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Removal of hazardous Ponceau S dye from industrial wastewater using nano-sized ZnO

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ABSTRACT

The present work deals with the removal of Ponceau S dye from industrial wastewater using nano-sized semi-conductor ZnO as photocatalyst. The ZnO nanoparticles were synthesized by sol–gel method from precursor zinc acetate dihydrate. Effect of different parameters like catalyst concentration, dye concentration, pH, contact time, UV radiations and catalyst on the rate of photocatalytic degradation has been studied. Fourier transform infrared spectroscopy and X-ray diffraction were used for characterization of powdered material. The size of ZnO nanoparticles calculated is 20.6 nm.

Keywords: Nano-sized ZnO; FTIR; XRD; Photocatalytic degradation

1. Introduction

The growth of industrialization and urbanization caused environmental pollution. The pollutants produced from rapid industrialization and urbanization not only affect our own lives but also all other living beings. The effluent discharged from textile and printing is highly toxic and causes pollution [1]. Dye industries release different harmful coloured effluents to the water bodies. The wastewater from the dye industry is highly coloured and high in chemical oxygen demand. Removing colour from wastes is often more important than other colourless and organic substances, because the presence of small amount of dye (below 1 ppm) is clearly visible and influences the water environment considerably [2]. In this work, we made a successful attempt to remove hazardous Ponceau S dye; being an azo dye, the Ponceau S dye may be allergic and can also cause symptoms of asthma. There are different methods for removal of colour from dyeing wastewater. The conventional methods for removal of colour from dyeing wastewater are filtration, coagulation, adsorption by activated carbon, treatment with ozone, etc. The method of advance oxidation process (AOP) can be used for a variety of organic and inorganic compounds. Traditional physical techniques like adsorption on activated carbon, coagulation, ultra filtration, ion exchange, etc. have been used for the removal of dye pollutants [3,4]. Several workers have also tried wastewater treatment of various dyes by adsorption over low-cost materials [5–7]. Nowadays, the AOP is applied for the treatment of contaminated water from dyeing industry [8,9].

AOPs are alternative techniques for the removal of dyes and many other organics in wastewater and effluents [10]. Advanced oxidation processes based on photocatalytic degradations are of huge importance for the effective oxidation of a wide variety of organics and dyes [11]. Since few years, photocatalytic degradation of organic compounds using semi-conducting materials as a photocatalyst is widely used for

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degradation of organic compounds in wastewater [12,13]. Semiconductors like TiO_2, ZnO, Fe_2O_3, CdS and ZnS can act as sensitizers for light-induced redox processes due to filled valence band and an empty conduction band in them [14].

In this work, we have used ZnO as a photocatalyst for the degradation of Ponceau S dye in aqueous medium. ZnO is known to be a good photocatalyst for the degradation of several organic compounds due to their high photosensitivity and large band gap [15,16]. The zinc oxide (ZnO) semiconductor has a band gap of 3.37 eV [17]. Joshi and co-workers have synthesized ZnO by sol–gel method [18]. The sol–gel method has proved to be very useful for the production of metal oxides [19,20].

2. Experimental

2.1. Materials and methods

All the chemicals were of analytical grade. The water soluble Ponceau S dye (M.F. $C_{22}H_{12}N_4O_{13}S_4Na_4$ and M.W. 760.56 gm) and nano-sized ZnO were used for photocatalytic study. The nano-sized ZnO was synthesized by sol–gel method. The structure of Ponceau S dye is shown in Fig. 1. A stock solution of 100 ppm of Ponceau S dye was prepared in distilled water. Different concentrations (10, 20, 25, 30, 40, 50, 60 and 70 ppm) of Ponceau S dye were prepared from the stock solution. The pH of Ponceau S dye solution was adjusted by adding HCl and NaOH. The rate of photocatalytic degradation was followed by measuring the absorbance of sample at different time intervals using UV–Visible spectrophotometer (Systronics-2203) using quartz cell of 1 cm path length at lambda max 519 nm.

2.2. Instrumentation

The photocatalytic degradation of Ponceau S dye was carried out in a photocatalytic reactor with a 400 W medium pressure Mercury lamp with nominal wavelength range 220–1400 nm. The reactor consists of a cylindrical Pyrex glass reactor and a double-walled quartz cooling water jacket to maintain the temperature and prevent the reactor from excessive heating. The reaction solution was stirred with magnetic stirrer at a constant speed. The changes in dye concentration were detected using spectrophotometer (Systronics 2203). The pH measurements were carried out using an Equiptronics digital pH metre (Model-E610).

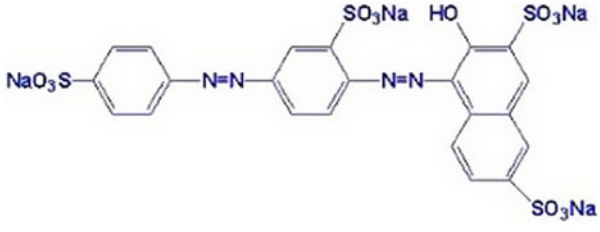

Fig. 1. Structure of Ponceau S dye.

2.3. Photocatalyst preparation

A Nanoparticle is a particle that has one dimension that is 100 nm or less in size. In this work, nanocrystalline ZnO has been synthesized by sol–gel method from the chemicals zinc acetate dihydrate, ethylene glycol, isopropyl alcohol and glycerol. In this synthesis, 20 gm of zinc acetate dihydrate was dissolved in 5 mL of ethylene glycol and it is heated in a round bottom flask fitted with a condenser at 130°C for 30 min. Then, it is cooled to room temperature and 1 mL of glycerol and triethylamine are added. The solution was centrifuged, washed and dried. The product is annulated at 400°C.

3. Results and discussion

3.1. Effect of catalyst dose

The effect of amount of nano-sized semi-conductor photocatalyst on the rate of photocatalytic degradation of Ponceau s dye was studied, the results are shown in Fig. 2. The dosage of photocatalyst was varied between 1 and 7 gm by keeping the initial dye concentration to 25 ppm and pH 9. The rate of photocatalytic degradation is found to increase with increasing amount of catalyst. The increase in rate of degradation is rapid initially, but further addition of catalyst does

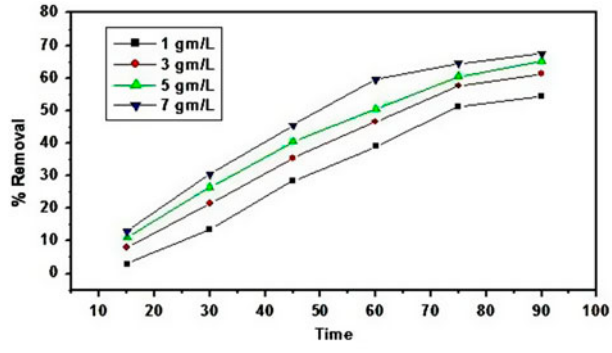

Fig. 2. Effect of catalyst dose on % removal of Ponceau S dye by ZnO at dye conc. 25 ppm and pH 9.

not cause a considerable increase in the rate of degradation. The increase in the rate of degradation with addition of catalyst is due to greater availability of exchangeable sites or surface area at higher concentration of catalyst [21].

3.2. Effect of initial dye concentration

The progress of photodegradation of Ponceau S dye was studied by varying the dye concentration between 10 and 70 ppm; because for fixed catalyst concentration, the active sites remain the same, the number of substrate molecules accommodating the interlayer space increases so degradation decreases. The results for the study are shown in Fig. 3. During the study, parameters like pH was 9, the catalyst concentration was 2 gm/L and contact time was 60 min 2 gm/L.

3.3. Effect of pH

The effect of pH on the rate of photocatalytic degradation of Ponceau S dye was studied by varying the pH of solution in between 3 and 11, keeping ZnO catalyst dose 2 gm and time 60 min. The results are shown in Fig. 4. The pH of Ponceau S dye solution was adjusted by adding HCl and NaOH. The rate of photocatalytic degradation increases with increasing pH. The results show that the rate of photocatalytic degradation increases with increase in pH and the maximum rate was obtained at pH 9.

3.4. Effect of contact time

The effect of contact time on the rate of photocatalytic degradation of Ponceau S dye at different dye concentrations (10, 30, 50 and 70 ppm) was studied. The results are shown in Fig. 5, which show that the rate of removal increases rapidly at start with increasing time and after some time reaches to equilibrium.

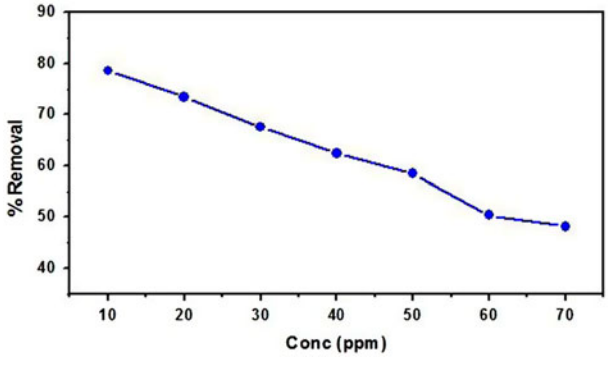

Fig. 3. Effect of initial dye concentration on % removal of Ponceau S dye with ZnO photocatalyst does of 2 gm for 60 min at pH 9.

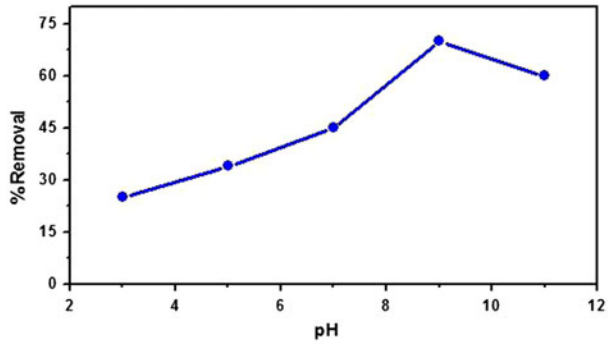

Fig. 4. Effect of pH on the removal of Ponceau S dye using nano-sized ZnO photocatalyst dose 2 gm and irradiation time 60 min.

3.5. Effect of UV light and catalyst

The effect of UV light and catalyst on the rate of photocatalytic degradation of Ponceau S dye was also studied. The results are shown in the Table 1. The results show that the rate of removal is highest in presence of UV light and catalyst. The rate of removal is lowest in presence of UV light only. The results are obtained by keeping ZnO catalyst dose 2 gm and time 60 min.

3.6. Characterization

3.6.1. Fourier transform infrared spectroscopy

Infrared spectroscopy is an important technique to identify the functional groups. Different functional

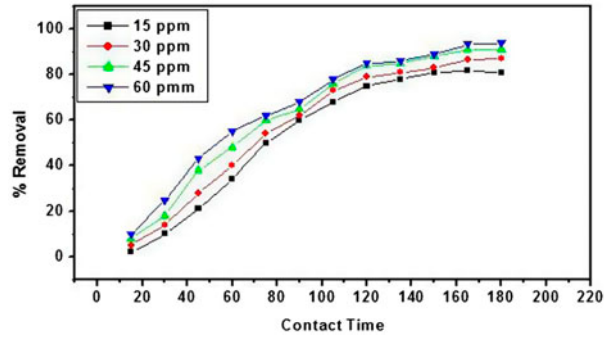

Fig. 5. Effect of contact time on % removal of Ponceau S dye with different dye concentration with 2 gm ZnO photocatalyst dose and pH 9.

Table 1
Effect of UV light and ZnO photocatalyst on % removal of Ponceau S dye with ZnO photocatalyst dose 2 gm and time 60 min

Conditions	UV light	Catalyst only	UV light + catalyst
Removal percentage	10	19	63

groups absorb at characteristic frequencies. Fourier transform infrared spectroscopy (FTIR) spectra of powdered ZnO sample dispersed in KBr was recorded using FTIR-7600 (Lambda Scientific) spectrometer with a 4 cm^{-1}. The FTIR spectrum of ZnO is shown in Fig. 6. The band around 500 cm^{-1} is due to Zn–O metal bond.

3.6.2. X-ray diffraction

The X-ray diffraction (XRD) patterns were recorded on D8 ADVANCE (BRUKER) model X-ray diffractometer using Cu-Kα1 radiation of wavelength 1.54060 Å as X-ray source. The diffractograms were recorded in the 2θ range of 10°–80°. XRD is an important technique used for quantitative and qualitative analysis of crystalline materials. The average grain size can be calculated from XRD data using Scherer's formula [22,23].

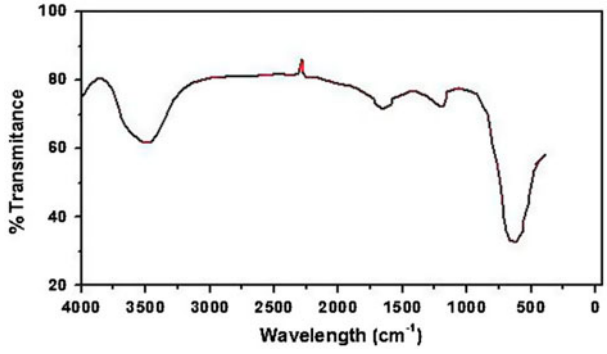

Fig. 6. FTIR spectra of ZnO.

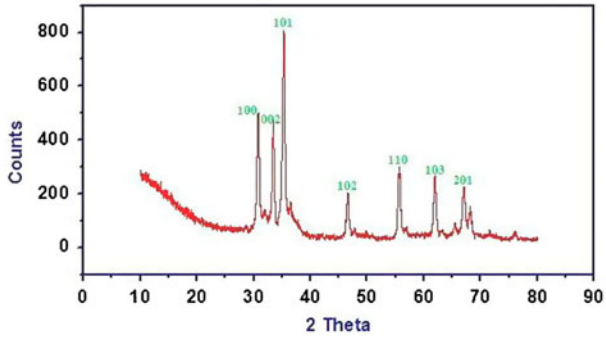

Fig. 7. The XRD diagrams of ZnO nanoparticle.

Fig. 7 shows the XRD pattern of powdered ZnO synthesized by above-mentioned procedure. The average grain size of ZnO particles calculated using the Scherer's formula confirms the nanocrystalline nature of the crystal. The calculated grain size for ZnO nanoparticles is 20.6 nm.

4. Conclusion

Removal of hazardous Ponceau S dye was successfully carried out using nano-sized ZnO synthesized from zinc acetate dehydrate in presence of UV light. The rate of removal of Ponceau S dye increases rapidly with increasing amount of ZnO-semi-conducting photocatalyst; addition of further photocatalyst does not affect the rate of removal considerably and reaches equilibrium. The removal of dye was more rapid in an alkaline pH of 9. The removal rate decreases with increasing initial concentration of Ponceau S dye and increases with catalyst concentration. The most effective removal of Ponceau S dye is obtained by combination of catalyst and UV light. The nano-sized semi-conducting ZnO was successfully prepared by sol–gel method and its formation and nano-sized nature was confirmed by FTIR and XRD technique.

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