oxide nano particles. XRD spectrum is dominated with peaks at 2θ value of 31.85°, 34.5°, 36.3°, 47.75°, 56.75°, 63.1° and 68.2° corresponding to the (100), (200), (101), (102), (110), (103) and (112) planes of the hexagonal wurtzite structure of ZnO respectively in accordance with JCPDS No. 89-1397 [11].

Moreover, all diffraction peaks of the product show stronger peak intensities, indicating that the obtained ZnO NPs have high crystallinity and purity. The ZnO NPs

have an average crystallite size of about 11.8 nm as calculated by Debye Scherrer's formula. Furthermore, as there is no difference in XRD pattern of fresh and used sample, therefore it can be concluded that present zinc oxide catalyst is stable in degradation experiments which can be recycled [12-17].

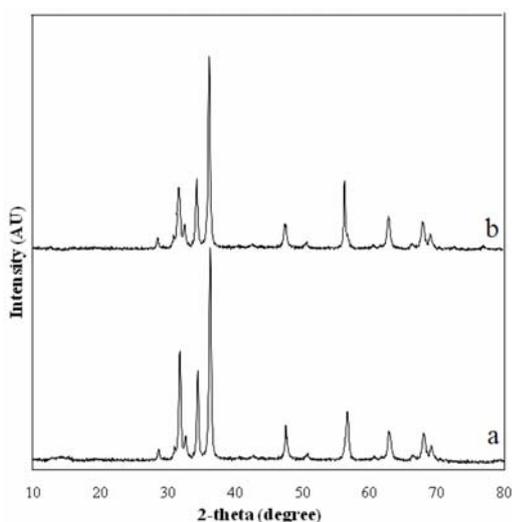


Figure 1. XRD of ZnO catalysts a) fresh sample b) used sample.

Figure 2 shows the scanning electron micrographs of fresh and used catalysts which shows that particles are plate like in morphology and are not agglomerated. The zinc oxide nano particles are homogeneous, smooth and uniform in shape. SEM image of unused and used catalyst show no difference representing that the catalyst is stable. The morphology and shape does not change during the catalytic reaction. BET surface area of the catalyst was determined using a Quanta Chrome (Nova 2200e) surface area and pore size analyzer. Samples were degassed at 383 K for 2 hours prior to analysis. $59.7 \text{ m}^2\text{g}^{-1}$ was determined as BET surface area.

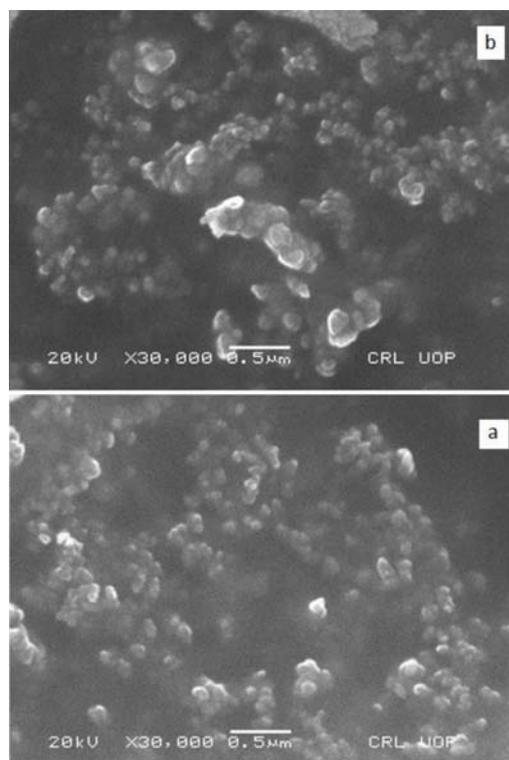


Figure 2. SEM of ZnO catalysts a) fresh sample b) used sample.

3.2 Degradation of Methyl Orange

ZnO catalyzed degradation of methyl orange dye is given in Figure 3. This investigation was accomplished with 100 mgL^{-1} as initial concentration of methyl orange dye in the presence of 0.2 g of ZnO catalyst while stirring the reaction mixture at 500 rpm. Separate experiments were carried out at 303, 313 and 323 K. It was noted that about 11% of dye solution degraded within first 10 minutes and gradually increased to 43% after 60 minutes at 303 K. Degradation achieved after 10 minutes was 15% at 313 K which was increased to 52% after 60 minutes. Finally, degradation of methyl orange increased from 20% in 10 minutes to 61% after 60 minutes at 323 K.

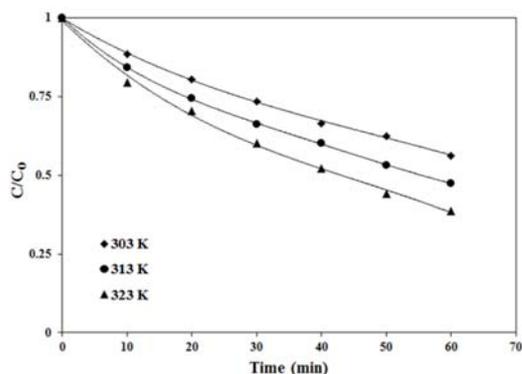


Figure 3. ZnO catalyzed degradation of methyl orange at various temperatures.

The cleavage often takes place on the azo linkage (-N=N-) of the aromatic azo compounds, because these π bonds are comparatively more diffusive than other parts within the molecule. Ultimately methyl orange dye was completely mineralized to water and carbon dioxide; however, existence of benzene sulfonate, naphthoquinone and carboxylic acids like phthalic, fumaric, succinic, maleic, malonic, oxalic and formic acids was observed with HPLC which were then mineralized to water and carbon dioxide. Figure 4 shows the FTIR spectra of catalyst sample. Peaks at 555, 670 and 774 cm^{-1} are related to metal oxide (Zn-O) bond. The peak at 3405 cm^{-1} indicates the presence of -OH residue. The peaks in the range of 1300-1550 cm^{-1} corresponds to the C=O and O-H bending vibration. The peaks at 1626 cm^{-1} can be attributed to O-H bending vibrations. The bands at 3400 and 2925 cm^{-1} originated from the O-H stretching of water. Peak at ~ 2400 cm^{-1} could be due to adsorbed carbon dioxide [18, 19].

As methyl orange was degraded to carbon dioxide, therefore peak at ~ 2400 cm^{-1} was pronounced in spectra b and c. Hua and his co-workers [20] have assigned this peak to N-H bond and carbonyl group. Band at 1482 cm^{-1} in spectrum b and c

was attributed to characteristic azo (-N=N-) functional group. Kim and Lee [21] have assigned the band at 1183 cm^{-1} to SO_3Na group of methyl orange. Band at 1637 cm^{-1} in spectrum c was observed which was attributed to stretching vibration of C=O of carboxylic acids formed in degradation reaction. Peak appearing at 1383 cm^{-1} was attributed to N-O stretching and N-H bending vibrations. Peak at 992 cm^{-1} in spectrum b is due to benzene ring [21].

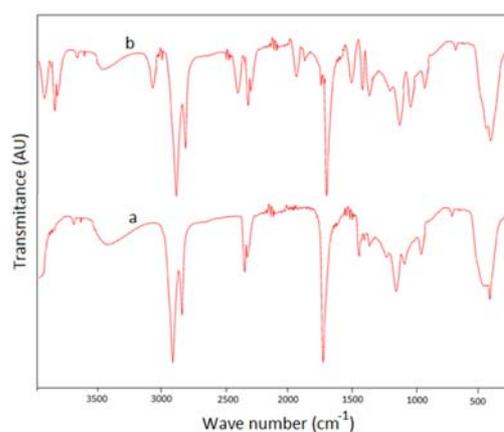


Figure 4. FTIR of ZnO catalysts a) Fresh sample b) Used sample.

3.4 Effect of Catalyst Dosage

For investigation of effect of catalyst dose on degradation, experiments were performed with different amount of ZnO catalyst from 0.05 to 0.3 g in 50 mL aqueous solution of methyl orange dye at pH of 1.5. Figure 5 represents the effect of catalyst dosage. It was observed that the rate of degradation increases linearly with increase in the amount of catalyst up to 0.5 g, and then decreases (leveling off). With the increase of catalyst dose, the number of photons and the number of methyl orange molecules adsorbed increase. With increase in the number of catalyst particles, it leads to increase in photo catalytic efficiency.

From Figure 5, beyond 0.2 g, there is a decrease in the photo catalytic process, i.e. the rate levels off. This may be due to increased concentrations of catalyst, although more areas are available for constant MO molecules to absorb the number of substrate molecules present in the solution remains the same, but the solution turbidity increases and it interferes the penetration of light and also cause scattering of radiation. Hence at a certain level presence of catalyst in excess amount may not involve in catalysis and thus the rate levels off.

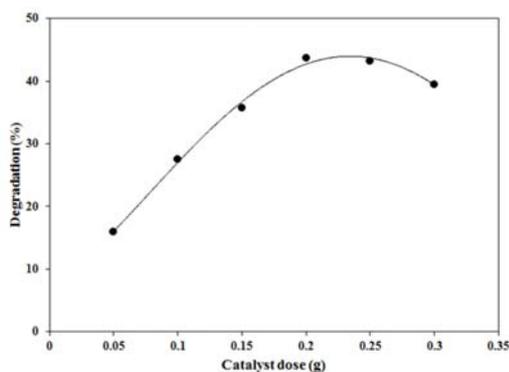


Figure 5. Effect of catalyst dose on degradation of methyl orange.

3.5 Effect of Concentration of Methyl Orange

The dye concentration is a very important parameter in wastewater treatment. A set of experiments were conducted varying the concentration of methyl orange from 50 to 200 mgL⁻¹ at a constant ZnO loading of 0.2 g and a solution pH of 1.5 at 303K. The results from the graphical representation are given in Figure 6 which indicates that increase in concentration of dye decreases the rate of degradation, because the increase in concentration of dye increases the number of molecules and competition with hydrogen peroxide for active sites of the catalyst. The effect of decrease in degradation of

methyl orange with increase in initial concentration of dye can be indicative of some kind of dye self-inhibition. For this reason, the effect of the catalyst loading and speed of agitation has been investigated.

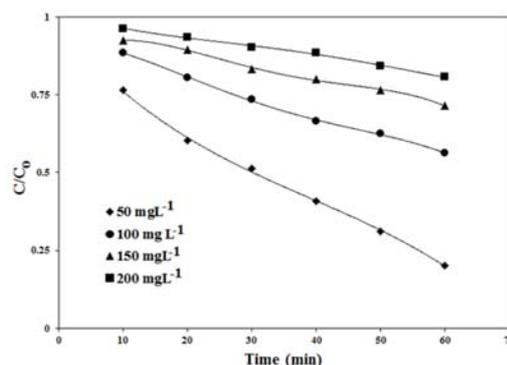


Figure 6. Effect of concentration of methyl orange on rate of degradation.

3.6 Kinetics Investigation

The kinetics of ZnO NPs catalyzed degradation of methyl orange in present investigation can be described by Eley-Rideal mechanism. The Eley-Rideal mechanism requires one of the reactants to be in the gas phase [22-24]. According to Eley-Rideal mechanism the gaseous reactant, oxygen adsorbs at the surface of catalyst while methyl orange dye reacts in fluid phase. It has been proposed that an electron-hole pair is formed between conduction and valence band of zinc oxide. Oxygen adsorbed at the surface of ZnO NPs scavenges the electron and yields superoxide anion (O₂⁻). Protonation of superoxide anion produces active OOH radicals. The hole in valence band of ZnO shifts to surface where it reacts with water and produce active OH radicals. These active species play a vital role in degradation of methyl orange dye [25].

The Eley-Rideal mechanism can be described by kinetics expression

$$-\frac{dC}{dt} = k_r C \theta_{O_2} \quad (3)$$

C and θ_{O_2} represent concentration of methyl orange dye and surface concentration of oxygen respectively. Continuous flow of oxygen makes the reaction zero order with respect to oxygen, hence the kinetic expression becomes as

$$-\frac{dC}{dt} = k_{Ap}C \quad (4)$$

k_r and k_{Ap} is true rate constant and is the apparent pseudo-first-order rate constant respectively.

Integration of that equation (with the same restriction of $C = C_0$ at $t = 0$, with C_0 being the initial concentration and t the reaction time) will lead to the expected relation:

$$\ln \frac{C_0}{C} = k_{Ap}t \quad (5)$$

Plot of $\ln(C_0/C)$ versus t is given in Figure 7. The slop of the curve gives apparent rate constant for degradation of Rhodamine B dye. Meanwhile, the linear relationship between $\ln(C_0/C)$ and t indicates that the catalytic degradation reaction follows the pseudo first-order kinetics. The apparent rate constants were 0.0163, 0.0128 and 0.0098 min^{-1} at 323, 313 and 303K respectively. For determination of activation energy, Arrhenius equation was applied to rate constants at different temperatures. Activation energy was calculated from the slop of curve and was found as 20.7 kJmol^{-1} . It has been reported that photo catalytic reactions are usually not very temperature dependent; therefore, the activation energy is low.

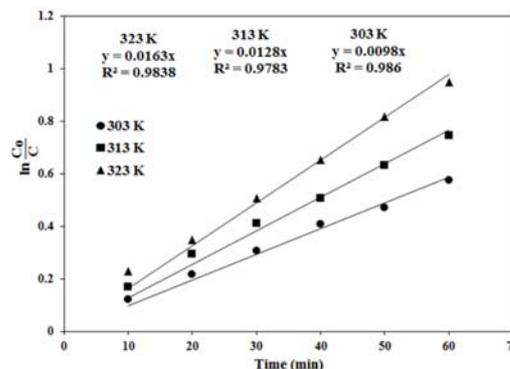


Figure 7. Fitting of kinetic model (equation 5) to experimental data at various temperatures.

4. CONCLUSION

Nano sized zinc oxide particles were successfully prepared by precipitation methods with zinc acetate and sodium hydroxide. XRD, FTIR, SEM and surface area measurement were used for characterization of prepared nano particles. The prepared ZnO NPs were employed as catalyst for degradation of methyl orange in aqueous medium. Methyl orange was degraded to inorganic products like water and carbon dioxide through a number of intermediate species. In this study ZnO acted as heterogeneous catalyst and was easily separated from mixture by filtration. Reaction followed the Elay-Rideal mechanism. According to the mechanism reaction take place in two steps. In 1st step O_2 get adsorb at the surface and produce electron-hole pair at ZnO which resulted in production of reactive radicals. The reactive radicals degraded the dye in second step.

ACKNOWLEDGMENTS

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