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Photo-catalytic degradation of methyl violet dye using zinc oxide nano particles prepared by a novel precipitation method and its anti-bacterial activities

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ABSTRACT

Synthesis of different shaped nano-particles using novel methodologies always attracts great importance in research. This report details with the preparation of zinc oxide nano particles (ZnO NPs) using a very simple, efficient precipitation method. ZnO NPs were obtained by the calcination of zinc oxalate powder precipitated from a reaction mixture containing zinc acetate and ammonium oxalate. As obtained ZnO NPs were characterized using field emission scanning electron microscopy (FESEM), X-Ray Diffraction analysis (XRD), Fourier transform infrared spectroscopy (FTIR), photo-luminescence spectroscopy, etc. The photo-catalytic property of ZnO NP was studied using UV–vis spectroscopy for the degradation of methyl violet (MV) by exposing to sunlight. Complete degradation of methyl violet was noticed on exposing the suspension containing sonicated ZnO NPs in an aqueous medium with MV in 60–80 min. Antibacterial studies of ZnO NPs were performed against bacterial strains such as *Pseudomonas aeruginosa*, *Escherichia coli* and *Staphylococcus aureus*. ZnO NPs exhibit high inhibition towards *P. aeruginosa* and *E. coli*; however it shows minimum inhibition towards *S. aureus*. A difference of 0.461 a.u was observed in the mean of optical densities between *P. aeruginosa* and *S. aureus*. Statistical *t*-test was performed to find the significance of this difference and the results confirmed that this difference was due to the influence of the prepared ZnO NPs on the bacterial strains.

1. Introduction

Dyes and pigments were used as colouring materials in various industries like textile, cosmetics, printing, paints, etc. These dyes have to be properly treated before dumping it to the environment. Continuous exposure of improperly or partially treated or untreated dyes may create different kinds of problems to human being such as serious eye damage, damage to organs, toxic to aquatic life, skin cancer, cell lysis etc. Researchers were extensively tried to degrade these types of dyes using various methods which include bio-degradation, photo-degradation, electrochemical degradation, ion exchange, laser degradation etc. [1–3]. Obviously, photo-catalytic degradation method is technically viable and user friendly than other methods since the degradation occurs by the irradiation of sunlight which converts the harmful pollutants into harmless components. Methyl Violet (MV) has been efficiently used in textile, ink, ink jet printing, ball point pens, printing industries, etc., while on discharging the dye in an untreated manner results in harmful effects, since MV is one of the classes of carcinogenic dyes. Moreover, photo catalytic degradations of various types of synthetic pollutants have been well established by many researchers [4–7]. Efficiency of photo catalytic degradation mainly depends on the percentage of UV radiations found on the total solar spectrum. However, the solar spectrum consists only less than 3% UV radiation, which is not sufficient to degrade the dye effectively. Normally, a photo-catalyst based on semi-conducting nano particles were used to increase the photo-degradation rate of methyl violet.

ZnO is a well-known photo-catalyst for the degradation and complete mineralization of certain environmental pollutants. Rao et al. [4] studied the variation of photo-catalytic degradation rate of crystal violet by changing various parameters such as concentration of crystal violet, the pH of the solution, amount and nature of semiconductor used and incident light intensity. Hong et al. [5] prepared sheet like ZnO nanoparticles and reported their photo-catalytic behaviour with methyl orange as model dye. Habib et al. [6] reported the photo-catalytic property of nano-ZnO suspension with irradiation of visible light for the degradation of crystal violet dye. Ameen et al. [7] studied the photo catalytic property of Zinc oxide nano flower against crystal violet. It shows a rapid

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degradation of about 96% within a time interval of 80 min. Mohan et al. [8] enhanced the photocatalytic property of ZnO nanorods by doping it with Cu. Ameen et al. [9] also reported the photo catalytic degradation of crystal violet using zinc oxide/graphene oxide nano hybrid composites and showed that 95% of the crystal violet was degraded at an interval of 80 min. Pant et al. [10] prepared TiO_2 incorporated Zinc oxide flower and reported the blend as an effective photo catalyst material. Pudukudy and Yaakob [11] studied the photo catalytic degradation and reusability of hexagonal zinc oxide structures against industrial dyes. Dodd et al. [12] studied the effect of photo catalytic activity with respect to the size of zinc oxide nano particles. Mohan et al. [13] studied the photocatalytic activity of ZnO nano wires with respect to diameter, indicating size dependent property of ZnO. Becheri et al. [14] used zinc oxide nano particles as UV absorbers in textiles and studied their ultraviolet protection factor.

Apart from photo catalytic activity, zinc oxide nano-particles were widely studied by researchers in the field of microbial activity too [15]. Rajendran et al. [16] prepared ZnO incorporated fabric and their anti-bacterial activity was tested against *Escherichia coli* and *Staphylococcus aureus*. Xie et al. [17] examined the inhibition and inactivation mechanism of cell growth of *Campylobacter jejuni* by ZnO nano particles. Liu et al. [18] studied the mechanism of cell death of *E. coli* O157:H7 bacteria by the activity of ZnO nano particles. Premanathan et al. [19] reported about the selective toxicity of the prepared zinc oxide nanoparticles toward prokaryotic and eukaryotic cells and also studied the cytotoxicity of ZnO to mammalian cells using human myeloblastic leukemia cells (HL60) and normal peripheral blood mononuclear cells (PBMCs). They also evaluated the anti-microbial activity against *E. coli*, *P. aeruginosa* and *S. aureus*. Many literatures dealt only the study of ZnO nano particles either as an efficient photo catalyst or predominant anti-microbial agent. Some of the literatures dealt about the photo catalytic cum antibacterial activity of nano particles. This fact triggers us to study the complete analysis of as obtained ZnO NPs as a photo catalyst towards the degradation of MV dye in aqueous medium and anti-microbial effects against the bacterial strains such as *E. coli*, *P. aeruginosa* and *S. aureus*.

2. Experiments and methods

2.1. Preparation of ZnO NPs

ZnO NPs were prepared using a novel precipitation method. 0.01 M Zinc acetate (2.19 g) was dissolved in 50 mL of distilled water. 0.01 M of solid ammonium oxalate (1.42 g) powder was accurately weighed and added to the zinc acetate solution. The suspension was stirred till the dissolution of ammonium oxalate took place. Ammonia solution was added drop wise to raise the pH of the solution to 10. Slowly a white precipitate of zinc oxalate was formed. The obtained precipitate was separated by filtration and washed repeatedly with distilled water. The wet zinc oxalate particles obtained was dried in air for 24 h, and then dried in hot air oven at 110 °C for 90 min. The dry powder obtained was carefully collected in silica crucible and heated in a muffle furnace at 700 °C for about 3 h. During calcination, zinc oxalate had undergone decomposition as per the following equation and leads to the formation of ZnO NPs.

$$Zn(CH_3COO)_2 + (COONH_4)_2 \xrightarrow[(pH10)]{NH_4OH} ZnC_2O_2 + CH_3COOH + H_2O + N_2 \uparrow$$

Zinc acetate — ammonium oxalate — zinc oxalate

$$2ZnC_2O_4 + O_2 \xrightarrow{\Delta 700^\circ C} 2ZnO + 4CO_2 \uparrow$$

2.2. Photo-catalytic degradation studies

100 mg of ZnO NPs was accurately weighed and mixed with 100 mL of distilled water, followed by sonication using a probe type sonicator (SONICS, 750 W, US). 1.25 mg of methyl violet (3×10^{-6} M) was dissolved separately in 100 mL of distilled water. Both the contents were mixed together, immediately 3 mL of ZnO NPs dispersed MV solution was taken for measuring its absorption characteristics using UV–vis spectrometer (time = 0). The contents were then kept in sunlight for the degradation of MV. Once in 15 min, 2–3 mL of stirred suspension containing ZnO NPs were taken and the change in absorption behaviour of MV at an absorption band at 584 nm was measured. The process was continued till the absorption band at 584 nm was completely vanished.

2.3. Anti-bacterial test

The ZnO NPs have anti-bacterial activity since the commonly occurring bacteria can not withstand in the oxidative stress produced on the surface of the ZnO NPs. Ultimately, the use of this nanoparticle leads to the damage of the bacterial cell membrane and causes leakage of the cellular fluid through cell lysis. However, there will be a variation in the inhibition of bacteria due to the dissimilarity in various factors such as surface morphology, crystallite structure, defects, size and shape of the particles. Here, the obtained ZnO NPs were tested for the anti-bacterial activity against three bacterial stains, a gram negative *E. coli* and two gram positive—*P. aeruginosa* and *S. aureus*. To check the bacterial inhibition property of prepared ZnO NPs, minimum inhibition concentration (MIC), zone of inhibition, cell viability test etc. were evaluated.

2.3.1. Optical density

The serial dilution method was performed by employing different compositions of ZnO NPs with the growth medium in separate test tubes. These tubes were then inoculated with the bacterial strain for which the activity has to be checked. The test tubes were incubated overnight at 37 °C. The optical density of the nutrient medium containing the sample and the microbes was analysed using UV–vis spectrometry at a wavelength of 600 nm. The appearance of turbidity in the test tubes indicates bacterial growth while those tubes contain clear medium after inoculation indicates the absence of bacterial growth.

2.3.2. MBC/MIC

The minimum inhibitory concentration assay is a technique used to determine the lowest concentration of ZnO NPs needed to kill bacteria. The differently concentrated cultures in test tubes were spread onto a nutrient agar plate and were incubated at 37 °C for 8 h for colony counting which were counted using the colony counter. The concentration at which the number of colonies falls below 30 cfu/mL was considered as minimum bactericidal concentration (MBC) and the concentration at which the growth of bacteria was completely absent was taken as MIC.

2.3.3. Zone of inhibition (ZOI)

Fresh overnight cultures of all strains were inoculated in 5 mL nutrient broth and were incubated at 37 °C. Sterile swabs were taken and the cultures were swabbed on Muller Hinton agar plates. The wafer dipped with ZnO NPs placed was kept in each quartile of the plate. The plates were then incubated at 37 °C for 24 h and were observed for the zone of inhibition (the colour change around disc indicates the dead microbe).

2.3.4. Cell viability test

In order to assess the antibacterial activity of as obtained ZnO NPs, the number of live and dead cells has to be identified after