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Characterization of Synthesized ZnO Nanoparticles and their Application in Photodegradation of Methyl Orange Dye Under Fluorescent Lamp Irradiation

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***Abstract*—** *Nanotechnology is promising field in waste water treatment. The aim of this study thus was to assess the use of synthesized ZnO nanoparticles in photo degradation of dyes under fluorescent light source of irradiation. on the surface of zinc oxide nanoparticles. The basis of ZnO/UV photo-catalytic process is the semi-conduct optical stimulation of ZnO as a result of electromagnetic ray absorption. Precipitation technique was used to synthesize ZnO nanoparticles. By varying experimental conditions two samples L_1 and L_2 were synthesized. They were characterized using Power X-ray Diffraction (PXRD). The PXRD results showed diffraction peaks which were indexed to ZnO reference as per JCPIDS file 80-0075. The size of ZnO nanoparticles was found to be 26 nm. The effect of process parameters like, amount of the photocatalyst, initial dye concentration and contact time on the extent of photodegradation have been investigated. The results showed that percentage removal of the dye increases with increase in contact time and amount of photocatalyst, it decreases with increase in initial dye concentration. The results revealed that dyes could be removed by semiconducting nanomaterials assisted by photocatalytic degradation*.

***Keywords*—** *Photodegradation, ZnO Nanoparticles, Organic dyes,fluorescent irradiation source*.

I. INTRODUCTION

Dyes are important class of synthetic organic compounds used in textile industry, paper, dyeing and plastic industries as colour for dyeing their products. A huge amount of water is used which results in production of dye-containing wastewater (Wojnarovits & Takacs, 2008). One of the main sources of severe pollution problems worldwide is the textile industry and its dye-containing wastewaters. These industries use approximately 10000 dyes and pigments (dos Santos *et al.*, 2007). 10-25% of the textile dyes and pigments are lost during the dyeing process, and 2-20% are directly discharged as aqueous effluents in different environmental components (Ali, 2010). These residual dyes pose a great danger to the environment especially the natural water resources. The discharge of dye-containing effluents into the water environment is undesirable, not only because of their colour, but also because many of dyes released and their breakdown products are toxic, carcinogenic or mutagenic to life (dos Santos *et al.*, 2007). Without adequate treatment, these dyes can remain in the environment for a long period of time. For instance, the half-life of hydrolyzed reactive methyl blue is about 46 years at pH 7 and 25°C (Fazli *et al.*, 2010).

The treatment and recycling of dye-containing wastewater has been highly recommended by environmental protection agencies like WHO and UNEP. This is due to the high levels of pollutants in dyeing and finishing processes (i.e. dyes and their breakdown products, pigments, dye intermediates, auxiliary chemicals and heavy metals. In an effort to reduce the environmental effects of organic dyes, various techniques have been employed. These techniques include coagulation and sedimentation in which sediments again create disposal problems. These methods are not only expensive but also highly ineffective. The use of synthesized nanoparticles in photo degradation of dyes is a new promising field in waste water treatment. This involves the degradation of organic dyes by irradiating them with ultraviolet light on the surface of zinc oxide. The entire process is called photo-catalytic degradation of dyes on ZnO. The basis of ZnO/UV photo-catalytic process is the semi-conduct optical stimulation of ZnO as a result of electromagnetic ray absorption. ZnO has an energy band of 3.2 eV which can be activated by radiation of UV in the wavelength of 387.5 nm. On the earth's surface, sunlight begins in the wavelength of 300 nm and only 4-5 percent of solar radiation may be used by ZnO (Chatterjee & Dasgupta, 2005).

The use of ZnO nanoparticles in photo catalytic colour removal is cheaper and does not pose disposal challenge, also the technology uses small amount of energy. The use of nanomaterial's like ZnO nanoparticles offers a promising technology for reduction of global environmental pollutants. This semiconductor catalyst has been preferred because of its wide energy band gap, high photo sensitivity, stability and low cost (Nishio *et al.*, 2006).

This study examined the use of fluorescent light sourse of irradiation and synthesized ZnO nanoparticles in photodegradation of dyes. Methyl orange (MeO) is an organic dye with a chemical formula of $C_{14}H_{14}N_3SO_3Na$ and characterized by sulphonic groups, which are responsible for high solubility of these dyes in water (Guettai & Amar, 2005).

II. MATERIALS AND METHODS

ZnO nanoparticles were synthesized using precipitation method. In this method, ZnO nanoparticles were prepared in two ways. In the first set, 100ml of 1M $ZnSO_4$ solution was added to 100ml of 2M NaOH solution in drops. When the addition was complete, the mixture was kept at room temperature under constant stirring using magnetic stirrer for a period of 2-4 hours.

The resultant precipitate obtained was filtered then rinsed with distilled water. The formed white precipitate of $Zn(OH)_2$ was allowed to settle, filtered using filter paper of pore size

0.4µm in a suction pump, washed with distilled water several times and dried in hot oven at 150^0C for 45 minutes. The synthesized ZnO nanoparticles were further irradiated at 180 W with microwave radiation in a microwave oven for 30 minutes. This was named as sample L_1. The above procedure was followed to synthesize ZnO nanoparticles in different experimental conditions. $ZnSO_4$, NaOH and oxalic acid were used as stabilizing agent.

The resultant ZnO nanoparticles particles after irradiation were collected and stored in brown bottles.

The synthesized ZnO nanoparticles were subjected to PXRD,

Preparation of dye solution: The stock solution (1,000ppm) was prepared and stored in brown bottles. The stock solution was diluted to get different required initial concentrations of the dye used. Dye concentration was determined by using absorbance measured before and after the treatment using UVVIS spectrometer.

Measurement of concentration of dye solution: The stock solution was diluted to different initial concentrations10, 20, 30, 40 and 50 ppm for methyl orange in standard measuring flasks by making necessary dilutions with required volume of distilled water. The optical density of each dye solution was measured using UV-VIS spectrophotometer (model – No-SL-150 Elico) at maximum wavelength value for MeO dye. A plot of optical density versus initial concentration was drawn. This plot was used as standard graph for estimation of dye by interpolation technique. The values of optical density for dye solutions before and after removal of dye were obtained by using UV-VIS spectrophotometer. Using these optical densities the corresponding dye concentration was obtained from the graph.

Determination of extent of removal of the dye: Stock solution of MeO dye (1,000ppm) was suitably diluted to get the required initial concentration from 15 – 45ppm. A 10ml of the dye solution of known initial concentration (C_1) wastransferredto 50ml beaker. Required amount of the photo-catalyst (L_1 and L_2) was exactly weighed and then transferred to the dye solution with different C_1. The beaker wasthen exposed to fluorescent light and direct sunlight for a fixed period of contact time.

After bleaching, the optical density (OD) of these solutions was measured using UV-Vis spectrophotometer and the final concentrations (C_2) obtained from the standard graph. The extent of removal of the dye in terms of percentage removal was calculated using the following relationship.

$$Percentage\ removal = \frac{100(C_1 - C_2)}{C_1}$$

Where

C_1 = initial concentration of dye (ppm)

C_2 = final concentration of dye (ppm)

Factors that govern degradation process: The effect of various experimental parameters on degradation of MeO dye in the aqueous suspension by ZnO nanoparticles were studied by varying the experimental conditions; concentration of the dye, amount of the sample and contact time.

III. Results and Discussion

Powder X-Ray Diffraction (PXRD)

Figure 1 below show the XRD patterns of the synthesized Zinc oxide nanoparticles.

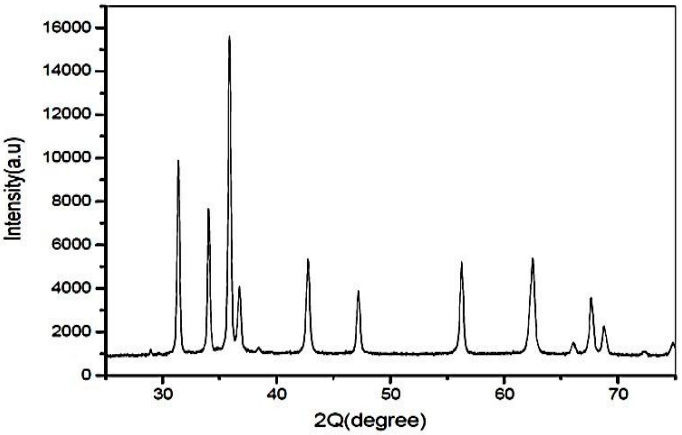

Fig. 1. XRD patterns of the synthesized zinc oxide nanoparticles.

The diffraction peaks at 31.7, 34.4, 36.2, 47.4, 56.4, 62.5, 67.6, and 68.7 can be indexed to ZnO as per the standard JCPDS file 80-0075. Powder diffraction patterns are characteristic of a particular substance. It is its ―fingerprint‖ and can be used to identify a compound. Powder diffraction data from known compounds have been compiled into a database by the JCPDS. The synthesized sample can be confirmed to be ZnO nanoparticle. Clear crystallinity of the ZnO nanoparticles was observed. The samples had similar patterns. This suggests that the oxalic acid added as stabilizing agent had no effect on the wurzite structure of ZnO (Herrmann and Helmoltz, 2010).

Similar results were obtained by Gu *et al*. (2004) who obtained XRD peaks at scattering angles (2θ) of 31.3670, 34.0270, 35. 8596, 47.1635, 56.2572, 62.5384, 67.6356, and 68.7978, corresponding to reflection from 100, 002, 101, 102, 110, 103, 200 and 112 crystals. They indexed the XRD patterns to ZnO nanoparticles reference JCPDS file 80-0075 as well.

The average crystallite size of ZnO nanoparticles was estimated according to the diffraction reflection by using Debye-Scherrer equation (Holzwarth& Gibson, 2011):

Photodegradation Studies

The optical density of each dye was measured using UV-VIS spectrophotometer at maximum wavelength of 480 nm. A plot of optical density versus initial concentration is shown in figure 2. This plot was used as standard graph for estimation of dye concentration by interpolation technique.

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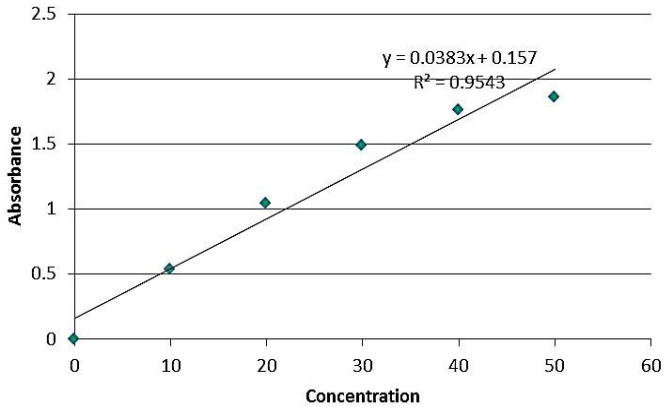

Fig. 2. Standard curve for methyl orange dye.

Effect of variation of initial concentration of dye on photo degradation of methyl orange dye

Table I below shows the effect of variation of initial concentration of Methyl orange dye on photodegradation.

TABLE I. Effect of variation of initial concentration of dye on photo degradation of methyl orange dye.

Radiation	Sample	Concentration of dye		
		15 mgL^{-1}	30 mgL^{-1}	45 mgL^{-1}
Fluorescent	L_1	14.23	26.40	41.31
	% removal	92.0 %	89.0%	88.2%
	L_2	14.04	29.81	38.03
	% Removal	91.8%	88.9%	88.0%

Photo catalytic degradation of the dye was found to decrease with increase in initial concentration of methyl orange. This could be due to more dye molecules than ZnO nanoparticles; in this case the photocatalyst became the limiting factor. It was noted that degradation rate decreased with increase in dye concentration. The decrease in dye degradation could be attributed to reduction of OH^- radicals on the catalyst surface when covered by dye ions (Poulis and Tsachpinis, 1999).

The results are similar to those reported by *Li et al.* (2005) when methyl orange was irradiated with sunlight source, the degradation of the dye decreased as the dye concentration increased. This due to the fact that the generation of $OH^·$ Radical on the catalyst surface is reduced since the active sites are covered by dye ions. Also Kansal *et al.* (2006) concluded that photo-catalytic degradation of methyl orange decreased as the dye concentration increased.

This decrease is as a result of increasing the number of photons absorbed by catalyst lower concentration (Davis, 2006). According to Shanthi and Muthuselvi (2012), the decrease in photo degradation is as a result of dye molecules imparting darker colour to the solution which acts as a filter to the incident light reaching the photo catalyst surface. Sampa and Biney (2004) further explained that the increase in the concentration of a dye solution result in the photons getting intercepted before they can reach the catalyst surface, thus decreasing the absorption of Photons.

Effect of variation of dose of photo catalyst (L1 and L2) on photo degradation of MeO dye

The initial concentration 30 mgL^{-1} of the dye and pH in all beakers were kept constant at pH 7.0 and the dose of photo-catalyst was varied from 200 mgto 400mg with a contact time of four hours and the results are shown in table II.

TABLE II. Effect of variation of dose of photo catalyst (L1 and L2) on photo degradation of MeO dye.

Radiations	Sample	Amount of photo-catalyst		
		200mg	300mg	400mg
		6.57	2.39	1.50
Fluorescent	L_1	26.40	26.88	26.55
	% removal	92.0	96.4	98.5
	L_2	29.81	27.46	25.23
	% removal	92.6	97.5	97.9

Photo catalytic degradation of methyl orange dye increased with an increase in concentration of ZnO particles. This is due to increase in photo-catalyst molecules available to degrade the dye. Further increase of ZnO concentration increase turbidity of the solution and decreases light penetration into the solution and therefore, removal efficiency decreases (Kartal *et al*., 2001).

The results of this study are similar to those of Joshi and Shrivastava (2012) who studied removal of methylene blue using ZnO nano particles, by varying the dose of photo catalyst from 2.0 g/l to 5.0 g/l and degradation increased from 86.0% to 92.8% as shown in table. The increase in the amount of catalysts increased the number of active sites of the photo catalyst surface, which in turn increased the number of hydroxyl and superoxide radicals (Sampa and Biney, 2004).

Effect of variation of contact time on photo degradation of MeO dye

The results are presented in table III below.

TABLE III. Effect of variation of contact time on photo degradation of MeO dye.

Radiations	Sample	Contact time in hours				
		1	2	3	4	5
Fluorescent	L_1	10.95	8.77	5.95	2.68	1.32
	% removal	63.5	70.8	80.2	91.1	95.6
	L_2	11.57	8.15	5.33	2.06	0.70
	% Removal	61.4	72.8	82.2	93.1	97.7

The results indicated that, the percentage removal of dye increases with increase in contact time. This is in agreement with the results reported by Shanthi and Muthuselvi (2012), who studied the effects of contact time on removal of malachite green using ZnO nano particles. The increased contact time causes the photo-generated OH^- radicals and other peroxide radicals all being highly oxidant species decompose the dyes completely to mineral end products (Hofman *et al*., 1995).

IV. CONCLUSION

Photocatalytic degradation of dye was found to decrease with increase in initial concentration of methyl orange possibly due to higher dye molecules than ZnO nanoparticles.

Photocatalytic degradation of methyl orange dye increased with an increase in concentration of ZnO nanoparticles to degrade the dye.

The findings indicate four hours as the optimum contact time. Photodegradation can be used for treatment of industrial effluents containing heavy metals and dyes. In place where we have plenty of sunlight solar radiation can be used for degradation. Light intensity is a major factor in photocatalytic degradation because electron hole pairs are produced by light energy.

Recommendations

In future, researchers should focus on the development of novel nanomaterials/nanocomposites with a high surface area, sufficient surface functional groups and high sorption ability, for the removal of organic dyes. The environmental threat of organic dyes is becoming more and more thus; further improvements must be made in the direction of the development of materials with greater stability (resistance to pH changes and concentrations of chemicals present in contaminated water) and the capacity for the simultaneous removal of multiple contaminants, such as toxic metal ions, organic dyes and bacterial pathogens.

Considering the economics of adsorbents, it is necessary to synthesize low-cost effective and recyclable adsorbents for their extensive application in our daily life. Treatment technologies should be developed for the purification of water in order to meet the demand of increased environmental pollution.

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