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Photocatalytic Degradation Efficiency of Nanoparticle For The Degradation of Azo Dye in Wastewater Effluents

KEYWORDS: Textile Wastewater; Degradation; Organic contaminants.

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ABSTRACT *The present work involved synthesis, characterization of ZnO nanoparticles for the photodegradation of textile effluents in wastewater. ZnO nanoparticle was synthesized by sol-gel process followed by calcination at 500°C and XRD, SEM and BET surface area methods were used to analyze its crystallite size, particle size and surface area. The crystallite size of ZnO nanoparticles was found to be comprised of 25-35 nm and the particle size was confirmed as 30 ± 5 nm with the large agglomerates with individual nanoparticles are heterogeneous and spherical in shape. The photocatalytic activity of ZnO nanoparticle was evaluated using reactive red 198 as a model compound. Under optimum conditions, nano ZnO has undergone complete degradation within 90 minutes of degradation time and it has showed higher degradation rate under the same condition.*

INTRODUCTION

Dyes play an important cause of waste water effluents because they are discharged in large quantity from various manufacturing industries. They create severe environmental problems due to the presence of organic and inorganic chemicals present in it. It creates the attention of many research workers due to the presence of potentially carcinogenic pollutants in contaminated water. Various approaches have been implemented to decontaminate these effluents [1]. Semiconductor photocatalysis is one of the most important photocatalytic processes has a great potential to the contribution of environmental problems. The important aspect of photocatalysis is selection of semiconductor material such as ZnO as a efficient photocatalysts because of its inexpensiveness, chemical stability, non-toxicity, higher efficiency and provide photo-generated holes with high oxidizing power due to their wide band gap energy for the degradation of wide range of organic chemicals and synthetic dyes [2].

Photocatalytic degradation process has extensively applied to textile water treatment because it is effective, eco-friendly, cheaper and rapid technique for the complete removal of toxic pollutants from wastewater [3]. Heterogeneous photocatalysis has been emerged as an efficient method for purification of water and air. In most cases, the effective materials for photocatalytic applications are nano-sized semiconductor oxide (ZnO), which has been proven as excellent catalysts because of its highly reactive surfaces. This oxide has been extensively examined as heterogeneous semiconductor photocatalysts primarily because of their high capacity for degradation of toxic and recalcitrant chemical species via relatively simple and low-cost procedure [4]. So nanosized ZnO has been chosen as one of the photocatalysts due to its direct energy gap EG of about 3.3 eV, large volume to area ratio, high ultraviolet (UV) absorption, and long life-span, gas sensor, active filler for rubber and plastic, UV absorber in cosmetics and anti-virus agent in coating and it absorbs UV radiation due to the band-to-band transitions. In the present work, ZnO nanoparticle was used for degrading textile dye pollutant such as reactive red 198 was tested. ZnO nanoparticles were prepared via sol-gel method and it was characterized by XRD, SEM, BET surface area analysis methods. The photocatalytic degradability of ZnO nanoparticle was investigated under UV light irradiation.

EXPERIMENTAL

Materials

Zinc acetate dihydrate, oxalic acid dihydrate and ethanol and all the organic reagents were analytical grade purchased from Merck, Qualigens, India. Reactive red 198 was one of the textile dye purchased from Textile Industry, Thirupur, Tamilnadu, India without any further purification. Solutions have been prepared using double distilled water was used for all the measurements.

Synthesis of ZnO nanoparticles

The ZnO nanoparticles were synthesized by sol-gel method. In this experiment, 10.98 g of zinc acetate dihydrate was treated with 300 ml of ethanol in an oil bath at 60° C in magnetic stirrer. Simultaneously 12.6 g of oxalic acid dihydrate was dissolved in 200 ml of ethanol on constant stirring at 50° C. Oxalic acid in ethanol was added drop wise to the warm ethanolic solution containing zinc (Zn^{2+}) ions drop wise with continuous stirring. After this the thick white gel of zinc oxide obtained was dried in a vacuum oven at 80° C for 20 hrs to get xerogel and it was calcined at 500° C to yield ZnO nanoparticles.

Analytical techniques and procedures

The XRD analysis was done to analyze the crystallite size of ZnO nanoparticle. Sample for powder X-ray Diffraction (XRD) was prepared by making a thin film of powder with ethanol on a glass plate and the measurement was performed with a Rigaku Geigerflex X-ray diffractometer with Ni-filtered CuKα radiation (λ=1.5418 Å, 30kV, 15mA). The particle size and morphology of ZnO nanoparticle was observed using Scanning Electron Microscopy (SEM) using FESEM-SUPRA55, CARL ZEISS, Germany was used in the experiments. Cary-50 ultraviolet spectrophotometer (Varian) was used in all the measurements of absorbance of dye solution at an incident wavelength of λ_{max} of 532nm.

Experimental set up

The photodegradation studies of reactive red 198 dye solution have been carried out in a batch reactor system. The slurry is stirred magnetically and low-pressure mercury vapour lamp has been used as an irradiation source. The lamp emits 8W of UV radiation with a peak wavelength of 254 nm. The optimum condition consists of a batch volume of 250 ml, stirring speed of 70 rpm and 30 minutes for adsorption equilibrium. The experimental procedure consists of irradiation of the dye solution of known concentration mixed with a known weight of catalyst powder at a constant volume of 250 ml. The slurry was stirred well using a magnetic stirrer throughout the period of experiment. In all the studies the suspensions have been stirred well for about 30 minutes to allow equilibration of adsorption process before exposure to UV light. Samples of 3 ml have been withdrawn at regular in-

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tervals of time, centrifuged, absorbance measured at 532 nm and returned to the reactor. All studies have been carried out at 30°C. The pH of the solution has been adjusted by using dilute solutions of HCl or NaOH. The intensity of the sunlight during the reaction in the range 808–1070 W/m^2. The intensity was constant during the experiments.

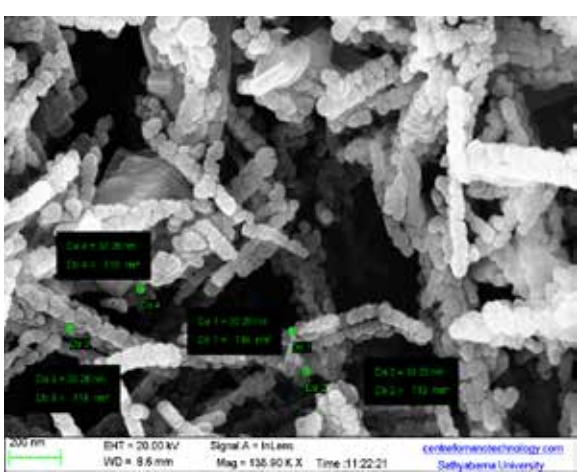
RESULTS AND DISCUSSION

XRD pattern

The XRD peaks correspond to the (100), (002), (101), (102), (110), (103), (200), and (112) planes of ZnO nanoparticle and it can be seen that all these peaks are in good agreement with wurtzite ZnO (a = 0.3249 nm and c = 0.52 nm),and the obtained spectrum has the first ZnO main peaks at 2θ: =31.7,34.4, 36.2, 43.2, 47.5, 56.5, 62.8, 66.4 and 67.9 which is in exact agreement with the 36-1451 standard card from the Joint Committee for Powder Diffraction Studies (JCPDS). No impurities are observed, which indicates high purity, crystallinity and ultra fine nature of the crystallites of the as-obtained wurtzite ZnO nanoparticles. The average crystallite size of ZnO nanoparticles obtained with calcination temperature at 500°C is estimated to be 30 ± 5 nm by applying the Debye–Sherrer formula. The calcinating temperature (at 500°C) provides energy of atoms to enhance mobility that could decrease the structural defects and improve the crystalline degree. This was confirmed using Scanning Electron Microscopy which revealed that the material consisted of agglomerates of hexagonal wurtzite structure whereas the electron microscopy can be used to determine almost any crystallite size.

SEM micrograph

Figure.1 shows the SEM micrograph of ZnO nanoparticles at the calcination temperature of 500 °C which revealed that the nanoparticles are grown in a very high-density due to the concentration of zinc ions. It has a certain impact on the particle size and distribution of ZnO nanoparticles and the particle size was around 35 ± 5 nm and the average particle size 30.2 ± 5 nm. It shows heterogeneous nanoparticles are spherical shape in nature which are coherent with each other. The calcinating temperature (500°C) had noticeable effect on the particle size and morphology of the ZnO nanoparticles. Also it indicated that activation energy barrier for the formation of well-dispersed ZnO nanoparticles could not be overcome. Surface area of ZnO was analyzed by using BET analysis and the surface area of ZnO nanoparticle was found to be 11.09 sq.m /g.



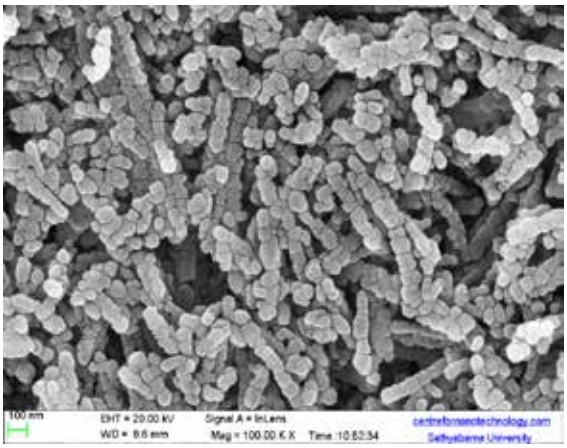
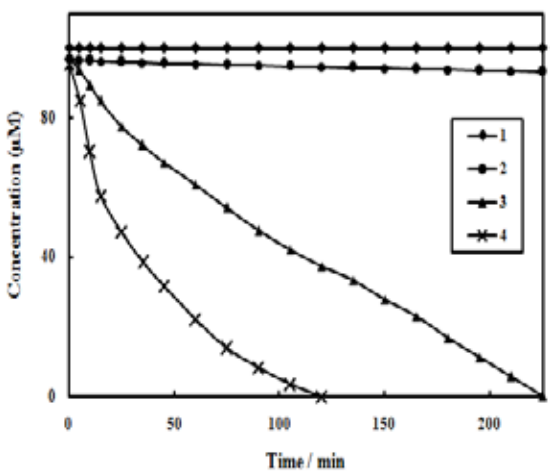


Figure 1: SEM micrograph of ZnO nanoparticle calcined at 500°C

Photodegradability of ZnO nanoparticle



1. Dye solution irradiated with UV light in the absence of nano ZnO
2. Dye solution treated with 1.0 g/l of nano ZnO in the dark
3. Dye solution irradiated with UV light in the presence of nano ZnO
4. Dye solution irradiated with solar light in the presence of nano ZnO

Figure 2: Photocatalytic degradability of reactive red 198; pH = 7.0; Weight of nano ZnO catalyst = 1g/L; Concentration= 100 μM; Temperature = 30 ± 0.1°C; Incident wavelength = 254 nm; Absorbance measured at 532 nm.

The photodegradability of the dye solution has been investigated by exposing to UV light or solar light in the absence and in the presence of nano ZnO photocatalyst in a batch reactor. It is seen from the Figure.2 that in the presence of both UV light or solar light and nano ZnO, complete degradation was occurred at an irradiation time of 225 minutes. But in the absence of UV light and in the presence nano ZnO, the dye solution is stable though adsorption has been found to be responsible for the decrease in dye concentration. For the same experiment performed in the absence of nano ZnO, only 0.5% of dye solution undergoes degradation when the UV lamp had been switched off and the reaction was allowed to occur in the darkness. The photocatalytic degradability experiment demonstrated that both UV light or solar light and a photocatalyst were needed for the effective destruction of textile effluent such as reactive red 198 in aqueous solution. The photocatalysed degradation of textile dye solution is

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initiated by photo excitation of the semiconductor, followed by the formation of an electron–hole pair on the surface of nanophotocatalyst [5].

Reusability of nanophotocatalyst

Reusability of ZnO nanoparticle for the photocatalytic degradation of reactive red 198 was evaluated. The nanocatalyst was separated from dye solution by filtration, washed with water and dried at 100 and 200˚C.The dried ZnO nanoparticles were used for the degradation of dye solution, employing under similar experimental conditions and procedures. The results showed that the degradation extent decreases after four runs as 94, 86, 76 and 63 % for drying temperature of 100˚C. The decrease in the degradation percentage is explained by adsorption of organic intermediates and by-products of the photodegradation process in the cavities and on the surface of the photocatalyst that influences the surface activity of the nanocatalysts.

CONCLUSIONS

ZnO nanoparticles was prepared by the sol-gel method and confirmed by XRD and SEM and BET surface area methods. The industrial textile pollutant like reactive red 198 was studied effectively. The XRD data showed ZnO nanoparticle has wurtzite structure with crystallite size as 35 ± 5 nm and SEM micrograph showed the heterogeneous and spherical shape with the particle size of 30.26 ± 5. ZnO nanoparticle was found to be highly efficient in degrading the textile pollutant in wasterwater.

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