

# Environmentally Friendly Preparation of Zinc Oxide, Study Catalytic Performance of Photodegradation by Sunlight for Rhodamine B Dye

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## ABSTRACT

This study includes the photocatalytic degradation of Rhodamine B (Rh.B) employing a heterogeneous photocatalytic process by using ZnO nanoparticles that was prepared by green sol-gel process. The structural, morphological, and its optical properties of ZnO Photocatalyst was studied using different characterization techniques such as X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), The influencing factors studied were the amount of the catalyst, the concentration of dye and pH on photocatalytic degradation of Rhodamine B. The experiments were carried out by irradiating the aqueous solutions of dyes containing photocatalysts with Sunlight. The rate of decolorization was estimated from residual concentration spectrophotometrically. Similar experiments were carried out by varying pH (3–11), amount of catalyst (0.25–2.0 g/L) and initial concentration of dye (5–50 mg/L). The experimental results indicated that the maximum degradation (71%) of dyes was achieved using ZnO photocatalyst at pH 10 after 240 min.

**Keywords:** environmentally friendly, ZnO, photodegradation, rhodamine B, sunlight

## INTRODUCTION

Pollution problem is getting worse day by day, so Researchers are looking for ways to get rid of this problem. Among the most common contaminants are dissolved dyes in industrial wastewater from textile [1] and paper mills [2]. Synthetic dyes are extensively used for dyeing and printing in textile industries. Over 10,000 dyes with an once a year production over 10<sup>5</sup> metric tons worldwide are commercially available and about 50% among them are azo dyes [3]. It is estimated that approximately 15% of the dyestuffs are lost in the industrial effluents during manufacturing and processing operations [4]. Color is usually the first contaminant to be recognized in wastewater. Many dyes may be decomposed into potential oncogenic amines under anaerobic conditions in the environment [5]. There are many ways for pollutant elimination such as adsorption on activated carbon [6], reverse osmosis [7], ultrafiltration [8], and ozonation [9] etc. Photodegradation is also one of the most important technologies used in the disposal of pollutants in industrial wastewater. Researchers want to use natural resources available to obtain the energy needed for the degradation of dyes in industrial wastewater, the most important source of natural energy is sunlight that consists of about 5–7% UV light, 46% visible light and 47% infrared radiation [10]. Photocatalytic oxidation of various harmful organic dyes in industrial wastewater has been carried over ZnO semiconductor oxides under UV light irradiation [11]. Research is now focused on to achieve high photocatalytic efficiency with ZnO [12] especially with sunlight. Zinc oxide can be prepared in more than one way, each method has its own conditions that determine product characteristics, preferably use environmentally friendly methods. Green chemistry is generally accepted as “the design, development, and implementation of chemical processes and products to reduce or eliminate substances hazardous to human health and the environment” [13]. There has been an explosive growth in the field of green chemistry both in preparing green Nanocatalysts [14] as well as green conditions during catalysis of industrially important reactions. Preparing green Nanocatalysts refers to manufacturing the nanocatalysts using green solvents or processing the nanocatalysts so that they are finally

dispersed in green solvents. Green nanocatalysis refers to doing the catalytic reaction in green solvents and rather by the use of green nanocatalysts for these reactions [15]. According to the fourth principle of Anastas' and Warner's 12 principles of green chemistry "Chemical products should be designed to preserve efficacy of function while reducing toxicity," [16], should of course also be applied to the synthesis of Nanocatalysts [17]. This is typified by the synthesis of nontoxic ZnO nanoparticle catalysts [18,19].

## MATERIAL AND METHODS

### Materials

Zinc acetate, potassium hydroxide were obtained from B.D.H Company, Rhodamine B dye, were supplied from Sigma-Aldrich. All materials were used directly without further purification.

### Instruments

UV-vis spectrophotometer double beam PC 1650 SHIMADZU, UV-vis spectrophotometer 780 Sunny China, The crystalline character of the solid has been identified by X-ray diffraction (XRD) analysis using a D/Max 2,550 V diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ) (Japan), and the XRD data were collected at a scanning rate of  $0.03 \text{ s}^{-1}$  for  $2\theta$  in a range from  $10^\circ$  to  $80^\circ$ , The morphology of prepared materials was noted by field emission scanning electron microscopy (FE-SEM) with (MIRA3 TESCAN - Czech), The optical band gap  $E_g$  was projected from the UV-Vis-NIR diffuse reflectance spectroscopic (UV-Vis-NIR DRS) determined in a wavelength range from (200 - 1100) nm with UV-1800 UV-VIS Spectrophotometer from SHIMADZU, pH meter (Sartorius, Germany), 100 mL Teflon-lined autoclave.

### Preparation of ZnO

In a typical synthesis, of ZnO nanoparticles is carried out by sol-gel process, at  $80\text{-}90^\circ\text{C}$ . Solution of zinc acetate  $\text{Zn}(\text{CH}_3\text{COO})_2$  was prepared by dissolving 2.195 g of zinc acetate in 100ml distilled water, and stirred in ambient atmosphere. Potassium hydroxide KOH 1.122g is dissolved in 10 ml distilled water and was added to the above solution drop wise under continuous stirring. After few minutes solution turn into jelly form and a milky white solution was obtained, the mixture was then further heated for 3 h at  $80\text{-}90^\circ\text{C}$  without stirring. The resulting suspension was centrifuged to retrieve the product, and the mixture was washed with distilled water and then the powder was dried at  $70^\circ\text{C}$  overnight and determined in terms of their structural, morphology and optical properties [20,21].

### Photo-catalytic Degradation Experiment

ZnO was added to 100 ml of Rhodamine-B dye solution and it is undergo irradiation by sunlight. After adding the catalyst and stirrer it at a constant speed. The samples were taken at different times. Before the irradiation, the dye catalyst suspension was kept in the dark with steering for 90 min to ensure an adsorption-desorption equilibrium. The solution was separated from the catalyst by the centrifuge. Measure the absorbance of each sample, absorption spectra were recorded and rate of decolorization was seen as far as change in power at  $\lambda_{\text{max}}$  of the colors. The decolonization efficiency has been ascertained as equation 1:

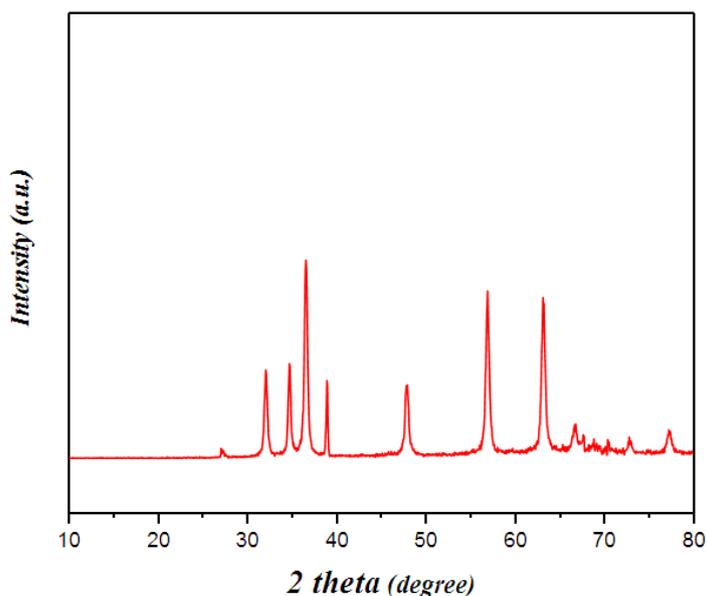
$$\text{Efficiency (\%)} = \frac{C_0 - C}{C_0} \times 100\% \quad (1)$$

Where  $C_0$  is the initial concentration of dye and  $C$  is the concentration of dye after photo irradiation. Similar experiments were carried out by varying the pH of the solution (pH 3-11), concentration of dye (10 - 100 mg/L) and catalyst loading (0.25-2.0 g/L), pH of aqueous solution was adjusted with 0.1M  $\text{H}_2\text{SO}_4$  or 0.1M NaOH.

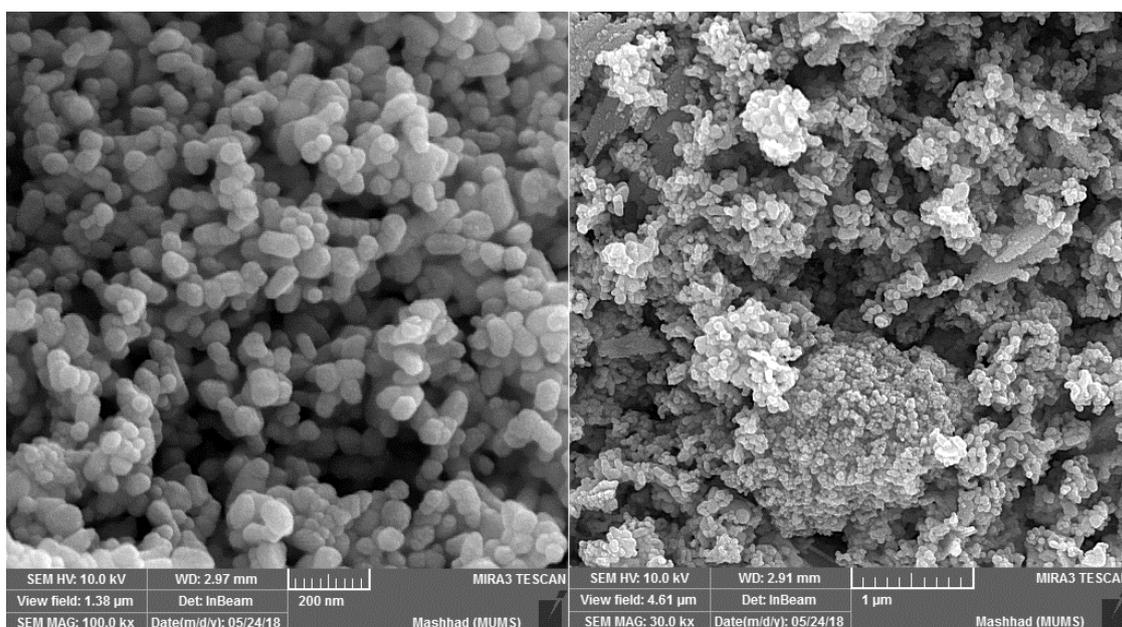
## RESULT AND DISCUSSION

### X-ray Diffraction

XRD pattern of synthesized ZnO nanostructures by sol-gel reaction at  $90^\circ\text{C}$  is shown in **Figure 1** All peaks of the obtained product are corresponding to the cubic structure of ZnO reported in many research works [21-23]. The detected peaks are at  $2\theta$  values of 32.0253, 34.6686, 36.4966, 47.7734, 56.8286 and 63.0893 corresponding to the following lattice planes: (100), (002), (101), (102), (110) and (103) respectively.



**Figure 1.** X-rays diffraction spectra of ZnO nanocrystals



**Figure 2.** FE-SEM image of ZnO nanoparticles

### FE-SEM

The surface morphology of catalyst is one of the important parameters that impact on the photocatalytic efficiency. The nanoparticles were investigated by FE-SEM image as shown in **Figure 2**. The FE-SEM images show that the ZnO particles were formed in a very uniform manner in the form of cubes and a few of them appeared spherically.

### UV-vis Diffuse Reflectance Spectra (DRS)

The properties of semiconductor nanoparticles are strongly size dependent. It is well known that the nano-scale systems show interesting properties, for example, increasing of the semiconductor band gap due to electron confinement [24]. The UV-vis diffuse reflectance, (Tauc's plot) of synthesized ZnO was shown in **Figure 3**, the calculated band gap energy for synthesized ZnO is 3.39 eV, the determination of optical band gap is obtained by Tauc's equation [25].

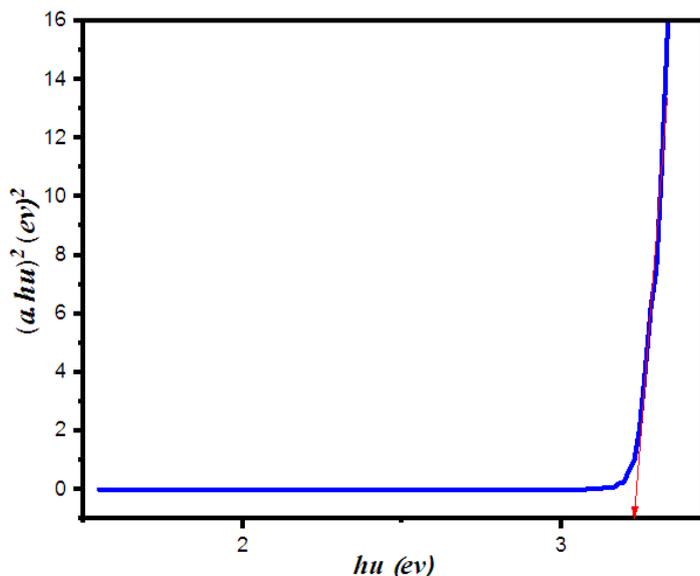


Figure 3. Band gap energy (Tauc's plot) of ZnO

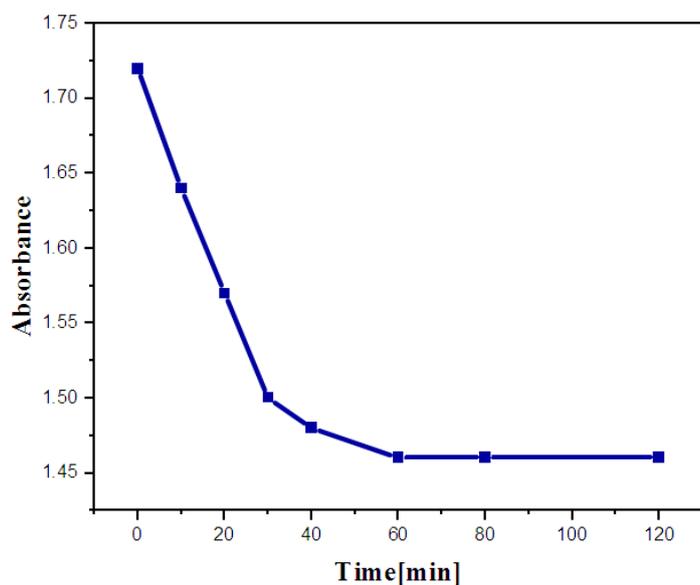


Figure 4. Time of adsorption equilibrium ((dye concentration 20 mg/L and catalyst amount 0.8 g/L, 35°C)

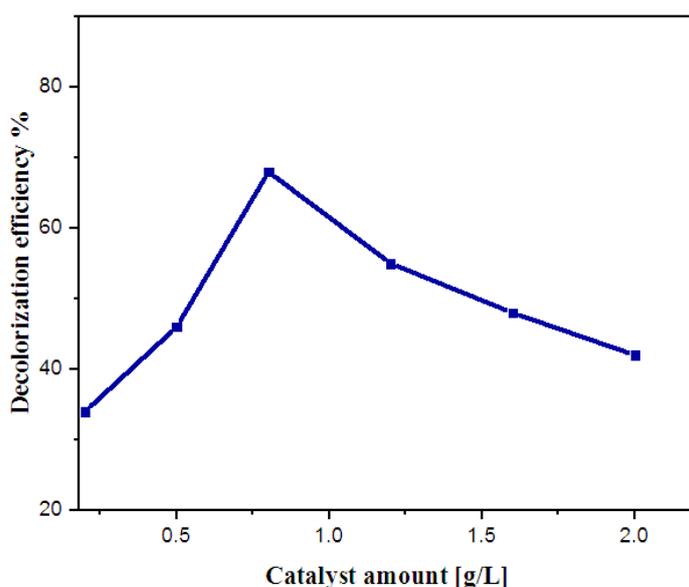
## Decolorization of Dye by ZnO Photocatalyst

### *Adsorption of the dyes on ZnO-photocatalyst*

Degradation of the dyes occurs predominantly on the photocatalyst surface [26]. In order to investigate the adsorption behavior of Rhodamine B, the suspension was prepared by mixing 100 ml of dye solutions 20 mg/L with fixed photocatalyst ZnO amount (1 g/L) at 35 °C, natural pH of Rhodamine B. The suspensions were kept for different times in the dark under shaking for 120 min. The absorbance measured at the  $\lambda_{\max}$  553 nm to determine the concentration of dyes. The experimental results are shown in Figure 4 from the results, it was noticed that the adsorption equilibrium under 20 mg/L initial concentration was reached at about 60 min of equilibration time.

### *Photocatalyst loading*

The experiments were carried out by varying ZnO photocatalyst amount from 0.25 to 2.0 g/L for dye solutions of 20 mg/L at natural pH of Rhodamine B. The decolorization efficiency for various photocatalysts amount for Rhodamine B has been depicted in Figure 5. It is observed that rate increases with increase in catalyst amount and becomes constant above a certain level then will be decreased. The optimum photocatalyst amount for

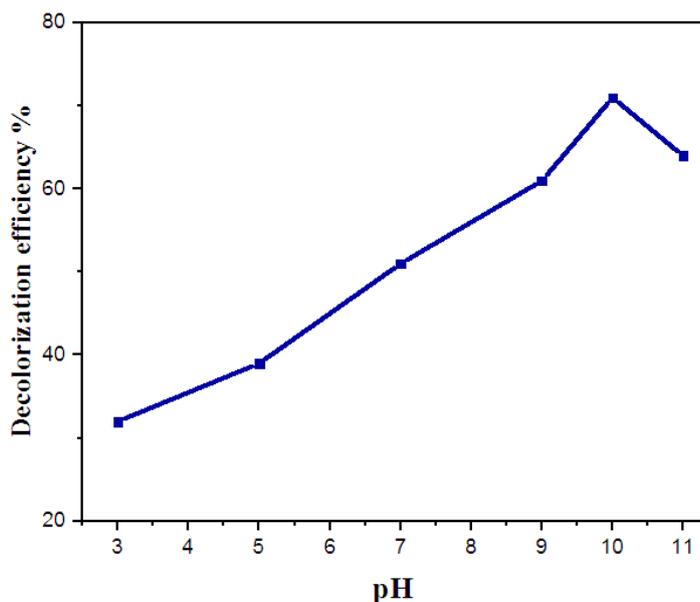


**Figure 5.** Effect of catalyst dose on decolorization efficiency (dye concentration 20mg/L, natural pH, irradiation time 240 min, 35C°)

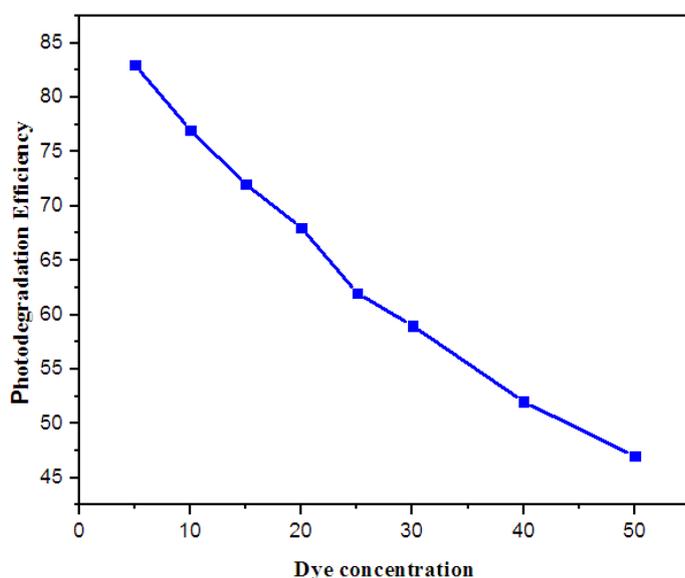
decolorization efficiency of dye is 0.8 g/L. The reasons for this decrease in decolorization efficiency at given time it aggregation of catalyst particles at high concentrations causing a decrease in the number of surface active sites [27,28] and increase in light scattering of catalyst particles to decrease in the passage of irradiation through the sample [29,30].

### *Effect of pH*

Wastewater containing dyes at different pH therefore it is important to study the effect of pH on degradation efficiency of dye [29], the amphoteric behavior of most semiconductor oxides influences the surface charge of the photocatalyst [31]. The effect of pH values on the degradation efficiency is studied in the pH range 3–11 at the dye concentration 20 mg/L and catalyst amount 0.8 g/L, 35C°. **Figure 6** illustrated the results of the decolorization efficiency after 160 min irradiation with different pH values (3, 5, 7, 9 and 11) It can be observe increase in the decolorization efficiency of Rhodamine B with increase of the pH value from 3 up to 11, exhibiting maximum efficiency at pH 10, This behavior could be explained by  $pH_{pzc}$  of the material, as well as the molecular nature of the dyes, the zero point charge of ZnO equal to 9.0, Therefore photocatalysts surface is positively charged below  $pH_{zpc}$ , whereas it is negatively charged when  $pH > pH_{zp}$ .



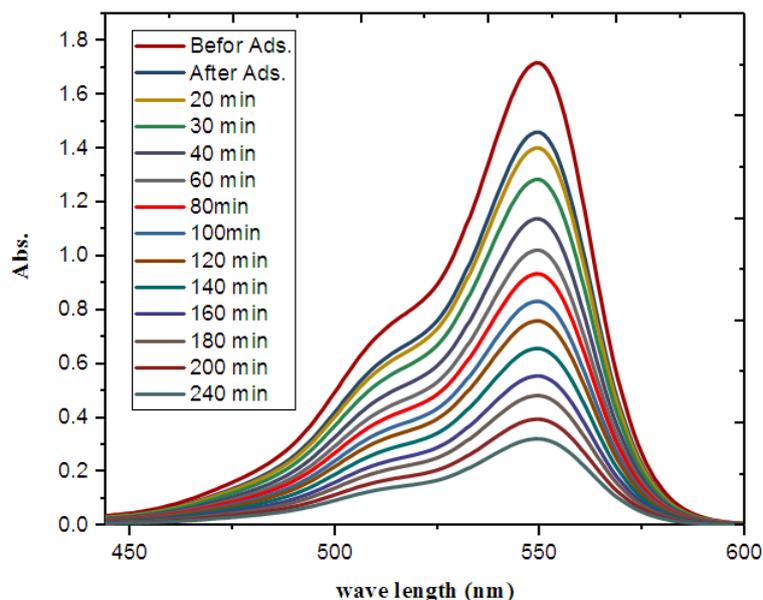
**Figure 6.** Effect of pH (dye concentration 20 mg/L, catalyst amount 0.8g/L, irradiation time 240 min, 35°C)



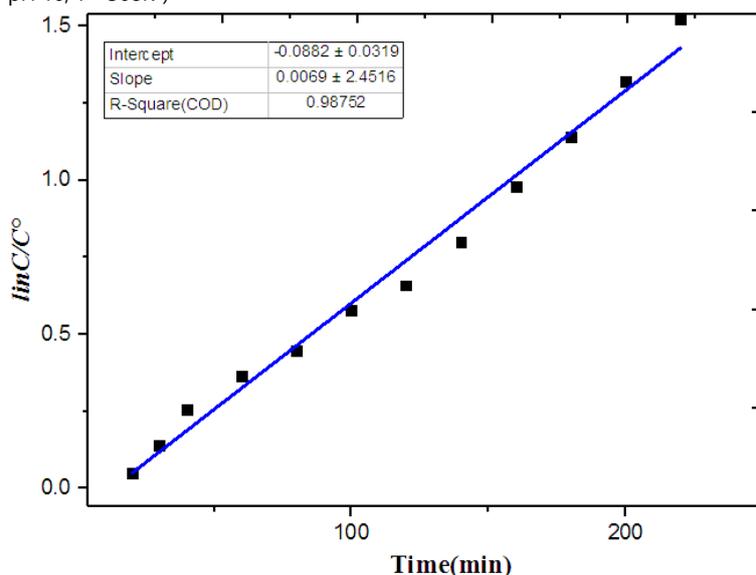
**Figure 7.** Effect of dye concentration on decolorization efficiency (catalyst dose 0.8 g/L, pH 10, irradiation time 240 min, 35°C)

### *Effect of initial dye concentration*

The results reported that the initial dye concentration effects the degradation efficiency strictly. With the increase of initial dye concentration, the degradation efficiency decreases remarkably [27]. The negative effects of the initial dye concentration are attributed to the competency between dye and  $\text{OH}^-$  ion adsorption on the surface of catalyst. The adsorption of dye reduces the  $\text{OH}^-$  ion adsorption, which results in the reduction on the formation of hydroxyl radicals [32]. The rate of degradation relates to formation of  $\text{OH}$  radicals, which is the critical species in the degradation process. At the same time, as the initial dye concentration increases, the path length of photons entering the solution decreases [33]. Hence in the solution with constant catalyst concentration, the formation of hydroxyl radicals that can attack the pollutants decreases, thus leading to the lower decolorization efficiency. **Figure 7** shows the effect of initial dye concentration on degradation efficiency by varying the initial concentration from 5 to 50 mg/L with the constant ZnO catalyst loading (0.8 g/L) and pH 10.



**Figure 8.** Absorption spectra of aqueous solution of Rhodamine B at different times (catalyst amount 0.8g/L, dye conc. 20 ppm, pH 10, T= 308K°)



**Figure 9.** Kinetic analysis of Rhodamine B under optimized conditions (catalyst amount 0.8g/L, dye conc. 20mg/L, pH 10, T= 308K°)

### *Kinetic of photodegradation*

**Figure 8** shows a typical UV-Vis spectrum of Rhodamine B solution during photo-irradiation time (dye conc.10 ppm, pH10, catalyst amount 0.8 g/L, T= 308K°). The absorption peaks, corresponding to dye, diminished and finally disappeared under reaction which indicated that the dye had been degraded. No new absorption bands appear in the visible region. The spectrum of Rhodamine B in the visible region exhibits a main band with a maximum at 553 nm. **Figure 9** shows the kinetics of disappearance of Rhodamine B for an initial concentration of 20 ppm at pH10, catalyst amount 0.8 g/L. The results show that the photodegradation of the dye in aqueous ZnO can be described by the first order kinetic model,  $\ln(C_0/C) = kt$ , where  $C_0$  is the initial concentration and  $C$  is the concentration at any time,  $t$ . The semi logarithmic plots of the concentration data give a straight line.

## CONCLUSION

In this study, Photocatalytic degradation of Rhodamine B dye has been investigated using ZnO photocatalyst. The following conclusions have been obtained about photodegradation:

- Photocatalytic degradation process is more suitable for low concentration of the pollutants.
- Photocatalytic degradation process is more suitable with low concentration of photocatalyst.
- Photocatalytic degradation process is more suitable with pH more than 9.

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