

Preparation, Characterization of Zinc Oxide Nanorods and Its Sonocatalytic activities in Oxidation of an Organic Dye Molecule from Aqueous Phase

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ABSTRACT: Large quantities of different types of dyes are used in leather, textile, food processing and allied industries. These industries are released huge quantities of toxic organic and inorganic compounds through effluents into the aquatic environment. The most suitable method is Advanced Oxidation Process (AOP) plays a major role in the oxidation of toxic organic and inorganic molecules from aqueous phase. Hence, the present study is focused on the oxidation of a model organic molecule, Eosin yellow dye using zinc oxide nanorods under power ultrasound. Zinc oxide nanorods catalyst was prepared by precipitation method using zinc precursor and ammonia as a precipitating agent. The prepared ZnO nanorods were characterized by FT-IR, XRD, FE-SEM and BET techniques. The prepared catalyst was highly crystalline with hexagonal structured nano rods which has Wurtzite crystal phase. The crystallite size was found to be 56.35 nm. Sonocatalytic activities of the prepared ZnO nanorods were studied under ultrasonic irradiation for the oxidation/degradation of Eosin yellow (EY) dyes in aqueous medium. Various experimental parameters like effects of pH, dye concentration, catalyst dosage and electrolytes on dye degradation were carried out in detail. The % degradation of the dye molecule was increased at acidic pH then it starts decreasing in the alkaline pH. The above 95% degradation was observed at lower dye concentrations. The kinetics of the degradation of EY dye molecules with and without catalyst by power ultrasound was also carried out and it was found that the reaction rate decreases with increasing dye concentrations of all the kinetic systems. The degradation of dye molecules were monitored by UV-Visible spectrophotometer, Chemical Oxygen demand (COD) and Total Organic Carbon (TOC) analyses. The interference of electrolytes such as NaCl, KCl, Na₂CO₃, NaHCO₃, and MgSO₄ on the oxidation of dye molecules has also been carried out. The by-product analysis was also analysed by ESI-MS. The reusability of the catalyst showed that the efficiency of the catalytic activities was not affected even up to five cycles of usage on the degradation of EY dye molecules.

KEYWORDS: Ultrasound, degradation, nanorods, Eosine yellow dye, TOC, COD

I. INTRODUCTION

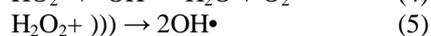
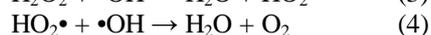
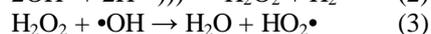
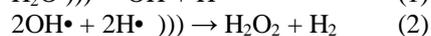
Environmental pollution is becoming a very serious problem now a day. Waste waters discharged from leather, textile, cosmetics, food processing, pharmaceutical industries due to its suspended solids, high COD, pH and colour, the effluents should be treated by advanced technologies. In the recent years, semiconductor nano materials have been used for the degradation of organics and inorganics using advanced oxidation technologies under UV-visible irradiations through the production of highly reactive OH radicals. Many oxidation and/or reduction methods are reported in the literature on the degradation of organic and inorganic compounds [1] into nontoxic substances [2]. Fenton's reagent [3], Ozone [4], semiconductor catalysts like ZnO [5], TiO₂ [6], iron oxide [7] etc., are used to degrade organics into harmless substances like carbon dioxide and water under photocatalytic and sonocatalytic procedures [8]. Ultrasonic irradiations may be exploited for the degradation of pollutants. Ultrasonic irradiation assisted semiconductor metal oxide catalyst is considered to be a better option for the degradation of organic and inorganic pollutants in water and/or wastewater, such as dyes, pesticides, aromatic compounds, pharmaceuticals, and chlorinated

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hydrocarbons etc. Removal of toxic substances by Fenton's reagent [9], ozone [10], TiO₂[11] and ZnO [12] are widely reported in the literature. Investigations on oxidation of organic compounds by ultrasonic irradiation with heterogeneous catalysts are not studied well. Hence, it is worth to investigate the catalytic activities of the semiconductor ZnO nanorods catalyst under power ultrasound for the oxidation of organic molecules from aqueous phase. Sonochemical techniques involve the use of ultrasonic waves to produce an oxidative environment via a cavitation through hot spot that yields localized microbubbles and supercritical regions in the aqueous phase. The collapse of these bubbles leads to generate high temperatures and pressures around the localized area [13]. The sonication of water produces hydroxyl radicals as shown in Eqns. [1-5] below:



Where, $\xrightarrow{\text{ultrasound}}$ refers to the ultrasonic irradiation. Eosin yellow is a fluorescent acidic dye useful for staining purposes, dyeing textiles, ink manufacturing, in coloring cosmetics and gasoline and as a toner however, it is listed as a carcinogen [14]. Hence, the present study is focused on preparation and characterization of ZnO nanorods and its catalytic activities on the degradation of a model organic compound for example, Eosin yellow under ultrasound is reported in detail.

II. EXPERIMENTAL

II.1 Chemicals

Eosin yellow was purchased from Sigma-Aldrich, (USA). Sodium chloride and Calcium chloride were procured from Rankem (AR). Magnesium chloride, Silver sulphate, Sulphuric acid, Hydrochloric acid, Sodium hydroxide and Potassium hydrogen phthalate were supplied by S.d. Fine. Chem. Ltd. Potassium chloride and Sodium bicarbonate were received from E-Merck, Mumbai, (India), Potassium dichromate and Ammonium ferrous sulphate were supplied by Qualigens, Mumbai, (India)

II.2 Preparation of the catalyst:

Zinc oxide nanorods were prepared using precipitation method with metal acetate as precursor and ammonium hydroxide as a precipitating agent. The typical procedure as follows: Appropriate amount of metal acetate dissolved in double distilled water to obtain a required stoichiometry. Aqueous ammonia added into the precursor solution with vigorous stirring till the formation of white precipitate. Then the precipitate formed was filtered under vacuum. The white crystalline precipitate thus formed was washed with double distilled water for several times to remove excess ammonia and impurities, filtered and transferred to a silica crucible. Then the precipitate was heated in a hot air oven for 1h and then sintered. The resultant ZnO formed were ground, collected and stored in an airtight container.

II.3 Characterization

The prepared ZnO powders were characterized by FT-IR, XRD and FE-SEM techniques. The stretching frequencies of vibrations were measured by FT-IR (Perkin Elmer FT-IR spectrophotometer). The crystallinity of the prepared catalyst was measured by (PAN analytical X-ray diffractometer, Germany) with Cu K α radiation in the 2 θ scan range between 0-70 $^\circ$ theta. An accelerating voltage of 40 kV and an emission current of 25 mA were used. The surface morphology and particle size of the catalyst was studied by FE-SEM (Oxford INCA ENERGY-350). The pH meter was calibrated using buffer solutions between pH 4 and 7 at 25 $^\circ$ C (Elico pH meter, Hyderabad, India). Sonochemical experiments were performed using (Sonics, Vibracell, USA, 20 kHz, 750 W, USA) horn and split type probes. The COD analysis was carried out in the (Thermoreactor Spectroquant TR-320, Merck, Germany) block digester.

II.4 Sonocatalytic studies

Sonocatalytic degradation experiments were performed in an ultrasound sonicator with horn type and split probes. The sonochemical reactor consists of a 250 ml jacketed glass reactor fitted with accessories for withdrawing samples. The sonotrode is capable of supplying a maximum power output of 750 W. A typical procedure for the kinetics measurement (10 ppm of initial dye concentration) is as follows: required amount of EY dye with catalyst and water

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was charged in a batch reactor (total volume of 200 ml), was introduced in the sonication bath, thoroughly mixed, then immediately withdrawn 5 ml of the sample for 0 minute and ultrasonic irradiation was passed through the mixture. 5 ml of the samples were withdrawn at regular time intervals during the experiment. The degraded samples thus collected were filtered and the filtrate was analyzed for the reduction in absorbance by UV-Visible spectrophotometer. The calibration graphs were drawn against dye concentration with optical density of the dye samples. The unknown concentrations of the degraded dye samples were computed from the standard graphs. The final concentration of the dye samples after degradation was determined from the measurement of the optical density. From this the efficiency of the degradation was calculated using eq. (6)

$$\text{Degradation efficiency (\%)} = \frac{C_o - C_e}{C_o} \times 100 \quad (6)$$

Where, C_o and C_e are the initial and final dye concentrations in the aqueous phase respectively. The samples were withdrawn from the reaction mixture was also analyzed for COD reduction by closed reflux method.

III. RESULTS AND DISCUSSION

III.1 FT-IR Spectroscopy

The functionality of the prepared catalyst was determined by FT-IR measurement for the pristine ZnO catalyst. FT-IR spectra of the pristine ZnO catalyst is given in Fig. 1a show a broad band between 430-419 cm^{-1} and this corresponds to the Zn-O stretching vibrations.

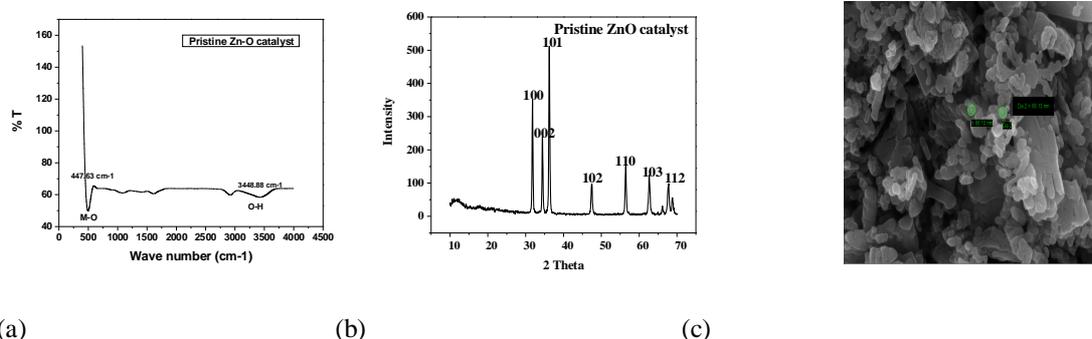


Fig. 1(a). FT-IR spectrum of the pristine ZnO nanorod catalyst; (b) XRD pattern of the prepared pristine ZnO catalyst; (c) FE-SEM image of pristine ZnO nanorod catalyst.

The spectrum shows bands at 3250 and 3500 cm^{-1} which may be due to O-H stretching vibrations of adsorbed moisture. The peaks are narrow and sharp which shows good degree of crystallinity.

III.2 X-ray diffraction studies (XRD)

Phase identification and estimation of the crystallite size of the prepared ZnO catalyst was determined by XRD method. The XRD pattern of the prepared ZnO is illustrated in Fig. 1b shows the phase composition of the prepared ZnO catalyst. It is observed that the ZnO catalyst was in a crystalline state and gave rise to the diffraction peaks at $2\theta = 31.778^\circ, 34.428^\circ, 36.258^\circ, 47.548^\circ, 56.608^\circ, 62.868^\circ, 66.388^\circ$ and 67.968° corresponds to their miller indices ((100), (002), (101), (102), (110), (103), (200), and (112)), indicating that the phase of the ZnO catalyst is in a hexagonal (wurtzite) structure. The planes are closely matched with the literature data (JCPDS Card, No. 36-1451). The crystallite size of the prepared pristine ZnO catalyst was calculated using Debye-Scherrer equation (7).

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (7)$$

Where, 0.89 is the Scherrer's constant, λ is the wavelength of X-rays (0.154 nm), θ is the Bragg diffraction angle and β is the full width at half-maximum (FWHM) of the diffraction peak. The average particle size of the sample was found as 56.35 nm. The sharp and narrower peaks showed that the obtained catalyst is highly structured and crystalline nature.

III.3 Field emission scanning electron microscopy (FE-SEM)

The prepared pristine ZnO catalyst was characterized by FE-SEM analysis to determine the surface morphology. The results are shown in Fig. 1c. It is found out that the catalyst was formed in an independent hexagonal rod-like arrangement which were spread in an indiscriminate manner.

IV. SONOCATALYTIC DEGRADATION OF THE EY DYE

IV.1 Effect of aqueous phase pH on catalytic activity

The effect of pH on sonocatalytic degradation of EY was carried out with split probe to find out the optimum pH for the degradation process. The aqueous phase of the dye molecules were adjusted using 0.1N of HCl and NaOH respectively. The optimum pH is the important parameter which mainly depends on the degradation efficiency of the dye under ultrasonication. Degradation of the EY dye molecule was favored for acidic pH. Then it starts decreasing towards alkaline pH as illustrated in Fig 2a. At low pH, as EY dye species mainly exist in the neutral form and EY molecules can penetrate into cavitation bubbles and subsequently may undergo oxidation/pyrolysis, which accounts for the increased degradation efficiency of EY at low pH values [15]. Catalyst surface is positively charged in acidic pH whereas it is negatively charged under alkaline media. The acidic dye solution favors adsorption of the dye molecules onto the catalyst surface that enhances the efficiency of the degradation of dye molecules. Secondly, increase in the degradation rate in acidic conditions might be due to the adsorption of dye molecules onto the surface and consequently its degradation with more hydrophobic character of the resulting dye molecule with respect to the basic conditions in which the dye molecule has more hydrophilic character.

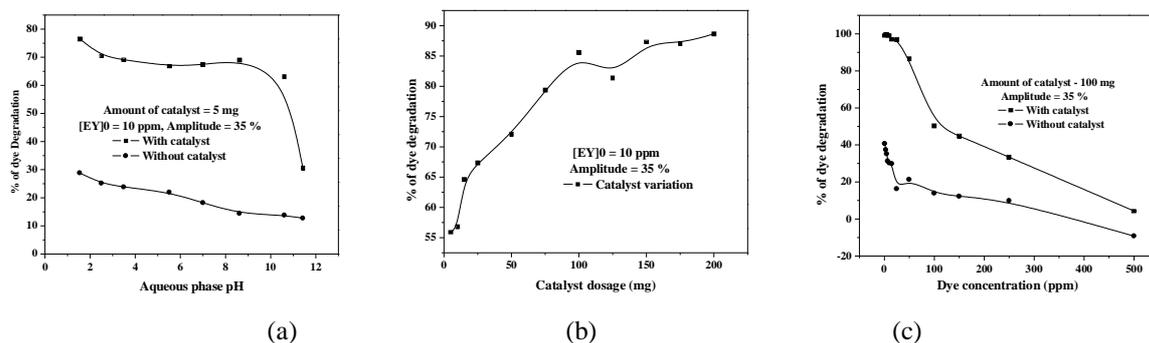


Fig. 2 (a) Effect of initial pH for the degradation of EY dye with and without catalyst; (b) Effect of catalyst dosage on the degradation of EY dye; (c) Effect of dye concentration on the degradation of EY dye with and without catalyst.

As the hydrophobic character of the molecule increases, the chance of presence of the molecule near the cavitation is higher and this leads to further degradation. On increasing the pH above 7, the rate of degradation of dye decreases, as the pH of the solution is increased, more OH⁻ ions will be available and these ions are absorbed on the surface of semiconductor making it negatively charged and as a result of repulsive force between two negatively charged species, the approach of electron rich dye to the semiconductor surface will be retarded. This will result into a decrease in the rate of degradation [16].

The influence of ultrasound on the degradation of dyes with different pH with and without the catalyst has also been carried out. It was observed that in the presence of catalyst with the passage of ultrasound irradiation enhances the percentage of degradation process but in the absence of the catalyst there was a lowest percentage of degradation was observed as shown in Fig. 2a.

IV.2 Variation of catalyst dosage

The effect of catalyst dosage on the degradation of the dye molecule was performed. The catalyst dosage was varied and the dye concentration was kept constant (10 ppm) with 35 % amp of energy input. It was observed that the percentage degradation of the dye molecules was increased with increasing catalytic amount as shown in Fig. 2b. The maximum degradation occurred up to 85.5% for 100 mg of catalyst dosage. These results confirm that the dye molecules not only undergo decolorization but may be completely oxidized under the present experimental conditions.

IV.3 Variation of initial dye concentration

The variation of initial dye concentrations that will give an idea about the degradation efficiency of the EY dye molecule with optimized dose of catalyst was carried out. The dye concentrations were varied with optimized amount of catalyst in neutral pH with 35% amplitude energy input (total volume of 10 mL). It was observed that under the present

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experimental conditions, the greatest percentage of degradation proceeds up to 50 ppm of initial dye concentration (86.4 % degradation) after that, the percentage of dye degradation decreased upto 4.3% degradation for the 500 ppm of initial dye concentration. The variation of dye concentration was also carried out in the absence of catalyst also is presented in Fig.2c. It is noted that minimum amount of percentage degradation was occurred in the absence of catalyst.

IV.4 Kinetics of EY dyedegradation

Kinetics of EY dye degradation with and without catalyst was studied in detail for different initial dye concentrations under ultrasonicirradiations and the results are shown in Fig.3a.

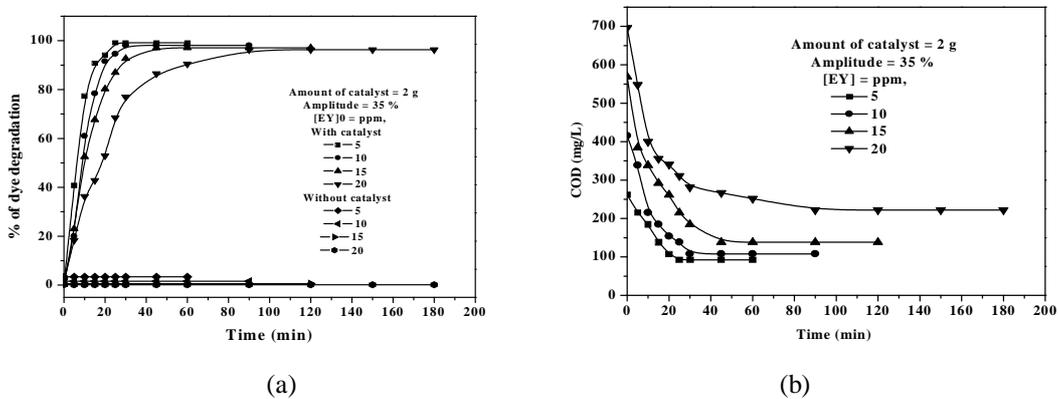


Fig. 3(a) Degradation kinetics of 10 ppm of EY dye at 35 % amplitude energy input; (b) COD reduction for the degradation kinetics for 5, 10, 15 and 20 ppm of EY dye at 35% amplitude.

For eg., 99.0% degradation was achieved for 5 ppm of dye concentration in 25 min and 96.3% degradation for 20 ppm of dye concentration in 90 min. The kinetic measurements such as 5 to 20 ppm of dye concentrations show more than 90% degradation is represented in Table. 1. The results proved that the dye molecule was almost completely degraded under the present experimental conditions. The reduction of chemical oxygen demand (COD) as a function of time during degradation of dye molecule for various initial dye concentrations like 5, 10, 15 and 20 ppm were also shown in Fig. 3b. All the kinetic data were analyzed by pseudo first order rate equation using equations 9 and 10

$$-dD_{eq}/dt = (1)kD_0 \quad (9)$$

$$\ln(D_{eq}/D_0) = kt$$

$$(10)$$

where, pseudo-first order kinetic plots are shown in Fig.4. The % degradation and kinetic rate constant values are shown in Table. 1.

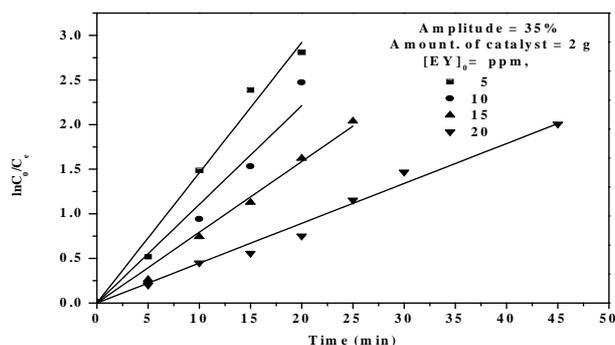


Fig. 4 Pseudo first order kinetic plots of EY dye degradation.

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Table.1 Pseudo-first order kinetic rate constants and percentage of EY dye degradation

Initial EY conc. (ppm)	Energy input (% amp)	Time (min)	% Degradation	Rate constant, k (min ⁻¹)	R ²
5	35	25	99.1	14.60×10 ⁻²	0.99204
10	35	30	98.0	11.057×10 ⁻²	0.98152
15	35	45	97.0	07.93×10 ⁻²	0.99731
20	35	90	96.3	4.469×10 ⁻²	0.99241

Rate constant (k) values were calculated using the slope of the straight lines. Reaction rate constant decreases with increasing dye concentrations.

IV.5 Effect of electrolytes on dye degradation

Industrial waste waters may contain many electrolytes in the dissolved state it may interfere in the degradation of organics. Therefore, the investigations on the effect of dissolved electrolytes such as NaCl, KCl, Na₂CO₃, NaHCO₃ and MgSO₄ on the degradation of dye molecules has been carried out and the concentration of electrolytes varied from 0.5-5 wt % and all other experimental parameters were kept constant. The results are shown in Fig. 5.

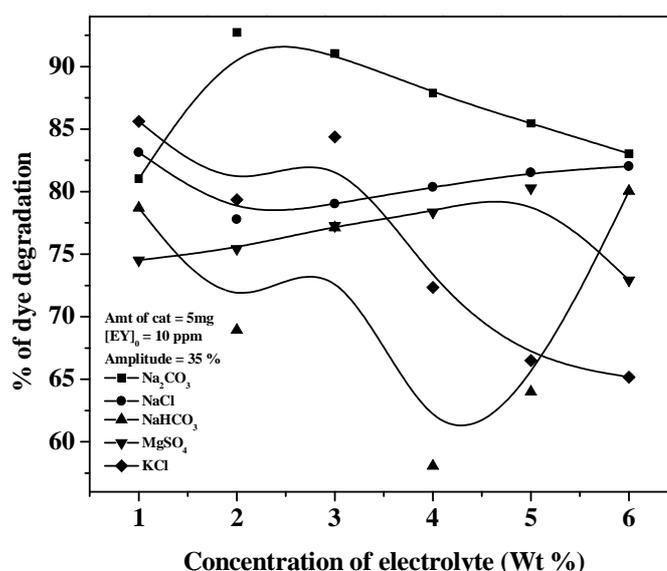


Fig. 5 Effect of electrolytes on the degradation of EY dye for 10 ppm of dye concentration at 35% amplitude.

Interference of electrolytes on the degradation processes were of lesser impact except that of chloride ions. It is observed that there is reduction in the presence of bicarbonate and this is because of bicarbonate halide ions act as scavengers for radicals like hydroxyl and sulfate ions in the oxidation processes.

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V.CONCLUSION

ZnO nanorod catalysts were prepared by precipitation method and the nanorods were characterized by FT-IR, XRD and FE-SEM techniques. The catalytic activities were studied by taking Eosin yellow as a model pollutant with power ultrasound in the presence and absence of catalysts. Characterization of the ZnO nanorods confirmed that the prepared catalyst are nanorods and nano crystalline. The sonochemical degradation occurs via bubble collapse and hot spot mechanism in aqueous solution through sonication. Interference of electrolytes on the degradation processes were of lesser impact except that of KCl. It was confirmed that almost complete mineralization of dye may be achieved without the formation of toxic by-products.

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