

Synthesise of ZnO nano particle as an alternative catalyst for Photocatalytic degradation of brilliant red azo dye

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To cite this article:

Jayamadhava P., Sudhakara A., Ramesha S., Nataraja G. Synthesise of ZnO Nano Particle as an Alternative Catalyst for Photocatalytic Degradation of Brilliant Red Azo Dye. *American Journal of Environmental Protection*. Vol. 3, No. 6, 2014, pp. 318-322.

doi: 10.11648/j.ajep.20140306.13

Abstract: A simple and a very convenient solution combustion method have been described to obtain ZnO nanoparticle. The band gap energy, particle size and morphology were studied by absorption spectra, XRD and SEM. The photocatalytic activity of synthesized ZnO nano particle on Brilliant red dye was studied by varying pH, amount of catalyst and dye concentration respectively. According to the XRD the average crystallite size of ZnO was found to be 41nm and the band gap energy of ZnO was found to be 3.2 eV. The photocatalytic degradation efficiency of this nanoparticle was found to be 100%, 98.6%, and 87.3% for 25, 50 at 75 mg/L dye concentrations respectively against Brilliant Red dye.

Keywords: Brilliant Red, Nano Particle, Photocatalyst, ZnO

1. Introduction

Water is the wellspring of life and is the most important liquid in the world to maintain the plant and animal life. Since the two thirds of the earth's surface covered by water and human body consists of 75% of it, water is one of the prime element responsible for life on earth. Water is fouled due to the disposal of wastes generated from the various developmental activities and causes pollution problem. There are two choices to overcome these problems, *i.e.*, normally prevention and control by adopting various strategies to minimize the waste generation and by different treatment methods. Liquid waste is of great concern because of their harmful effects. Industrial wastewater contains wide variety of materials of both organic and inorganic nature including toxic substances like dyes and pigments, which are usually discharged with or without treatment.

Since the beginning of industrialization, the variety and quantity of pollutants discharged into the environment have steadily increased. But the rates of development of waste production are not likely to diminish; efforts to control and dispose of wastes are also rising. Among the pollutants currently thousands of tons of organic dyes discharged from textile mills. Out of nearly 80,000 tons of annual production of

dyes, 10-15% of the world product dye is lost during the dyeing process and is released in textile effluents [1]. These colored dye effluents create several environmental problems by releasing toxic and potential carcinogenic substances into the aqua sphere. This massive influx of untreated organic chemicals into the waterways not only introduces aesthetic concerns, but they promote eutrophication and adversely affect the environment [2]. Several studies have been carried out for biological, physical and chemical treatment of dye containing effluents [3]. Among these, biodegradation, adsorption, chlorination and ozonization are the most commonly used conventional methods. Dyes are usually resistant to aerobic degradation. Hence bio treatment alone has been found to be ineffective for the treatment of dye effluents [4]. On the other hand, physical methods such as flocculation, reverse osmosis and adsorption are not destructive and mainly create pollutant concentrated phases, and many of this process are not found economically feasible [5]. The use of heterogeneous photocatalytic treatment is more attractive for the degradation of organic dyes contrary to physical process; it can facilitate the complete mineralization of organic compounds to carbon dioxide, water and mineral acids [6-8]. Moreover, Photocatalysis does not require expensive oxidant and can be carried out at natural sunlight.

Hence, in the present work, the photocatalytic degradation

of Brilliant Red (BR), a textile azo dye on synthesized ZnO nanoparticles under natural sunlight was investigated by varying other parameters such as initial dye concentration, solution pH and catalyst dosage.

2. Experimental

2.1. Materials and Reagents

Chemicals such as Zinc nitrate $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{NH}_2\text{CO NH}_2$, all are of A.R grade obtained from Hi media chemicals Mumbai, and used without further purification. Brilliant Red (The molecular mass = 958, $\lambda_{\text{max}} = 517 \text{ nm}$) and distilled water was used for preparation of various solutions.

2.2. Apparatus and Instruments

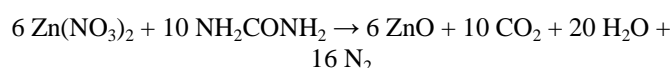
A 119 UV-Vis single beam spectrophotometer from Systronics has been used for recording absorbance at λ_{max} . Later the absorbance was recorded in UV-Vis spectrophotometer 169 (Systronics).

2.3. Synthesis of Nanoparticles

The photocatalyst ZnO was synthesized by solution combustion method. Stoichiometric compositions of Zinc nitrate and urea were calculated using the total oxidizing and reducing valencies of the components which serve as numerical coefficients for stoichiometric balance [9-10].

2.4. Synthesis of ZnO

The stoichiometric amounts of Zinc nitrate, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (17.85g) was dissolved in a minimum quantity of water along with $(\text{NH}_2\text{CO NH}_2)$ (6g) in a silica crucible (with a volume of 100 cm^3). The mixture was introduced into the muffle furnace which was preheated at 600°C . Initially the solution foils, boils and undergoes dehydration followed by decomposition with the evolution of gases (N_2 and CO_2). Then, it burns to yield the residue. The gases evolved not only yield fine particles of metal oxides but also help to dissipate the heat which inhibits sintering of the product. Thus, combustion reaction was completed within a few minutes [11]. The combustion reaction for the synthesis of ZnO by the redox mixture method (urea) can be written as:



2.5. XRD and SEM of Synthesized ZnO Nanoparticle

The powdered sample of ZnO nanoparticle was examined by XRD and analysis was carried out on fresh sample to assess the purity of the expected phases and the degree of crystallization *i.e.*, size, composition and crystal structure. XRD was performed by Rigaku diffractometer using Cu-K_α radiation (1.5406 \AA) in a θ - 2θ configuration. According to the XRD the average crystallite size of ZnO was found to be 41 nm (Fig. 1). Also, Figure 2 illustrates SEM photographs of single crystals of ZnO. The photographs revealed plate like crystal

morphology which looks like scattered. The individual plates are having sharp edges. The enlarged image shows the particles are attached on the other particles.

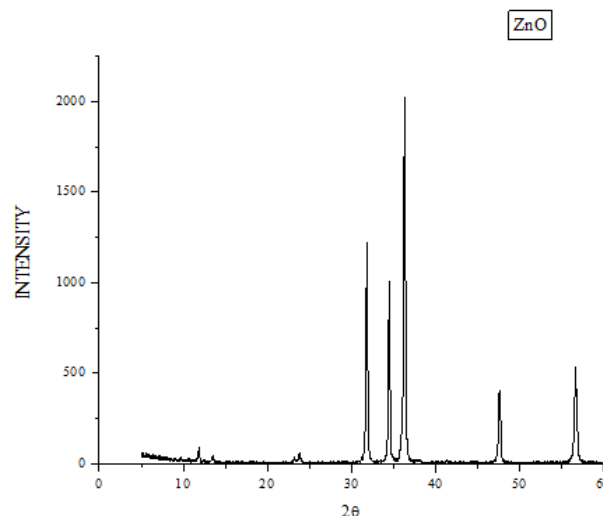


Fig 1. XRD of synthesized ZnO nanoparticle

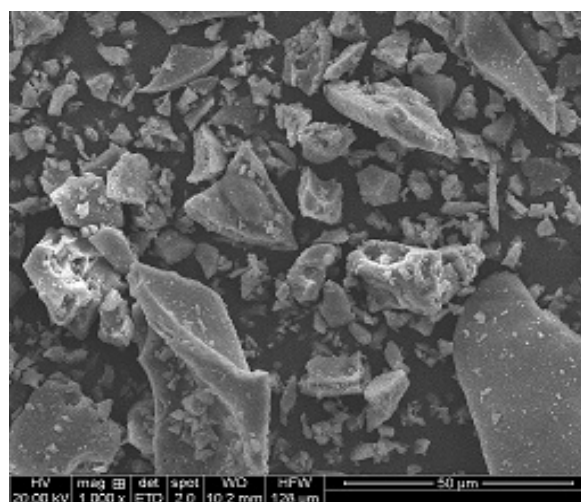


Fig 2. SEM micrographs of ZnO

2.6. UV Absorption Spectroscopy

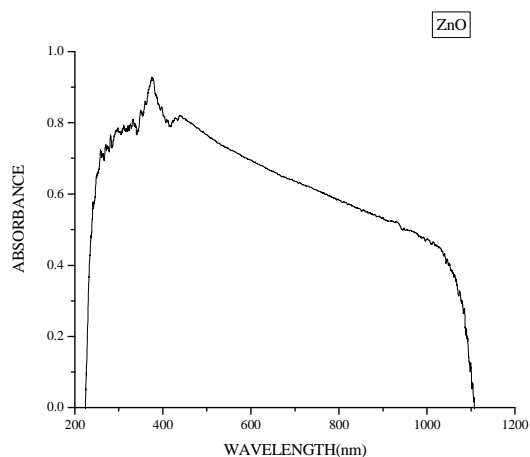


Fig 3. Absorption spectra of ZnO

Absorption spectra of ZnO nanoparticle was recorded using a UV-Vis spectrophotometer over the wavelength range of 200-1200 nm at Nano Research Laboratory. From the spectrum, it has been inferred that ZnO nanoparticle has sufficient transmission in the entire visible and IR region. (Fig-3).

The band gap energy of the ZnO was calculated using the following simple conversion equation [12], the band gap equation is calculated using the Planck's equation as follows.

$$e = hc/\lambda$$

h = Planck's constant, C = Velocity of light, λ = wavelength
 $h = 4.135 \times 10^{-15}$ eV, $C = 3 \times 10^8$ m/s

$$\lambda = \dots \times 10^{-9} \text{ nm}$$

$$\text{Band Gap Energy (eV)} = 4.135 \times 10^{-15} \times 3 \times 10^8 \times 10^9$$

$$\text{Band Gap Energy (eV)} = 12.405 \times 10^2 / \text{wavelength (nm)}$$

$$\text{Band Gap Energy (eV)} = (1240 / 376) = 3.2 \text{ eV}$$

The band gap energy of ZnO found to be 3.2 eV.

2.7. Procedure

Photo degradation experiments were carried out with BR dye (Fig 4) concentration 50mg/L prepared using distilled water. A known concentration of ZnO nanoparticle was added to beakers containing BR dye solution. The suspension pH values were adjusted at desired level using dilute NaOH and H₂SO₄ and then the pH values were measured with pH pen. After that, the beakers were kept in the sunlight. During irradiation, agitation was maintained to keep the suspension homogenous. The concentration of dye in each degraded sample was determined with UV-Vis spectrophotometer 169 (Systronics) at $\lambda_{\text{max}} = 517\text{nm}$. The percentage of photo degradation D was determined by using the following equation⁶, where C_0 is initial concentration of BR and C_t is the concentration of BR at time 't'.

$$D = \left(\frac{C_0 - C_t}{C_0} \right) \times 100$$

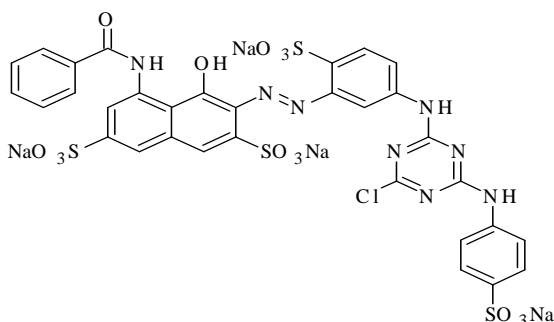


Fig 4. Structure of Brilliant Red

3. Results and Discussion

3.1. Catalyst Type

Initially, blank experiments were performed under direct

sunlight without the addition of catalyst and no degradation was observed. To enhance the efficiency, different dose of catalysts were added. The results are shown in fig 5, at dye concentration=50mg/L, catalyst concentration = 0.4g/100ml, initial solution pH = 9, and reaction time =120 min respectively. The results showed that the ZnO nanoparticle exhibited higher photocatalytic activity. The similar result was also obtained in other studies with other type of azo dyes [13]. The decolourization result was explained on the basis of higher quantum efficiency of ZnO. The band gap energy of ZnO was found to be 3.2 eV. The Sun light energy was found to be sufficient to cause excitation in ZnO nanoparticle [14]. Beside the band gap energy, the charge carrier density as well as the catalyst structure and the crystallinity may also have significant impact on the photocatalytic activity [15-16].

3.2. Effect of Catalyst Concentration

To determine the effect of the catalyst concentration, a series of experiments were carried by varying the amount of catalyst from 0.1 to 0.7g/100ml (dye concentration = 50 mg /L , solution pH=9) respectively. The photo degradation efficiency is as shown in Fig 5. As per the figure, for a constant reaction time (120 min), the degradation efficiency was found to increase sharply by increasing concentration up to 0.4g/100ml, and then decreased gradually. At lower concentration, the catalyst surface and adsorption of light by the catalyst surface are the limiting factors and increase in catalyst greatly enhances the degradation efficiency. On the other hand at higher concentration levels, the irradiation field inside the reaction medium was reduced due to the light scattering by catalyst particles [15].

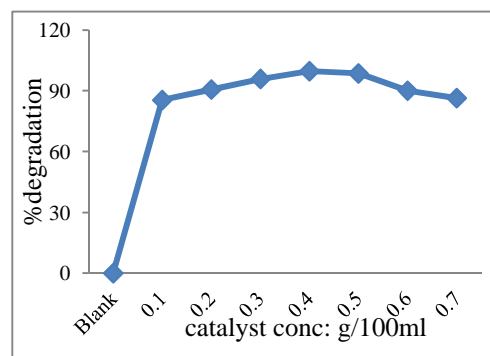
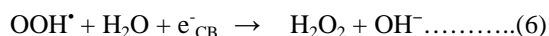
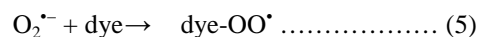
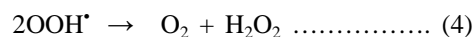
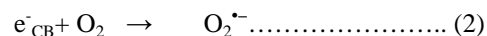
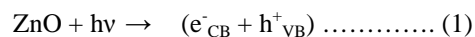
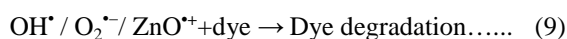


Fig 5. Effect of catalyst concentration on photocatalytic degradation of BR (BR= 50mg/L, pH=9, Time=120min)





It has been established that the photocatalysed degradation of organic matter in solution is initiated by the photo excitation of the semiconductor, followed by the formation of electron-hole pair on the surface of the catalyst. The mechanism of photocatalytic degradation for an azo dye are characterized by nitrogen to nitrogen double bonds ($\text{N}=\text{N}$). The color of azo dye is determined by the azo bonds and their associated chromophores and auxochromes. Azo bonds are the most active bonds in azo dye molecules and can be oxidized by positive hole or hydroxyl radical or reduced by electron in the conduction band. The cleavage of $\text{N}=\text{N}$ leads to the discoloration of dyes [17]. Mechanism of the photocatalytic degradation is as follows [18]. The mechanism of photocatalytic activity of ZnO nanoparticle can be predicted based on the equations as shown above. Under sunlight irradiation ZnO molecules get excited and transfer electron to the conduction band (Eq 1). Electron in the conduction band of ZnO can reduce molecular oxygen and produce the super oxide radical $\text{O}_2^{\bullet-}$ ions (Eq 2). This radical may form hydrogen peroxide or organic peroxide in the presence of oxygen and organic molecule (Eq 3, 4, 5). Hydrogen peroxide can be generated in another path (Eq 6). Hydrogen peroxide can form hydroxyl radicals which are powerful oxidizing agents (Eq 7, 8). The radicals produced are capable of attacking dye molecules and degrade them (Eq 9) [19].

3.2. Effect of PH

In order to study the effect of pH on the degradation efficiency of ZnO catalyst, the experiments were conducted at various pH (ranging from 2 to 11). The results showed that pH significantly affected the degradation efficiency. As shown in fig.6, the degradation rate of BR increased from 70.5% to 98.6% when the pH was increased from 2 to 9 and then decreased to 89.6% at pH 11. The maximum degradation rate of BR was achieved at pH 9. BR is an anionic dye which contains sulphonated groups. Its photocatalytic activity was maximum at pH 9. More efficient formation of hydroxyl radicals occurs in alkaline medium. Excess of hydroxyl anions increases the formation of OH^{\bullet} radicals. These OH^{\bullet} radicals are the main oxidizing species responsible for photocatalytic degradation. (Eq 7-8)[20]. But at above pH 9, the decrease in the degradation efficiency can be explained on the basis of amphoteric nature of ZnO catalyst and the ZnO surface becomes negatively charged for higher pH values. This causes the electrostatic repulsion between the catalyst and negatively charged BR dye [21].

3.3. Effect of Initial Dye Concentration

The effect of initial dye concentration on the degradation efficiency was investigated by varying the initial dye concentration. The initial concentration of dye was varied from 25, 50 and 75 mg/L. ZnO resulted in 100%, 98.6%, and 87.3% for 25, 50 and 75 mg/L dye concentrations respectively

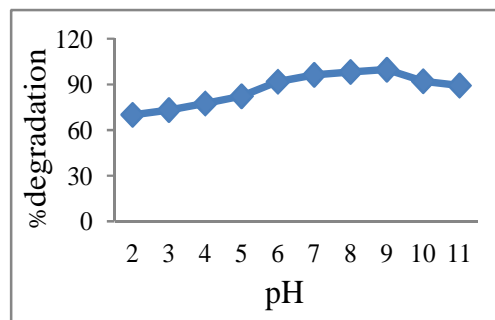


Fig 6. Effect of initial pH on photocatalytic degradation of BR, (BR= 50mg/L, ZnO =0.4g/100ml, Time=120min)

These series of experiments illustrated that the degradation efficiency was inversely affected by the concentration (Fig. 7). The decrease in the degradation with an increase in dye concentration was ascribed to the equilibrium adsorption of dye on the catalyst surface which results in a decrease in the active sites. This phenomenon results in the lower formation of OH^{\bullet} radicals which were considered as primary oxidizing agents of the organic dye [22]. On the other hand, according to Beer-Lambert law: as the initial dye concentration increases, the path length of photons entering the solution decreases. This results in the lower photon absorption on the catalyst particles, and consequently decreases the photocatalytic reaction rate [23].

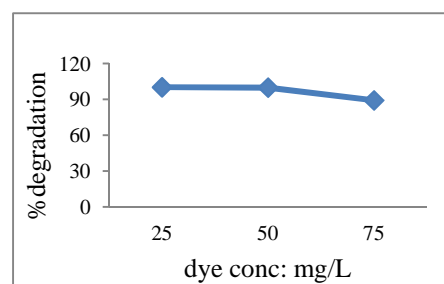


Fig 7. Effect of initial dye concentration on photocatalytic degradation of BR (pH= 9, ZnO =0.4g/100ml, Time=120min)

4. Conclusions

A simple and very convenient solution combustion method was described to obtain ZnO nano particle. According to the XRD the average crystallite size of ZnO was found to be 41nm and the band gap energy of ZnO was found to be 3.2 eV. The photocatalytic degradation efficiency of this ZnO nanoparticle was found to be 100%, 98.6%, and 87.3% for 25, 50 at 75 mg/L dye concentrations respectively against Brilliant Red dye. The degradation efficiency increases with increase in pH, and attaining maximum value at pH 9. The above pH 9, the catalyst surface is negatively charged by means of adsorbed OH^- ions, which causes electrostatic repulsion between catalyst and negatively charged BR decreases the degradation efficiency. Hence the experiment was proved that the ZnO having 41nm in size and the band gap energy of 3.2 eV was found to be very active catalyst and hence could be utilized in

large scale for degradation of different azo dyes with suitable technology.

Acknowledgements

Authors are grateful to the Mr. Nagenrda Prasad. R., Director, R&D Center SS College Bangalore, for valuable support for this research work and we also thank to Indian institute of science, Bangalore for spectral studies.

Nomenclature

1 XRD	x ray Diffraction
2 SEM	Scanning Electron Microscopy
2 ZnO	Zink Oxide
3 Zn(NO ₃) ₂ .6H ₂ O	Zinc nitrate

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