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Chemical Synthesis of Zinc Oxide Nanoparticles and Its Application of Dye Decolourization

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Abstract

In the present study, various size of Zinc Oxide Nanoparticles (ZnO NPs) was synthesized via Sol-gel method. The photocatalytic activity of the synthesized ZnO NPs was investigated for the Decolourization of three different colored dyes viz. Congo Red, Acid Blue 9 and Coomassie Brilliant Blue R-250 under UV lamp. Zinc Chloride ($Zncl_2$) and Sodium Hydroxide (NaOH) were used for the chemical synthesis. The SEM and FTIR analysis shows that the synthesized ZnO NPs are crystalline in nature. The synthesized NPs were then checked for its efficiency to decolorize the above same dyes under the condition of 20 mg/L dye and 0.3 g/L of photocatalyst dosage. The investigation results showed that each size of ZnO NPs was able to effectively decolorize the dye solution and the efficiency was found to be 88% for Congo red (CR: 27-29 nm), 73% for Acid Blue 9 (AB: 24-27 nm) and 70% for Coomassie Brilliant Blue R-250 (BB: 29-32 nm). Out of which CR dye oxidation rate was higher than the other dyes and especially BB dye possible to decolorize by using synthesized ZnO NPs. Hence, it was concluded that ZnO NPs by itself is strong enough to decolorize these dye aqueous solutions. Moreover, the photocatalytic activity of NPs on dye was the decisive factor/unique property for dye reduction rather than size and morphology of the ZnO NPs.

Keywords: *Chemical Synthesis, Decolourization, Dye, Photocatalyst, Sol-gel Method, Zinc Chloride.*

1. INTRODUCTION

Nanotechnology deals with the particle size about 1 to 100 nm according to the specified novel applications. Nanosized particles of semiconductor materials have engaged more interest in recent years because of their special properties *viz.* large surface area, electronic and optical properties which are compared to their bulk components [1]. The large surface to volume ratio justified the unique properties (as a catalyst) of nanoparticles (NPs) [2]. The nanostructured metal oxides are an important class of semiconductors [3]. Among the various semiconducting and photocatalyst oxides, Zinc Oxide (ZnO) is an intrinsic electronic and photonic wide band gap semiconductor with an energy gap of 3.37ev and a high exciton binding energy (60 meV) at room temperature [4]. It has been used considerably for its catalytic, electrical, electronics, optical, dermatological, antibacterial and photochemical properties [5-7]. The nano zinc oxide is an important raw material for many applications for the design of gas sensors and solar cell, panel display, photocatalysis, machineries, environmental protection-waste water treatment and biomedical-antibacterial applications [8-11].

Many methods have been studied in the literature for the synthesis of ZnO NPs such as laser ablation [12], hydrothermal methods [13], sol-gel method [14], electrochemical depositions [15], thermal decomposition [16], chemical vapor deposition [17], and combustion method [18]. Recently published methods are ultrasound [19], anodization [20], micro-wave assisted combustion method [21], co-precipitation [22], two-step mechano-chemical thermal synthesis [23], and electrophoretic deposition [24]. However, chemical route is one of the potential methods for synthesizing NPs with high surface properties and purity [25]. Chemical synthesis techniques have been mostly used due to their low cost, less hazardous, high yield, simplicity and capable of easy scale up [26].

Large quantities of colored dye effluents emitted from textile and manufacturing dyeing industries create serious environmental pollution due to their contrary effect [27]. Dye effluents are aesthetic pollutants that accommodate chemicals which display toxic effect on living organisms and generate carcinogenic compounds such as aromatic amines and mutagens are toxic to mammals [28]. More than 53% of these commonly used dyes are identified as completely non-biodegradable compounds [29]. Removal of dyes from textile waste effluents has been carried out by flocculation, membrane filtration, coagulation, adsorption and fungal decolourization [30].

In recent years as a promising tool to surrogate the long-established wastewater treatment, photocatalysis among the Advanced Oxidation Process (AOP) has attracted the public concern for its capacity to convert the pollutants into the innocuous substances directly in the wastewater [31]. The process uses atmospheric oxygen as the oxidant and is processed under ambient conditions to be used as a semiconductor catalyst for converting organic pollutants to CO_2, water and mineral acids [32]. Electrochemically assisted ZnO NPs also was investigated to degrade reactive azo dyes in recently [33]. In this regard, ZnO nanoparticles can be used as an effective, inexpensive and non-toxic semiconductor photocatalyst to the degradation of a wide range of synthetic dyes [34]. Some researchers have reported that the performance of ZnO is well in both acidic and alkaline conditions than the Tio_2 [35]. Also it is well known that the highly reactive $OH^{\bullet}$ radicals and holes are created on the surface of photocatalyst under the radiation of UV. Therefore, a surface characteristics of ZnO NPs which is determined by synthesis method will influence this property well in final degradation efficiency. The size of photocatalyst is one of the most important factors. There were many comparative studies developed about the photo catalytic efficiency of pollutants on ZnO nanostructures [36]. Other investigations also have been reported on removal of dyes using NPs such as Congo Red (ZnO Nps-90.63%) [37], Acid Blue 9 (TiO_2 Nps-97%) [38] and Coomassie Brilliant Blue R-250 (coir pith-70%) [39]. Hence, 50 nm of ZnO NPs are most effective photocatalyst in decolourization which has been reported in literature [40]. Except for size, morphology and fabrication methods of the photocatalyst are the crucial factor that influences the degradation efficiency [41]. Hence, comparison of dye degradation efficiency by ZnO NPs with various size scale results indicated preparation method was the crucial factor rather than size and morphology because of surface area significant effects on photocatalytic activity [40].

In this study, the specific aim is to investigate the possible application of the synthesized and characterized ZnO NPs for decolourization of aqueous solution containing selective dyes *viz.* Congo Red, Acid Blue 9 and Coomassie Brilliant Blue R-250. Usually, CR dye is used in most of the NPs decolorize studies, whereas in this study, an attempt was made to decolorize the AB and BB dye using chemically synthesized ZnO NPs. In order to evaluate the percentage decolourization effect on the particle size, morphology, temperature and dripping time by prepared different size of nanoparticle for dye reduction. To compare the decolourization efficiency of the selective dyes using different size ZnO nanoparticles under the conditions, studies were carried out for the same.

2. EXPERIMENTAL SECTION

2.1. Materials

$ZnCl_2$ (min. 98%), NaOH (pellet min. 99%) and 2-propanol (min 99.5%) all of analytical grade reagents were used for the synthesis and de-ionized water is used for the preparation of solutions.

2.2. Synthesis of ZnO NPs with Various Size Scales

10 g of NaOH (1.0 M) was dissolved in 100 ml distilled water; the resulting solution was heated under constant stirring at the desired reaction temperature (50-90°C). After obtaining the desired temperature, 17 g of $ZnCl_2$ (0.5 M) was dissolved in 100 ml distilled water, the resulting solution was added drop by drop (dripping for 20-60 min) into the NaOH solution. This procedure was performed under different dripping time and the reaction temperatures. The dripping of the $ZnCl_2$ solution in an aqueous alkaline solution results in immediate precipitation of ZnO, and the color changes from transparent to white. After completing dripping, each solution is agitated for a period of two hours, maintaining the desired temperature. The particles were detached from the supernatant dispersion. The supernatant was discarded, and suspension was washed for five times with distilled water for the complete removal of NaCl from the suspension. Each time, the dilution ratio of the concentrated and washing solution was about 1:10. The purified particles were peptized by 2-propanol in an ultrasonic bath for 10 min at 27°C. The peptization process is necessary to disrupt the micro-agglomerates and release the nanounits from bulk suspensions [42]. The particles were then collected by centrifugation at 6,000 rpm for 15 minutes. Accumulated particles were filtered and washed several times with de-ionized water and dried in a vacuum oven at a maximum temperature of 70°C for several hours. Synthesis conditions of different ZnO NPs are shown in Table 1.

Table 1. *Synthesis conditions of different ZnO nanounits (Zinc Chloride, Sodium Hydroxide and water used as a medium).*

Run	Temperature (°C)	Dripping Time (min)	Mean particle size (nm)
1	50	20	32-37
2	60	30	29-32
3	70	40	27-29
4	80	50	24-27
5	90	60	21-24

2.3. Characterization

The synthesized ZnO NPs were characterized by using Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). The FTIR spectra were recorded on a PERKIN ELMER – SPECTRUM RX 1 (%T, ATR) in KBr media in the range 400 to 4000 cm^{-1} at a scanning rate of 4 cm^{-1}/min. The SEM analyses were carried out to determine the morphology and the mean particle size of nanoparticles. The samples were prepared on a carbon coated grid, and then the samples were allowed to analysis for SEM using JEOL-JSM-5610LV with resolution of 1μm at 15 kV with 11 mm.

2.4. Photocatalytic Decolourization of Dyes Using Synthesized ZnO Nanoparticles

The photo catalytic decolourization of synthetic dyes like CR, AB and BB were carried out to evaluate the performance of the synthesized ZnO NPs. About 0.002 g of dye is dissolved in 100 ml distilled water and 0.03 g of synthesized nanoparticles were added to it. The solution was sonicated for 15 minutes and then stirred in dark for 20 minutes [43]. All the experiments were performed at temperature of 27±3°C and under the UV light. The pH value of pure dye solutions such as CR, AB and BB were also corrected to neutral. During the experiments, samples were withdrawn at regular intervals from each dye solutions. The photo-decolourization efficiency was quantified by detecting the absorbance of the solutions at its maximum absorption wavelength of 497 nm for CR, 640 nm for AB and 595 nm for BB with UV-Vis spectrophotometer. The decolourization efficiency as a function of time was calculated by the absorbance value of the original and analytical samples. Decolourization efficiency is defined as

$$\text{Decolourization Efficiency, \%} = \frac{C_O - C_T}{C_O} \times 100$$

where, C_0 (mg/L) and C_t (mg/L) are the dye concentration at initial and after time ‘t’ (min) respectively.

3. RESULTS AND DISCUSSION

3.1. Nanoparticles Characterizations

The morphology of ZnO NPs was analyzed via scanning electron microscopy under lower magnification.

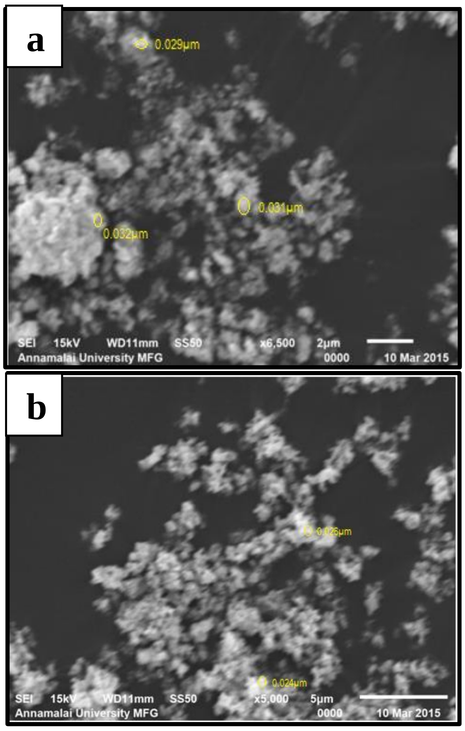

Figure 1. *SEM images of ZnO NPs a) 60°C, 30 min. b) 80°C, 50 min.*

From the Figure 1a and 1b, it was observed that the increase in reaction temperature from 50-90°C resulted in decrease in size of the particle. This is in agreement with the statement as being reported [44]. In this study, the mean diameter of the crystalline shape ZnO nanoparticles were found to be in the range of 21-37 nm. The size confirms the presence of nanoparticles. The size of ZnO NPs synthesized by sol-gel method is much smaller than the nanoparticles prepared by chemical deposition method. The size of ZnO NPs found to be decreases with increasing reaction temperature and dripping time.

FTIR measurements were carried out to identify the composition and their efficient stabilization of the synthesized metal nanoparticles (ZnO NPs).

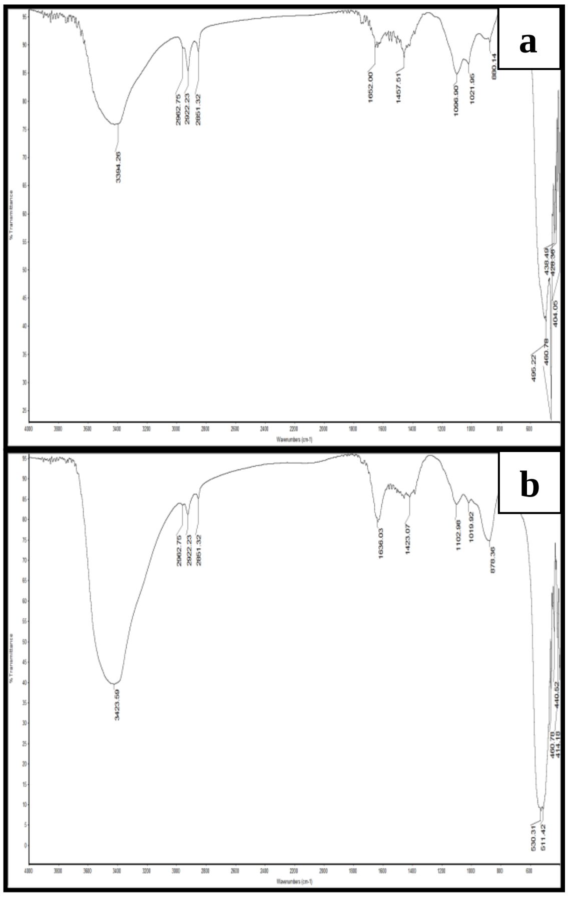

Figure 2. *FTIR result for ZnO NPs a) 70°C, 40 min. b) 90°C, 60 min.*

Figure 2a and 2b show that the characteristic band with strong absorption band at lower energy region 490 cm^{-1} is attributing to the stretching vibration of Zn-O [37]. Two characteristic bands at 2900 cm^{-1} and 1400 cm^{-1} can be described as stretching vibration mode of C=O residues probably due to atmospheric moisture and CO_2. Absorption band at about 1423 and 1630 cm^{-1} corresponds to

C-O, C=O stretching in acetate groups, which further verifies the coverage state of ZnO colloidal nanoparticles [40]. The peak at 3300 cm^{-1} is assigned to the O-H bending vibration of physisorbed water [37]. The FTIR data of the synthesized ZnO NPs indicated its preparation has been successfully achieved for evaluation of this potential study.

3.2. Evaluation of the Photocatalytic Activities of ZnO NPs on Different Dyes

The dosage of photocatalyst is a crucial factor for photocatalytic activity because a fixed amount of adsorbate only can be adsorbed on a given mass of catalyst [13]. The smaller sizes of the synthesized ZnO nanoparticles have large surface area i.e. high number of active sites on the surface. It leads to more amount of dye molecules to get attached on the surface of the ZnO NPs [37]. All the synthesized ZnO NPs were evaluated for its photocatalytic activity under the UV light.

The effect of concentration of CR dye on the efficiency of the sol-gel process was investigated at various sizes of the synthesized ZnO NP in the range of 21-37 nm. The maximum decolourization efficiency of 88% was attained in 150 minutes. Dripping time is a major factor that generates well dispersed NPs with more number of well active site on the surface of ZnO nanoparticles [45]. Chromophores are only the reason for appearance of dye color which is attributing to benzene and naphthalene rings in the mother molecule. Disappearance of the visible bond suggests the sensitivity of the oxidized model molecule towards ZnO NPs, it has to be noted that ZnO reacts with conjugated systems such as dye molecules through either direct or indirect oxidation [46]. Hence, the free radicals ($OH^{\bullet}$) generated breaks the double bonds (–N N–) in the conjugated chains of the dye molecule and hence decolourization is achieved via photocatalytic activity [46]. Figure 3 shows that the highest decolourization efficiency 88% on CR dye under the various condition of 70°C temperature, 40 minutes dripping time and in the range of 27-29 nm size. Banisharif et al. revealed that the 95% of decolourization efficiency was obtained during the treatment of Congo red dye by using TiO_2/Fe_3O_4 nanocomposite [47]. However, this outcome comparatively high than our present study (88%) but economically the ZNO NP is excellent precursors for dye decolourization.

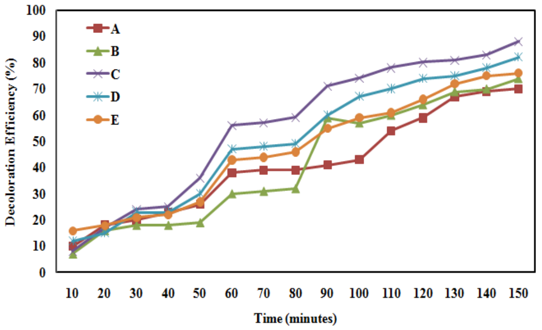

Figure 3. *Decolourization Efficiency of different size ZnO Nps on Congo Red dye: (A) 50°C, 20 min, 32-37 nm, 70%; (B) 60°C, 30 min, 29-32 nm, 74%; (C) 70°C, 40 min, 27-29 nm, 88%; (D) 80°C, 50 min, 24-27 nm, 82%; (E) 90°C, 60 min, 21-24 nm, 76%.*

The decolourization efficiency of AB dye was found to be decreases with increasing reaction temperature and dripping time of NPs synthesis preparation. The maximum efficiency was declared as 73% in 130 minutes for AB dye. Fewer hollow-electron pairs are produced and an extraordinary reaction time is needed to create the $OH^{\bullet}$ radical which is required for degradation of the acid dye. In this study, the chromophore group, this has low bond energy and therefore breaks at a high rate. This is reflected in the fast disappearance of the colour in the acid dye solution [38]. Figure 4 shows that the highest decolourization efficiency 73% on AB dye under the various condition of 80°C temperature, 50 minutes dripping time and size of 24-27 nm. This efficiency occurs because a greater number of photons are absorbed by ZnO and greater concentrations of OH$^\bullet$ radicals are available for the decolourization of the dye [38].

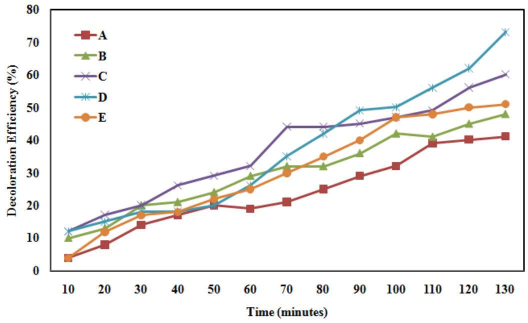

Figure 4. *Decolourization efficiency vs. time for different Size ZnO Nps on Acid blue 9 dye: (A) 50°C, 20 min, 32-37 nm, 41%; (B) 60°C, 30 min, 29-32 nm, 48%; (C) 70°C, 40 min, 27-29 nm, 60%; (D) 80°C, 50 min, 24-27 nm, 73%; (E) 90°C, 60 min, 21-24 nm, 51%.*

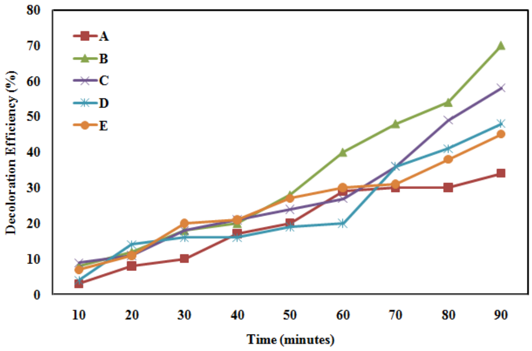

Figure 5. *Decolourization efficiency vs. time for different Size ZnO Nps on BB R-250 dye: (A) 50°C, 20 min, 32-37 nm, 34%; (B) 60°C, 30 min, 29-32 nm, 70%; (C) 70°C, 40 min, 27-29 nm, 58%; (D) 80°C, 50 min, 24-27 nm, 48%; (E) 90°C, 60 min, 21-24 nm, 45%.*

Figure 5. shows that the decolourization efficiency on BB dye. It was found that particle size decreases with increasing reaction temperature and dripping time. The maximum efficiency was declared to 70% in 90 minutes. ZnO nanoparticle creates more reactive free radicals. Reduction of the terminal nitro groups alters the absorption of the dye. The central azo bond breaks the conjugation between the stilbene units. This is reflected in the disappearance of the color in the BB dye solution [39].

3.3. Comparison of Decolourization Efficiency on Selective Dyes

The chromophore groups in the dye solution can be eliminated by the advanced oxidation process using suspensions of ZnO NPs with artificial UV light. The decolourization effect of the competence between dye and OH$^-$ ion helps in the adsorption on the surface of catalyst which results on the formation of hydroxyl radicals. Hence in the solution with constant catalyst concentration, the generation of hydroxyl radicals is possible which can attack the pollutants effectively, thus leading to the higher decolourization efficiency [37].

Table 2. *Operating conditions for the decolourization of Selective Dyes.*

Selective Dyes	Effective Parameters				Decolourization Efficiency (%)
	pH	Temperature (°C)	Dripping Time (min)	ZnO size (nm)	
Congo Red (CR)	6	70	40	27-29	88
Acid Blue 9 (AB)	6	80	50	24-27	73
Coomassie Brilliant Blue R-250 (BB)	5	60	30	29-32	70

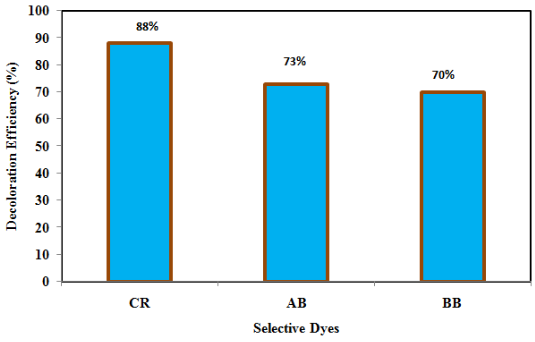

Figure 6. *Comparison of the three selective dyes decolourization efficiency*

In selective dyes, decolourization efficiency varied by the creation of hydroxyl radicals based on the different size ZnO nanoparticles. Using thermal effect induces; the nanoparticle size decreased which is more capable for potentially reducing dye molecule. In some cases, at large temperature, the reduced ZnO nanoparticle size were not increased thus reducing the decolourization efficiency. Hence for this reason, the Nano ZnO might not get stable due to particle agglomeration. The overall results tabulated in Table 2, the operating condition for the respective dye solutions proved to have better efficiency. Figure 6 clearly shows the robustness of the chemically synthesized ZnO NPs on dyes decolourizations. Moreover, the results concluded that the nanomaterial like metal oxide (ZnO) is one of the most promising candidate to remove dyestuffs from real industrial dye effluents [48].

4. CONCLUSION

Various sizes of ZnO NPs with crystalline nature were obtained quickly by following sol-gel method, using Zinc chloride and Sodium Hydroxide. Different size of ZnO NPs was synthesized in the temperature which ranges from 50-90°C and dripping time 20-60 min yielding 21-32 nm size of NPs which are further characterized by SEM and FTIR analysis. The smallest crystalline size was obtained in the highest temperature at 90°C with dripping time playing an effective role. Photocatalytic performance was done by various sizes of NPs on selective dye solutions. Thus, size of the nanoparticle played a key role in photocatalytic degradation of various dyes in this study. Amongst the three dyes being used, the CR dye showed more dye removal efficiency as compared to others. Moreover, BB dye also potential to decolourized by using ZnO NPs with maximum efficiency.

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