Chapter - 3

Synthesis and Photocatalytic Activity of ZnO Composite-II Against Coralene Red F3BS Dye in the presence of Solar Radiation
INRODUCTION

Textile industries occupy a unique place in industrial sector since they consume high quantity of water and chemicals. The estimated global dye production in an year is over 7,00,000 tons (Robinson et al., 2001) and it is reported that, about 2% of the huge quantity is discharged as effluent from the manufacturing and dyeing operations in the textile dyeing, leather tanneries and painting industries (Easton, 1995).

Due to the higher stability of modern synthetic dyes, the release of these coloured effluents into the rivers is harmful to the aquatic ecosystem which results in pollution, eutrophication and perturbations in the aquatic life (Acosta et al., 2005; Denizli et al., 2000; Herrmann et al., 2001). Further, these water bodies are very undesirable for the water user due to aesthetic reasons, since they may cause eye and skin irritation, irritation of the digestive tract and may be severely harmful if swallowed (Alcantara Licudine et al., 1999; Chen et al., 2005).

Conventional, biological and physical treatment methods for treatment of textile wastewater have been ineffective because, either they fail to achieve complete colour removal (Souther and Alspaugh 1957; Hamazam and Hamoda 1980) or ineffective on pollutants which are not readily adsorbable or volatile and have further disadvantage that, they simply transfer the pollutants to another phase, which again creates disposal problems. Other methods include
the techniques like coagulation, filtration, adsorption on activated carbon and treatment with the ozone (Lorimer et al., 2001), each of them have their own disadvantages. However, the disposal of toxic sludge shows a severe drawback in all the above methods, except ozone treatment, which has high operational cost.

In the past few decades, metal oxide nanoparticles have attracted much attention, since its introduction to the field of environmental remediation by photocatalytic degradation of toxic organic compounds in the aqueous suspension. Photocatalytic reaction takes place when the semiconductor particles absorb a photon of light energy, which is more energetic than its band gap. The electron excited from the valence band to the conduction band, creates electron–hole pairs, which are able to initiate the oxidation and reduction processes of adsorbed substrates (Gouvea, 2000) or the holes scavenged by the surface hydroxyl ions generating the strong oxidizing hydroxyl radical (OH*), which can promote the oxidation of organic compounds (Shourong et al., 1997; Poulios and Tsachpinis, 1999; Zhang et al., 1998). Factors influencing the photodegradation rate of aqueous systems are pH value, initial dye concentration and amounts of photocatalyst added to the aqueous solution (Yang et al., 2001; Chaterjee and Mahata, 2001; Herrera et al., 2000; Hachem et al., 2001).

The present research has focused on non-conventional synthesis method of ZnO composite-II and its photocatalysis against colour induced by the
Coralene Red F3BS in lab scale, which combines effectiveness and least expensiveness in treating these coloured effluents.

MATERIALS AND METHODS

Chemicals and Instruments

Commercially available water soluble Coralene Red F3BS azo dye (Colourtex Limited, Surat, Gujarat, India), 99% LR grade hydrazine hydrate (SD fine-chem limited, Mumbai, India) and dry zinc nitrate (Jobal Chemie, Mumbai, India) were procured and used without further purification. UV-vis Spectrophotometer 169 (Systronics) was used for recording the absorbance and $\lambda_{\text{max}}$.

![Chemical structure of Coralene Red F3BS dye](image)

**Figure 1. Chemical structure of Coralene Red F3BS dye**

Preparation of ZnO Composite-II

ZnO composite-II was prepared by drop wise addition of 5.02g hydrazine hydrate (99%) to the beaker containing 11.88g of zinc nitrate with vigorous stirring. The obtained white precipitate was diluted to 50ml by distilled water and stirred for one hour. After centrifugation at 2000rpm and washing with water several times, the product was dehydrated at 100-120°C in
hot air oven for 2-3 hours. The final white powder was then crushed manually and stored for further use.

**Photocatalytic Experimental Procedure**

Photodecolourization of Coralene Red F3BS dye solution was studied in the presence of ZnO composite-II particles and with solar radiation. Coralene Red F3BS is widely used azo dye in silk yarn dyeing industries and most of the textile industries. Photocatalytic reaction experiments were performed in the presence of direct sunlight. Standard dye stock solution of 50ppm was prepared by dissolving 50mg of Coralene Red F3BS in 1000ml of distilled water and the initial absorbance was recorded at 521nm ($\lambda_{\text{max}}$). 100ml of this standard dye stock solution was taken in set (6 numbers including control sample) of Borosil® glass beakers and prepared ZnO composite-II at various concentrations (0.1g, 0.2g, 0.3g, 0.4g, 0.5g) were directly dispersed to each beakers simultaneously. Absorbance readings at regular time intervals (15 minutes) was compared with initial absorbance for the investigation of photocatalytic activity of prepared ZnO composite-II at different concentrations and pH (12.0, 7.0 and 3.0). The percentage of decolourization was calculated by using the following formula.

$$\frac{(A_0 - A_t)}{A_t} \times 100$$

Where, $A_0$ is the initial absorbance of the dye solution

And $A_t$ is the absorbance at time interval ‘$t$’.
RESULTS AND DISCUSSION

X-Ray Diffraction and Scanning Electron Micrographs of Prepared ZnO Composite-II

The x-ray diffraction (Figure 2) of the synthesized ZnO composite-II confirmed the presence of other contaminants in the prepared composite sample. However, it is very similar to that of ZnO molecular precursors (Joint Committee of Powder Diffraction Standards (JCPDS) card no 80-0075) indicating that the obtained product under the current experimental conditions gives a molecular composite containing ZnO particles. The presence of ZnH₂ (JCPDS card no 47-0982) in traces along with ZnO was also identified. Hence, the new composite product obtained has been named as ZnO composite-II in this chapter. The scanning electron micrograph images of composite sample have shown the typical texture and morphology of ZnO composite-II. The x-ray diffraction results showed the crystallite size of the ZnO composite-II particles were between 8 to 145 nm respectively (Debye Scherrer's formula).
Figure 2. X-ray diffraction spectra and scanning electron micrographs of ZnO composite-II
Effect of pH

Decolourization of Coralene Red F3BS by the synthesized ZnO composite-II at different pH levels with respect to amount of catalyst load has been shown in Figure 3. The pH of dye solution (50ppm) was adjusted with dilute NaOH and HCl solutions. It was found that, the decolourization of selected dye solution was highly pH sensitive and achieves the maximum colour removal of 98% at pH 12.0 within 45 minutes. At pH 3.0 (acidic condition), the decolourization was 10-15 times less at lower composite dosages and 1-2 times at higher dosages than that of pH 12.0 condition at maximum time interval of 105 minutes.

Photograph No. 1. Effect of pH on decolourization efficiency of ZnO composite-II after 90 minutes in presence of solar irradiation

The possible explanation for dependence of decolourization on pH of dye solution was, as the pH increases the catalyst represents positive charge and thus promotes the adsorption of dye since dye contains negative sulphonate
group. An additional explanation for the pH effects can be related to specifications of the selected model azo dye, i.e., protonation or deprotonation of the dye can change its adsorption characteristics and redox activity.

Further, dependence of photocatalytic adsorption on pH was expected to rely on different reaction mechanism, such as hydroxyl radical attack, direct oxidation by positive hole and direct reduction by the electron in the conduction band can contribute to colour removal. All these reactions were dependent on the nature of dye and pH of dye solution. In this study, the prepared ZnO composite-II was found to have optimal and rapid photocatalytic activity at pH 12.0 under the given experimental conditions.
Figure 5. Effect of pH of dye solution on percentage of decolourisation of 50ppm Corelene Red F3BS dye solution at different catalyst load; (a) 0.1g, (b) 0.2g, (c) 0.3g, (d) 0.4g and (e) 0.5g.
Effect of Catalyst Loading

To determine the effect of the catalyst loading, a series of experiments were carried out by varying the amount of catalyst from 0.1 to 0.5g/100ml. The decolourization as shown in figure 4 (a), 4(b) and 4(c). The maximum decolourization was recorded at the higher catalyst dosage range of 0.3 to 0.5g/100ml.

Photograph No. 2. Effect of catalyst dosage on decolourization efficiency of ZnO composite-II after 90 minutes of solar irradiation at pH 12.0

The extreme point results from the conflicting effects of catalyst load on the photocatalytic process; at lower loading levels, such as 0.05g/100ml, photonic adsorption which controlled the reaction extent due to the limited catalyst surface area and an increase in catalyst loading, which greatly enhances the process performance. The initial decolourization rate was very fast and decreased exponentially with time. In contrast, at lower dosage the colour removal proceeded with uniform rate and reaching upto 73%.
Figure 4. Effect of catalyst load on the decolourization of 50ppm Coralene Red F3BS dye solution at different dosages at pH levels [(a) at pH 12.0, (b) at pH 7.0 and (c) at pH 3.0]
Effect of Reaction Time

It can be seen that, the dye removal process using prepared ZnO composite-II as semiconductor photocatalyst was found to proceed with two phases at pH 7 and 3 (Figure 5(b) and Figure 5(c)). At maximum catalyst dosage (0.5g/100ml), the first rapid phase was for the first 45 minutes and was found to achieve 13% and 27% decolourization respectively as shown in Figure 5. The colour removal thereafter attains saturation and finally increased to reach 87% and 80% colour removal at pH 3 and 7 respectively in a reaction time of 105 and 90 minutes. The first rapid adsorption phase, i.e., 0-45 minutes, at pH 3 and 7, was may be due to an increased number of vacant sites available at the initial and as a result, of the decrease in the concentration of dye in solution. As time proceeds, due to adsorption of dye molecules on vacant sites previously available adsorbent surface decreased and thus, virtually saturation stage was perceived. The reaction rate was at uniform speed in the initial 30 minutes, which achieved ~90% decolourization for all catalyst loads and attained the optimum saturation of 98% after 45 minutes at pH 12 (Figure 5(a)).
Figure 5. Percentage of decolourization of Coralene Red F3BS dye solution (50 ppm) at different pH levels [(a) at pH 12.0, (b) at pH 7.0 and (c) at pH 3.0]

SUMMARY AND CONCLUSION

ZnO composite-II nanoparticles were prepared by simple solution combustion method and investigated for its photocatalytic activity against the Coralene Red F3BS azo dye. The x-ray diffraction results showed that, the size
of ZnO composite-II particle was in the range of 8 to 142nm. The systematic study performed at different pH levels to investigate the photocatalytic efficiency of ZnO composite-II showed that, the composite was most active photocatalyst at alkaline pH condition. The results also indicated that, decolourization efficiency of synthesized ZnO composite-II was affected by irradiation time, pH of the dye solution and catalyst concentration. The optimal catalyst load and pH level was 0.5g/100ml and 12.0 against the Coralene Red F3BS dye concentration of 50ppm. Approximately 98% colour removal has been achieved in a relatively short solar irradiation time of 45 minutes at pH 12.0. Further, at pH 7 and 3.0, only ~80% and ~90% colour removal was recorded for 90 minutes respectively. The presented synthesis (solution combustion) method of ZnO composite-II and the photocatalytic Coralene Red F3BS dye degradation protocol was helpful in treating Coralene Red F3BS dye containing textile effluents. It is economically feasible and easily adaptable dye degradation technique by photocatalytic process under the natural sunlight.

REFERENCES


