

Photolytic Degradation of Organic Dyes Using Photocatalyst Nanoparticles for Waste Water Treatments



Chemistry

KEYWORDS : XRD, FTIR, UV-spectroscopy, TGA and SEM , MAS NMR spectroscopy, photocatalysts, MOD

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ABSTRACT

Nanotechnology has the impressive developments in the field of synthesis, characterization & application in material and chemical science. In the present study the photolytic degradation is done using metal oxides like ZnO, AgO and TiO₂. The prepared nanoparticles are studied with XRD, FTIR, UV-spectroscopy, TGA and SEM, MAS NMR spectroscopy. The ZnO, AgO and TiO₂ are loaded with activated carbon and degradation are studied separately. Intense study of ZnO, Ag₂O and TiO₂ as a photocatalyst because of its high chemical stability, no toxicity, low cost and excellent degradation of organic compound from waste water form textile, paper, dairy, plaint and sugar industry. This method is superiority of photocatalytic degradation by semiconductor in waste water treatment is due to its advantages over the traditional techniques.

1. INTRODUCTION :- In the field of Chemistry, Physics and material science nanotechnology play an important role in semiconductors insulators and catalyst. The presence of large amount of toxic and waste materials in waste water from industry caused various healthcare problems. Purification of waste water by using photocatalyst like ZnO nanoparticle has an important role in photodegradation of organic dyes like methyl orange. In the field of nanotechnology, aim to prepare the nanoparticles with same chemical and physical properties with their limited size and a high density of corners must have a low surface free energy. In the water purification technology nanoparticles act as photocatalyst in the presence of sun light. The synthetic dyes are used almost in all branches of textile, paint and research laboratory. About 8000- 12000 tones of dye are produced per year for the various industrialization activity, and various dyes will be thrown out in waste water as a byproduct. It is a serious problem in environmental ecosystem so that requirement of removal of such organic compound from waste water is essential for nature stability.

In present work oxidation processes include of heterogeneous catalyst to degradation of a wide range of Methyl Orange Dye (MOD) from waste water of textile, paint and other industry. The photocatalyst ZnO are used as a catalyst due to its high efficiency, high stability, low costs and no toxic properties. The used ZnO catalyst have higher catalytic activity under sun light to adsorb large amount of organic compound. The chemical structure of Methyl Orange Dye is

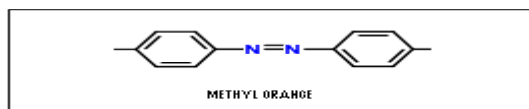


Fig- 1 Structure of Methyl Orange

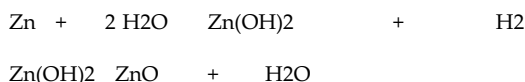
2. MATERIALS AND METHOD :-

2.1 Chemicals and Reagents :-

Distilled Water are prepared in laboratory distilled water plant, Sodium bicarbonates 99.8% pure A.R. and Zinc metal are purchased from LOBO Chem. Pvt. Ltd.

2.2 Preparation of ZnO powder

powder are prepared from Zinc Oxide in the laboratory by electrolyzing a solution of sodium bicarbonate with Zinc metal. Zinc hydroxide and hydrogen gas are produced. The prepared zinc hydroxide decomposed to form Zinc Oxide.



2.3 Photocatalytic reactor

Textile dye degradation experiments were carried out in the experimental equipment schematically depicted in Figure 2. The basic part of the apparatus is the photo reactor with the immobilized ZnO. The body of the reactor was made of the polycarbonate. The body was covered with the UV light transparent quartz glass. The inner dimensions of the reactor are: 70 mm × 45 mm × 3 mm (length × width × depth). The inner space of the reactor was divided by 3 spacers to ensure required liquid flow pattern.

The immobilized ZnO was irradiated through the quartz glass by UV-lamps. Three UV-lamps were tested in our experiments: 500 W high pressure mercury lamp, 6 W lamp (UVGL 58, UVP) and 4 W lamp (UVGL-25, UVP). The last two lamps emitted monochromatic light at wavelengths 254 or 365 nm, respectively, and were placed directly at the surface of the quartz glass. Only a half of the 6 W lamp was used to irradiate the inner space of the photo reactor. The stock solution containing dissolved dye was pumped from a bottle by the peristaltic pump through the reactor with the immobilized ZnO and then it was returned back to the bottle. The volumetric flow rate of the liquid was set to 0.5 mL min⁻¹ or 2 mL min⁻¹. The entire volume of the liquid in the apparatus equalled 65 mL. The stock dye solution in the bottle was stirred by the magnetic stirrer and the concentration of the dye in the liquid was measured by the immersion probe of the UV-VIS spectrophotometer.

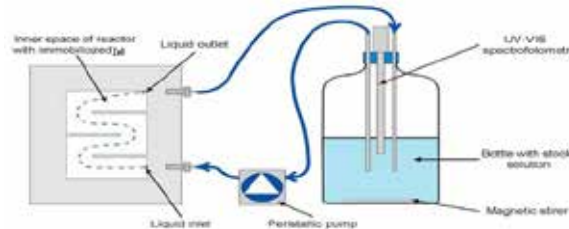


Fig- 2 Photodegradation of Methyl Orange Dye (MOD)

2.4 Experimental Method

Five immobilizers are used for the study of degradation of methyl orange from waste water of textile and paint industry. The prepared nanoparticles of Zinc Oxide are applied inner side of the reactor with concentration 0.8 mg/ml; 1.0

gm/ml ; 1.2 mg/ml ; 1.4 gm /ml and 1.6 mg/ml with poly-vinyl alcohol solution by syringe needle to the saturated boric acid solution. The formed particles were then thoroughly washed with the distilled water.

2. 5. Characterization techniques

Structural and optical properties of the ZnO nanoparticles were determined by using Transmission Electron Microscopy (TEM) (Hitachi: H-7500; Resolution: 2 Å), X-ray Diffraction (XRD) (Rikagu Mini-2 using CuK α 1, λ = 0.15406 nm radiations), Differential Scanning Calorimetry (DSC) (TA Instruments USA, DSC Q10) in the range 50-600 °C, Fourier Transform Infra-Red spectroscopy (FTIR) (Thermo-USA, FTIR-380) in the wavelength range of 400 - 4000 cm⁻¹ and UV-Visible spectroscopy (Systronic-2203).

3. RESULT AND DISCUSSION

3.1 XRD Analysis

Figure 3.1 represents the X-ray diffraction pattern of ZnO Nanoparticles. In this XRD patterns analysis, we determined peak intensity, position and width, Full-width at half-maximum data. The diffraction peaks located at 31.84°, 34.52°, 36.33°, 47.63°, 56.71°, 62.96°, 68.13°, and 69.18° have been keenly indexed as hexagonal wurtzite phase of ZnO with lattice constants $a=b=0.324$ nm and $c=0.521$ nm, and further it also confirms the synthesized nanopowder was free from impurities. The synthesized ZnO nanoparticle diameter was calculated using Debye-Scherrer formula

$$d = 0.89\lambda / \beta \cos\theta$$

Where Scherrer's constant=0.89 ,

λ is the wavelength of X-rays,

Bragg diffraction angle= and Full width at half-maximum = β diffraction peak corresponding to plane (101).

The average particle size of the sample was found to be 16.23 nm which is derived from Full width at half-maximum

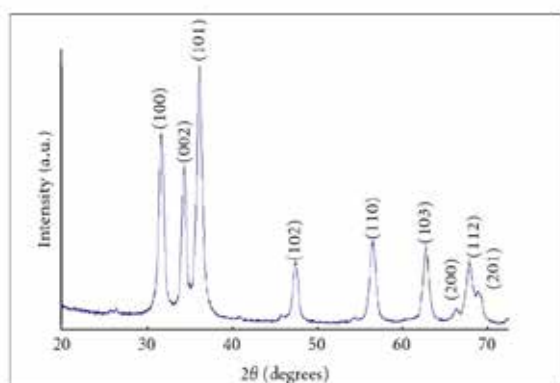


Fig - 3.1 XRD Pattern of ZnO nanoparticles

3.2 FTIR Analysis :

Figure 3.2 shows FTIR spectra of ZnO nanoparticles. Infrared studies were carried out in order to ascertain the purity and nature of the metal nanoparticles. Metal oxides generally give absorption bands in fingerprint region i.e. below 1000 cm⁻¹ arising from inter-atomic vibrations. The peak observed at 3453cm⁻¹ and 1120 cm⁻¹ are may be due to O-H stretching and deformation, respectively assigned to the water adsorption on the metal surface. The peaks at 1636 cm⁻¹ and 621 cm⁻¹ are corresponding to Zn-O stretching and deformation vibration, respectively.

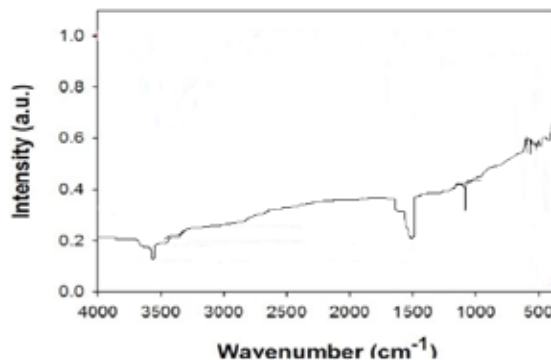


Fig.3.2 FTIR analysis

3.3 UV-Visible Absorption

Figure 3.3 shown the absorption spectrum of ZnO nanopowder. The size of the nanoparticles plays an important role in changing the entire properties of materials. Thus, size evolution of semiconducting nanoparticles becomes very essential to explore the properties of the materials. UV-visible absorption spectroscopy is widely being used technique to examine the optical properties of nanoparticles.

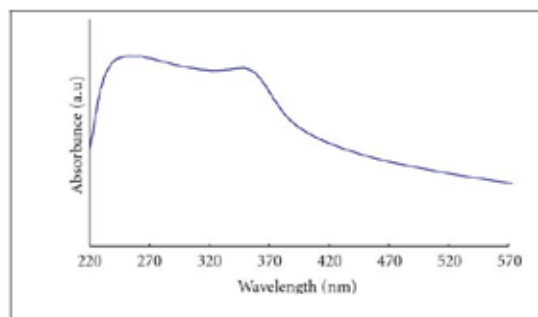


Fig-3.3UV-Visible Absorption

3.4 TGA Analysis

Figure 3.4 show the result of Transmission Electron Microscopy (TEM) (Hitachi: H-7500; Resolution: 2 Å)

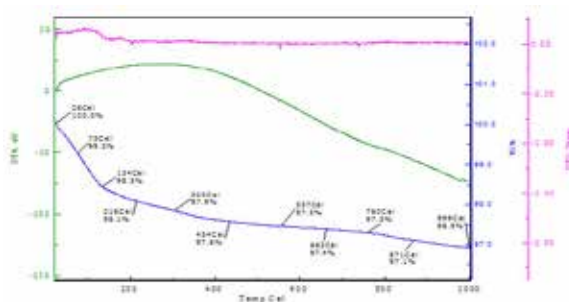
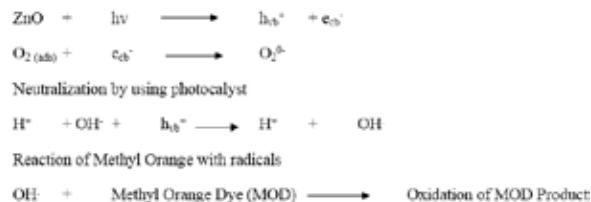


Fig-3.4 TGA Analysis

4. PHOTODEGRADATION MECHANISM

The degradation of Methyl Orange dye(MOD) by ZnO nanoparticles could be obtained by photogeneration of electron-hole pairs between the conduction and valence band due to excitation of ZnO under UV radiation. This phenomenon create a separation, which might be helpful for the generation of active radicals for the degradation of organic dyes from industrial waste water. Holes could be trapped by hydroxyl group to form highly reactive hydroxyl radical , while electrons can be reacted by the adsorbed

oxygen molecule to produce superoxide radicals of oxygen molecules which can finally be reduced to OH radicals. The Produced radicals are highly reactive and could effectively degrade organic dyes like MOD from waste water of industry . The degradation mechanism are as below.



From the above reactions it is evident that the photocatalytic process mostly depends on the efficiency to form oxygenated radicals via capture of electrons and holes that are generated in metal oxide nanoparticles. Oxide materials can present ionic or mixed ionic/electronic conductivity and it is experimentally well established than both can be influenced by the nanostructure of the solid. The number of electronic charge carriers in a metal oxide is a function of the band gap energy according to the Boltzmann statistics When MOD oxidized with superoxide radicles to produce product of Methyl Orange Dye.

5. CONCLUSION

The combination of the photocatalyst used in the immobilization with concentration 0.8 mg/ml ; 1.0 gm/ml ; 1.2 mg/ml ; 1.4 gm/ml and 1.6 mg/ml with polyvinyl alcohol solution to constant time 150 min. It was absorbed that the photocatalyst applied in proportion 1.2 mg/ml with time 150min gives 94.3 % removal of methyl orange dye (MOD) of the waste water from the industry like textile , plant , dairy and sugar. The tabulated result as

Sr. No.	Photocatalyst Concentration (mg/ml)	10 % Polyvinyl Alcohol (ml)	Time (Min)	% Removal Of MOD
1	0.8	10	150	76.02
2	1.0	10	150	82.7
3	1.2	10	150	94.3
4	1.4	10	150	91.0
5	1.6	10	150	89.0

Now I will suggested that by using the mixture of photocatalyst applied in immobilization inner site of column increases the adsorption gives more separation of organic compound from waste water. The given method of purification is vary easier and more economic for the waste water purification.

6. ACKNOWLEDGMENT

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