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RESEARCH ARTICLE

Photocatalytic Performance of Nanocatalyst for the Effective Removal of Dye in the Wastewater†

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Abstract: Excess use of various dyes in the textile industry has led to the severe surface water and groundwater contamination by releasing the toxic and coloured effluents. For solving the problems of water contamination new set of technologies have implemented in both water and wastewater recently. Among them, the photocatalytic oxidation process using the nano-photocatalysts is a promising alternative method for treatment of polluted water in textile industries. Nanostructured ZnO is an attractive material for its unique performance in the elimination of waste from the water. The present study investigates the synthesis of ZnO nanoparticle by sol-gel method and characterized by X–ray diffraction (XRD) and SEM. The results showed that pure nano ZnO was composed of uniform distribution particles of ~15 nm and with spherical morphology. The present study aims in the photocatalytic degradation of dye reactive red 198 on the surface of nano ZnO in a batch reactor. The photocatalytic activity for the degradation of azo dye under UV light irradiation in aqueous solutions at different pH has been studied. All the experiments were performed in a photochemical batch reactor equipped with 8-W UV lamp emitting a peak wavelength around 254 nm. Under optimum conditions complete degradation of the organic dye was achieved.

Keywords: Removal of Dye, Wastewater, Textile industry, Photocatalytic performance

Introduction

Azo dyes account for the majority of all textile dye stuffs produced and have been the most commonly used synthetic dyes in the textile, food, paper making, color paper printing, leather and cosmetic industries[1]. It produces large quantities of coloured dye effluents from manufacturing and processing processes in the textile industry mainly, create severe environmental pollution problems due to their negative impact on photosynthetic activity[2]. Conventional methods used to treat dye effluents are classified as physical, biological or chemical methods[3], each having its own drawbacks. Physical methods such as chemical or electro-flocculation, reverse osmosis and adsorption are not destructive and mainly create pollutant concentrates. Activated sludge process does not work efficiently due to high solubility of synthetic dyes and their resistance to aerobic degradation[4].

Thus, new treatment methods are necessary for the removal of persistent dye chemicals or converting them into harmless compounds in water. Advanced oxidation processes

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(AOPs) offer new routes for the oxidative degradation of organic compounds[5]. Semiconductor photocatalysis has become more and more attractive and important since it has a great potential to contribute to such environmental problems. One of the most important aspects of environmental photocatalysis is in the selection of semiconductor materials like ZnO[6]. It is relatively inexpensive and they provide photo-generated holes with high oxidizing power due to their wide band gap energy and a large exciton binding energy (60 meV). Zinc oxide (ZnO) nanostructures have gained intense interests due to their potential applications in optoelectronic devices, ultraviolet (UV) laser devices, chemical sensors, solar cells and photocatalysts[7]. Researches show that ZnO can be also used as a very efficient semiconductor photocatalyst compared. Furthermore, ZnO has attracted significant attention in the degradation and complete mineralization of environmental pollutants[8]. For enhancement of the photodegradation efficiency, many efforts have been made related to size, morphology and preparation method on the photocatalytic property of ZnO.

The present work was to prepare the ZnO nanoparticle by modified sol-gel method and to characterize the material by XRD study. The photocataltyic activity of the nanoparticle was investigated by taking Reactive Red 198 azo dye as model compound. The photocatalytic activity for the degradation of azo dye in aqueous solution at different pH has been studied.

Experimental

Zinc acetate dihydrate, oxalic acid dihydrate and all the organic reagents were procured from SRL, Qualigens, India. Double distilled water was used for all the measurements.

Synthesis of nanocatalyst

Nanocatalyst was synthesized by modified sol-gel method. 5.49 g of zinc acetate dihydrate was treated with 150 mL of ethanol in a rotary evaporator at 60 °C under slightly reduced pressure. The salt was completely dissolved in 10-15 minutes. 6.3 g of oxalic acid dihydrate was dissolved in 100 mL of ethanol was simultaneously prepared by stirring for 10 minutes at 50 °C. Then the oxalic acid in ethanol was added drop wise to the warm ethanolic solution containing Zn^{2+} ions. The thick and white gel obtained was dried at 80 °C for 20 h to get xerogel was calcined at 500 °C.

Catalyst characterization

The XRD analysis was done to analyze the crystallite size of nano ZnO. Sample for powder X-ray Diffraction (XRD) were 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 XRD patterns were recorded in the range of 20-80°, with a scan speed of 2°/min. The Cary-50 ultraviolet spectrophotometer (Varian) was used to measure the absorbance values.

Experimental set up

The photodegradation studies have been carried out in a batch reactor system. The slurry was 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 conditions consist 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 organic dye solution of known concentration mixed with a known weight of catalyst powder at a constant volume of 250 mL. The slurry has been 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 intervals of time, centrifuged, absorbance measured at 532 nm, respectively and returned to the reactor. All studies have been carried out at 30 ºC. The pH of the solution has been adjusted to the desired values between 4.0 and 10.0 by using dilute solutions of HCl or NaOH.

Results and Discussion

XRD study of ZnO nanoparticle

Powder X-ray diffraction pattern of nano ZnO is shown in Figure 1. It can be seen that all the peaks are in good agreement with wurtzite ZnO. The XRD peaks correspond to the (100), (002), (101), (102), (110), (103), (200) and (112) planes of ZnO nanoparticle. No impurities were observed, which indicates the high purity and crystallinity of the as-obtained wurtzite ZnO nanoparticles. The average crystallite size of ZnO nanoparticles obtained with calcination temperature at 500 ºC is estimated to be 26.3 nm by applying the Debye–Scherrer formula.

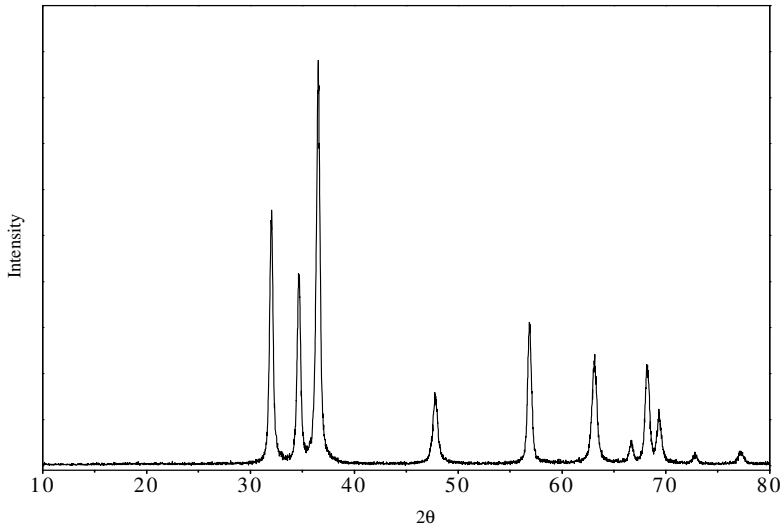

Figure 1. X-ray powder diffraction plot of nano ZnO at 500 ºC

Photodegradability of reactive red 198

The photodegradability of dye has been investigated by exposing the dye solution to UV 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 and ZnO about 90% of the dye was degraded at an irradiation time of 300 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.

Effect of pH

The wastewater from textile industries usually has a wide range of pH values. Generally, the pH of the solution is an important parameter in the photocatalytic processes. Since it is not only plays an important role in the characteristics of textile wastewater but also determines the surface charge properties of ZnO, the size of aggregates formed, the charge of dye

molecules, adsorption of dyes on surface of nano ZnO and the concentration of hydroxyl radicals. The photocatalytic degradation of reactive red 198 has been studied in the pH= 3, 5.7 (natural) and 8. The effect of pH on the photodegradation of dye solution as a function of time is shown in Figure 3. It has been observed that, with the increase in pH value from 3 to 8 the time required for degradation from 105-135 minutes. From the figure it has been observed that photocatalytic activity is enhanced at lower pH values. Lower pH favors the degradation and is hindered in alkaline conditions. At pH greater than 7 the catalyst surface becomes negatively charged. Negatively charged dye and the hydroxide anion prevent it from adsorbing onto the surface of catalyst. It can explain the reduced degree of degradation in alkaline conditions[9].

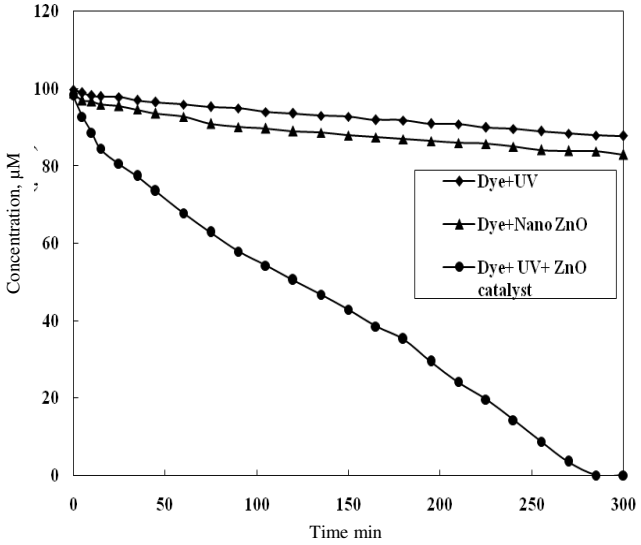

Figure 2. Photodegradability of dye pH = 7.0; Concentration= 100 µM; Weight of nano ZnO catalyst =1 g/L; Temperature = 30±0.1 °C

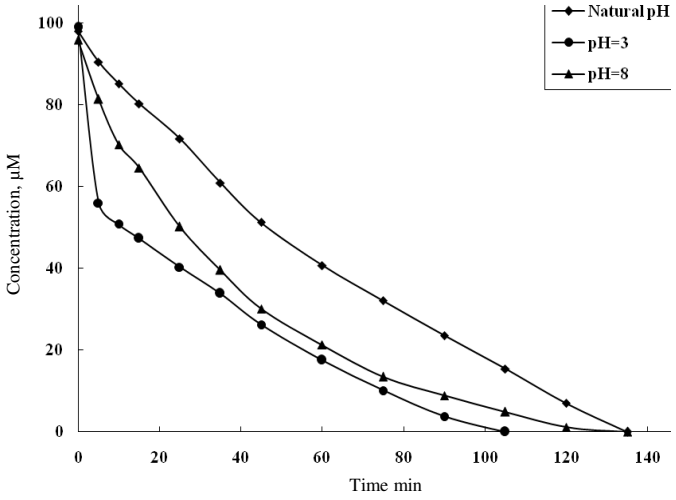

Figure 3. Effect of pH on the photocatalytic degradation of the dye; Concentration = 100 µM; Weight of nano ZnO catalyst = 1 g/L; Temperature = 30±0.1 °C

Conclusion

Nanocatalyst ZnO was successfully synthesized via sol-gel method. XRD result reveals that the synthesized nanoparticles were well-crystalline and wurtzite ZnO structure. For application point of view, the photocatalytic performance of ZnO nanoparticles was evaluated by degradation of reactive red 198. The performance of the synthesized nanoparticle developed good photocatalytic activity at different pH values. Therefore, prepared ZnO nanoparticles can be utilized as a photocatalyst in wastewater treatment for environmental applications.

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