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Photocatalytic degradation of Direct Brown RN dye in the presence of ZnO nanoparticles

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Abstract

The ZnO nanoparticle was prepared by using $Zn(NO_3)_2.6H_2O$ and NaOH under optimum reaction conditions and the prepared nanoparticle was characterized by UV-visible spectroscopy, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), energy dispersion X-ray spectroscopy (EDX) and scanning electron microscopy (SEM). The sunlight irradiated photocatalytic degradation of Direct Brown RN dye was studied using ZnO nanoparticle. The results of this investigation revealed that in the presence of sunlight, catalyst load of 0.5 g·L^{-1} and time of contact of 40 min, ZnO nanoparticle showed substantial capability of destroying Direct Brown RN dye from solution. An actual leather effluent containing Brown RN as a major constituent along with other dyes and dyeing auxiliaries was treated using ZnO and the reduction in the chemical oxygen demand (COD) of the treated effluent revealed almost complete destruction of the organic molecules along with color removal.

**Keywords**: ZnO; Nanoparticles; Photodegradation; Direct Brown RN dye

Introduction

Dyes can easily contaminate the water bodies through their discharge from the industries. Non-biodegradable nature of most of the dyes which result in perturbation in aquatic diversity by blocking the passage of sunlight through the water represents serious problems to the environment. It is reported that less than 1 ppm of dye content causes obvious water coloration (Al-Degs *et al.,* 2000). There are more than 100,000 commercially available dyes and globally over 7×10^5 tons of dye is produced in a year and 15% of which is lost during the dyeing process (Martinez-Huitle and Brillas, 2009). Leather processing and leather products manufacturing are important export-orientated industries in Bangladesh. The full flourishing of this sector is significant for the country's economy. Most of these processing plants have no effluent treatment plant. They directly dispose untreated colored and toxic effluent into the nearby rivers and other waterways, thereby causing serious environmental pollution.

Development of technological systems for the removal of organic dyes has recently been on the rise. These include physical methods such as adsorption (McKay, 1982, Chatterjee *et al.,* 2010), coagulation (Zargar *et al.,* 2009), biodegradation (Moore *et al.,* 1989) and chemical methods such as chlorination, ozonation etc (Slokar and Le Marechal 1998). Physical and biological methods do not destroy the pollutants but simply transfer the pollutant to another phase which again creates disposal problem. On the other hand chemical methods have the disadvantages of using strong oxidants like chlorine and ozone which are themselves hazardous in nature. However, photocatalytic technology as an advanced oxidation process (AOP) promotes the degradation of pollutants through producing hydroxyl radicals (·OH) from water molecules as strong oxidizing agent which eventually converts the organic dye molecules into CO_2 gas.

The most important reason for choosing ZnO as photocatalyst is its ability to show photo catalytic efficiency in both UV and visible range of light i.e. direct sunlight can be used as light source. The focus of the present work is to synthesize ZnO nanoparticles and use it in the photocatalytic degradation of Direct Brown RN (disodium4-[4-[4-[2,4-diamino-5-(4-sulfonatophenyl) diazenylphenyl]diazenylphenyl] phenyl] diazenyl-2-hydroxybenzoate, Figure 1.), using sunlight irradiation.
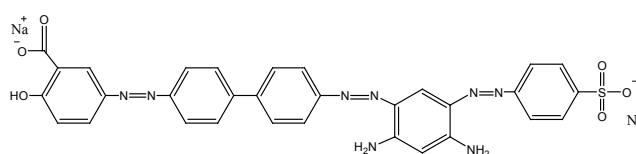
Fig. 1. Chemical structure of Direct Brown RN.

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Materials and methods

Materials

Zinc nitrate hexahydrate [$Zn(NO_3)_2.6H_2O$] was purchased from JHD group, Guandang, China. Sodium hydroxide (NaOH) was obtained from NEN Tech. Ltd. Brixworth, UK. Direct Brown RN dye (molecular formula: $C_{31}H_{22}N_8Na_2O_6S$, formula weight: 680.615, C.I. No: 30045) was supplied by Apex Tannery Ltd, Hazaribag, Bangladesh. Stock solution of Direct Brown RN dye (2.5×10^{-5} mol·L^{-1}) was prepared daily by dissolving appropriate amount of dye solid in deionized water. All experiments were performed with analytical grade reagents and directly used without further purification. Doubly deionized water was used throughout.

Apparatus

Ultraviolate visible (UV-vis) spectral measurements were performed on a UV-1700 (Shimadzu, Japan) spectrophotometer. ZnO crystal structures were characterized by X-ray diffractometry (XRD) using a D8 ADVANCE diffractometer (Bruker, Germany). The morphology and chemical composition of the ZnO nanoparticles were observed by means of JSM-6490 scanning electron microscopy (SEM) and EDX analysis (JEOL, USA). FTIR spectra were recorded on a Prestidge-21 IR (Shimadzu, Japan) spectrophotometer from samples in KBr pellets.

Nanoparticle preparation

ZnO nanoparticles were prepared following the procedure described elsewhere (Kawano and Imai, 2008). A 0.2 M solution of zinc nitrate and a 4.0 M alkali solution of sodium hydroxide were separately prepared by dissolving zinc nitrate hexahydrate $Zn(NO_3)_2·6H_2O$ and NaOH, respectively, in deionized water. To prepare ZnO nanoparticles, 2 mL of the alkali solution (4.0 M NaOH) was dropped at an approximate rate of 0.5 mL/min into a 20 mL aqueous solution of 0.2 M $Zn(NO_3)_2.6H_2O$ with stirring. The final pH of the mixture was fixed at 13 as highly basic conditions are conducive to the direct preparation of ZnO crystals (Nejati *et al.,* 2011). The products obtained by centrifugation were washed with deionized water and dried at 60º C in air. Prepared ZnO was then characterized by UV, FTIR, EDX, XRD and SEM analysis.

$$\text{Decolorization Efficiency (\%)} = \frac{C_0 - C}{C_0} \times 100 \qquad (1)$$

Photocatalytic Degradation of dye

In photocatalytic experiments, Direct Brown RN dye solution (50 mL) and the catalyst (ZnO), were taken in a beaker and exposed to sunlight for upto 40 min. Dye samples of about 2–3 mL were taken out at a regular intervals of 10 min from the test solution, centrifuged for 4–5 min at 950–1000 rpm and their absorbance were recorded using a spectrophotometer. The percentage decolorization efficiency (%) was calculated from the equation given below

where C_0 is the initial concentration of dye and C is the concentration of dye after photo irradiation at varying reaction time (expressed in mol·L^{-1}).

Effluent Treatment

Colored effluent containing Direct Brown RN dye as a major constituent along with other dyes and dyeing auxiliaries were collected from the discharge line of a local leather processing plant (Apex Tannery Ltd, Hazaribag). The effluent was treated using the prepared ZnO nano under varying conditions. The same photocatalytic experimental set up, as used for the dye solution, was employed here for effluent treatment. The chemical oxygen demand (COD) of the untreated and treated (with ZnO nanoparticles) effluents was determined using $KMnO_4$ oxidation method (Clesceri *et al.,* 1998).

## Results and discussion

Analysis of ZnO Nanoparticle

A characteristics peak for ZnO nanoparticle was found at 350 nm wavelength in UV analysis (Figure 2a). Figure 2b shows the FT-IR spectra of the synthesized ZnO particles. The IR spectra of samples of ZnO particles are generally influenced by the particle size and morphology (Nejati *et al.,* 2011). The peaks at wavenumber 671 and 559 cm^{-1} are related to the stretching vibrations of Zn–O bonds. The peak at 3414 cm^{-1} indicates the presence of –OH residue, probably due to atmospheric moisture (Nejati *et al.,* 2011). The comparison of the synthesized ZnO peak in various plane with the JCPDS (Joint Committee on Powder Diffraction Standards) data shows presence of peak in similar position (Figure 2c). In case of synthesized ZnO, broad peaks of higher intensity affirm the smaller particle size (Nejati *et al.,* 2011, Kale *et al.,* 2009). The crystallite size was calculated using Scherrer's formula (Scherrer, 1918) and found to be 18.79 nm. The SEM (Figure 2d) shows that the particles are uniform in shape and well dispersed with particle size below 200 nm. The chemical stoichiometry of ZnO nano particle was investigated with EDX (Figure 2e), which affirmed an atomic ratio of Zn:O = 48.02 : 51.98 ≈1:1. No characteristic peaks of any other phase of ZnO or of any impurity were observed in XRD or
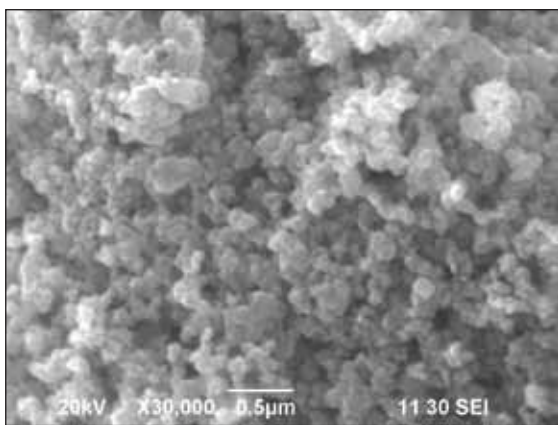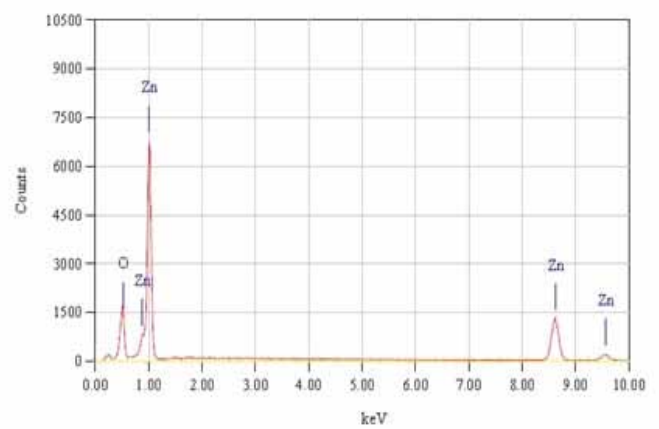
a.

b.

2-Theta-Scale
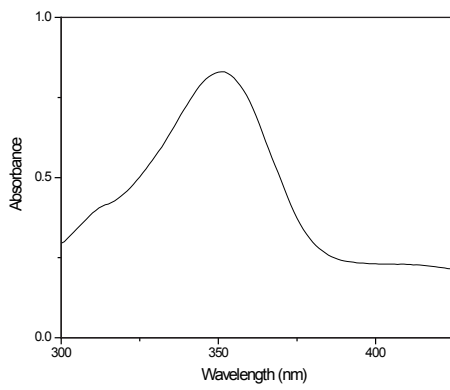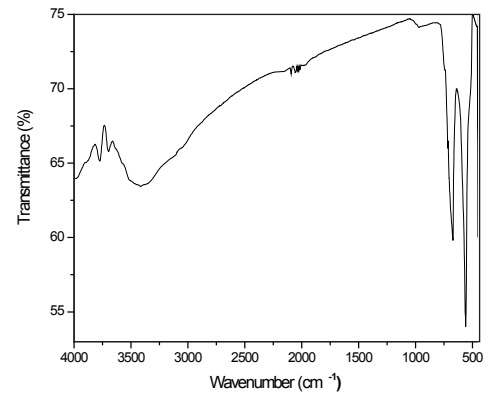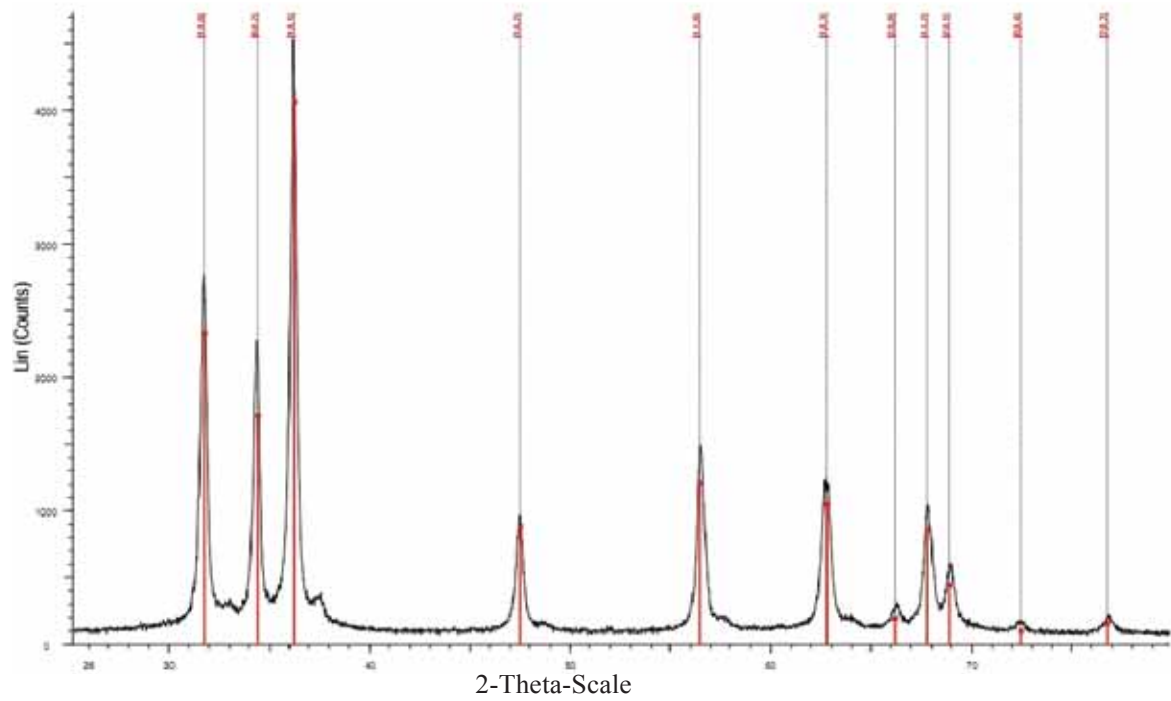
c.

d.

e.

**Fig. 2. Characteristics of prepared ZnO nanoparticle. a. UV-Visible; b. FT-IR; c. XRD d. SEM and e.EDX spectrum.**

EDX analysis. This result indicates the high purity of the ZnO nanoparticles.

Photodegradation studies

The UV spectral characteristics of the Direct Brown RN dye at different time intervals are shown in Figure 3. The dye was irradiated under sunlight at a 10 minutes interval for 40 minutes to observe if there is any degradation effect. The absorption peak gradually decreases as the
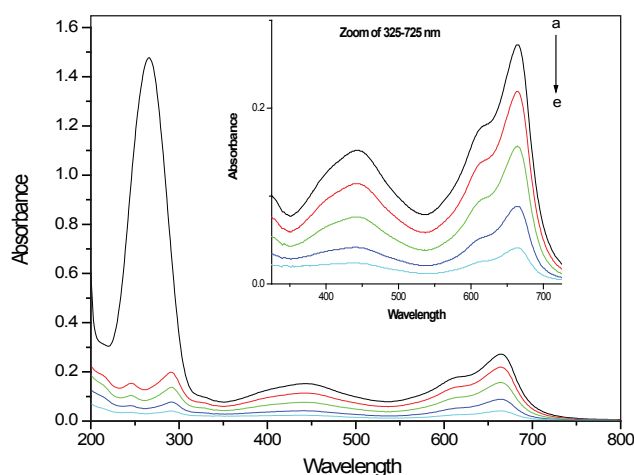

Fig. 3. UV spectra of Direct Brown RN dye at regular intervals (a→e) after applying ZnO nanoparticles. (INSET showing zoom from wavelength 325 to 725 nm). Conditions: Dye concentration, 2×10-5 mol·L-1; Catalyst loading, 0.5 g·L-1; Degradation time, 0, 10, 20, 30 and 40 min.
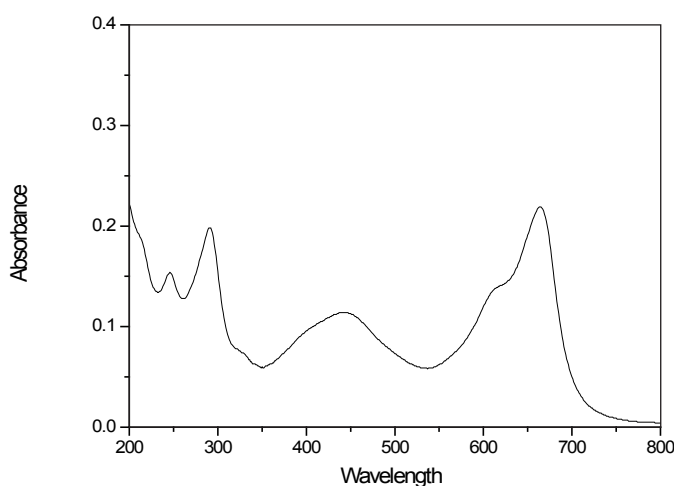
Fig. 4. UV spectra of Direct Brown RN dye showing no change after exposure to sunlight for 40 mins in the absence of ZnO nanoparticles.

concentration decreased. This is in agreement with the knowledge that the amount of organic compound contained is less for solution with lower concentration. The decreasing of the absorption peak at 440 nm indicates that the decomposition of organic compound in the solution has taken place. To check the significance of the catalytic effect of ZnO nanoparticles, the dye was irradiated under sunlight without the presence of ZnO. The result showed that no degradation of the dye took place in the absence of ZnO nanoparticles after 40 mins of sunlight exposure (Figure 4). The effect of initial dye concentration on the decolorization efficiency was studied by varying the concentration from 5×10^{-5} mol·L^{-1} to 2.5×10^{-6} mol·L^{-1} and keeping ZnO (0.5 g·L^{-1}) as constant. The results are presented in Figure 5. It is seen that the decolorization efficiency of Direct Brown RN dye decreases with the increase of initial dye concentrations. This follows from the fact that the active surface on the
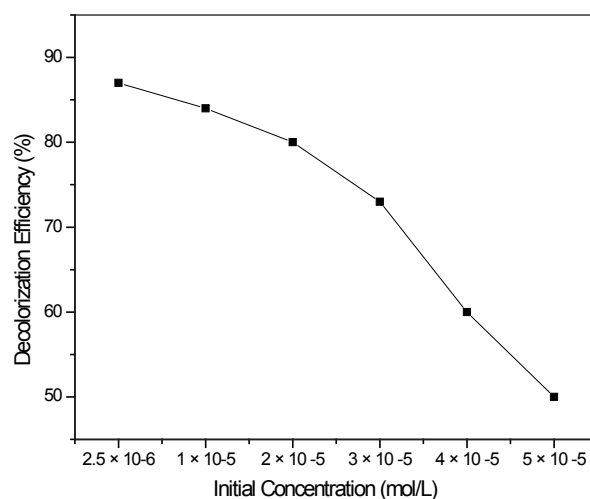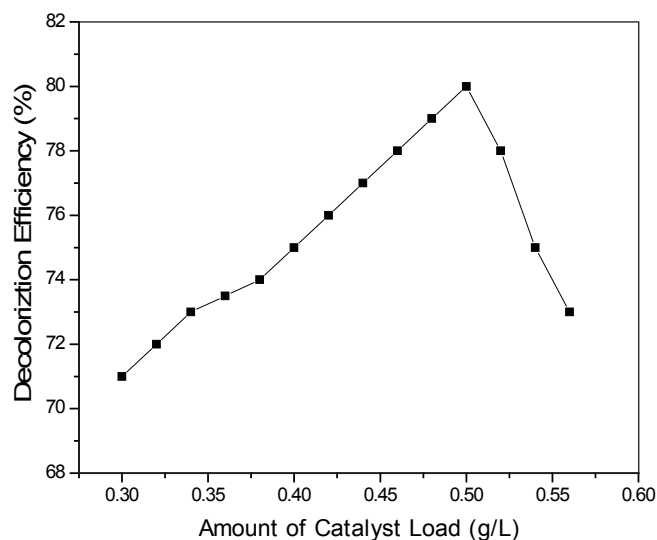

Fig. 5. Effect of initial concentration of Direct Brown RN dye on decolorization efficiency. Conditions: Catalyst loading, 0.5 g·L-1; degradation time, 40 min.

Direct Brown RN (mol·L^{-1})	K (m^{-1}) (10^{-2})	$t_{1/2}$ min
5×10^{-5}	2.41	27.12
4×10^{-5}	3.53	18.50
3×10^{-5}	4.8	14.22
2×10^{-5}	5.06	13.20
1×10^{-5}	5.52	12.79
2.5×10^{-6}	5.79	11.55

catalyst available for reaction is very crucial for the degradation to take place. As the dye concentration is increased and the catalyst amount is kept constant, this results in fewer active sites for the reaction. The rate constant (K) and $t_{1/2}$ values for experimental values of different concentrations of Direct Brown RN dye are summarized in Table 1. It is observed that as the initial concentration decreases the rate constant increases and half life decreases. This means that the reaction became faster and more feasible with the decrease in concentration.

Figure 6 shows the variation of decolorization efficiency with the amount of catalyst loaded. The decolorization efficiency is found to increase when catalyst load was increased upto 0.50 g·L⁻¹ and then it decreases. The reduction in the decolorization efficiency when the catalyst amount is increased above 0.50 g·L⁻¹ may be due to light scattering and reduction in light penetration through the solution. With a higher catalyst loading the deactivation of activated molecules by collision with ground state molecules dominates the reaction, thus reducing the rate of reaction (Neppolian *et al.* 2001).

The ZnO used in the photocatalytic treatment was centrifuged, dried at 60° C in an oven and it was reused as

Fig. 6. Effect of different amount of catalyst load on decolorization efficiency. Conditions: Dye concentration, 2×10-5 mol·L-1; degradation time, 40 min.

such in the succeeding photocatalytic experiments. The efficiency of photocatalytic degradation of dye solution using this regenerated ZnO was observed to be nearly the same.

Effluent treatment

A sample of colored effluent from the leather processing industry which uses Direct Brown RN dye and other chemicals was subjected to the photocatalytic degradation of dye molecules using ZnO nanoparticle. The degradation efficiency of the effluent was evaluated in this study through the COD of the treated and untreated effluent. Thus the degradation efficiency of the effluent under the given experimental conditions was obtained as 72.86%.

Conclusion

ZnO nanoparticle was successfully prepared with a cheap, easy to operate and reproducible procedure and the physicochemical properties of ZnO nano crystals were analyzed. The prepared ZnO nanoparticle photocatalyst effectively treated Direct Brown RN dye leading to its degradation. The developed method was successful in reducing COD values of tannery effluent. Thus, a simple and environmentally benign photocatalytic degradation method has been described for removal of Direct Brown RN, a common dye used in tannery industries of Bangladesh.

Acknowledgement

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