A Study of the Morphology of Synthesized ZnONa nophotocatalyst and their Application in removal of Dyes under Solar irradiation

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ABSTRACT

Environmental pollution by toxic organic contaminants is a global menace and its magnitude is increasing significantly and therefore declining water quality has become a global issue. Waste products produced from the textiles, dyeing, paper and plastic industries are predominantly responsible for contaminating the water bodies. Organic dyes produce toxic aromatic amines that are carcinogenic to human beings and harmful to the environment yet they are non-biodegradable. In an effort to lessen the environmental effects of these dyes, various techniques have been utilized. However, these techniques are expensive and ineffective resulting in intensively coloured discharge and high concentration of dyes from the treatment facilities. 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. This involves the degradation of methyl orange dye using sunlight and fluorescent light as sources of radiation 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), Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy. 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 images obtained by SEM showed rod shaped clusters of nanoparticles. They were distributed well within a range of 100 nm which is a favorable property to exhibit better photo catalytic activity. 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.

Key Words: Photodegradation, ZnO, Nanoparticles, Organic dyes

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 10,000 dyes and pigments (dos Santos*et al.,* 2007). Between 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 andtheir breakdown products are toxic, carcinogenic and mutagenic to life (dos Santos *et al.,* 2007). Without adequate treatment, these dyes can remain in the environment for a long period oftime. For instance, the half-life of hydrolyzed reactive methyl

blueisabout 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, that is, 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 byirradiating them with ultraviolet light on the surface of zinc oxide. The entire process is called photo-catalytic degradation of dyes onZnO. The basis of ZnO/UV photo-catalytic process is the semi-conduct optical stimulation of ZnOas a result of electromagnetic ray absorption. ZnOhas 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 nanomaterials like ZnO nanoparticles offers a promising technology for reduction of global environmental pollutants. This semi-conductor 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 synthesized ZnO nanoparticles in photodegradation of dyes.Methyl orange (MeO) was used as a model dye since it is an organic dye similar to that used in the textile and paper industries. Methyl orange 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).
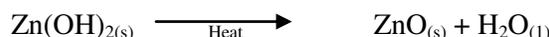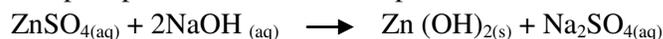
MATERIALS AND METHODS

ZnO nanoparticles were synthesized using precipitation method. In this method, ZnO nanoparticles were prepared in two ways. In the first set, 100 ml of 1 M $ZnSO_4$ 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 constant stirring using magnetic stirrer made the precipitation homogeneous and minimal particles which reduce the specific surface free energy of crystal nucleus which inhibit agglomeration and growth of the crystal nucleus so the particle size of the product is reduced (Zhang *et al.*, 2008).

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 procedure was repeated to synthesize ZnO nanoparticles in different experimental conditions. $ZnSO_4$, NaOH and oxalic acid were used as stabilizing agents. Thus one more sample was obtained and referred to as L_2.

The precipitation reaction was represented as

$$ZnSO_{4(aq)} + 2NaOH_{(aq)} \longrightarrow Zn(OH)_{2(s)} + Na_2SO_{4(aq)}$$

$$Zn(OH)_{2(s)} \xrightarrow{\text{Heat}} ZnO_{(s)} + H_2O_{(1)}$$

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

The synthesized ZnO nanoparticles were subjected to SEM, PXRD, FTIR and EDX, to confirm the nanostructure.

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 UV-Vis spectrometer.

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.

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:

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

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 (L_1 and L_2) and contact time.

RESULTS AND DISCUSSION

Powder X-Ray Diffraction (PXRD)

Figure 1shows the XRD patterns of the synthesized ZnO nanoparticles.
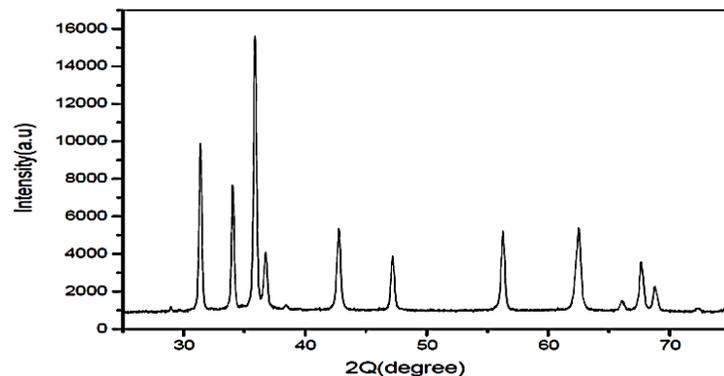
Figure 1: XRD patterns of the synthesized ZnO nanoparticles

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 and it's "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 &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):

$$T = \frac{0.9\lambda}{\beta cos\theta}$$

Where

λ -the wavelength of incident X- ray (1.5406A^0)

β - the full width for half maximum (FWHM),

Ө -the Bragg's angle for the peak

β- can be calculated using the equationβ = $(2\theta_2 - 2\theta_1)$, obtained to be 0.2755 radians. The

average crystallite sizes of synthesized ZnO nanoparticles were found to be around 26 nm. Similar results were obtained also by Shanthi and Kuzhalosai (2012), who characterized synthesized nano-ZnO using PXRD. For their three samples prepared. The sizes obtained were about18nm, 16nm and 12nm.

SEM Analysis

Figure 3 and Figure 4 shows the SEM diagram for sample $L_1$and L_2 at high magnification respectively.
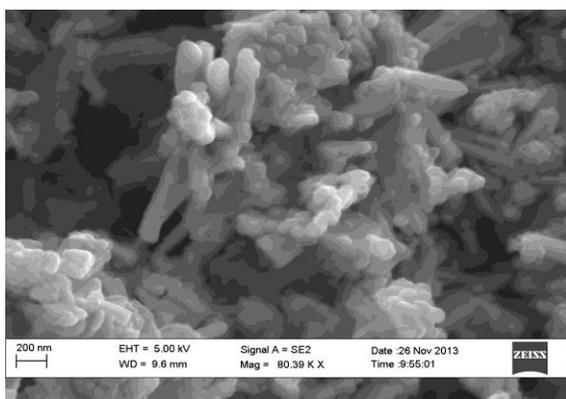
Figure 3: Magnified L_1 SEM
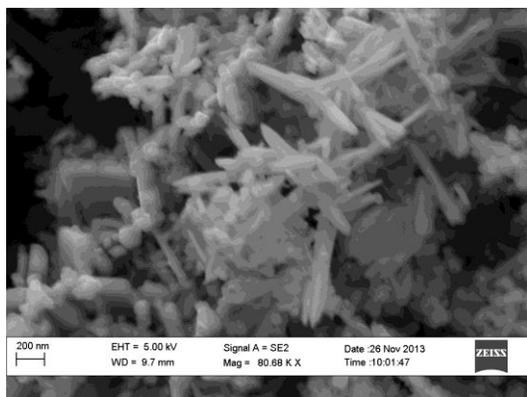
Figure 4: Magnified L_2 SEM

These images showed that the ZnO nanoparticles obtained formed rod shaped clusters distributed within the range of 100nm. The diagrams also show that the surface was not uniform but porous in nature. It shows that the nanocatalyst has considerable number of pores where there is a good possibility for the heavy metals to be trapped and adsorbed onto these pores and it is a good sign for effective adsorption of heavy metals (Joshi and Shrivastava, 2012).The photographs also showed

different surfaces for $L_1$and L_2. The L_1showed round ended while L_2 showed sharp ended nanoclustures. This showed that the stabilizing agent had an influence on the morphology of the samples.

Similar studies were made by Soltaninezhad and Amrnifar (2011). They studied surface morphology of ZnO nanoparticles produced by Spray Pyrolysis. The pictures observed showed particles that were spherical in shape. However Joshi and Shrivastava, (2012) determined the surface texture which was found to be rough and porous in nature.

Due to these close similarities, the ZnO nanoparticles were confirmed. The difference in distribution range is attributed to the level of accuracy during synthesis and also method of synthesis (Joshi and Shrivastava, 2012).

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.This plot was used as standard graph for estimation of dye concentration by interpolation technique.

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

Table 1 shows the effect of variation of initial concentration of methyl orange dye on photodegradation.

Table 1: 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}
Sunlight	L_1	0.85	2.68	10.77
	% removal	98.4%	96.1%	94.7%
	L_2	2.49	6.83	20.89
	% removal	97.4%	97.2%	93.6%

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 photo-catalyst 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 surfacewhen covered by dye ions (Poulis&Tsachpinis, 1999).

The results agrees with 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 generation of OH$^.$Radical on the catalyst surface which is reduced since theactive 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'slower 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 results 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 (L_1 and L_2) on photo degradation of MeO dye

The initial concentration 30 mgL⁻¹ of the dye and pHin 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 2.

Table 2: Effect of variation of dose of photo catalyst (L_1 and L_2) on photo degradation of MeO dye

Radiations	Sample	Amount of photo-catalyst		
		200mg	300mg	400mg
Sunlight	L_1	6.57	2.39	1.50
	% removal	92.1	94.2	96.0
	L_2	10.99	6.83	4.06
	% removal	93.4	97.2	96.5

Photo catalytic degradation of methyl orange dye increased with an increase in concentration of ZnOparticles. This is due to increase in photo-catalyst molecules available to degrade the dye. Further increase

of ZnO concentration increased 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 ZnOnano 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%. 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 3:

Table 3: Effect of variation of contact time on photo degradation of MeO dye

Radiations	Sample	Contact time in hours				
		1	2	3	4	5
Sunlight	L_1	11.84	6.83	5.99	1.45	0.58
	% removal	60.5	77.2	80.0	95.2	98.0
	L_2	9.12	4.23	2.68	0.97	0.53
	% removal	69.6	85.9	91.1	96.8	98.2

The results indicated that, the percentage removal of dye increased with increased 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 ZnOnano 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, 1995).

Conclusion

Photocatalytic degradation of dye was found to decrease with increase in initial concentration of methyl orange.Photocatalytic degradation of methyl orange dye increased with an increase in amount of ZnO nanoparticles. The optimum photocatalyst concentration was found to be 45mg/l with dye removal of 96.0% at contact time of 2 hours.

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The contact time for maximum removal of methyl orange was four hours.

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.

Acknowledgements

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