# Zinc Oxide, a UV light active photocatalyst for the degradation of anionic dye

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**Abstract:** Zinc oxide, a UV-light active photocatalyst has been successfully synthesized in laboratory by co-precipitation method. The $ZnAC_2.2H_2O$ and NaOH were used as precursor materials. The EDTA was used as a capping agent to confine the size and to control the over-growth of the photocatalyst. Characterization of as prepared photocatalyst was done by X-Ray Diffraction and Fourier Transform Infrared Spectroscopy. The peak at 32.2° (100), 35.0° (002), 36.6° (101), 47.8° (102), 57.0° (110), 63.2° (103), 68.2° (200), and 69.4° (112) at 2θ degrees indicated the crystalline phase of as prepared material and average crystalline size was calculated by Debye-Scherer equation and was found to be 17.81 nm. The FTIR spectra showed the clear bands of Zn-O, C-H, and O-H at 400 to 600 $cm^{-1}$, 1650 $cm^{-1}$ and 3350 $cm^{-1}$ respectively. Then, as synthesized ZnO material was used as catalyst to degrade anionic dye: methyl orange (MO), under UV light irradiation. The results revealed that ZnO showed an excellent photocatalytical performance at pH 7, and an optimum catalyst dose of 0.1 g per 100 mL of 10 mg/L dye concentration. The 81.20% MO dye degredation was observed within 5 hrs. The removal efficiency of MO dye was found to be increased significantly up to 89 % when oxidant $H_2O_2$ was added. It may be due to scavenging effect of $H_2O_2$ oxidant. It also helps to reduce recombination of electron- hole pair during photocatalytic application. The degradation followed the pseudo first-order kinetics with rate constant k = 0.5507 also signifies the efficiency of ZnO. Hence, an economical and environment-friendly ZnO photocatalyst can be prepared and used to degrade anionic dye from the wastewater contaminated with synthetic azo dyes.

**Keywords**: Degradation; Methyl-orange; Photocatalyst; ZnO.

## Introduction

Different industries like paper, textile, leather, cosmetics, printing, are the sources of national economy. On the contrary, those industries discharge a large amount of dyeing effluents to the environment and are one of the most serious challenges that the world is facing these days. Removing those effluents before entering to the water bodies is utmost. Adsorption, ultrafiltration, photocatalytic action, sedimentation, reverse osmosis, precipitation, chemical oxidation processes, etc. are the different methods for the removal of dye[1]. Among them, photocatalytic application is considered as one of the most important, innovative, and green technology for the wastewater treatment. Due to the narrow band gap between the valence and the conduction band, semiconductors are generally used as photocatalysts. Different metal semiconductor materials, including $TiO_2$ ZnO, $Fe_2O_3$, $Bi_2WO_6$, CuO, CdS, $BiVO_4$/HAP composite, and ZnS[(2-9)] are employed as photocatalysts because they are economical and environmentally responsible. Among them zinc oxide (ZnO) is one of the economical, versatile and interesting semiconductor material that have been widely used in degradation of dyes. Zinc oxide generally synthesized by laser ablation technique[10], hydrothermal technique[1], co- precipitation method[11], sol-gel method[12],

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chemical vapour deposition technique, molecular beam epitaxy, sonochemical route[13].

In this study, ZnO nanoparticles were prepared by co-precipitation method using zinc acetate dehydrate and NaOH as precursor. As prepared material was characterized by X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR). Then it was used as photocatalyst for the degradation of anionic methyl orange (MO) dye in water. In order to improve the photocatalytic efficiency of ZnO for the degradation of MO dye, ZnO along with $H_2O_2$ oxidant in presence of UV-light was also performed which is not reported so far. The impact of various parameters such as pH, catalyst (ZnO) dose, concentration of methyl-orange (MO), time of degradation on the degradation of MO dye were also investigated.

## Materials and Methods

### Reagents

Zinc acetate dehydrate ($ZnAC_2.2H_2O$) was obtained from Merck Life Science Pvt. Ltd., India, Sodium hydroxide (NaOH) was procured from Central Drug House Pvt. Ltd., India and EDTA was purchased from Thermo Fischer Scientific India Pvt. Ltd. All reagents were of analytical grade and used without further purification.

### Preparation of zinc oxide

The ZnO was synthesized by the co-precipitation method. In a typical experiment, 10.75 g of zinc acetate dehydrate was dissolved in 100 mL deionized water to obtain solution A. Solution B was prepared by dissolving 4 g of NaOH in 100 mL deionized water. Solution A and solution B were prepared in a ratio 1:2 i.e. 0.5M and 1M concentration respectively. These prepared solutions were then mixed into a beaker at room temperature. Likewise, 0.015M EDTA was prepared by weighing 1.40 g of EDTA in 250 mL deionized water and 20 mL of it was then transferred into the mixture containing zinc acetate dehydrate and sodium hydroxide. The mixture was stirred in a magnetic stirrer for 2 hours and was then shaken in shaker for 18 hours at 150 rpm. During mixing and shaking white precipitate was formed in the solution. Then the obtained precipitate was separated by centrifugation. Eventually, ZnO nanoparticles were obtained by washing several times with deionized water and acetone, and the washed particles were dried at 60°C.

### Instrumentation

A pH-meter (Deluxe pH meter, Max Electronics, India) was used for measuring the pH values of solutions. An UV-visible Spectrophotometer (2306, AB1908003, Electronics, India) was used for analyzing the dye by measuring absorbance with the maximum absorbance at wavelength of 464 nm for MO. A Fourier Transform Infrared Spectroscopy (Shimadzu IRAffinity-1) was used to study the functional groups present in the material and were recorded from 4000-400 $cm^{-1}$ wavenumber. X-Ray Diffraction (Bruker D2 Phaser) was used to study the phases, structures, orientation and different structural parameters of the material.

### Photocatalytic activity

The photocatalytic activity of as-prepared ZnO was measured by degradation of methyl orange (MO) at ambient temperature. To perform the photocatalytic activity, UV cabinet (model number-BLE 8T254, Spectronics corp, Westbury New York) was used as the irradiation source. The temperature of the reaction system was maintained at 20-25 °C. In a typical process, 100 mL of 10 ppm dye solution was taken in a 250 mL. Then, 0.1 g prepared photocatalyst was added and magnetically stirred for 30 min for the adsorption-desorption process. After that, the solution containing beaker was kept in dark for 30 min for adsorption-desorption equilibrium. Before irradiation, solution was withdrawn for absorbance studies prior to irradiation of light. Then again solution was pipetted out at required interval of irradiation and double centrifugation was done at 4000 rpm for 20 min. Then the absorbance was noted at 464 nm using UV-visible Spectrophotometer.

## Results and Discussion

### Phase analysis by X-ray diffraction (XRD)

The XRD pattern of as prepared ZnO powder is shown in Figure 1. In the XRD pattern of as prepared material, one can see the major peaks at 32.2° (100), 35.0° (002), 36.6° (101), 47.8° (102), 57.0° (110), 63.2° (103), 68.2° (200),

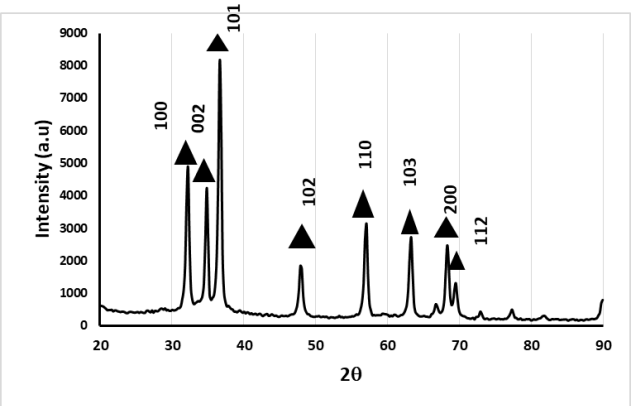


**Figure 1: XRD pattern of as prepared material.**

and 69.4° (112) of 2θ degrees. These sharp diffraction peaks indicate the crystallinity of the material and peaks are assigned for ZnO according to JCPDS Card No. 36-1451[14]. These 2θ values are assigned for the zincite structure of ZnO. Similarly, the average crystallite size of the material has also been calculated using Scherrer's equation (1)[3]:

$$\mathbf{D = K\lambda / \beta \cos\theta} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where K (0.9) is the shape factor for spherical particles, λ is the wavelength of incident radiation, β is the line width at half-maximum height, θ is Bragg's angle and D is the crystallite. The average crystalline size was found to be 17.81 nm. Thus obtained material was found to be nano-sized.

## Fourier transform infrared spectroscopy (FTIR)

The FTIR spectrum of as-prepared material is shown in Figure 2.

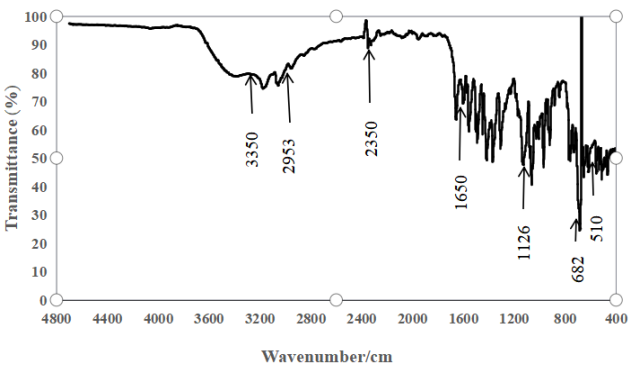


**Figure 2: FTIR spectrum of ZnO nanoparticles.**

As can be seen in the FTIR spectra of ZnO nanoparticles, clear bands have been observed. The stretching band of ZnO could be seen at around 400cm$^{-1}$ to 600 cm$^{-1}$. Similarly, a weak and broad bands around 3350 cm$^{-1}$ indicates the stretching bond of hydroxyl groups. It may be due to some moisture and impurities.

A weak vibration band at 1650 cm$^{-1}$ could be seen which indicates the presence of little water absorbed on the surface of metal oxide. Similarly, a peak around 1126 cm$^{-1}$ was seen which revealed the stretching band of C-H vibration. These results are also in agreement with previously reported literature [12, 15].

## Effect of pH in dye degradation

The pH of the solution is significant in the photodegradation process. For this study, the concentration of dye was fixed at 10 ppm with 0.01 g of ZnO. Different solutions with different pH were prepared and irradiated under UV light for 2 hours. The results are presented in Figure 3.

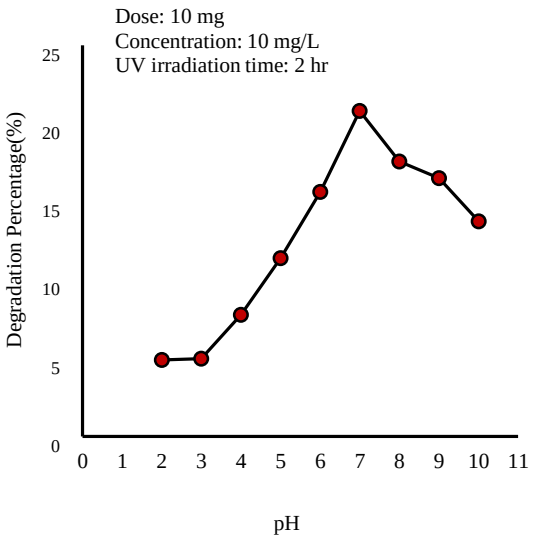


**Figure 3: Effect of pH in dye degradation.**

Figure 3 demonstrates the unfavourable condition for photocatalysis in the acidic medium due to the dissolution of ZnO. Decline in the degradation rate was due to the production of $H^+$ ions. Also in the basic medium, there was a decrease in the degradation rate which may be due to the properties of the dye and the surface-charge properties of the photocatalyst that means the strong

electrostatic repulsion may have occurred between the dye and the negatively charged photocatalyst. Since, there was a maximum degradation observed at pH 7, further experiments were carried out at optimized pH of 7.

**Effect of catalyst dose**

For this study, the catalyst dose have been varied from 0.005 g to 0.2 g keeping constant pH of 7, the concentration of dye 10 mg/L, and 2 hrs irradiation time.

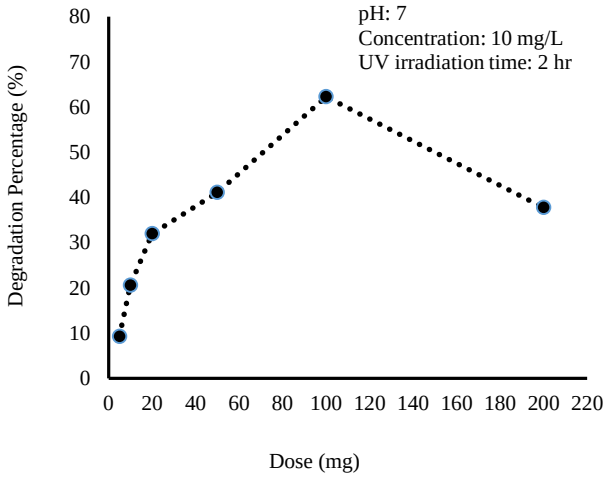


**Figure 4: Effect of catalyst dose in MO degradation in presence of ZnO.**

As can be seen in Fig. 4, nearly 10% degradation was observed when 0.005 g of catalyst was used. As we increased the catalyst dose the degradation rate also increased. The increment in degradation rates may be due to the increased number of electron-hole pair formation. The highest degradation rate of 62.3% was observed with the use of 0.1 g catalyst. However, when the catalyst dose increased to 0.2 g, there was a significant decrease in the photocatalytic activity of the catalyst. In this case, a high dose may cause turbidity in the solution system. Increased turbidity lowers the penetration of irradiation light into the bottom of the solution, resulting in a slow response rate. There may also be agglomeration of the catalyst particles at a higher concentration, which lowers the catalyst's efficiency.

As a result, the outline of this component of this experiment provides insight into the increased turbidity with increased photocatalyst level. As a result, the optimum catalyst dose for photodegradation of MO dye is 100 mg catalyst per 100 mL dye solution. Other literature has also reported similar optimum conditions [16].

**Effect of dye concentration**

The optimum dye concentrations for the study of MO degradation were investigated using 100 mg ZnO nanocatalyst with a pH of 7. The results of different concentrations irradiated for 2 hrs are presented in Figure 5.

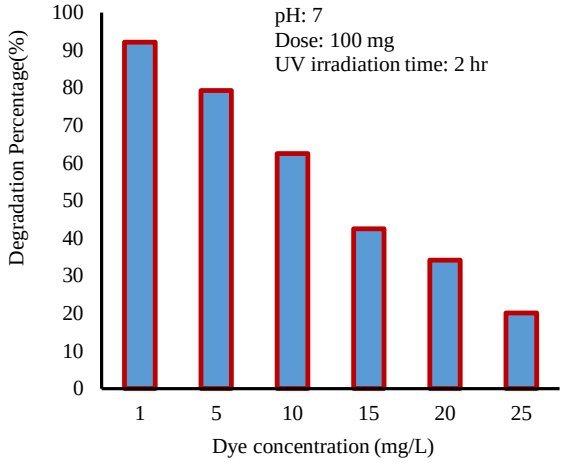


**Figure 5: Effect of dye concentration on MO degradation.**

Figure 5 demonstrates the very high degradation percentage when dye concentration was 1 mg/L and 5 mg/L which may be due to the production of high electron-hole pairs and the lesser amount of dye molecule acted upon the photocatalyst at an instant. The 62.5% degradation was observed when 10 mg/L dye solution was used. When the concentration was increased, the degradation rate gradually decreased. This decrease in degradation may be due to the chance of aggregation of dye molecules on the surface of the catalyst which may result in the quenching of the excited molecules[17]. Furthermore, it may be due to the decrement in the path length of photon entering the solution which decreases the number of photons absorbed by the catalyst particles which eventually decrease in degradation efficiency[18]. Also, all the active sites of the catalyst are fully occupied when the concentration increases which decrease the formation of hydroxyl radical which results in the degradation efficiency of dye[2].Hence, 10 mg/L was found

to be the best concentration and was chosen for further experiments.

**Photocatalytic degradation of MO with respect to time**

As can be seen in Figure 6, there was a gradual increase in percentage degradation with an increase in irradiation time as the dye solution containing 100 mg of ZnO photocatalyst was introduced into UV irradiation. There was a 50.85 % degradation for the first hour of irradiation. Likewise, after 2hr, 3hr, and 4hr, the degradation % was

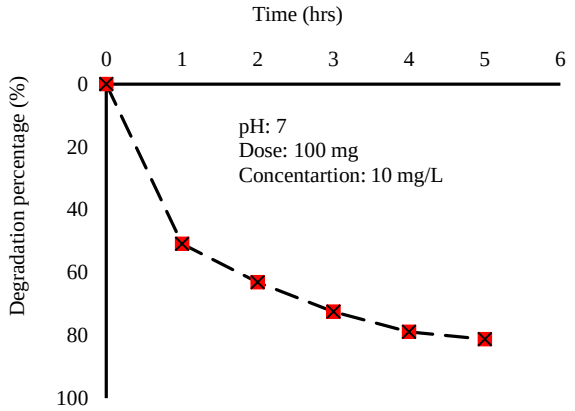


**Figure 6: Effect of time on MO degradation in presence of ZnO.**

increased to 63.05%, 72.42%, and 78.84 % respectively. Finally, the degradation percentage reached to 81.20 % after the fifth hour of irradiation. After 5 hrs of irradiation, there was a clear solution which insured MO dye had been almost decomposed within 5 hrs. Thus in this experiment, 81.20 % of the MO dye degraded in 5 hrs.

**Photocatalytic degradation in different conditions**

Other experiments were designed by varying the reaction conditions to enhance the photocatalytic degradation in short time which is shown in the Figure 7.

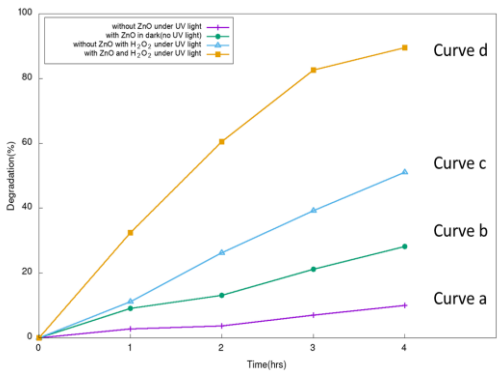


**Figure 7: Photocatalytic degradation of MO by ZnO in different conditions.**

Figure 7**,** curve (a) shows the degradation of MO in UV light irradiation without the presence of ZnO. The curve shows no any significant degradation. The degradation of MO in presence of ZnO in dark is shown by Figure 7, curve (b) but adsorption was observed rather than degradation as it was carried in dark. Similarly, the Figure 7, curve (c) indicates the degradation curve of MO without ZnO but with the introduction of $H_2O_2$ oxidant under UV light. As the curve shows slight increment in degradation but due to the absence of catalyst, the increment was not satisfied. Figure 7, curve (d) depicts the degradation curve of MO with $H_2O_2$ along with ZnO in presence of UV light which resulted in 89% degradation within 4 hrs. It may be due to scavenging effect of oxidant $H_2O_2$ where the generation of more and more OH radicals occurred and ZnO get successively activated and triggered the photocatalysis process.

**Reaction rate and order of reaction**

The further investigation on reaction rate was carried out using Langmuir Hinshelwood kinetic model ln ($C_0$/C) =kt after confirming catalyst dose, dye concentration, and reaction condition. Here, 10 ppm initial MO dye concentration was taken and 0.1 g ZnO catalyst was added to the reaction flask with $H_20_2$ under UV light. The results are then presented in a graph (Figure 8) as ln $C_O$/C in as a function of irradiation time. The rate constant k was found to be 0.5507 which followed the pseudo first-order kinetics. The co-relation coefficient $R^2$ which was found to be 0.9809 signifies the efficiency of ZnO photocatalyst.

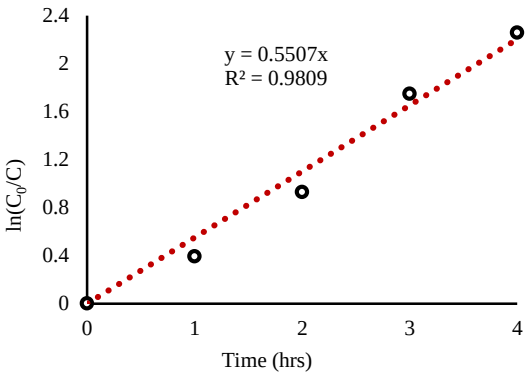


**Figure 8: Plot for pseudo first-order kinetics for MO degradation by ZnO in presence of oxidant.**

**Possible reaction mechanism and photodegradation over ZnO**

The rate of MO photocatalytic degradation was accelerated when the produced catalyst was combined with $H_20_2$ under UV light. The increase in the degradation rate may be due to the free radical species which may be produced during the time of irradiation. These species can react with the organic component and brings about its degradation. Initially, the nanocatalyst ZnO is in contact with model organic pollutants MO under UV irradiation, which corresponds to its optical band gap. Then the electrons are promoted from the valence band to its conduction band. The charged species OH, H, and $O_2$ diffuse rapidly towards the catalyst ZnO surface where oxidation-reduction may occur resulting in the formation of the excited photoelectron. The electron may react with adsorbed oxygen molecules $O_2$ to form electronically active superoxide anion radicals ($O_2^-$). Similarly, photo-induced holes in the valence band may oxidize $OH^-$ which results in the formation of hydroxyl radical species ·OH. Also, ·OH may be formed from the adsorbed water on the surface of ZnO and the peroxide radicals from the molecular oxygen in the conduction band. The reaction can be illustrated in the following equations (2 to 8):

$ZnO + h\mu \rightarrow ZnO [h^+ + e^-]$ …… (2)

$ZnO [e^-] + O_2 \rightarrow ZnO + O_2^-$ …… (3)

$ZnO + [h^+] + OH^- \rightarrow ZnO + \cdot OH$ …… (4)

$ZnO [e^-] + O_2 + H^+ \rightarrow \cdot HO_2 + ZnO$ …..… (5)

$\cdot HO_2 + H^+ \rightarrow H_2O_2$ ……..…….(6)

$H_2O_2 + e^- \rightarrow \cdot OH + OH^-$ ……..…….. (7)

$ZnO + \cdot OH + O_2 + MO \rightarrow ZnO + CO_2 + H_2O$…(8)

Here sufficient amount of hydroxyl radicals have been generated which is a powerful oxidizing agent, may attack the organic dye and is capable to mineralize these toxic and bio-resistant compounds into a harmless products. These photodegraded products can be completely converted to $CO_2$.

The degradation pattern of MO using ZnO is illustrated in Figure 9.

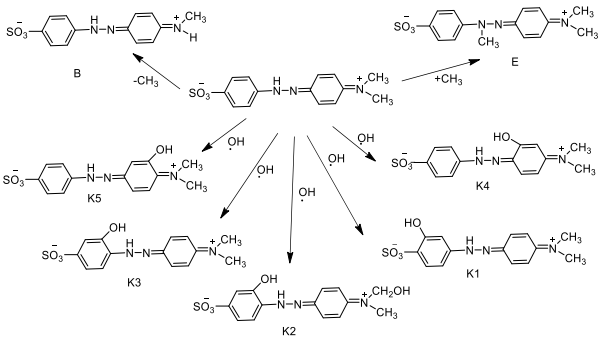


**Figure 9: Possible reaction pattern for the degradation of MO dye in UV light.**

Figure 9 shows the detail step denoting B, E, K1, K2, K3, K4, and K5. In this system, K1, K2, K3, K4, and K5 are the intermediate formed by introducing hydroxyl group on MO. Similarly, E is the intermediate formed by introduction of methyl group on MO. In the same way, B is also the intermediate followed by loss of methyl group from MO. Such type of degradation was also reported in literature [21].

**Comparison with literature value**

The photocatalytic performance of prepared ZnO was compared with other reported literatures which are shown in Table 1. Results revealed that the findings of present work are quite comparable with previous reports.

**Table 1: Photocatalytical degradation of MO dye for various catalysts.**

| Catalyst used | Dye (mg/L) | Catalyst Dosage (mg) | UV Irradiation time (min) | Degradation (%) | Ref. |
|---|---|---|---|---|---|
| ZnS | 10 | 60 | 75 | 72.99 | [13] |
| ZnO @ ZnS | 40 | 50 | 120 | 50.00 | [3] |
| $TiO_2$ | 20 | 60 | 120 | 76.00 | [19] |
| $BaF_2$-$TiO_2$ | 20 | 300 | 60 | 79.38 | [20] |
| ZnO | 10 | 100 | 300 | 81.20 | * |
| ZnO-$H_2O_2$ | 10 | 100 | 240 | 89.00 | * |

***-** Present study

## Conclusion

The laboratory prepared ZnO nanoparticles by co-precipitation method was employed for the photocatalytic degradation of MO dye. The prepared photocatalyst was characterized by XRD which showed the average crystalline size of 17.81 nm and clear bands of ZnO were observed as characterized by FTIR. As the solution was irradiated under UV light, the degradation efficiency was achieved within 4 hrs with pH 7, 0.1 g of catalyst, and dye concentration of 10 mg/L. The removal efficiency of MO dye was found to be increased significantly when $H_2O_2$ along with ZnO catalyst in UV-light was applied which showed almost 89% of the dye was degraded within 4 hrs. The order of reaction and reaction rate was investigated and results showed the pseudo first-order kinetics with rate constant k= 0.5507 which signifies the efficiency of ZnO photocatalyst. All the results exposed that the laboratory prepared ZnO was found to be one of the promising UV light active material for the practical removal of acidic dyes like MO.

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