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Facile Synthesis of Zinc Oxide Nanoparticles with Antibacterial, Humidity Sensing and Photocatalytic Behaviour

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Abstract- Synthesis of zinc oxide (ZnO) nanoparticles was carried out by simple co-precipitation technique. The synthesized ZnO nanoparticles were characterized by powder X-Ray Diffraction (XRD) for phase analysis, Scanning electron microscopy (SEM) for morphology, Dynamic light scattering (DLS) for particle size analysis, Ultra-violet absorption spectra for optical properties. The antibacterial activity of the synthesized ZnO nanoparticles was assessed against both the gram-positive and gram-negative bacterial strains. *Staphylococcus aureus* and *Escherichia coli* were test pathogens under study that were tested for its bacterial growth against synthesized ZnO nanoparticles. The ZnO nanoparticles shows prominent zone of inhibition towards growth of bacteria's. The humidity sensing capability of synthesized ZnO nanoparticles was analyzed at different relative humidity ranges. It exhibits the sensitivity factor of 922 with quick response and recovery characteristics. The photocatalytic ability was analyzed using synthesized ZnO nanoparticles as photocatalyst for the degradation of an organic dye – Rhodamine B (Rh B) under visible light source. The degradation efficiency was above 98% within 45 minutes of irradiation, this proves the stupendous degradation of the Rh B dye solution.

Keywords: ZnO nanoparticles, Antibacterial activity, Humidity sensor and Photocatalyst.

1. INTRODUCTION

In the modern era, nanotechnology grasps the attention; as it paves way to the modern innovations in the field of science and technology. Nanotechnology dealing with particle size in nanometer range finds application in the environmental, sensing, medical, optical, communication and electromagnetic fields. The various synthesis techniques of these nanoparticles greatly influence in its size, morphology and applications. Among the nanoparticles, the metal oxides were known to possess exorbitant physico-chemical properties and finds plausible applications in various sectors. Among the metal oxides, Zinc oxide (ZnO) was remarkable due to its astounding properties. ZnO, an n-type semiconductor with wider band gap were found to be useful in several applications in the field of sensors, medical, optical, solar cells, photocatalysis and electromagnetic areas. There were various techniques of the synthesis of the ZnO nanoparticles such as sol-gel, hydrothermal, microwave assisted method, co-precipitation, solid state reaction. Amongst which the eco-friendly, economic, simple and user-friendly approach was the requisite characteristics for its efficient application in various sectors. The zinc oxide leads to its plentiful applications; widely in electrical and biological sectors [1-4]. The urbanized world with modern amenities was in an urge to focus on medical field; as the infectious diseases caused by multidrug resistant microorganisms were the serious issue leading to several medical complications day-by-day. Bacterial infections were the serious issue; as it also affects the pleasant life of mankind by indirectly affecting the various processes in food, textile, medicine and several industries. ZnO nanoparticles possess the antibacterial properties against several gram-positive and gram-negative species. Nanoparticles have properties that differ from the bulk materials due to its surface-to-volume ratio, size and morphology. Among the different pathogens, antibiotic-resistant pathogens are the area of concentration as they are culpable for various intricate infectious diseases. Therefore, there arises a need for biologically active, antibacterial material against those multi-drug resistant bacteria's. The antibiotic-resistant, multidrug resistant (*Staphylococcus aureus, Escherichia coli*) pathogens are known to be more infectious as the infections and diseases caused by them are more complicated to cure [5-7]. Following the health sector, humidity monitoring, detection and control had been vital in wide areas as it possess many domestic applications as in intelligent control,

cooking control and serves in medical sectors in sophisticated maintenance processes. Humidity monitoring also plays role in agriculture for maintaining and acquiring proper level of moisture for plant growth and humidity had inevitable position in food processing and many production processes. The existence of humidity sensing material of various types drags the focus towards miniaturization, fabrication and production of humidity sensors with low cost, user-friendly characteristics. Relative humidity sensors were the preferable and commonly used due to its economic and user-friendly characteristics. The surface of the sensing material and the water molecules shows surface related interaction such as adsorption mechanism, thus the sensing ability of the material was monitored by electrical measurements which were closely related to the changes in the relative humidity percentage. Several metal oxides and nanoparticles possess sensing behavior; but there remains the need for commercial grade sensor with the high sensitivity, low response time, high accuracy and low cost material [8-10]. Now-a-days, the water pollution had been the great threat to the society. The majority of contaminants, impurities in the water bodies were the dyes from industrial effluents. This contaminant not only affects the water table, but also leads to acute health issues and affecting both the aquatic as well as terrestrial lives. Among the various ways of treatment of the effluents, photocatalysis had been the solution for the removal of dye contamination from water, as it was cost effective and environmental friendly approach. Metal oxides, in particular semiconductor materials were known to be efficient in photocatalysis. ZnO have been known to possess the photocatalytic property and it was seemed to be environment-friendly, biocompatible material. The redox reactions of the photocatalysis process degrade the dyes without leaving any secondary pollutants to the environment [11-13].

Thus, the aim of the work was to synthesize material with multiple applications. In the present work – we synthesized multifunctional ZnO nanoparticles which were analyzed for its antibacterial activity, humidity sensing capability and photocatalytic studies.

2. EXPERIMENTAL SECTION

2. 1. Synthesis of ZnO nanoparticles

0.2M solution of sodium hydroxide and 0.1M solution of zinc nitrate were mixed and magnetically stirred for two hours. The precipitate obtained was washed several times and filtered; followed by the calcination of the precipitate in muffle furnace at 500°C for four hours. The calcined precipitate of ZnO nanoparticles were synthesized by template-free, surfactant-free technique.

2. 2. Characterization

"XPERT-PRO" was used to study the powder XRD for phase analysis. Surface morphology was analyzed using AU Quanta 250 FEG scanning electron microscope, the particle size was measured using Zetasizer 3000HS instrument and the UV-spectral studies were done using JASCO V-630 spectrophotometer.

2. 3. Antibacterial, humidity sensing and photocatalytic studies

The antibacterial activity of the ZnO nanoparticles was assessed using agar well diffusion technique. The synthesized ZnO nanoparticles were taken with DMSO solvent. The DMSO also acts as control [14]. The synthesized ZnO nanoparticles were prepared into stock solution of 1mg/ml concentration which was then diluted to 25µl/ml, 50µl/ml, 75µl/ml and 100µl/ml. Gram-positive *Staphylococcus aureus* and gram-negative *Escherichia coli* were selected as test pathogens. The agar medium swabbed with pathogens was loaded with different concentrated solutions and control. All the tests were done in triplicates and the average zone of inhibition was noted which was used to predict the antibacterial activity of the synthesized ZnO nanoparticles.

Anhydrous phosphorus pentoxide; saturated solutions of potassium acetate, calcium chloride hexahydrate, zinc nitrate hexahydrate, calcium nitrate tetrahydrate, sodium nitrite, ammonium chloride, barium chloride dihydrate and copper sulphate petahydrate were placed in a closed apparatus which serves as controlled humidity arrangement with relative humidity (RH) of 5%, 20%, 31%, 42%, 51%, 66%, 79%, 88% and 98% respectively [15]. The synthesized ZnO nanoparticles were used as sensing element in the two-probe set-up, which was used to analyze the relative humidity. The ZnO nanoparticles infused two-probe sensing set-up was kept undisturbed for two hours. After the resting time, the sensitivity was measured using electrical measurement of DC resistance. The response and recovery time was also studied.

The photocatalytic activity of the synthesized ZnO nanoparticles was analyzed by

using ZnO nanoparticles as photocatalyst for the photodegradation of the organic dye – rhodamine B (Rh B) [16]. 0.025g of the synthesized ZnO nanoparticles was taken to degrade 100ml of aqueous Rh B solution of concentration (2×10^{-5}M). The suspensions of photocatalyst and dye were stirred in dark for 30 minutes for attaining equilibrium; followed by which the suspensions were kept under 250W tungsten-halogen lamp as visible light source. After irradiation, the suspension collected at regular intervals was centrifuged and filtered. The supernatant liquid was subjected to UV-absorption studies to analyze the concentration of the Rh B dye.

3. RESULTS AND DISCUSSION

3. 1. Analyses on Phase, morphology, size and optical properties

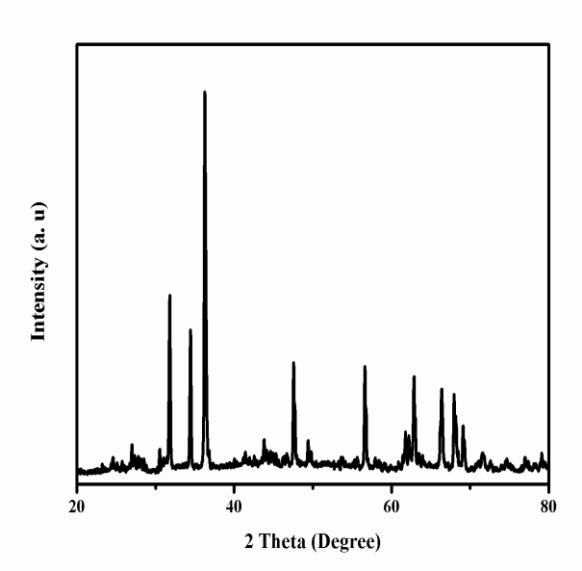

Fig. 1. Powder XRD of synthesized ZnO nanoparticles.

The powder XRD analysis of synthesized ZnO nanoparticles shows thorny diffraction peaks, which were found to be in accordance with JCPDS number: 89-0510. The Powder XRD pattern of synthesized ZnO nanoparticles recorded with 2θ values from 20 to 80 degrees was given in Fig. 1. According to the JCPDS, the synthesized ZnO nanoparticles possesses primitive lattice with hexagonal system and cell parameters a = 3.248A°, c = 5.205A°.

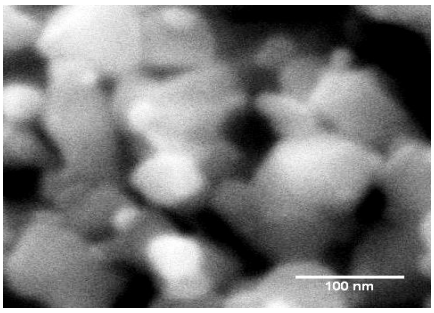

Fig. 2. SEM image of the synthesized ZnO nanoparticles

The SEM image of the synthesized ZnO nanoparticles was shown in Fig. 2. The SEM image shows irregular particles with uneven distribution and minor congregation. The template-free, surfactant-free synthesis procedure was reflected in this morphological behavior. Further, the particle size analysis using DLS shows the polydispersity of particles and the intensity percentage was greater between 30 nm to 90 nm. The most intense peak was recorded at 56.3 nm as given in Fig. 3. This shows that the synthesized nanoparticles lie under the nano-range.

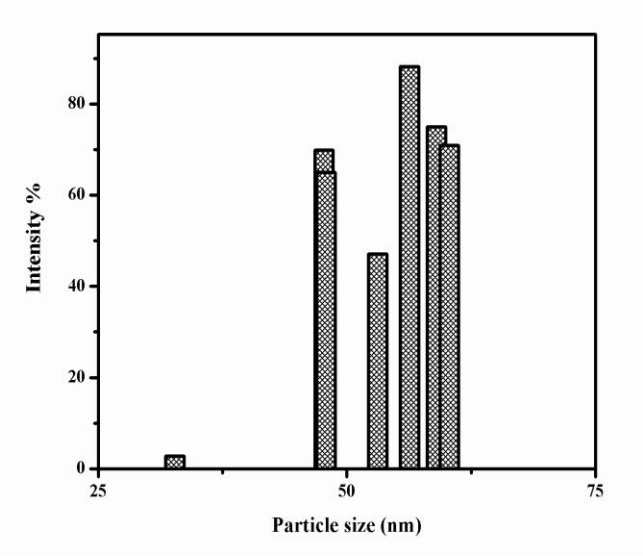

Fig. 3. Particle size analysis of ZnO nanoparticles

The optical property analyzed by UV-absorption spectra was shown in Fig. 4. The absorption edge was at 371 nm and the band gap value was calculated using the formula Eg = 1240/λ, where λ is the absorption edge [17]. The calculated

band gap value was 3.34 eV. This band gap facilitates electronic transitions, thereby increasing its potential towards applications as photocatalyst.

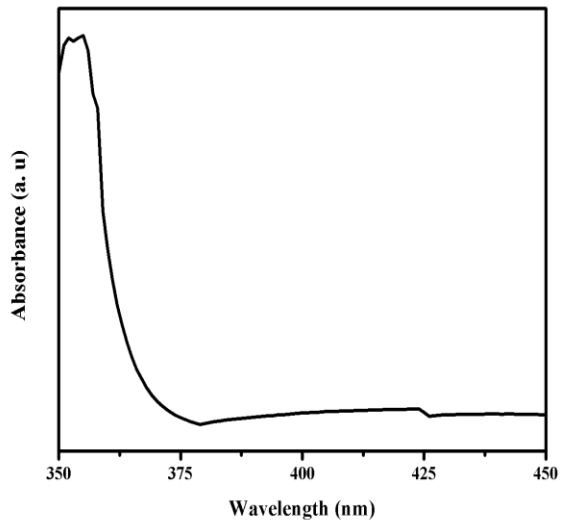

Fig. 4. UV-Absorption spectra of ZnO nanoparticles.

3. 2. Antibacterial activity of the synthesized ZnO nanoparticles

The antibacterial activity of the synthesized ZnO nanoparticles assessed against gram-positive and gram-negative bacterial strains which shows prominent zone of inhibition. As there was no inhibition zone observed with DMSO solvent, the antibacterial activity possessed by the DMSO was nullified and the zone of inhibition was entirely due to the synthesized ZnO nanoparticles. The zone of inhibition measured after 24 hours of incubation of agar wells loaded with ZnO nanoparticles exhibits the satisfactory zone of inhibition even with minimal amount of concentration of the ZnO nanoparticles.

The antibacterial activity of the synthesized nanoparticles was given in Fig. 5. The antibacterial activity of the synthesized ZnO nanoparticles against each bacterial species increases with the increase in the concentration of the nanoparticles. However, the concentration of ZnO nanoparticles had an impact on the antibacterial assay. It exhibits the variation in the zone of inhibition for each concentration. There was the fluctuation in the highest inhibition zone between the *staphylococcus aureus* and *Escherichia coli* with respect to each concentration. The bacterial resistivity monitoring was continued for 36 hours to estimate the time depending bacterial resistivity character of the antibacterial agent. Once the zone of inhibition was measured after 24 hours, the time dependence bacterial resistivity was assessed by continuously keeping the petridish undisturbed for 36 hours.

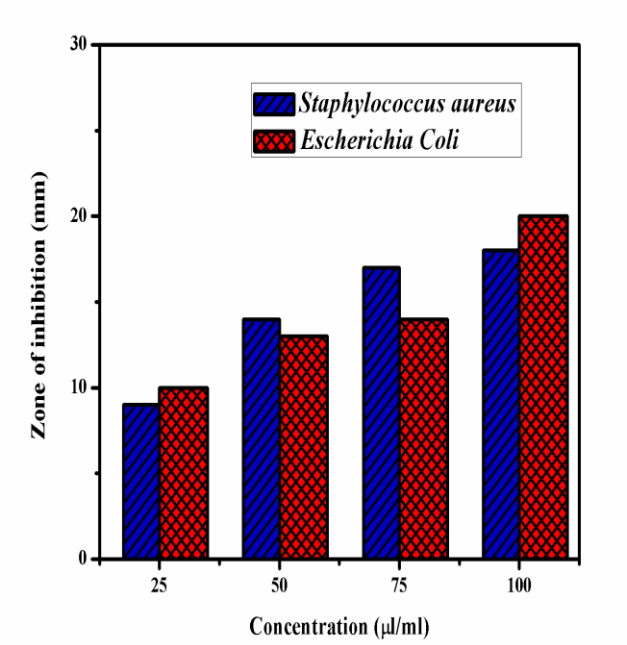

Fig. 5. Antibacterial assay of ZnO nanoparticles

As the time goes on increasing, the zone of inhibition decreases and there was decrease in the bacterial resistivity character of ZnO nanoparticles. The antibacterial activity assessed after 36 hours was given in Fig. 6. The bacterial resistivity of the ZnO nanoparticles was attributed to the biological mechanism involving at cellular level. The zone of inhibition varies due to the presence of thick layer of peptidoglycan in the gram-positive species; which was thin in gram-negative species. These are the characteristics responsible for difference in inhibition zone and interaction of nanoparticles at cellular level. The interaction of the synthesized ZnO nanoparticles with the bacterial cell followed by the reactions producing ROS were responsible to interlude the metabolism of the bacterial species. This mechanism would obviously result in impairment of bacterial cell, thereby causing cell damage and finally leads to the death of the bacteria [18, 19].

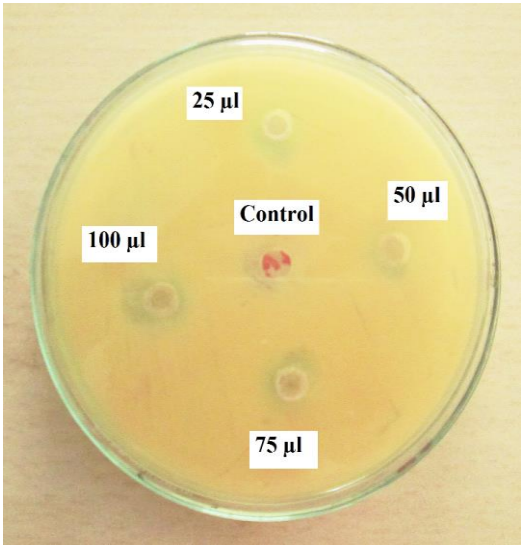

Fig. 6. Time dependent antibacterial assay after 36 hours.

3. 3. Humidity sensing behavior of ZnO nanoparticles

The humidity sensor studies of the synthesized ZnO nanoparticles were examined in the relative humidity range of 5% to 98%. The respective resultant resistance values were large numerical integers represented in the ohm units. Thus, the graph was plotted against log R versus RH%. The plot explains the sensitivity report on humidity sensing ability of ZnO nanoparticles; as the relative humidity increases, the log R values drops consistently as shown in Fig. 7.

The sensitivity factor (S_f) of the synthesized ZnO nanoparticles was calculated using the ratio of $R_{5\%}$ / $R_{98\%}$, where $R_{5\%}$ and $R_{98\%}$ are the DC resistances at 5% and 98% of relative humidity respectively. The sensitivity factor of 922 shows the prominent humidity sensing ability of the ZnO nanoparticles.

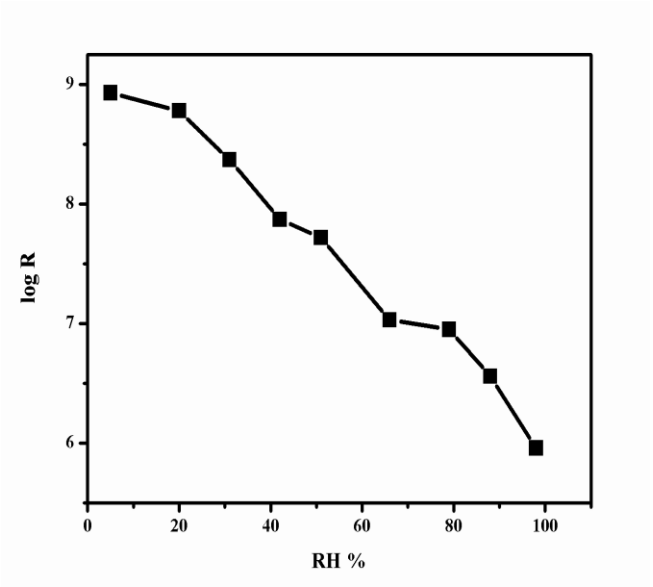

Fig. 7. Humidity sensing ability of ZnO nanoparticles

The mechanism of sensing behavior of the synthesized nanoparticles was attributed to the surface reactions. The adsorption of water molecules by the synthesized nanoparticles facilitates condensation through the microscopic pores between the nanoparticles. These surface changes were encountered by its impact and reflection in the changes of electrical measurements. However, the sensing ability and the mechanism of action were greatly influenced by the particle size, porosity, morphology and the synthesis technique [20]. The response and recovery characteristic of the synthesized ZnO nanoparticles towards humidity sensing nature was analyzed by varying the RH% from 5% to 98%. The response and recovery characteristic graph was shown in Fig. 8. As the quick response and recovery characteristic was a necessary criterion for better sensing material; the synthesized ZnO nanoparticles show response at 30 s and recovery at 100 s. This also evident the adsorption and desorption ability of the synthesized ZnO nanoparticles. The quick response and recovery characteristic of the synthesized zinc oxide nanoparticles makes it applicable in commercial grade.

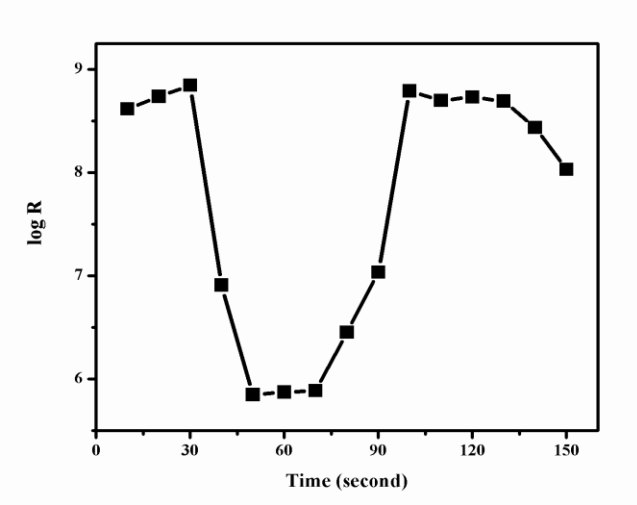

Fig. 8. Response and recovery characteristic of ZnO nanoparticles

3. 4. Photocatalytic activity

The photocatalytic activity of the synthesized ZnO nanoparticles against Rh B dye were demonstrated under visible light and the photodegradation of Rh B were clearly observed from the UV-absorption plot in Fig. 9.

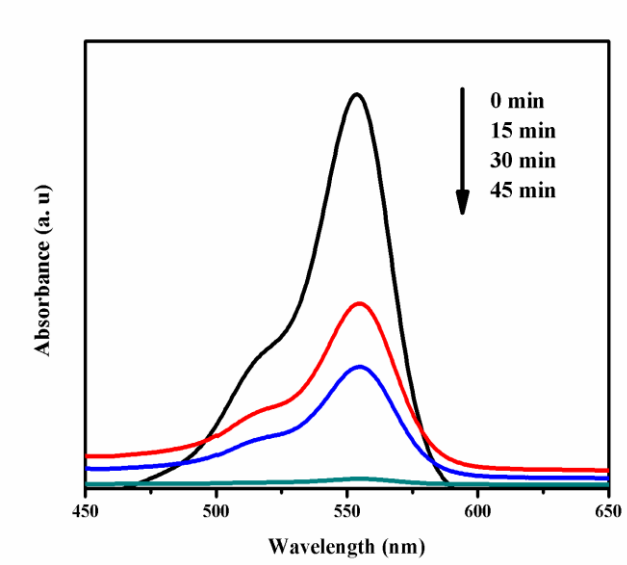

Fig. 9. Photocatalytic activity of ZnO nanoparticles towards Rh B degradation.

The concentration of the dye was observed to decrease with increase in irradiation time. The color of the Rh B dye slowly pales and become lighter from initial time to 45 minutes of irradiation. The diminishing of dark pink to pale color was clearly visible from the solution obtained at regular time intervals. The solutions obtained at regular intervals were displayed in Fig. 10 exhibiting Rh B solution from 0 minutes to 60 minutes. The sample bottle at position- 5, shows the Rh B at 60 minutes. There was no remarkable change noticed at the concentration of the Rh B dye between 45 and 60 minutes. Thus, minimum time of 45 minutes at that respective concentration of nearly zero was considered as the time for maximum degradation of the Rh B dye solution. The plot of C/C_0 versus time was given in Fig. 11. This explains that the Rh B was not photodegraded automatically in the absence of any photocatalytic material. The degradation in the absence of synthesized photocatalyst was not eminent. But, the degradation in the presence of ZnO nanoparticles shows decrease in the concentration of the Rh B with increase in time. The degradation efficiency was calculated using the formula,

$$\text{Degradation efficiency} = [(A_0\text{-}A) / A_0] \times 100$$

Where, A_0 is the initial concentration of the Rh B dye and A is the concentration of the Rh B dye after 45 minutes [21].

Fig. 10. Color of Rh B dye solution during degradation process.

The degradation efficiency after 45 minutes was found to be 98.54% and the concentration was reduced to approximately zero. The degradation by the synthesized ZnO photocatalyst was overwhelming and the mechanism/processes in the

degradation of Rh B were significantly via the decomposition of conjugated ring system in Rh B molecule. As there was no significant hypsochromic shift; the de-ethylation would not be the dominant process in the photodegradation reaction. Thus, the adsorption of the nanoparticles on the Rh B dye molecules; thereby facilitates the redox reactions producing free radical species followed by its attack towards the decomposition of conjugated chromophores were concluded to be the steps mainly involving in the photodegradation of the Rh B dye [22, 23].

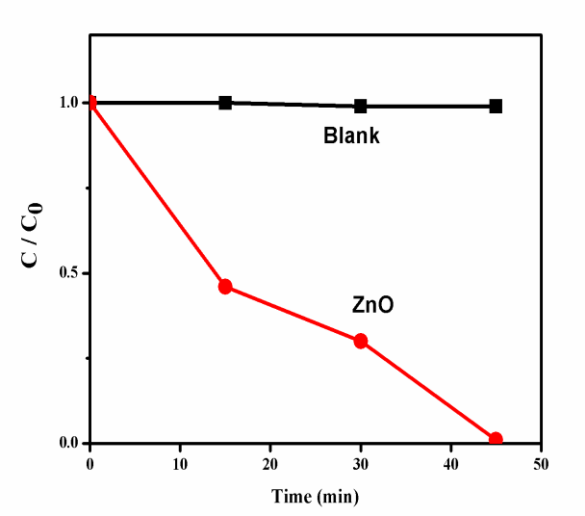

Fig. 11. Photodegradation – with ZnO and without ZnO nanoparticles.

4. CONCLUSION

The synthesized ZnO nanoparticles are known to possess hexagonal system in accordance with JCPDS number. The morphology of the ZnO nanoparticles shows irregular distribution of particles with small huddles and porosity thereby facilitating its application oriented properties. The particle size analysis of the synthesized ZnO nanoparticles shows particles with high intensity and maximum number of particles focused in the range of 56 nm. The band gap of 3.34 eV favors the potential of the nanoparticles towards its applications. The bacterial resistivity of the synthesized ZnO nanoparticles against the gram-positive (*Staphylococcus aureus*) and gram-negative (*Escherichia coli*) species was observed. The maximum zone of inhibition was against gram-negative (*Escherichia coli*) species with maximum concentration of ZnO nanoparticles. The humidity sensing behavior of the synthesized ZnO nanoparticles possesses sensitivity factor of 922 with fast response and recovery time period of 30 s and 100 s respectively. The relation between relative humidity and electrical measurements (resistivity) were exhibited by the decrease in log R (changes in the electrical measurements) with increase in RH%. The stupendous sensitivity factor of 922 makes the synthesized ZnO nanoparticles as an efficient humidity sensing material. The photocatalytic degradation of Rh B by the synthesized ZnO nanoparticles shows degradation efficiency of 98.54% within 45 minutes of irradiation which was significant, as it proves the photodegrading ability of the organic dye – Rh B. Thus, the synthesized ZnO nanoparticles can be known as multi-functional material as these nanoparticles were efficient with antibacterial, humidity sensing and photocatalytic applications.

Based on these antibacterial, humidity sensing and photocatalytic properties, the synthesized ZnO nanoparticles can be used in future; to be applicable in the variety of fields for numerous applications such as antibiotics, humidity sensor and in wastewater treatment.

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