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PREPARATION AND SOLAR ASSISTED PHOTOCATALYTIC PERFORMANCE OF AG- DOPED ZNO FOR ROSE BENGAL DYE DEGRADATION

B. Malini [*1], G. Allen Gnana Raj[*2],

[*1]Assistant Professor, Department of Chemistry, Government College of Engineering, Tirunelveli, Tamilnadu, India.

[*2]Associate Professor, Department of Chemistry, Scott Christian College (Autonomous), Nagercoil, Tamilnadu, India.

ABSTRACT

Rose Bengal (RB) is one of the dyes used in textile and dyeing industries. This paper focuses on degradation of RB, using silver-doped ZnO nanocatalysts. Silver- doped ZnO nanocatalyst is prepared by one-step impregnation technique. The synthesized nanocatalyst is characterized using XRD,SEM and EDAX. The experiments of RB degradation are performed under sunlight irradiation. The effect of various parameters on dye degradation like catalyst dosage, dye concentration, pH, effect of O_2 and COD are investigated systematically. The catalytic activity of the synthesized sample is evaluated by monitoring the degradation of Rose Bengal dye under sunlight. The dye degradation upto 98.49% is achieved in 120 minutes and the dye degradation upto 99.80% is achieved within 90 minutes in oxygen presence. The results reveal that Ag doped ZnO is an efficient catalyst to carry out the degradation of Rose Bengal.

Keywords: Rose Bengal, XRM, SEM, EDAX.

I. INTRODUCTION

Several environmental issues are caused by the usage of various synthetic dyes used in various industrial applications. These dyes contaminate the soil as well as water bodies to a large extent. Most of these compounds are toxic, mutagenic or at least cause an aesthetic problem in receiving water or soil. These dyes are found to be chemically stable and highly persistent in the environment. According to an estimate, nearly 2 million tons of wastes from dyeing industries are discharged into the water bodies per day. Their complete removal is mandatory but this is very hard to attain because of their complex structures and high stability. Remediation of these toxic dyes are based on various physical, chemical and biological techniques but there are shortcomings. The main drawback of these techniques is formation of secondary waste product which cannot be treated again and has to be dumped as such(1). Obviously, there remains great demand for exploration of inexpensive, eco-friendly materials that might be used for photodegradation of organic dyes in sunlight especially for effluents of textile waste water. The photo catalytic processes removes the pollutants even at low concentration and hence can be a viable solution for treating industrial waste water(2). The photocatalytic degradation of organic pollutants in water using semiconductors such as TiO_2 and ZnO has attracted extensive attention. Such semiconductors can degrade persistent organic pollutants leading to total mineralization of these pollutants into CO_2 and water. But the fast recombination rate of photogenerated e-/hole pair hinders the commercialization of this technique. This has led to great interest in enhancing the activity under sunlight by suitable modification of semiconductors to carry out the degradation of organic compounds. Among all the various materials, Titanium dioxide (TiO_2) has long been a promising material for photocatalytic applications. It is not a cost-effective method to use TiO_2 on a bulk scale to treat polluted water and so works on finding alternatives to TiO_2 are in progress (3). ZnO is a suitable alternative to TiO_2 owing to its low cost and high photo-activity. The salient advantage with ZnO is its large absorption of solar spectrum. ZnO has a band gap of 3.37 eV close to that of TiO_2 3.2 eV.(4). Doping heavy metals as Pt, Pd, Au and Ag on metal oxide semiconductors is found to accelerate the degradation reaction. In tropical country like India we can use the vast potential solar energy into utilization for degradation of hazardous compounds. Solar irradiation has been utilized for detoxification of dyes by many researchers and the photocatalytic approach has become a potential solution to the urgent global issues of environmental pollution and energy shortage. The synthetic dyes are classified in terms of their chemical structures in different ways. Among different types of dyes, those characterized by presence of xanthenes nucleus with aromatic groups as chromophore has been in use widely. Rose Bengal is a halogen containing fluorescent water soluble ,inorganic anionic pink coloured dye that is extensively used in dyeing, photochemical printing industries and also as an insecticide. Though being widely used for medical purposes, the dye however

is highly toxic and can cause irritation, itching reddening, blistering etc. to the human skin and also affects eyes causing inflammation, eye redness, itching (5). Moreover, earlier works reported longer degradation time of RB. It is therefore considered worth wile to develop a systematic method for degrading Rose Bengal.

II. METHODOLOGY

Characterization

One step impregnation method was used to prepare Ag doped ZnO(6). 10 mL of Silver nitrate(0.18M) was added to 10 g of uncalcined Zinc oxide. The sample was agitated and heated at 110°C for 30 minutes and then calcined at 400°C for 4 hour. Grayish powder of Ag doped ZnO nanoparticles formed in the crucible was removed from the furnace and crushed into a fine powder by using pestle and mortar.

Characterization

The XRD (X-ray diffraction) patterns were recorded on a PANAalyticalX′pert Por X-ray diffractometer as the X-ray source. The diffractograms were recorded in the 2θ range 20°to 100°. FESEM measurements were done using SEM(Vega 3 Tescan) with EDAX (Bruker). Absorbance changes of RB during photocatalytic degradation were studied using UV–vis spectrophotometer(PG instrument).

III. MODELING AND ANALYSIS

Photocatalytic degradation procedure

The photocatalytic degradation of the chosen dye was carried out under clear sky conditions. The light intensity was measured by Luxmeter. The sunlight intensity was recorded from 900 to 950 Wm^{-2} and the mean temperature was 31°C. A borosilicate glass of 250 mL capacity was used to carry out the degradation. Rose Bengal dye of desired concentration was prepared for 100mL using distilled water. Prior to irradiation, 100 mL of Rose Bengal dye solution having definite catalyst loading was stirred continuously in the dark for 30 minutes to achieve the adsorption equilibrium of dye on the surface of the catalyst. This concentration at this point was taken as the initial one. The solution was irradiated using solar light. At given regular intervals of irradiation, the dye solution along with catalyst particles was centrifuged and then filtered through a filter. The samples were analysed by uv-visible spectrophotometer. The determination wavelength is 549 nm for rosebengal and the degradation efficiency of rosebengal was calculated as per the following equation.

$$\text{Efficiency}(\%)=(C_0-C)/C_0*100$$

Where C_0 represents the concentration of Rosebengal solution before irradiation and C is the final concentration of Rosebengal solution after irradiation.

IV. RESULTS AND DISCUSSION

XRD

XRD pattern of Ag-ZnO is presented in Figure.1. The peaks at 2θ values of 32.24°,34.88°,36.71°,47.97°,56.99°,68.29° and 69.46° observed in the XRD spectra are indicative of the typical hexagonal wurtzite structure (JCPDS file No. 36-1451) of ZnO while those of 38.39°,44.47° and 63.24° can be indexed to face centered-cubic(fcc) metallic Ag (JCPDS file No. 04-0783). The appearance of Ag peaks in the diffraction patterns indicates clearly the formation of crystalline silver clusters in the nano particles. The average crystalline sizes of the as-synthesized photocatalysts were obtained using Scherrer equation: where D is the crystallite size in nm, K is the shape factor constant and taken as 0.9; K is the full width at half maximum (FWHM) in radians; λ is the wavelength of the X-ray (= 0.15406 nm)for Cu target K_ radiation and θ is the Bragg's angle. The calculated average crystallite size of the as-synthesized Ag-ZnO was 12 nm.

SEM

Figure.2 shows the typical SEM micrographs of the Ag incorporated ZnO nanoparticles that exhibit the formation of elemental Ag entities as a second phase. Figure.3 shows a typical EDS spectrum of the as-formed Ag-ZnO sample. The spectrum containing characteristic peaks of Zn and Ag confirmed the distribution of the constituent elements. The EDS spectrum depicts the presence of Zn,O and Ag in the synthesized photocatalyst.

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The degradation of Rosebengal using solar irradiation has been carried out using the prepared Ag –ZnO photocatalyst. It is observed that there is decrease in absorption maximum and almost complete degradation is observed in 120 minutes as shown in Figure.4.

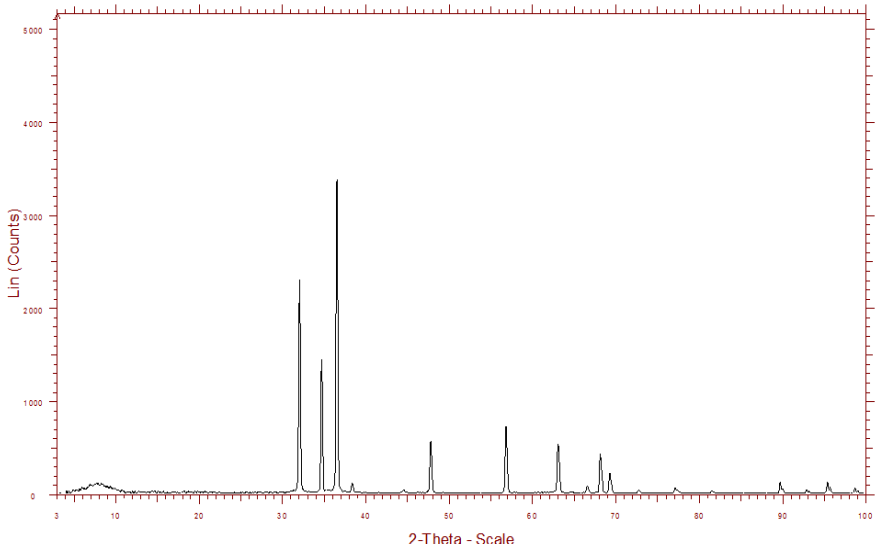

Figure 1: XRD of Ag-ZnO

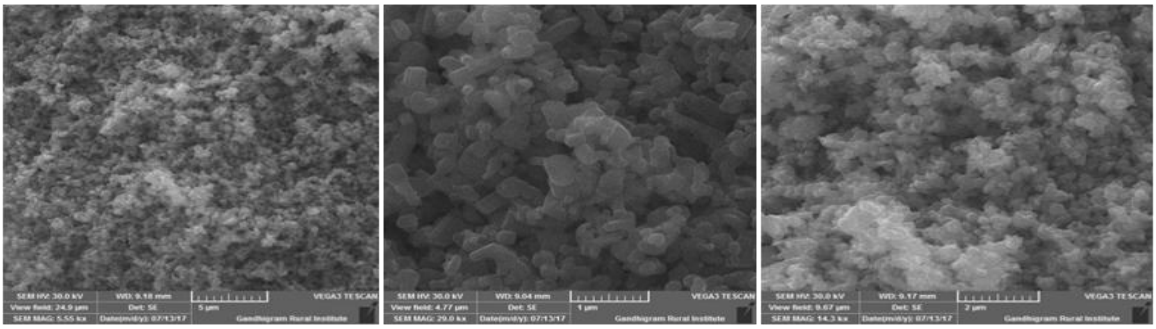

Figure 2:SEM images of Ag-ZnO

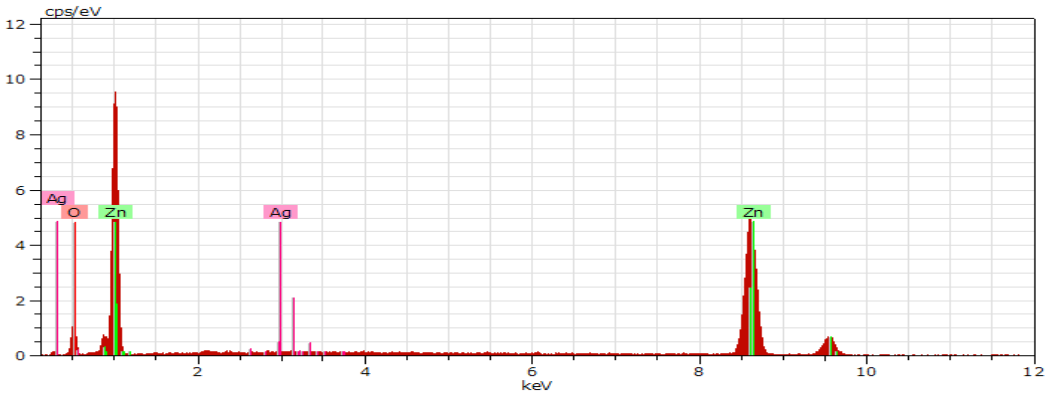

Figure 3 : EDX of Ag-ZnO

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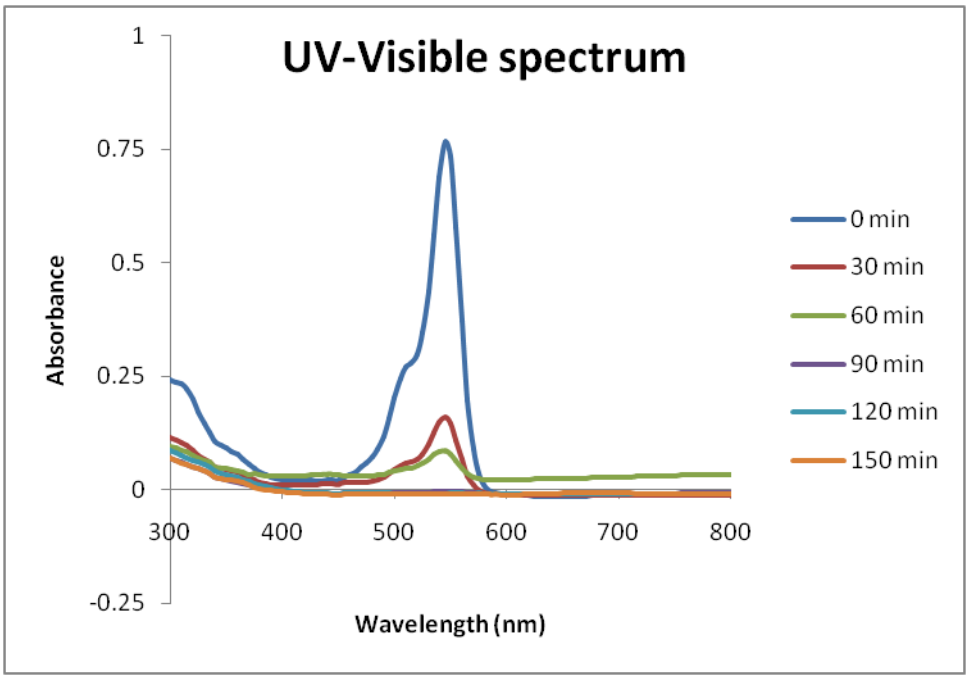

Figure 4: Time dependent UV-Visible spectra of Rose bengal

Effect of amount of catalyst

The catalyst loading has both positive and negative impact on the degradation rate. The catalyst loading increases the quantity of photons adsorbed which in turn increases the degradation rates. But it increases the opacity of the solution and decreases the penetration of photons and decreases the degradation rate (7). Hence, for efficient photomineralization a nominal amount of catalyst has to be present to ensure total absorption of light photons (8). The optimal amount of Ag-ZnO catalyst for rosebengal degradation was determined by varying the amount of catalyst from 0.02-0.1g/100mL at a constant dye concentration of 10 ppm. The percentage of dye degraded at different time intervals at various catalyst loadings is found out and shown in Fig.4. It is evident from Figure.5(a) that with increase in load of catalyst from 0.02-0.1g/100mL there is an increase in percentage of dye degradation upto 0.04g and then there is a decrease in the percentage degradation and hence the optimal amount of catalyst for the dye degradation was taken as 0.04g/100mL.

Effect of dye concentration

The initial concentration of dye solution plays a prominent role in deciding the rate of dye degradation. More dye molecules are available for excitation when the dye concentration is high (9,10).As the concentration of the dye increases more and more, the light penetration to the surface of the catalyst decreases. (11,12) Since the time of irradiation and catalyst loading are kept constant, the OH radical generated on ZnO surface is also constant. Hence, there is a decrease in free radical attacking the dye molecule decreasing the rate of dye degradation(13).In the present work, the dye concentration was varied from 5 ppm to 25 ppm in the steps of 5 ppm at a constant catalyst loading of 0.04g/100mL. Fig 5 shows the percentage degradation values of the dyes at different concentrations. At 20 ppm dye concentration there is maximum dye degradation. With increase in concentration of dye from 5ppm to 25 ppm initially there was increase in the amount of dye degraded from 5ppm upto 20 ppm and after thereafter the degradation rate decreases. So, the optimum dye concentration was fixed as 20 ppm.

Effect of pH of solution

The influence of pH on the degradation of dye has been investigated by slight variation of pH.Fig shows the percent of dye degraded at different time intervals at different pH. It is obvious from the figure 6 that as pH raises from5 to 9, there is an increase in degradation rate till pH 6 followed by decrease . The catalyst is positively charged in acidic medium and negatively charged in alkaline medium. The pH determines the surface

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charge of the photocatalyst . There is minimum dye adsorption when the pH of the solution is at the isoelectric point(14,15). Below isoelectric point the surface of the photocatalyst is positively charged and above that it carries a negative charge . As pH is lowered, the catalyst and dye molecules are positively charged. So, dye molecules and catalyst particles will repel each other. Thus, catalytic reaction Ag-ZnO will take place to smaller extent. But above pH 6 the rate of dye degradation goes down. The reason attributable is that Rose Bengal is an anionic dye and at higher pH, catalyst surface and dye molecules will exhibit repulsive force which in turn decreases the rate of dye degradation(16).

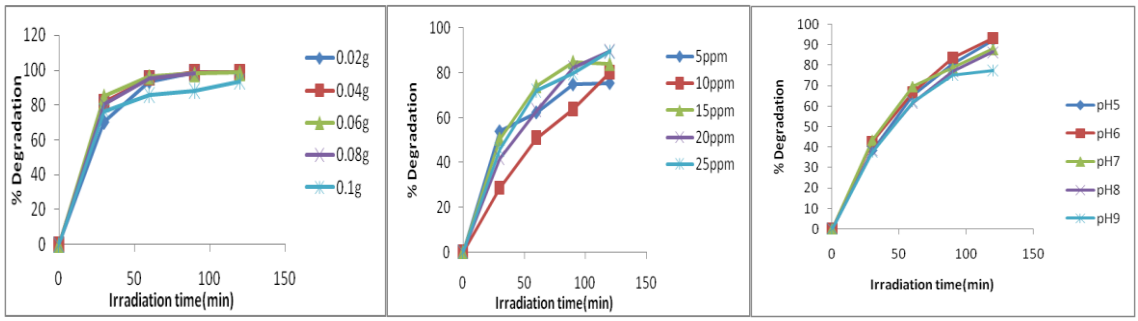

Figure.5: Variation of percentage degradation after 120 min irradiation as a function of a. catalyst loading b. concentration of dye c. solution Ph

Kinetics of the photocatalytic degradation of Rosebengal

In order to study the kinetics of the reaction, the photo degradation reaction of Rosebengal (20ppm) with photo catalyst (0.04g) was carried out at pH (6) in sunlight illumination as depicted in Figure.6. The plots are shown in Figure.7. The plot of lnC0/C vs. irradiation time shows a straight line behavior Fig 8 .The rate constant for the photo catalytic degradation of Rosebengal was obtained from the first order rate equation $\ln C_0/C=Kt$ where C_0 and C are the concentrations of substrate initially and at time t in minutes. K is the first order rate constant (min-1) determined from the slope of the straight line. The regression coefficient R^2 of the experimental values was 0.952 which confirms the degradation of the dye molecules principally obeys the pseudo first order linear kinetics.

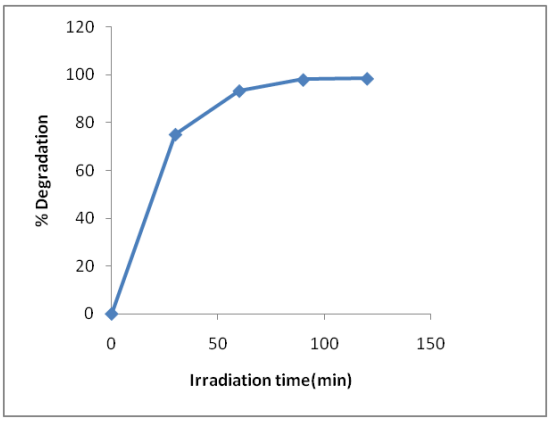

Figure.6 : Photocatalytic degradation of Rose Bengal under optimum conditions

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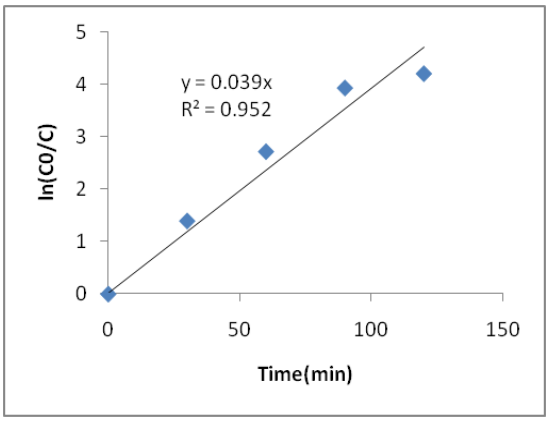

Figure 7: Kinetic plots for photocatalytic degradation of Rose Bengal under optimum conditions

Effect of Oxygen

The degradation was studied in the presence of atmospheric O_2 by taking Rosebengal (20ppm) photo catalyst (0.04g) at pH (6) under sunlight illumination. Figure 8 shows the percent of dye degraded at different time intervals. It is obvious from the figure.8 that the degradation at the end of 90 min irradiation was found to be greater in the presence of O_2 indicating that O_2 is a prerequisite for the photocatalytic degradation process and Figure 9 shows the kinetics plot for the photodegradation of RB dye in presence of oxygen.

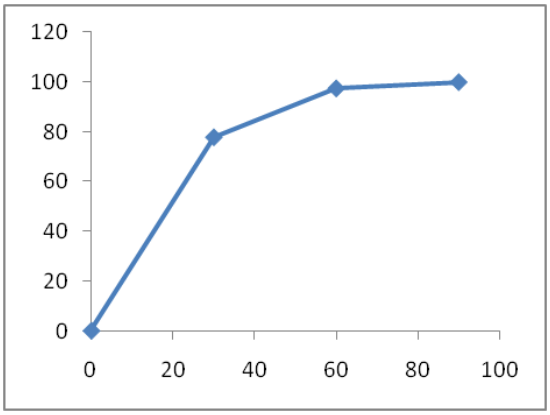

Figure 8:.Photocatalytic degradation of Rose Bengal under optimum conditions in presence of oxygen

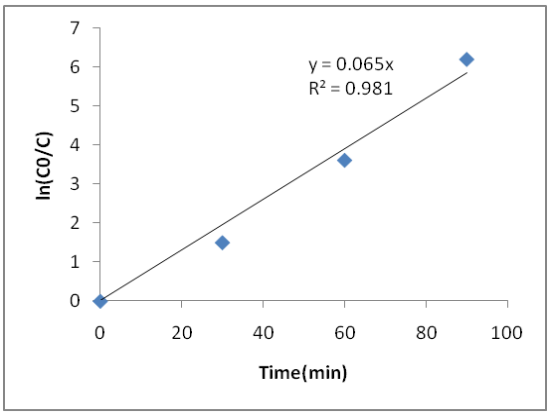

Figure 9: Kinetic plots for photocatalytic degradation of Rose Bengal under optimum conditions in presence of oxygen

Photo catalytic mechanism

The probable mechanism degradation of dye in the presence of sunlight and catalyst in an Advanced Oxidation Process is as follows. Rose Bengal molecule absorbs radiations and moves to its singlet excited state which then

undergoes inter system crossing and gives the triplet excited state. The Ag-ZnO photo catalyst utilizes the incident light energy to excite electron from its valence band(VB) to the conduction band(CB) .The hole left behind on the VB adsorbs an e- from OH- to generate $OH^{\cdot}$ radical. These radicals oxidize the dye to its colourless leuco form that gets degraded to harmless compound. The photo-catalytic mechanism in presence of Oxygen can also be explained through the electronic transition from VB to CB due to absorption of light followed by capturing by the adsorbed O_2 molecules to form O_2^- active species. The produced O2- also react with the photogene rated electrons to produce OH^- and $OH^{\cdot}$. Finally the OH^- reacts with photo-generated holes to form the active species $OH^{\cdot}$. Both O2- and $OH^{\cdot}$ then oxidize Rose Bengal dye.

Measurement of COD

The extent of mineralization of Rosebengal has been measured by using the disappearance of COD(17). The COD varies during the photo catalytic degradation of Rose Bengal (20ppm, 100mL). Estimation of COD had been done by standard methods .The efficiency of dye mineralization was estimated using the following expressions.

Mineralization %=(1-COD)/COD_0 * 100

where COD and COD_0 correspond to CODs initially and finally. It is noted that irradiation of the suspension for 2hours resulted in elimination of the COD of the solution, indicating the complete mineralization in two hours.

V. CONCLUSION

Ag doped ZnO particles have been synthesized. The surface morphology was studied by SEM and elemental composition was analyzed by EDX spectrum. The crystal size was revealed by XRD. The synthesized Ag doped is photoactive and is found to exhibit excellent photocatalytic activity towards degradation of RB dye.

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