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Use of ZnO Nanoparticles in the Degradation of Rhodamine B dye in Wastewater to Save the Environment

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ABSTRACT: Green Synthesis method was adopted to prepare nanoparticles of ZnO (average size 28 nm). The morphology of these particles was characterized by XRD, SEM, and TEM. The intensity and diffraction pattern of XRD peaks of the sample shows crystallite nanoparticles in the anatase phase. SEM and TEM images confirm the synthesis of nanorods. The photocatalytic activity of ZnO nanoparticles was examined by photocatalytic degradation of Rhodamine B dye, a major contributor to water contamination, under UV radiations. The effect of various parameters such as the presence or absence of ZnO nanoparticles, time duration, and effect of UV light were studied. It has been observed that photodegradation of Rhodamine B dye in wastewater occurs at a faster rate under UV light. The results inferred that the ZnO nanoparticles act as catalysts for the degradation of dye in wastewater.

Keywords: Green Synthesis, Photo catalytic, SEM, TEM, UV, XRD, ZnO

I. INTRODUCTION

Environmental pollutants are the major contributors to most of the health illness. Water is one of the largest sources of pollution, which affects health through bio-magnifications. Water gets contaminated by dyes, heavy metals, insecticides, pesticides, detergents, oils, solvents, and other inorganic salts. Among various pollutants, dyes present in textile wastewater are a major culprit for worsening the quality of water. The effluents with the high value of COD and BOD are extremely harmful to living beings. Roughly 1- 20% of residual of coloring dyes are discharged directly to water bodies. It is not surprising that these compounds have become a major environmental concern. These compounds show structural stability against sunlight, bacteria interactions, and microbial degradation in the treatment process. The environment can be protected if the textile industry can decrease the use of harmful dyes. The dye manufactures should develop biodegradable dyes so that the residuals of dyes cannot harm the environment. Although these steps are preventive the presence of dyes/color substances cannot be ruled out in wastewater. Therefore, the treatment of this colored water is of prime importance in the current scenario. Due to prolonged droughts, increasing population, and climatic changes, the freshwater sources are exhausting day by day. Thus, the demand for fresh water is increasing throughout the globe. The present water treatment, water resources, and their management are not sustainable with growing demand. The multidimensional field of nanotechnology can provide a viable solution for the effective treatment of wastewater efficiently. Due to unique properties of nanoparticles, which include the interaction with the coloring substance in deep, can provide a cost-effective treatment for wastewater in large scale, which can never be achieved by traditional methods. Nanoparticles are the smallest particles. Its size is about 1 to 100nm. They can perform transport properties; therefore, these behave like a complete unit. There are two groups of nanoparticles one is organic nanoparticles and the other is inorganic nanoparticles. Organic nanoparticles are those nanoparticles that are mainly of carbon and inorganic nanoparticles, nanoparticles having a band-gap in the region of semiconductors like (silicon and zinc oxide) and nanoparticles of metals (like gold, silver, palladium, and nickel). In today's world, the nanoparticles are a great source of attention as compared to bulkier particles due to a small size and greater surface to volume ratio [1-2], which is responsible for their interesting properties such as optical property, surface property, electrical property, thermal properties, and their wide range of shape. One can use different materials with their novel applications by controlling their size and shape at a nanometer scale. Nanoparticle have shape and size-dependent properties because of this, they have a wide area of applications like in cosmetic, an electronic application like these can be used in the domestic refrigerator, optical, sensor applications, biomedical applications, and medicinal uses. Biodegradable nanoparticles were used in drug delivery system because these have less toxicity, target specific properties, encapsulation, and bio-available properties, Target drug delivery system because they exhibit less toxicity and also have smaller size due to this they can be used for target and diagnose diseases like cancer and photocatalytic property, which make them useful for wastewater treatment. Photocatalytic treatment of wastewater by ZnO nanoparticles is a widely discussed topic in environmental research [3-7] and a potential technique for the degradation of pollutants. Photocatalytic treatment of wastewater by ZnO nanoparticles is finding

its importance in contemporary research because of the unique properties of ZnO. The broad-spectrum makes it more interactive for the degradation of organic and microorganism. It's cheap operating costs, high availability, and simple experimental design make it a potential candidate fit for the application. The surface treatment of these nanoparticles is another alternative to increase many folds the photocatalytic activity of these nanoparticles. The design of photocatalytic reactors is of utmost importance, where intense research is needed. An effective photocatalytic reactor should be simple, energy-efficient, economical to assemble and operate, and capable to handle the large volume of wastewater. The reactors having designs, which do not require any post-separation of catalysts and make use of solar energy holds good promise as future photocatalytic reactors. The doping of ZnO nanoparticles with non-metals and metals may be used to shift the absorption of light from the UV region to the visible region to reduce the bandgap of doped nanoparticles. However, the feasibility of using doped nanoparticles needs a review because of the risk of dopant leaching and low catalytic activity of doped ZnO nanoparticles in the visible region. Coupling of this technique with other available technologies has a great potential for the treatment of a large volume of water treatment. Therefore, in the present study, the emphasis is on the synthesis of ZnO nanoparticles having the potential to degrade the dyes present in the wastewater [3-7]. Rhodamine B (Rh B) is a xanthene class of dye, which had got its uses in painting and dyeing of clothes, paper, other household items, and industrial instruments. Rh B dye can be allergic to skin and eyes. It is one of the major culprits of pollution of water. Therefore, it is of great importance to degrade this dye at earliest.

In the present study, the ZnO nanoparticles are synthesized by green synthesis method. The green synthesis method isa straightforward, economical resourceful, non-toxic, environmentally benevolent and bio-safe approach, at room temperature. These nanoparticles are characterized by XRD study for evaluation of structural aspects. XRD analysis has confirmed that the synthesized particles are anatase phase ZnO and of nano size. In the study, the photocatalytic degradation of organic dye, Rhodamine B, by ZnO nanoparticles is studied.

II. EXPERIMENTAL DETAILS

Materials and methods: Zinc acetate dihydrate $Zn(CH_3COOH)2.2H_2O$, acetic acid, and Rhodamine B were used as procured from E-merk, German. Fresh leaves of Osmium tenuiflorum (Tulsi, Basil) were collected and washed with double distilled water. The leaves were dried at 30℃ temperature.

Green synthesis Method [8-9]: Two approaches to prepare nanoparticles are Top-down (lithographic, ball milling, etching, and sputting, etc.) and bottom-up CVD (chemical vapor deposition), hydrothermal, condensation, and wet chemical methods, etc. The bottom-up approach had been extensively used for various nanoparticle productions. The shape and size of the particles and a result, the properties of these particles depend upon the technique and initial precursors used. Since the objective of this study is to clean wastewater therefore, green synthesis technique is used to prepare ZnO nanoparticles. This technique avoids excessive use of chemicals and a result environment is safe. In Green preparation algae, bacteria, plants, leaves, and seeds can be used. Using Leaves is a simple and reliable approach, in which the yield is better. These green methods hold several useful attractions and have the potential for an effective and economical way to environmental protection. The basil leaves were dried at 32℃ temperature. These leaves were powdered. 2.5 gm of leaves powder was dissolved in 20 ml of double-distilled water. This solution was boiled at 70ºC for 1 hour. The light-yellow colored solution was formed and the solution was cooled at room temperature. After filtering the solution, it was stored at 40ºC. 0.2 N of Zinc acetate dihydrate solution was constantly stirred for 20 minutes. 1ml of leaves extract and 0.2 N of sodium hydroxide were added to the solution of Zinc acetate dihydrate in a drop-wise manner with the help of burette. The solution was stirred continuously for 2 hours and white precipitates were formed. This solution was filtered and washed with distilled water followed by ethanol several times. After this, precipitates obtained were dried overnight for 2 days at 700C and a white powder was obtained.

Experimental Techniques: The XRD technique was used for phase identification of the prepared sample. A finely grounded and homogenized samples were analyzed on Bruker D8" X-ray diffractometer using Cu Kα radiation, the energy of which was 8.04 keV and wavelength1.54Å. Hitachi U-330 UV-VIS Spectro - photometer was used to study UV studies. Surender *et al.* [10] described, an immersion type photochemical reactor, was used in the present study. The photocatalytic studies were carried out in UV light with a wavelength of 400 nm. Rh B dye was dissolved in water in molar ratio 5×10^{-6} M. In 100 ml of this solution, 0.10 gm of ZnO nanoparticles was mixed. 5 ml of this solution was taken out. This solution was centrifuged for 5 minutes. After this, the excessive dye present at the surface was removed. The photocatalytic studies were carried out for the 553 nm absorption peak.

III. RESULTS AND DISCUSSION

The phase composition and the crystallite size of the prepared ZnO sample are evaluated by X-ray diffraction pattern. The XRD images of ZnO nanoparticles is presented in Fig. 1. The crystal planes designated are mentioned in the figure itself. The most intense and dominating peak around 36.3320 denotes plane [011]. It is the most significant peak. The second most intense peak is around 31.8370 assigned to [010] planes. The third most intense peak is around 34.5020 representing [020] plane. The other peaks (intensity in descending order) are around 56.7260, 63.0120, 68.119o, 47.6500, 69.2540, 66.5400, 77.1550, and 72.7560 represents, the planes [110], [013], [112], [012], [021], [022], [020] and [040] planes, respectively. The lattice constant calculated are a =b= 3.251 Å and c= 5.211 (Å). No spurious diffraction peak was observed in the sample. The intensity of XRD peaks shows that nanoparticles formed are crystalline. The breadth of diffraction peaks shows very small size crystallite.

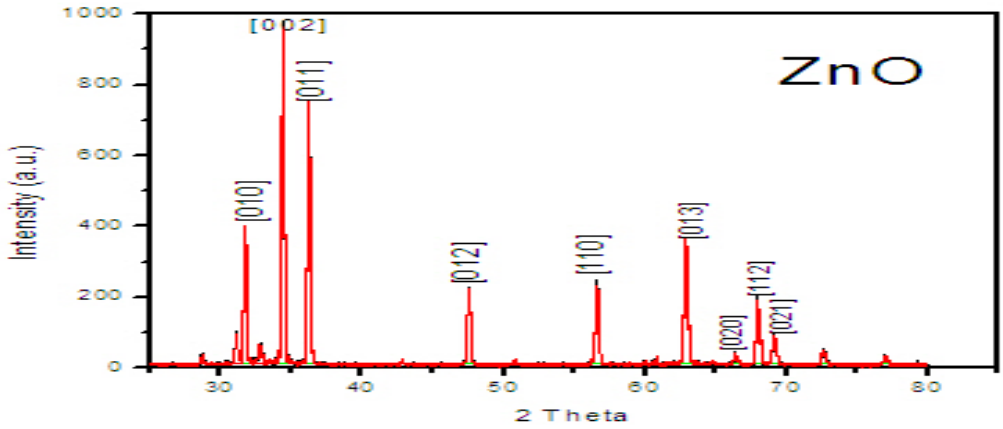

Fig. 1. XRD of ZnO sample prepared by Green Method.

Well known Scherer Equation was adopted to calculate average crystallite size. The average size of ZnO nanoparticles was found to be 28 nm. SEM (Fig. 2) and TEM (Fig. 3) studies of this sample were also carried out. SEM image (Fig. 2) shows that Nanorods are prepared. Micrograph indicates that a network had been formed. Grain boundaries are visible. It clearly shows that agglomeration had taken place. In Green, synthesis agglomeration is comparatively less.

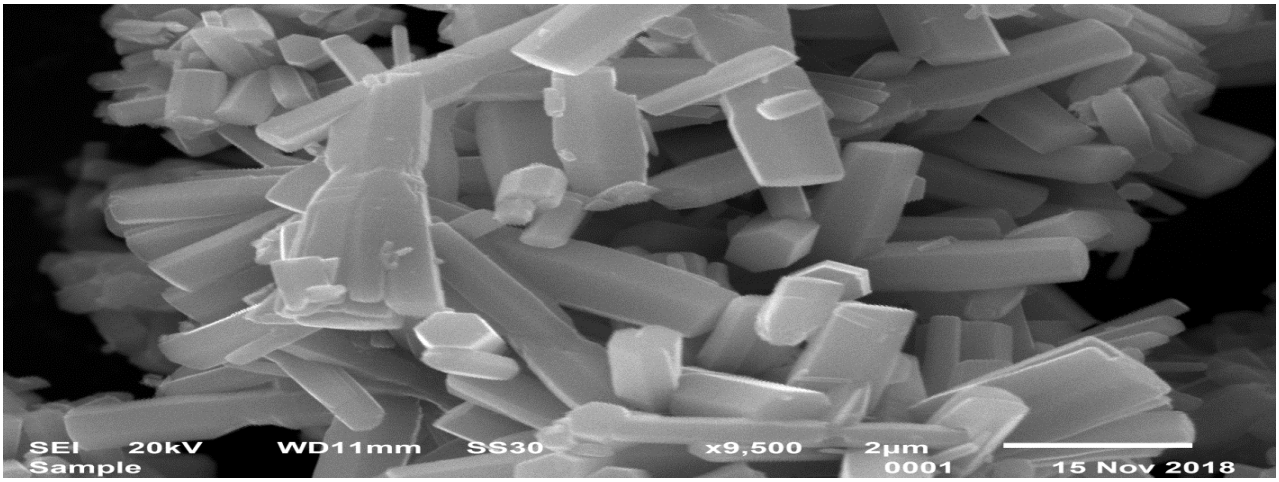

Fig. 2. SEM image of ZnO nano rods.

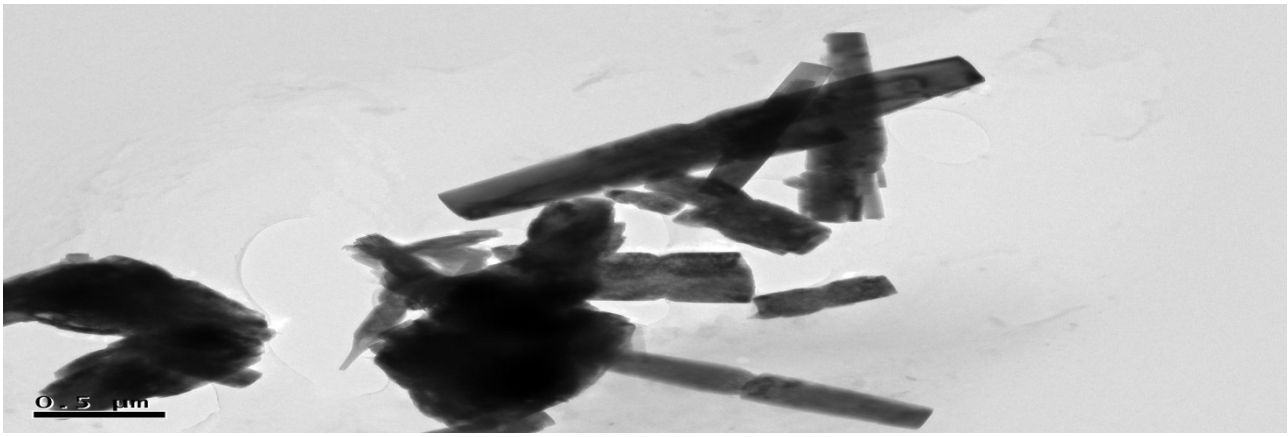

Fig. 3. TEM image of ZnOnao rods.

TEM (Fig. 3) of this sample also confirms the same. However, particle size comes to be 44nm. This may be attributed to agglomeration as confirmed by SEM. Agglomeration is a major concern which is due to high surface activity. To stabilize these nanoparticles vesicles and surface-active supports have been employed [10]. Of various methods for stabilizing nanoparticles, surface chemical modifications with organic molecules are of

particular importance; because it can be utilized for effectively prevent agglomeration and increase dispensability and stability of nanoparticles in many organic solvents [11-12]. Tulsi (Basil) extract acts as a surface capping agent during the reaction and doesn't allow the surface to react with any legend present during the synthesis and prevents the agglomeration of nanoparticles. However, the main focus was to perform this characterization to evaluate the particle size specifically. The shape and size of synthesized nanoparticles can drastically influence the photocatalytic activity of nanoparticles to degrade the dye molecules due to the change in the surface area. The photocatalytic activity of ZnO depends on many properties such as crystalline nature, phase composition, and surface area. As far as the particle size gets decreased, the number of surface defects gets increased. As a result, inter facial charge transfer get increased. On these sites, the photo-generated charge carriers react with engrossed molecules and hence hydroxyl and superoxide radicals are generated. Facade recombination turns out to be the foremost process because the charge carriers are formed very close to the face of the particle. Thus, the rate of recombination process is speedy than interfacial charge transfer [13-14].

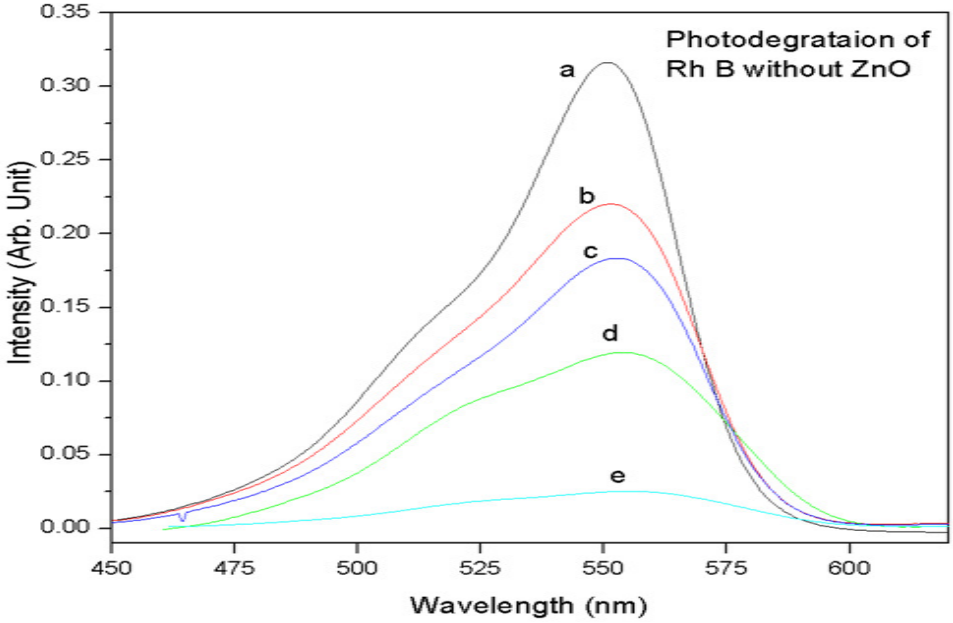

Fig. 4. Photo degradation of Rh B without ZnO nano particles at time (a) 0 minutes (b) 20 minutes (c) 75 minutes (d) 120 minutes (e) 160 minutes.

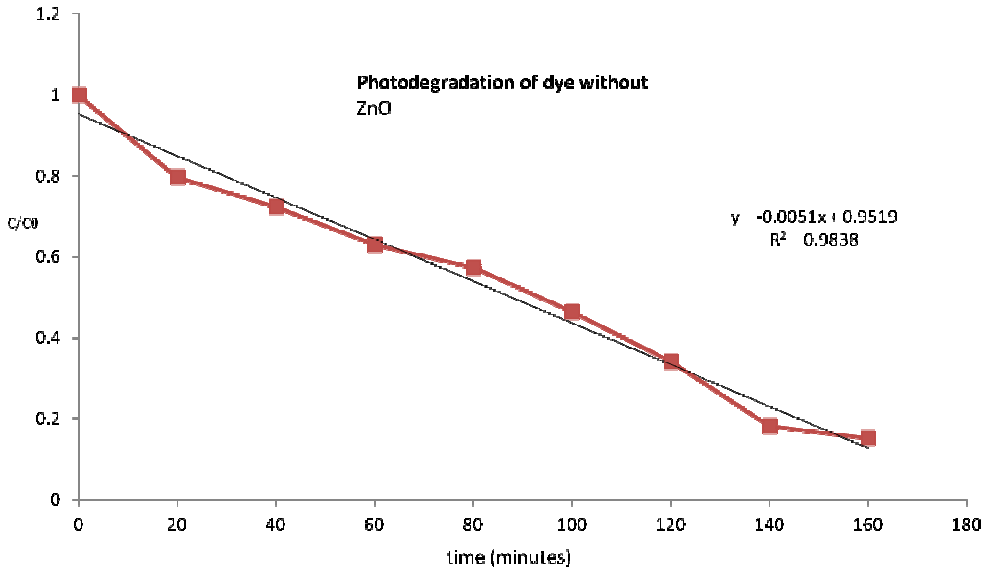

Fig. 5. Photo degradation of Rh B without ZnO nano particles.

On close observation of the absorption spectra of Rh B, two peaks may be identified. A broad and intense peak around 553 nm is assigned to π to π* transition. A weak peak around 440 nm is assigned to n to π* transition. Photodegradation (Fig. 4) of Rh B dye under UV irradiation without ZnO the study was carried out. The degradation curve is also shown in Fig. 4. On close observation of the absorption spectra of Rh B, two peaks

may be identified. It is quite visible that in the first twenty minutes the intensity of the broad peak decreases significantly. Later on, Rh B gets decolorized linearly. This slope is fitted with a linear trend. Slope equation and regression coefficients also shown in Figure. The slope is found to be 0.0051 and regression coefficient is 0.9838. This coefficient indicates that the linear decrement in intensity is observed. Further, a peak shift is also observed after some time. This may be attributed to non-radiative energy transfer between dye and ZnO nanoparticle. This non-radiative energy transfer may be due to TICT (Twisted interstate charge transfer). Total time of decolorization is 160 minutes approximately.

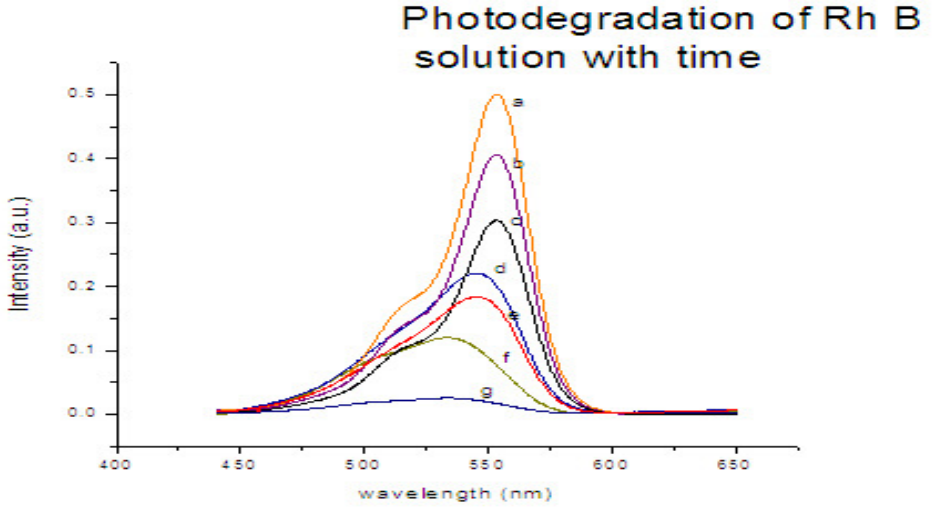

Fig. 6. Photo degradation of Rh B with ZnO nano particles at time (a) 0 minutes (b) 10 minutes © 20minutes (d) 30 minutes (e) 40 minutes (f) 53 minutes.

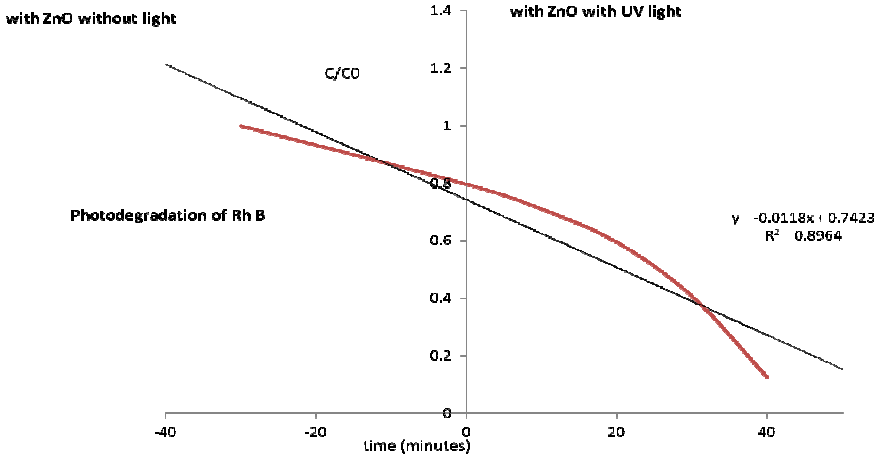

Fig. 7. Photo degradation of Rh B with ZnO nano particles.

The photodegradation of Rh B dye under UV radiations was also carried out for the different duration of time in the existence of ZnO nanoparticles and is depicted in Fig. 6 and 7. From the first thirty minutes, the adsorption is ruled out. Firstly, in dark, the dye solution and ZnO nanoparticles were stirred for 25 minutes to obtain equilibrium. When 5 ml solution of this master solution is centrifuged for 5 minutes the dye gets absorbed at the surface of ZnO. It was removed. Since the concentration is decreased as a result peak intensity get decreased. In this time no gas evolves. This cannot be attributed to photodegradation. This concentration was measured and maintained by UV peak intensity at 553nm. The slope and duration indicate that ZnO plays a vital role in photo-degradation. Rh B dye was decayed entirely after 53 minutes irradiated by UV light. For the linear trend, the slope is 0.0118 and regression coefficient is 0.8964. This coefficient indicates that now the trend is not linear A semiconductor ZnO nanoparticle starts its mechanism in the presence of photon energies larger than the bandgap of the acting substance. The valence band electrons are excited to the conduction band and holes are created in the valence band. Recombination of almost every electron-hole pair produced in the valence band takes some tens of pico-second and the energy is released in the form of phonon, photons and both [3-4]. The holes ensnared at outside contain an extremely reactive oxidation potential and the electron has a highly spontaneous reduction potential. Due to these holes and electrons, an induced catalytic reaction occurs at the surface, which is called photocatalytic reaction [15]. ZnO is largely used for air and water purification. It is used as an agent for the antifogging and self-cleaning surface. ZnO is an excellent semiconductor having certain limitations such as poor absorption of visible light and rapid electron/hole recombination of photo-generated electron/hole pairs. This problem can be overcome to a certain extent by various methods such as dye

sensitization, coupling, capping, and doping. The photons of UV acts on all parts of the solution (the catalyst, the dye, and the solvent). In catalyst, electron-hole pairs are generated. The dye also gets excited and as a result, singlet or triplet state produces free electrons by breaking the bonds in the dye. Insolvent also UV radiation generates H_2O_2 and OH- radicals for further catalysis [16-17]. A probable way of photoelectron transfer can be attributed to holes and electron pair formation due to UV light. The UV light excites dye and bonds get broken to form (Dye^+ + e-). These free-electron get injected in the conduction band of ZnO.

IV. CONCLUSION

Nanoparticles of ZnO were synthesized by green synthesis method, in a versatile, non-toxic and bio-safe approach, at room temperature. XRD analysis has confirmed that the synthesized particles are anatase phase ZnO and of nano size. From SEM and Tem, it is confirmed that the particle formed are of rod shape. Aggoliation is also present in the ZnO nanoparticles. Without UV light, the Rh B dye gets degraded in 160 minutes but it gets photodegraded in 53 minutes in presence of UV light. The presence of ZnO acts as a catalyst for the process. This method shows a potential way to treat wastewater on a large scale.

Conflict of Interest: No

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