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Research Article

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Antibacterial and photocatalytic activity of ZnO nanoparticles synthesized by sol-gel method

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ABSTRACT

ZnO nanoparticles were synthesized by sol-gel method and characterized by XRD, SEM, EDX and BET analysis. These nanoparticles were tested for its antibacterial activity against the clinical pathogens Escheria coli, Klebsiella pneumonia, Pseudomonas aeruginosa and Staphylococcus aureus using disc well diffusion method. Positive activity was observed against Pseudomonas aeruginosa and Staphylococcus aureus. The catalyst nanoparticles were also used for the removal of toxic organic pollutants such as, dye acid blue 113 under UV irradiation in a batch reactor. The different operational parameters such as the initial concentration of the dye, weight of photo catalyst and pH on the photo catalytic degradation of the dye were investigated. The optimum catalyst loading was found to be 2.0 g L^{-1}. It was noticed that the degradation of the dye was found to be more pronounced in neutral medium.

Keywords: ZnO nano particles, Acid Blue 113, degradation, photo catalysis, antibacterial activity.

INTRODUCTION

The environmental pollution is mostly arises due to the contamination of water streams by pesticides, dyes, industrial effluents and heavy metals. This has necessitated the researchers to seek solutions to mitigate the pollution problem [1, 2]. The pollutants can be completely degraded by photo catalytically active nano structural semiconductor metal oxides like TiO_2, ZnO, Fe_2O_3, CdS and ZnS etc under UV irradiation [3-7]. Though TiO_2 is found to be an excellent photo catalyst in the detoxification of waste water [8], but the large scale use of this catalyst is restricted due to its high cost. Literature reports have indicated the supremacy of ZnO over TiO_2 as a photocatalyst [9-12] and this has further confirmed by the rampant use of ZnO as a potential catalyst in several photo catalytic reactions [13-15]. ZnO is considered to be one of the best nano structural semiconductor photo catalysts owing to its high photo sensitivity, high catalytic activity, suitable band gap, low cost and eco-friendliness [16-19].

ZnO also possesses better anti-bacterial activity even at low concentrations [20]. It has many advantages as an antibacterial agent because of its good stability at high temperatures and pressures and long shelf life when compared to organic anti-bacterial agents. The materials and textiles coated with ZnO are widely used as useful antibacterial and antifungal agents [21-23].

The present study aims at the synthesis of ZnO nanoparticles by Sol-Gel method and its characterization is carried out using analytical techniques such as XRD, SEM, EDX, BET and FTIR. The as prepared ZnO nano particles are tested for its photo catalytic activity on the degradation of the dye acid blue 113 and also its antibacterial studies are being conducted against Escheria coli, Klebsiella pneumonia, Pseudomonas aeruginosa and Staphylococcus aureus.

EXPERIMENTAL SECTION

2.1 Materials

The dye and other chemicals used in the present study were of AR grade from Merck. The Acid Blue 113 (AB 113), the dye was used without further purification. Reagents used in the synthesis of ZnO nanoparticles, such as $Zn(NO_3)_2.4H_2O$, NaOH & ethanol were of AR grade. The double distilled water was used for the preparation of all the reagents. pH of the experimental solution was adjusted using 0.1M HCL or 0.1M NaOH, as the case may be.

2.2 Synthesis of ZnO nanoparticles

ZnO nanoparticles were synthesised by Sol-gel method. In a typical synthetic procedure 0.45M of $Zn(NO_3)_2.4H_2O$ and 0.9M of NaOH were dissolved in double distilled water. The beaker containing NaOH solution was heated to a temperature of about 60^0C. To this solution of NaOH, the $Zn(NO_3)_2.4H_2O$ solution was added drop wise under high speed stirring. The beaker containing the above solution mixture was then securely covered and left aside for 2h. The precipitated ZnO nanoparticles were then cleaned with double distilled water and ethanol and then dried in an air oven maintained at 60^0C.

2.3 Antibacterial Activity test

Antibacterial activity was performed by well diffusion method in Mueller Hinton Agar plates against the clinical pathogens *Escherichia coli, Klebsiella pneumoniae, Pseudomonas aeruginosa and Staphylococcus aureus*. To the sterile solid Mueller Hinton agar plates the above clinical strains were swabbed uniformly onto the individual plates using sterile cotton swabs. Wells were created using a cork borer to about 5 mm diameter in size. Different concentrations of 10, 25, 50, 75 and 100 ppm of dry powder of ZnO nanoparticles were dispersed in distilled water. The dispersed solution was amended into separate well using a sterile cork borer. After incubation at 37°C for 24 to 36 hours, the different levels of zone of inhibition of bacteria were measured. Chloramphenicol was used as positive control. The experiments were performed three times and data have been statistically analyzed.

2.4 Batch photo reactor set-up

The photo catalytic degradation of the dye was carried out in a batch reactor of 500ml capacity double walled reaction vessel made of borosilicate mounted suitably on a magnetic stirrer. The experiments were performed under identical conditions by using a low pressure mercury vapour lamp (6W, 18cm along) emitting UV radiation at a peak wavelength of 254nm. Constant stirring of the solution was ensured with the use of a magnetic stirrer. The temperature of the reaction mixture was maintained constant throughout the reaction time.

2.5 Absorbance measurement

In the present investigation, a batch volume of 250ml of dye solution was kept at a distance of 7cm from the UV source with a constant stirring of 60 rpm and the initial absorbance of the dye solution was measured by using UV-Visible spectrophotometer. A calculated weight of ZnO nanoparticles were added to this dye solution and the mixture was stirred in dark for about 30 minutes to ensure adsorption/desorption equilibrium. A 3ml aliquot was then withdrawn from this reaction mixture, centrifuged and then the absorbance was measured. Now the reaction mixture was irradiated with UV source. Subsequently, samples of 3ml of aliquot were withdrawn at regular intervals of time, centrifuged and the absorbance of the supernatant solution was measured by using UV-Visible spectrophotometer and then the solution was returned back to the reactor.

RESULTS AND DISCUSSION

3.1 Characterisation of the catalyst:

The synthesized ZnO nanoparticles were characterized by XRD, FESEM, BET, EDAX and FTIR analysis and reported earlier [24]. From the XRD pattern the average crystalline size was calculated as 33nm using Scherer formula. The FESEM image reveals that the ZnO nanoparticles were found to be spherical in nature with the average size of 30-35 nm (Fig.1). The surface area of these nanoparticles was observed to be 15 m^2/g. The EDAX studies confirmed the presence of Zn and O respectively.

3.2 Antibacterial Activity of ZnO nanoparticles

A significant antibacterial property was observed as a clear circular zone of inhibition after incubation against the clinical pathogens. There was no activity against *Escherichia coli* and *Klebsiella pneumoniae* at all concentrations. Whereas a significant activity was observed at 25, 50, 75 and 100 ppm of ZnO nanoparticles against *Pseudomonas aeruginosa* and subsequently against *Staphylococcus aureus*. The antibacterial activity of ZnO nanoparticle was observed to be almost similar when compared to the positive control. The higher concentration of nanoparticle exhibited more activity which can be inferred from the larger circular zones of inhibition. These inorganic materials kill bacteria by binding to intracellular proteins [25] and inactivating the bacterial replication and forming an

electrostatic interaction with cellular membrane and rupturing the lipid layer causing effusion of cytoplasm. Further, in addition they also generate a reactive oxygen species and lead to direct damage of cell walls [26].

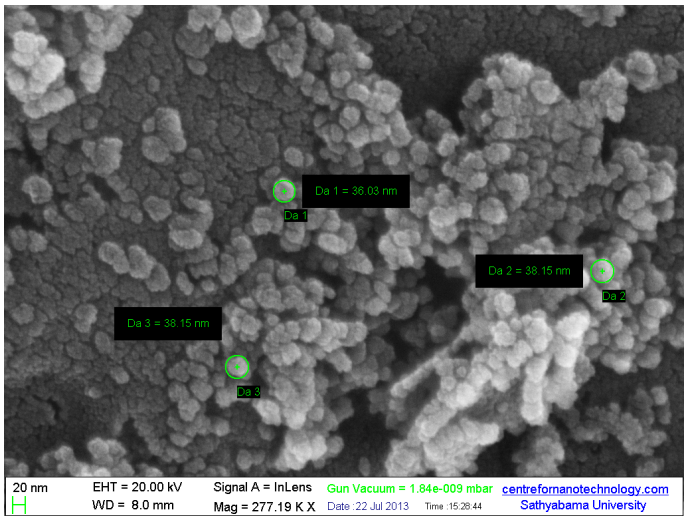

Fig.1. FESEM image of ZnO nanoparticles

Fig.2. Antibacterial activity of ZnO nanoparticles against *Pseudomonas aeruginosa*

Fig.3. Antibacterial activity of ZnO nanoparticles against *Staphylococcus aureus*

3.3 Photo degradation of Acid Blue 113

The progress in the absorption spectrum of the reaction solution was monitored by changing the various operational parameters such as initial dye concentration, catalyst loading and the pH. The changes in the absorption spectra of the dye, AB 113 during the photo degradation at various time intervals are shown in the figure 4 accordingly. The

effect of initial dye concentration was investigated by changing the from 25 µm-150 µm. The experimental results shows the fact that the photo degradation efficiency in inversely related to the dye concentration. This is due to the fact that as the dye concentration increases, the equilibrium adsorption of the dye on the catalyst surface active sites increases, therefore resulting in the lower formation rate of $OH^{\cdot}$ radicals which is the principle oxidant in this process [27]. The effect of added photocatalyst was carried out by varying the amounts of ZnO nanoparticles from 0.1g – 0.75g [Fig. 5]. The optimum catalyst loading in this process was found to be 2 g L^{-1}. The photo catalytic degradation of acid blue 113 was carried out in the pH range of 6 - 8.2. As shown in the (Fig. 6), the photo degradation efficiency was observed to reach a maximum at a pH of 6.9. The effect of pH on the photo catalytic degradation of the dye needs to be explained by multiple approaches. First, it is related to the acid-base property of the metal oxide surface and can be explained by taking into consideration the zero point charge (zpc) of ZnO which is reported as 8 [28].The adsorption of water molecules at surfacial metal sites is followed by the dissociation of OH^- charge groups, leading to coverage with chemically equivalent metal hydroxide groups (M –OH) [29]. The observed result indicating 98% degradation as shown in the figure 4 conform to the efficiency of the degradation process as expected. Similar results have been reported in literature for acid blue 113 [30], in the presence of H_2O_2/TiO_2.

Removal Efficiency: $X = (C_0 - C/C_0) \times 100$

where C_0 is the initial dye concentration and C is the concentration of dye at time t.

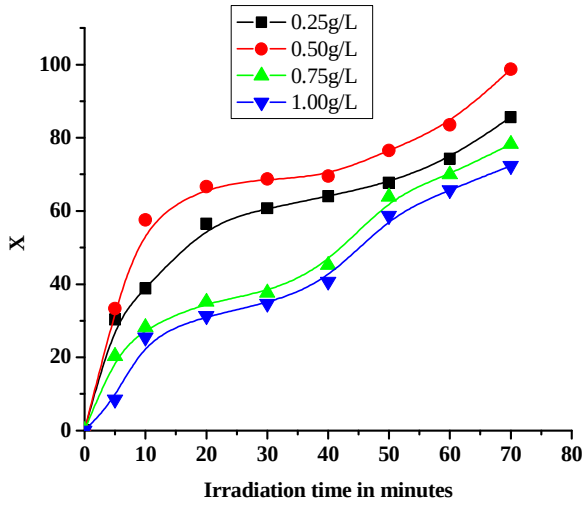

Fig. 4 Effect of initial concentration of the dye. Reaction conditions: pH=7.00, weight of catalyst=0.5g/250ml, Temp= 30°C, incident wavelength=254nm,Absorbance measured at 565.5nm

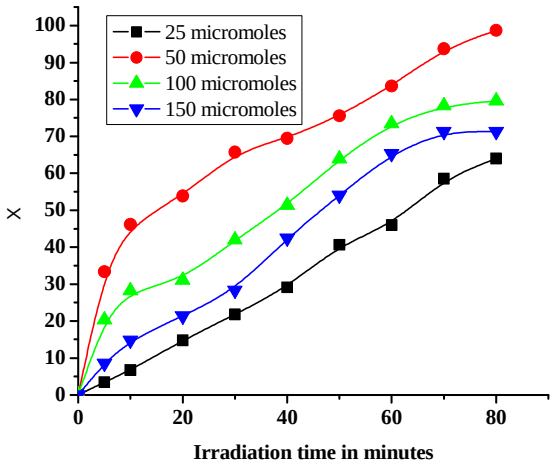

Fig. 5 Effect of catalyst loading. Reaction conditions: pH=7.00, concentration of acid blue 113=50µMol, Temp= 30°C, incident wavelength=254nm, Absorbance measured at 565.5nm

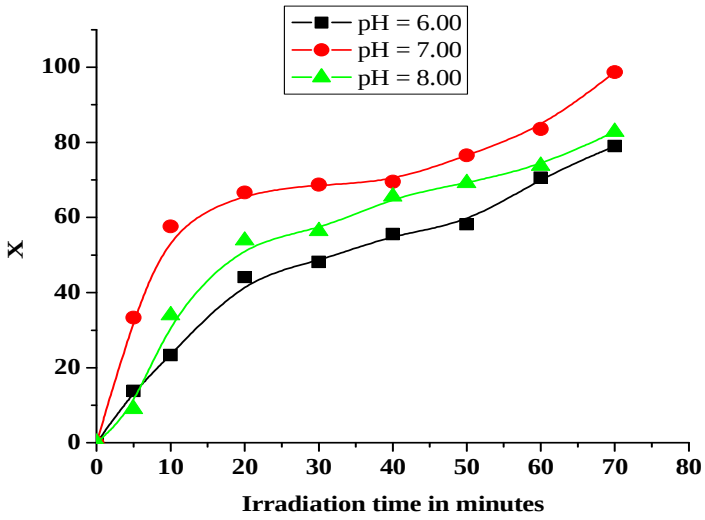

Fig. 6 Effect of pH. Reaction conditions: weight of catalyst=0.5g/250ml, concentration of acid blue 113=50µMol, Temp= 30°C, incident wavelength=254nm, Absorbance measured at 565.5nm

3.4 Kinetic Investigation

The photo catalytic degradation of the dye Acid Blue 113 was found to obey first order kinetics at low dye concentration. A plot of log C_O/C Vs irradiation time t, as shown in the figure 7 was found to be linear, confirming first order kinetics adherence. The first order rate constant k, was found to be 0.0101 min^{-1} from the plot shown in the figure 7.

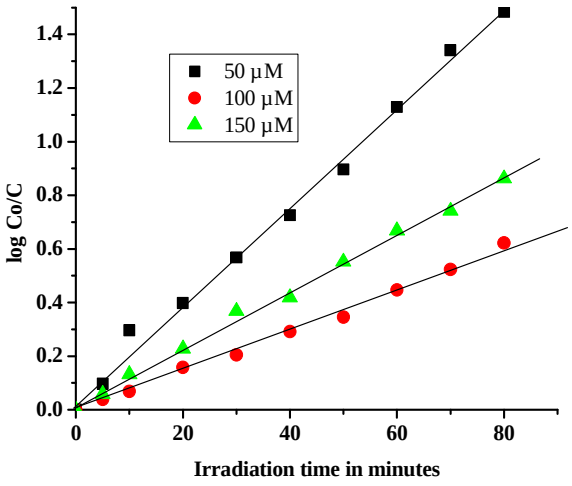

Fig. 7 Plot of logCo/C versus time for acid blue 113. Reaction conditions: weight of catalyst=0.5g/250ml, pH=7.00, Temp= 30°C, incident wavelength=254nm, Absorbance measured at 565.5nm

CONCLUSION

The ZnO nanoparticles were synthesized by sol-gel method and characterized by XRD, SEM, EDX, BET, FTIR analysis. The antibacterial activity of ZnO nano particles were tested using disc well diffusion method and possessed a positive antibacterial activity against Pseudomonas aeruginosa and Staphylococcus aureus. The photocatalytic degradation studies on the dye acid blue 113 have indicated that the dye underwent a complete degradation by 80 minutes in the presence of ZnO/UV. The optimum catalyst loading was found to be 2.0 g L^{-1}. The degradation of the dye was more pronounced in neutral medium.

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