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Comparison of photo catalytic and antibacterial activities of zinc oxide and copper oxide nanoparticles synthesised by sol-gel method

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ABSTRACT

In the present work zinc oxide nanoparticles (ZnO) and copper oxide nanoparticles were successfully synthesized by sol-gel method where zinc acetate and cupric acetate were used as the precursor materials. Sodium hydroxide takes care for the homogeneity and pH value of the solution and helps to make a stoichiometric solution to get Zinc oxide nanoparticles and Copper oxide nanoparticles. The ZnO powder and CuO powder obtained from this method were calcined at 400ºC temperatures. The samples were characterized by X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). The XRD spectra indicate that the ZnO nanoparticle has a hexagonal wurtzite structure and CuO nanoparticles has a monoclinic structure. The photo catalytic activities of the metal oxide nanoparticles on the degradation of Methylene Blue were studied. The results show that ZnO nanoparticles were far more superior to CuO in degrading methylene blue. The antibacterial activities of the nanoparticles against both Gram positive and Gram negative bacterial strains shows that both ZnO and CuO can be used as effective antibacterials.

KEY WORDS: Nanoparticles, ZnO, CuO, catalytic, antibacterial.

1. INTRODUCTION

Effluents released from textile industries pose a serious threat to environment as these contain organic dyes. Environmental pollution by organic dyes cause severe ecological problem, since most of them is often toxic to microorganisms and have long degradation times in the environment (Pagga, 1984; Parsons, 2006). Advanced oxidation processes using nanoparticles are found to be more efficient and cost effective compared to the conventional methods which include adsorption, coagulation, biological treatment etc. for the treatment of these effluent (Daneshvar, 2007; Nazar Elamin, 2013; Nirmala, 2010, Qu, 1998; Torimoto, 1996; Das, 2013; Zhang, 2011). In this process electrons (in conduction band) and holes (in valence band) are generated using light energy. These holes and electrons interact with H_2O and O_2, respectively, to yield OH and OOH radicals (Behnajady, 2007; Akyol, 2008; Anandan, 2007). These hydroxyl radicals are highly reactive with very high oxidation potential and can oxidize the dyes completely. It is a fast, clean and destructive method of dye degradation in which no secondary waste is generated (Fernandez, 2010). The effectiveness of nanoparrticles as antibacterials have been well established (Horiguchi, 1980; Dusan Zvekic, 2010; Li, 2002). A variety of methods have been developed for the synthesis of metal nanoparticles which include hydrothermal (Zhou, 2007), chemical precipitation method (Wang H, 2007; Wang, 2007), hydrolysis in polyol medium (Poul, 2001), thermal oxidation process (Zhang, 2007) template method (Kou, 2006) and microwave synthesis (Siddiquey, 2008). It is found that the method used for the synthesis affect the size, morphology, crystalline form and photocatalytic activity of the nanostructures (Zhang, 2007).

Here in this paper, we report the synthesis and characterization of ZnO and CuO nanoparticles and their photocatalytic ability for the degradation of Methylene Blue. We also report the antibacterial abilities of these nanoparticles and their activites are compared.

2. MATERIALS AND METHOD

All the chemicals used for the synthesis of metal nanoparticles were of analytical grade. Zinc acetate dehydrate (99%purity), cupric acetate (99% purity) and sodium hydroxide (pellet 99%) were used as the introductory material. The pH measurements of the colloidal solution were carried out using CYBER pH-14L pH metre.

2.1. Synthesis of ZnO and CuO nanoparticles: In a typical procedure, 2.7441 g of zinc acetate dehydrate was dissolved in 250 ml distilled water under vigorous stirring at room temperature. To 50 ml of this solution, aqueous 1.0M NaOH solution was added drop by drop to reach pH about12. It was then placed on a magnetic stirrer for 2 hours. The white precipitate formed after completion of the reaction, was washed thoroughly with distilled water followed by ethanol to remove the impurities. The precipitate was dried in a hot air oven for overnight at 60ºC and further calcined at 400^0C for 4 hours. Complete conversion of Zinc oxide in to ZnO nanoparticles took place during this period.

CuO nanoparticles were also prepared using the same procedure by taking 1.9965g of cupric acetate dehydrate.

2.2. Characterisation of the nanoparticles: The resulting products were analyzed by using X-ray diffraction (XRD) using Cu k α radiation (λ = 1.5404 Å) and the overall morphology of the obtained ZnO and CuO powders were observed by Scanning Electron Microscope (SEM).

2.3. Comparison of photocatalytic activities: The photocatalytic activity of the two samples was followed by measuring the degradation of Methylene Blue (MB). A 5mg/L aqueous solution of methylene blue was prepared by dissolving 0.0012g of commercially purchased methylene blue in distilled water and made up to 250 ml in a standard flask. Catalytic reactions were carried out at room temperature in a sealed glass beaker containing 20 ml of aqueous solution of methylene blue as follows. 0.02g of the prepared catalysts (ZnO) was added to the dye solution, the mixture was allowed to react, a definite amount of solution was withdrawn, filtered and absorbance measurements were taken at every half an hour interval. The absorption at 664 nm was measured, and degradation of MB was calculated by noting the decrease in absorption at 664nm.

MB degradation (%) = $(A_0\text{-}A)/A_0 \times 100$, where, A_0 is the initial absorption of MB and A is the absorption of Methylene Blue at sampling time during the processing.

The same procedure was repeated with CuO nanoparticles.

2.4. Comparison of antibacterial activities: Antibacterial activities of the synthesised colloidal dispersions of nano particles of ZnO and CuO samples were carried out against Gram-positive (*Staphylococcus aureus)* and Gram-negative (*Escherichia coli)* bacterial strains using disc diffusion method. Finally their activities were compared. Nutrient agar was used as the medium for the preparation of pure cultures of bacteria for detecting antibacterial activity. Test organisms were collected from Institute of microbial Technology, microbial Type culture collection centre, (IMTECH), Chandigarh.(ATCC 25922,MTCC 96/ATCC 9144).

The bacterial strains were maintained on their respective medium in slants at 2-8°c. Muller Hinton Agar (MHA) medium was used for bacterial culture. MHA was prepared and sterilized at 121°c for 15 minutes. After sterilization required volume of the medium (20ml) was poured in the sterile petridishes and allowed to solidify. Sensitivity of the 0.1m ZnO and 0.1m CuO nano particles were tested for both Gram-positive (*Staphylococcus aureus*) and Gram-negative (*Escherichia coli*) bacterial strains that are resistant to a broad band of antibiotics excluding ampicillin. Dimethyl sulfoxide (DMS) was used as the negative control to compare the antibacterial activity in all experiments.

3. RESULTS AND DISCUSSION

ZnO nanoparticles synthesised as discussed above was obtained as white powder and CuO as black powder. The XRD pattern obtained for ZnO nanoparticles calcined at 400^0C shows that ZnO (Fig 1) has hexagonal structure and CuO (Fig 2) has monoclinic structure. The intensities and positions of peaks are in good agreement with the reported values (JCPDS file No. 79-0208 for ZnO and JCPDS file No. 05-661 for CuO). The single phase sample formation was revealed from the absence of any impurity peaks. The crystallite size was calculated using the Scherrer formula, $D = 0.9\ \lambda/\ \beta \cos\theta$, where λ is the wavelength of X-ray radiation, β is the full width at half maximum (FWHM) of the peaks at the diffracting angle θ. Crystallite size calculated by the Scherrer formula was found to be 27.6 nm for ZnO nanoparticles and 19.7nm for CuO nanoparticles.

The SEM images of the ZnO nanoparticles calcined at 400^0C reveals rough surface morphology which consists of small aggregates of particles with sharp edges (Fig 3). The SEM data of CuO nanoparticles shows porous particle networks with almost spherical morphology (Figure 4). The morphologies of both the particles are suitable for improved catalytic activity.

Studies on the photocatalytic activity of the prepared ZnO and CuO samples on the degradation of Methylene Blue were carried out as discussed. The results shows that ZnO nanoparticles significantly affected the absorption spectra of Methylene Blue in an aqueous suspension solution with reduced Methylene Blue light absorbance and changed maximal absorption peak in a short time. It was found from the results that CuO has no catalytic activity for the photochemical degradation of methylene blue. This indicates that ZnO can photocatalytically degrade organic matter effectively. Figure 5 shows the graph % degradation plotted against time.

Figure 6 and 7, shows the zones of inhibitions. Table 1 presents the antibacterial effect of ZnO and CuO nanoparticles against *Staphylococcus aureus* and *Escherichia Coli*. The results show that ZnO nanopaticles show good antibacterial activity against gram negative *E.coli* and CuO shows good activity for the grampositive *S.aureus*.

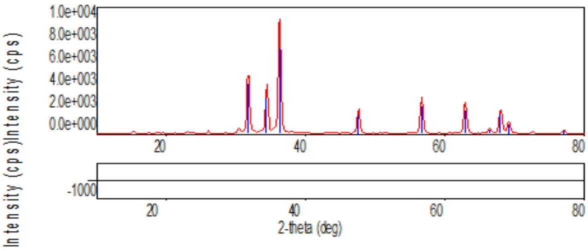

Figure1: Wide angle XRD patterns of ZnO nanoparticles calcined at 400^{0}C

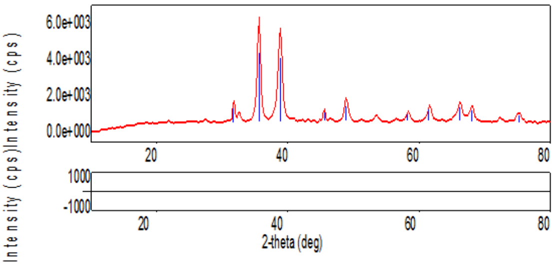

Figure 2: Wide angle XRD patterns of CuO nanoparticles

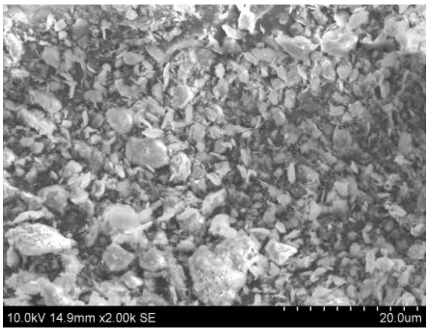

Figure 3: SEM image of ZnO nanoparticles

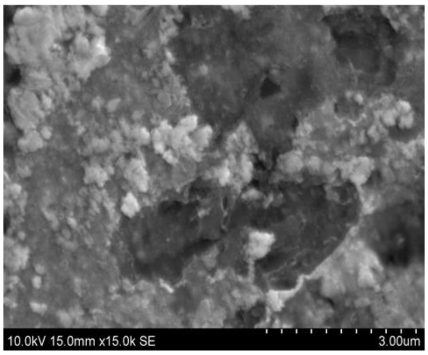

Figure 4: SEM image of CuO nanoparticles

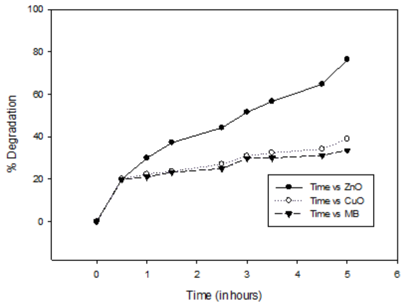

Fig 5. Comparison of the photocatalytic activities of the ZnO and Cuo nanoparticles

Table 1: Antibacterial effects of ZnO and CuO nanoparticles.

Sample	Organism	Zone of inhibition (mm) Diameter)
ZnO	*S. aureus*	0
	E.coli	9
CuO	*S. aureus*	7
	E.coli	0
Control	*S. aureus*	0
	E.coli	0

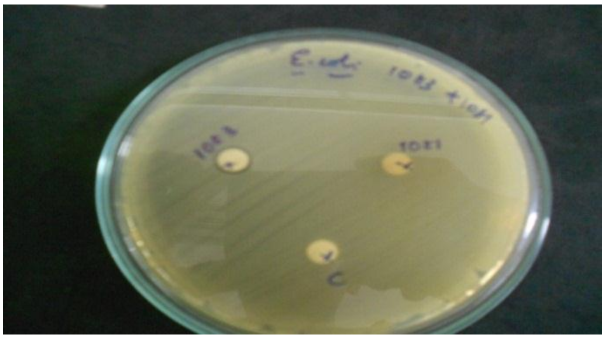

Fig 6 and 7 : Zones of inhibition

4. CONCLUSION

From the studies it is concluded that the nanostructured ZnO particles exhibits excellent photocatalytic activity and can be considered as a promising photocatalyst for treatment of dye effluents. Also Antibacterial activity experiments performed on the two microorganisms clearly demonstrated the higher effectiveness of ZnO nanoparticles for Gram negative bacteria and CuO nanoparticles for Gram positive bacteria. Due to the intense antibacterial, nontoxic nature and other noble properties the ZnO and CuO nanoparticles, these can be used in food nanotechnology as a food preservation material.

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