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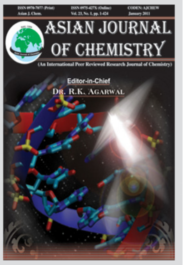

# Solution Combustion Synthesis, Characterization and Photocatalytic Activity of Nanosized ZnO Catalyst for Textile Industrial Dye Effluents Degradation

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We report here the synthesis of ZnO nanoparticles by solution-combustion method employing a mixture of zinc nitrate and sugar (O/F = 1) as reactants. Powder X-ray diffraction, scanning electron microscopy and ultraviolet-visible absorption spectra were employed to characterize the product. The studies showed that the ZnO nanoparticles could be used to catalytically degrade organic dyes present in waste water of textile dye effluent under UV light irradiation. More than 95 % decolourization of textile dye effluent occurs with ZnO as catalyst with in 8 min at basic medium under solar light. It was also found that chemical oxygen demand takes place at a faster rate under solar light as compared to that under UV light. The results further suggest that, ZnO nanoparticles are better catalyst than the calcined ZnO under solar and UV light irradiation.

**Key Words: ZnO, Nanomaterial, SEM, Photocatalysis, Solar light.**

## INTRODUCTION

It has been established that *ca.* 15 % of the total world production of dyes is lost during the dyeing process and is released as textile effluents[1]. These coloured waste waters in the ecosystem is a major source of toxic pollution, which leads to perturbations in aquatic life and is hazardous to human beings. As international environmental standards are becoming more stringent, development of technology for the removal (or degradation into non-toxic forms) of organic dyes have recently become more important. It includes both physical methods (*e.g.* adsorption)[2], biological methods (*e.g.*, biodegradation)[3,4] and chemical methods (*e.g.* chlorination, ozonation)[5]. Wide-band gap semiconductor materials have been the focus of interest in this context for quite some time, as photocatalysts for dye-degradation processes[6-8] which are commonly referred to as the materials which involve advanced oxidation processes (AOPs). The higher mobility of the photogenerated carriers (including holes and electrons) and deeper valence bands of a semiconductor can enhance its photocatalytic oxidative activity leading to the decomposition of the organic dyes[9,10]. Among such different advanced oxidation processes, the most preferred photocatalysts include $TiO_2$[11], CdS, ZnS[12,13], ZnO[14], Fenton[15] and polyoxometallates[16]. Photocatalyst assisted degradation is reported to be better achieved with nanomaterials upon exposure of the catalyst and dye solutions to ultra-violet light[17-21]. In this work, low cost ZnO nanoparticles have been prepared by solution combustion route and its photocatalytic activity on textile industrial dye effluents under both UV and solar light irradation was studied. Various parameters like catalyst dosage, pH of the dye solution, light irradiation on the photocatalytic effect was studied. The effect of crystallite size of the catalyst was also investigated.

## EXPERIMENTAL

Zinc nitrate [$Zn(NO_3)_2\cdot4H_2O$] and commercial sugar ($C_{12}H_{22}O_{11}$) were Merck chemicals and were used without further purification. Double distilled water was employed.

The powder XRD patterns of ZnO samples were obtained using a Philips PW/1050/70/76 X-ray diffractometer which was operated at 30 kv and 20 mA using $CuK_\alpha$ radiation with nickel filter at a scan rate of 20/min. The surface morphology of the powders was examined using JEOL (JSM-840A) scanning electron microscopy (SEM). FTIR spectra were recorded using a Nicollet IMPACT 400 D FTIR spectrometer in the range 4000-400 $cm^{-1}$ using KBr pellet. The absorption spectra were taken with a UV-visible spectrophotometer (Elico-159). Chemical oxygen demand of the sample was estimated by open reflux method and pH meter (Elico) was used to adjust the pH of the solution.

**Synthesis of nano ZnO:** Stoichiometric composition of the redox mixture used for combustion process was calculated using the total oxidizing (O) and reducing valencies (F) of the reactants so that the ratio is unity (F/O = 1) and the energy released during combustion is maximum[22]. The valencies taken are C = +4, H = +1, divalent and trivalent metal ions = +2 and +3 and the valence of O = -2 and that of nitrogen as zero. On this basis, zinc nitrate has an oxidizing valence of -10 and sugar ($C_{12}H_{22}O_{11}$), a reducing valence of +48. For the preparation of ZnO the required mole ratio of $Zn(NO_3)_2 \cdot 4H_2O$ to sugar is 1:0.2.

For the synthesis, zinc nitrate (5.0 g) and sugar (1.2 g) taken in a cylindrical pyrex dish of 300 mL capacity were dissolved in a minimum quantity of double distilled water and dispersed well using a magnetic stirrer for 0.5 h. The resulting homogeneous redox mixture was rapidly heated in a muffle furnace maintained at 300 ± 10 °C. The redox mixture boils, froths and dehydrates forming a honey like gel which burns with an incandescent flame. The product of combustion is voluminous, fluffy and porus. The gaseous products formed such as oxides of nitrogen by the thermal decomposition of metal nitrates at 300 ± 10 °C are hypergolic. The whole process takes place in less than 5 min. The reaction may be represented as:

$$Zn(NO_3)_2\ (aq) + C_{12}H_{22}O_{11}\ (aq) \rightarrow$$
$$ZnO(s) + N_2\ (g) + 11H_2O + 12CO_2\ (g)$$

## RESULTS AND DISCUSSION

**Characterization of ZnO nanoparticles:** Fig. 1 shows powder XRD of as-formed and calcined [at 600, 900 and 1000 ºC for 3 h] ZnO particles. All the samples show crystalline cubic phase, with no detectable secondary phase. The X-ray diffraction peaks have been indexed and found to be consistent with a hexagonal wurtzite structure [JCPDS 36-1451] with lattice parameters a = 3.249 and c = 5.206 Å. The crystallite size of the samples was calculated using Scherrer's formula and it was found to be 12, 25, 36 and 50 nm for as-formed and calcined samples at 600, 900 and 1000 ºC, respectively. Powder XRD results reveal that as calcination temperature increases the growth of the particles also increases.

The microstructure and morphology of the samples were studied by scanning electron microscope. The SEM images of as-formed and calcined ZnO samples are shown in (Fig. 2). The SEM images reveal that the particles are uniform, circular in shape and are weakly agglomerated with an average grain size of 0.5-3.0 mm. On calcination, particle size grows due to congregation effect, which is also reflected in powder-XRD profiles. The SEM micrographs show the pores and voids, which can be attributed to the large amount of gases escaping from the reaction mixture during combustion. It is well known that the morphological characteristics of the powder prepared are strongly dependent on the heat and gases generated during the reaction. Large volumes of gases facilitate the formation of tiny particles while the heat released is an important factor for crystal growth. The agglomeration of nanoparticles is usually explained as due to minimization of their surface free energy. However some investigators suggest that the agglomeration takes place due to the presence of organic radicals that act as binders.

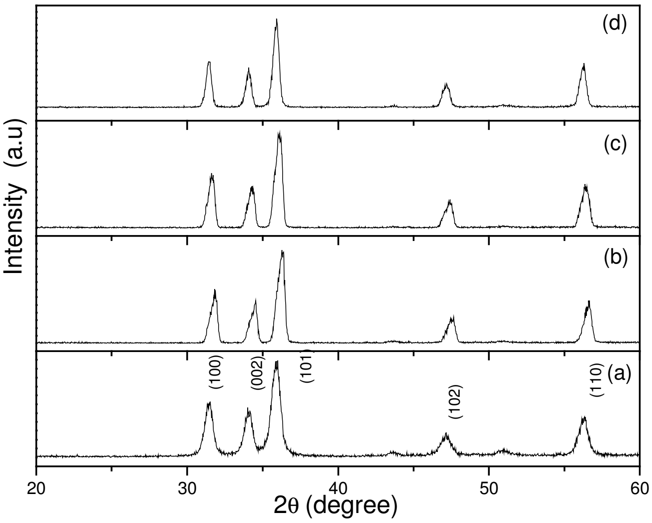

Fig. 1. Powder XRD of ZnO samples (a) as-formed and calcined for 3 h at (b) 600 ºC, (c) 900 ºC and (d) 1000 ºC

Fig. 3 shows a typical FTIR spectrum of as-formed ZnO nanopowder. There is only one intense band *ca.* 417 $cm^{-1}$ associated with the characteristic vibrational mode of Zn-O bonding[23]. The weak absorption peak at 3421 $cm^{-1}$ corresponds to the -OH group of water adsorbed on the surface of the ZnO powder.

**Photocatalytic activity of ZnO nanopowder:** In order to evaluate the photocatalytic activity of the ZnO particles, photocatalytic degradation of textile dye effluent was studied. A typical experiment, consisted of 100 mL of the dye solution and 0.03 g of the catalyst with the surface area of 39 $cm^2$ taken in a glass reactor. The mixture was stirred in dark for 20 min to establish the adsorption equilibrium of the dye molecules with the catalyst. The solution was irradiated with the UV light in the range of 350-400 nm of 125 W with a photon flux of 7.75 $mW/cm^2$. The experiments were performed in the presence of atmospheric oxygen. The distance between the light source and the reactor was kept at 29 cm. Experiments using solar light were carried out during the month of May between 1 to 2 P.M. (day temperature was 30 ºC) when variation in the solar light intensity is minimum. The decolourization efficiency (%) was calculated from the relation:

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

where $C_0$ and C is the concentration of textile dye effluent before and after solar light-irradiation respectively. Similar experiments were carried out by varying the pH of the solution and amount of the catalyst.

**Effect of ZnO loading:** Experiments were carried out employing different amounts of ZnO keeping the amount of textile dye effluent constant (Fig. 4). It was found that, the rate constant increases up to 30 mg/100 mL of the dye solution, beyond which it shows a drastic reduction. The increase in the degradation of the effluent with an increase in the amount of catalyst may be due to an increase in the active sites available on the catalyst surface for the reaction, which in turn increases

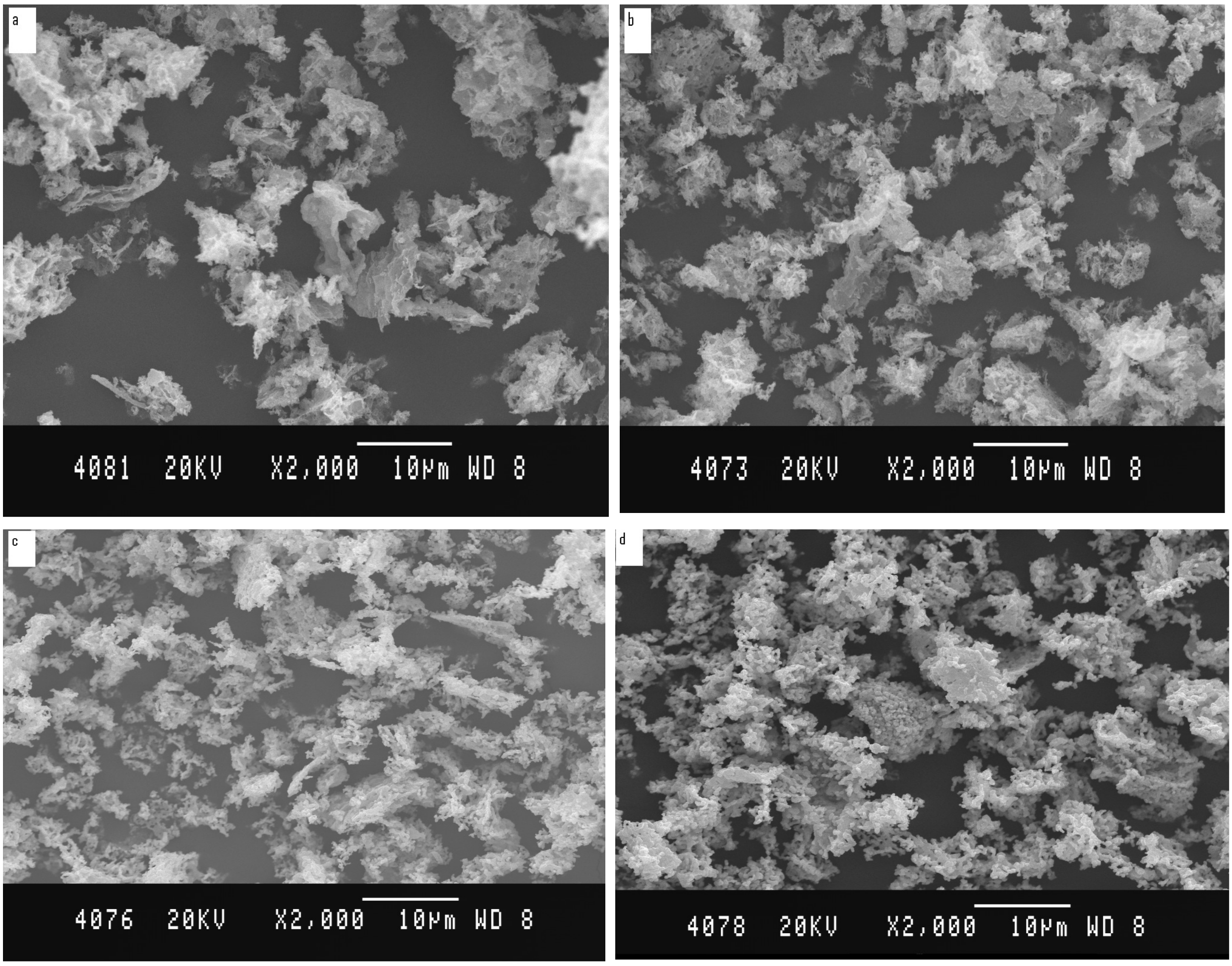

Fig. 2. SEM images of ZnO samples (a) as-formed and calcined at (b) 600 ºC (c), 900 ºC and (d) 1000 ºC

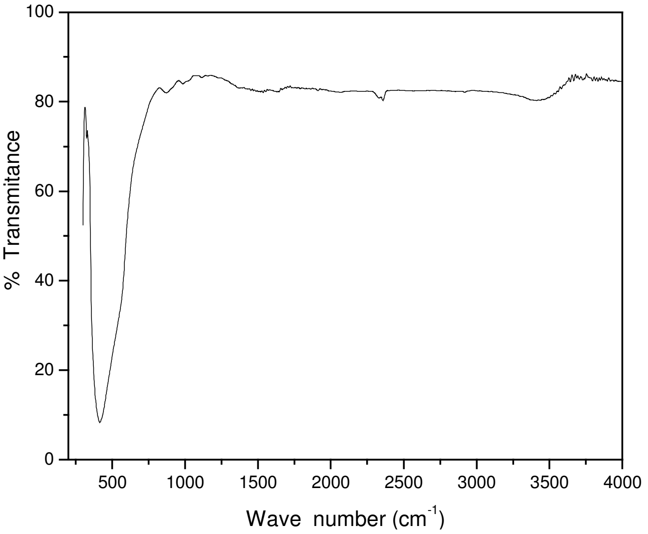

Fig. 3. Typical FTIR spectrum of ZnO nanopowder

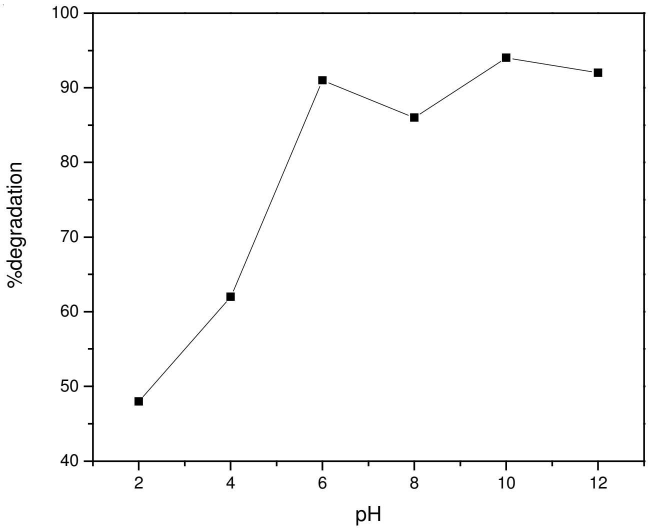

Fig. 4. Plot of ZnO dosage *versus* % degradation of textile dye effluent

the rate of radical formation. The reduction in the rate constant when the catalyst amount is increased beyond 30 mg/100 mL, may be due to light scattering and reduction in light transmission through the solution. With a higher amount of catalyst, the deactivation of activated molecules by collision with ground state molecules dominates the reaction, thus reducing the rate of reaction[24,25].

**Effect of pH:** The pH of the dye effluent solution was adjusted using HCl or NaOH solution. The maximum rate constant was recorded at basic pH (above 7.0) (Fig. 5). The pH affects not only the surface properties of ZnO but also the dissociation of dye molecules and the formation of hydroxyl radicals. Enhanced reaction rate under alkaline condition could be attributed to the increase in hydroxyl ions. In acidic condition,

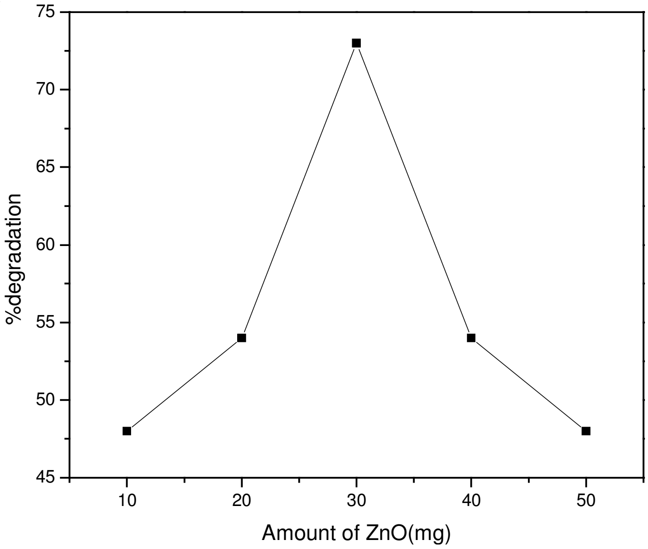

Fig. 5. Plot of pH against % degradation of textile dye effluent under UV light irradiation

the perhydroxyl radical may convert to hydrogen peroxide, which in turn gives rise to the hydroxyl radical. Thus, it is necessary to maintain alkaline pH.

**Effect of stirring:** The photo assisted decolourization of textile dye effluent was also carried out using optimum amount of ZnO at basic pH under solar and UV irradiation. Fig. 6 illustrates the results of photodecolourization of textile dye effluent using optimized conditions as a function of duration of stirring under solar light irradiation. It indicates that the decolourization of textile dye effluent occurs at a faster rate under solar light compared to that under UV light. Decolourization of 99 % was observed when stirred for 8 min under solar light, whereas in the presence of UV irradiation (Fig. 6), the decolourization was slow and it took *ca.* 0.5 h of stirring. The results are in agreement with the earlier findings that ZnO can harvest maximum solar energy by utilizing visible light for degradation of water bound organics[26]. Although sunlight has only 5 % of optimum energy for photocatalytic degradation of pollutants, it is a safe and cost effective source. UV source is not only hazardous but also expensive. In tropical countries like India, where intense sunlight is available throughout the year it could be effectively used for photocatalytic degradation of pollutants in wastewater. Further, there is no material deterioration in the case of sunlight.

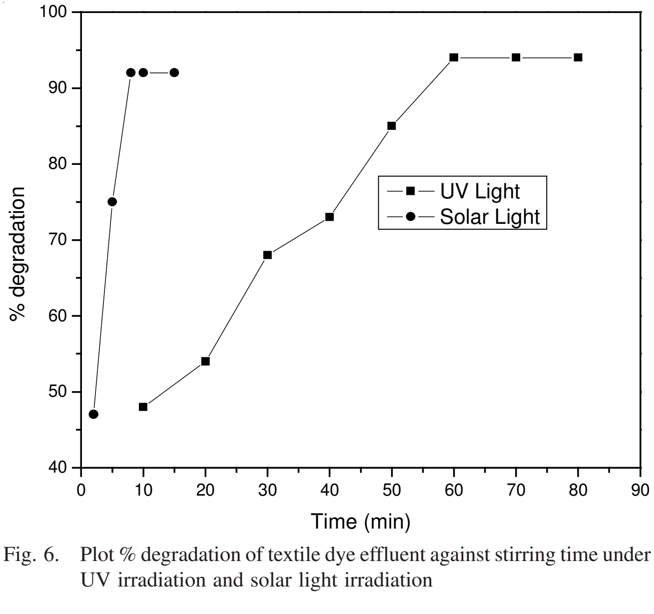

Fig. 6. Plot % degradation of textile dye effluent against stirring time under UV irradiation and solar light irradiation

**Estimation of chemical oxygen demand (COD):** The chemical oxygen demand test is widely used as a measure of the strength of organic matter in wastewater. It provides quantitative data of organic waste in terms of the total quantity of oxygen required for the oxidation of organic matter to $CO_2$ and water by a strong oxidant. The chemical oxygen demand of the dye solution before and after the treatment was estimated. The dichromate reflux method is adapted to estimate chemical oxygen demand[27]. The reduction in chemical oxygen demand values [85 %] of the treated dye solution is estimated.

## Conclusion

Textile dye effluent with diverse composition was effectively treated using ZnO nano particles. The reduction in chemical oxygen demand [85%] of the effluent suggests that the dye molecules are completely decolarized. Thus the ZnO assisted photocatalytic degradation of textile dye effluent is a versatile, economically and environmentally benign and efficient method of treatment.

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