

Application of Synthesized (Ni^{2+} , Ag^{2+}) doped ZnO Nanocatalyst for degradation of Acid Blue 113 by Advanced Oxidation Process

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ABSTRACT

The (Ni^{2+} , Ag^{2+}) co-doped zinc oxide (ZnO) nanocatalyst was synthesized by chemical co-precipitation method. The nanocatalyst was characterised by FT-IR, SEM, EDAX, UV-DRS and XRD. Crystal Structure and the sizes of ZnO nanoparticles were characterized by X-ray diffractometer. SEM and TEM were used to determine the surface morphology. The size of the nanoparticle is found to be 50-200nm. Energy dispersive analysis of x-rays spectroscopy (EDAX) spectrum indicated that the dopants of Ag, Ni peaks in the ZnO lattice and indicates the purity of the samples. These co-doped nanoparticles were used to determine the Photocatalytic activity of acid blue 113 dye solution in the presence of sunlight. The energy gap of the material was determined using Diffuse Reflectance Spectroscopy. The degradation of dye solution is monitored by measuring its concentration and chemical oxygen demand analyses. The Photocatalytic activity is influenced by three important parameters such as pH, Initial dye concentration and catalyst loading. The complete degradation was noticed at 120 mins of irradiation. The effect of these parameters on photocatalytic degradation were studied and optimized. Using these optimized conditions, the maximum Chemical oxygen demand (COD) of 94.5mg/l was obtained. The co-doped (Ni^{2+} , Ag^{2+}) ZnO nanoparticles show twice as potent in degrading acid blue 113 in the presence of sunlight compared to un-doped ZnO. This study has proved that co-doped ZnO nanoparticles could treat textile effluent constituting of azo dyes.

KEY WORDS: Co-doped ZnO nanoparticles, EDAX, UV-DRS, photocatalysis, COD.

1. INTRODUCTION

In recent years, the application of Zinc oxide in different fields has increased rapidly. Zinc oxide (ZnO) is a II-VI group semiconductor and has direct band gap energy of 3.37 eV and large exciton binding energy of 60 meV at room temperature. ZnO nanoparticles have been used as photocatalyst in many fields, such as environmental applications, namely air cleaning, water purification and water treatment. Most of the textile dyes are non-biodegradable and their release into the environment poses a major threat to the surrounding eco systems. Advanced oxidation processes (AOPs) have been proposed in recent years as an alternative for treatment of wastewater containing non-biodegradable organic pollutants. Among AOPs, ZnO mediated semiconductor photocatalysis is gaining more importance due to its high production of hydroxyl radicals. It is also inexpensive, nontoxic, abundantly available and stable. Hence the recent research is focused on the development of modified semiconductor photocatalysts to increase the efficiency of the advanced oxidation process. The photocatalytic activity of ZnO nanoparticles under ultraviolet light particularly is prominent, but it has been recently found that this oxide, when doped with transition metal ions, is also a photocatalyst under visible light. Transition metal ions doped nanostructure is an effective method to adjust the energy level surface states of ZnO, which can further improve by the changes in doping concentrations of doped materials and hence in its physical and especially optical properties. It is experimentally found that Ag particles in Ag doped ZnO increase the efficiency of ZnO by acting as electron traps. From our earlier studies it is noticed that silver (Ag) acts as an excellent neutralizer of native defect states in ZnO and enhances the photocatalytic activity. In this direction, trails have been made to minimize the native defect states by doping with Ag and then doping Ni as a co-dopant into ZnO. The surface area and surface defects play an eminent role in photo catalytic activities of metal oxides. The doping with a nickel metal ion increases the surface defects. This can presumably shift the absorption towards visible region. Thus enhancement in optical absorption and increases the photo catalytic activity.

Various types of nano structured materials are synthesized by using different physical methods such as simple vapour transport and condensation process, sol-gel method, solid state reaction method, chemical vapour decomposition, facile low temperature synthesis, chemical co-precipitation method, etc. Among these methods, chemical co-precipitation method is the best one, because it is simple, inexpensive and high yield rate.

In the present study, the (Ni^{2+} , Ag^{2+}) co-doped ZnO nanoparticles were synthesized by co-precipitation method and their composition and structural properties were investigated. The photocatalytic activity of the undoped and synthesized photocatalyst was determined using acid blue 113 as a pollutant. The effect of pH, initial dye concentration and catalyst loading on the degradation efficiency was optimized and the chemical oxygen demand was determined.

2. MATERIALS AND METHODS

2.1. Materials: Zinc acetate dihydrate, potassium hydroxide, nickel chloride hexa hydrate and silver nitrate. All the chemicals used were of analytical reagent grade obtained from Merck (Mumbai, India). Nano Zinc oxide powder was procured from SRL and deionized water is used for the preparation of solutions.

2.2. Synthesis of nano-structured materials: Ni²⁺, Ag²⁺ doped ZnO nanopowder were synthesized at room temperature by following the procedure as described by previous researchers. Zinc acetate and potassium hydroxide were used as precursors. They were mixed in 1:1 ratio in a stirrer. Then add 5 mole % of Nickel Chloride and 5 mole % of silver nitrate under a constant stirring of 8 hrs. After filtering, the precipitate is washed repeatedly with double distilled water to remove un-reacted chemical species. Finally, the product is dried at 70 °C for 2 hr, and then grounded and annealed in the furnace at 500°C for 1 hr.

2.3. Characterization: The structural properties including structure and crystallite-size of the samples were determined by Seifert 3003 TT X-ray diffractometer (XRD) using CuK α radiation by applying voltage and current of 40 kV and 30 mA, respectively. Concentration of dopants in ZnO was estimated by energy dispersive X-ray and spectroscopy (EDS) attached with scanning electron microscope (SEM) (Model: Hitachi, S-3000H). FT-IR were also taken for the samples using Tensor 27. The optical absorption properties were recorded using UV-Vis diffuse reflectance spectroscopy (Shimadzu UV 3600).

2.4. Photodegradation Experimental Procedure: The photocatalytic experiment of Acid Blue 113 dye (5, 15, 25 and 50 ppm) and the catalyst (un-doped ZnO and co-doped ZnO) was taken up in two beakers. The solutions were placed in the dark for 1 hr until adsorption equilibrium is reached. Once attained the solutions were exposed to the solar light between 12.30 pm to 2.30 pm. Aliquot samples were taken every 30min for 2hr, filtered and absorbance was recorded at λ_{max} 561 nm using UV-Vis Spectrophotometer (Shimadzu – 180A). Further the photodegradation of the dye was monitored by measuring its COD using open reflux method. The percentage of degradation (X) was calculated using Eq. 1:

$$X = \frac{(C_0 - C_e)}{C_0} \times 100 \quad \text{Equation.1}$$

3. RESULTS AND DISCUSSION

3.1. Structural Analysis: Typical XRD patterns of undoped ZnO and (Ni²⁺,Ag²⁺) co-doped ZnO nanostructures annealed at 500°C for 1 hr are shown in fig 1. The X-ray diffraction patterns of the all samples are found to be matching with the standard hexagonal wurtzite structure of ZnO corresponding to the data card no: JCPDS 01-079-2205. Also the XRD patter were found to matching with the standard Nickel Oxide and Silver Oxide corresponding to the datacard No: 03-065-2901 and 01-089-3081 respectively. It reveals that the co-substitution of Ni²⁺ and Ag²⁺ does not disturb the wurtzite crystal structure of parent ZnO.

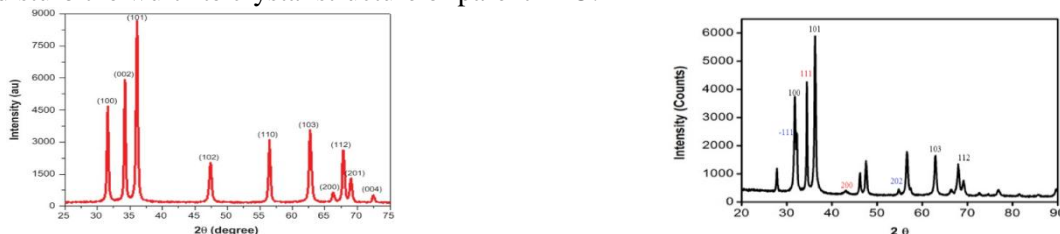


Fig.1.XRD pattern of (a) undoped ZnO and (b) Zn_{0.90}Ni_{0.05}Ag_{0.05}O nanostructures

However, a careful analysis of the peak (101) positions suggests a small shift toward lower 2θ values with Ni²⁺ doping as shown in **Fig. 1b**. The significant change in position of peaks is attributed to the different ionic radii of Zinc, Iron and silver (Zn²⁺ ~ 0.74 Å, Ni²⁺ ~ 0.70 Å and Ag²⁺ ~ 0.115 Å). The shifting of the XRD peaks with the co-doped ZnO suggests the substitution of Zn²⁺ by Ni²⁺ in the ZnO host lattice. The size of the particle is large in the nano scales, which could be the reason for narrow XRD peaks. By using Debye-Scheerer formula, the evaluated average particle crystalline size of pristine ZnO and Zn_{0.90}Ni_{0.05}Ag_{0.05}O nano powders are 3.7nm and 5.1 nm respectively.

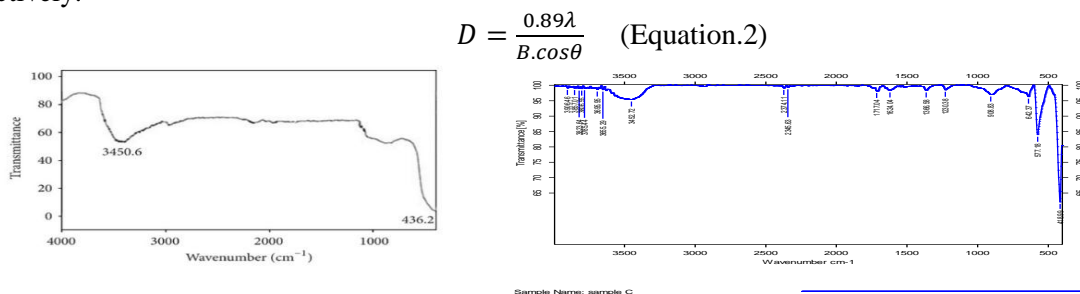


Fig.2. FTIR result of (a) Pure ZnO and (b) Zn_{0.90}Ni_{0.05}Ag_{0.05}O nanostructures

Pristine ZnO and co-doped (Ni^{2+} , Ag^{2+}) ZnO are further supported by FT-IR spectra as shown in figure 2. Un-doped ZnO and Co-doped ZnO have the similar spectra. The band at 2315 cm^{-1} attributed to C-H stretching vibrations; the band at 1366 cm^{-1} indicates ZnO peak and the band observed at 908 cm^{-1} is attributed to C-H bend. No peaks shifting in FT-IR spectra are observed, which are in good agreement with the results from the XRD.

3.2. Morphological and compositional analysis: The morphology of the samples was investigated by Scanning electron microscope (SEM) as shown in the figure 3. Un-doped ZnO nanoparticles appear rice-like in shape and co-doped (Ni^{2+} , Ag^{2+}) ZnO nanoparticles also appear like agglomerated clusters. All these nanoparticles present in the size range of 100-200 nm. Figure-4 (a) and (b) depicts the energy dispersive spectra (EDAX) of un-doped ZnO and co-doped (Ni^{2+} , Ag^{2+}) ZnO crystallites. EDAX spectra of un-doped ZnO having only two elements, Zn and O indicate the purity of the ZnO sample and that an additional Ni^{2+} , Ag^{2+} elements exist in ZnO: Ni: Ag crystals.



Figure.3. SEM result of (a) Pristine ZnO and (b) $\text{Zn}_{0.90}\text{Ni}_{0.05}\text{Ag}_{0.05}\text{O}$ nanostructures



Fig.4. EDAX result of (a) Pristine ZnO and (b) $\text{Zn}_{0.90}\text{Ni}_{0.05}\text{Ag}_{0.05}\text{O}$ nanostructures

Table.1 gives the ratio of Zn: Ni: Ag: O elemental composition. The atomic percentages of the elements are obtained from the spectra and the doping of nickel and silver ions are confirmed. From quantitative analysis, the dopants and atomic concentration in ZnO (atom %), could be found and the Ni^{2+} and Ag^{2+} contents in the ZnO samples based on the doping levels of 5 mol%.

Table.1. Compositional analysis of ZnO and ZnO: Ni: Ag nanostructures

Dopant Concentration (%)	Experimental Results (%)			
	Zn	Ni^{2+}	Ag^{2+}	O
0	49.63	-	-	50.37
5	27.80	2.13	2.98	67.09

3.3. Optical Studies: UV-Visible Diffuse reflectance spectroscopy was used to determine the energy band gap of the synthesized nanoparticles. It was measured at room temperature in the wavelength 200 – 800nm. The band edge absorption of un-doped ZnO was found to be at 3.20eV. The band gap energy of the photocatalyst was found by:

$$E = \frac{1240}{\lambda} \text{ eV}$$

Where λ is the wavelength in nanometres. From the equation the energy of the synthesised co-doped ZnO was found to be 2.95 eV.

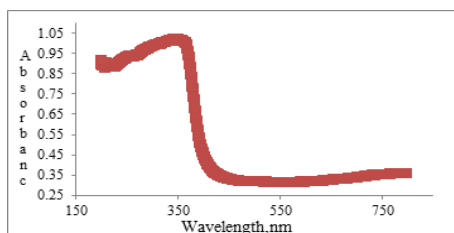


Fig.5. UV-DRS Spectra for co-doped ZnO calcined at 500°C

3.4. Photo-degradation Studies

3.4.1. Effect of pH: The effect of pH on the degradation of Acid Blue 113 was studied in the pH range from 6 to 10 with 50 ppm dye concentration and 2 g/L catalyst loading. The pH of the aqueous phase was adjusted using 0.1 N HCl and NaOH. For (Ni^{2+} , Ag^{2+}) Co-doped photocatalyst, the photocatalytic degradation efficiency increases from a pH 6 to 8 and then decreases for further increase in pH. The maximum degradation efficiency was found to be at pH

8. Thus for further photocatalytic degradation experiments pH 8 was kept constant. For un-doped ZnO, the photocatalytic degradation efficiency increases from pH 6 to 7 and then decreases from pH 7 to 10. The degradation efficiency was found to be optimum at a pH of 7.

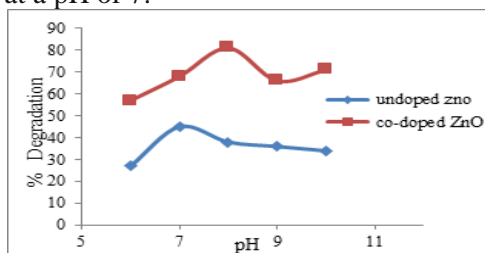


Fig.6a.Effect of pH on photocatalytic activity

3.4.2. Effect of Initial Dye Concentration: The degradation of Acid Blue 113 at different concentrations (5,15,25 and 50 ppm) for a catalyst loading of 0.2g and 0.3g of co-doped ZnO and un-doped ZnO respectively was investigated and shown in fig. 3c. The degradation efficiency was to be inversely proportional to the increase in concentration. The optimum degradation was found to at 5 ppm for co-doped ZnO particles. Also the graph in figure 3c shows that even at 50 ppm the degradation efficiency was 71% which means that co-doped ZnO worked well at high concentration. In the case of un-doped ZnO, the maximum efficiency was only 49 % at a dye concentration of 5 ppm under solar irradiation.

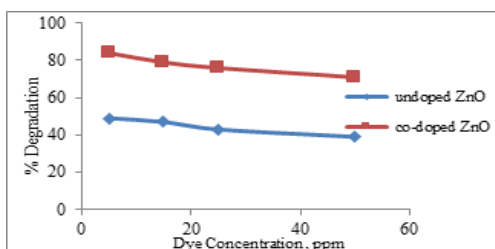


Fig.6b.Effect of dye concentration on photocatalytic activity

3.4.3. Effect of Catalyst loading: Experiments were carried out with different quantities un-doped and co-doped nano-crystalline ZnO for 50 ppm dye concentration in solar radiation to assess the efficiency of degradation as a function of the amount of catalyst. The degradation efficiency increases until 0.2g/50ml of co-doped photocatalyst. The degradation efficiency decreases on further increasing the quantity of co-doped ZnO. In the presence of un-doped ZnO the optimum degradation efficiency was found to be at 0.3 g/50ml.

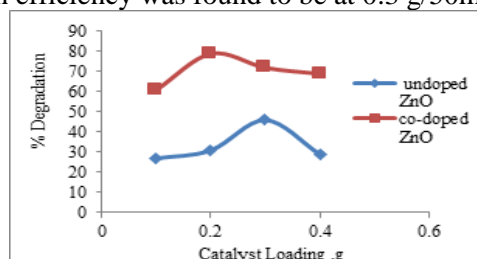


Fig.6c.Effect of catalyst loading on photocatalytic activity

3.5. Chemical Oxygen Demand: The effective technique used to measure the quantity of organic content present in waste water is Chemical oxygen demand (COD). This test measures the total quantity of oxygen required for the complete oxidation of organic matter to carbon dioxide and water. Thus the COD of the treated aqueous Acid blue 113 solutions in the presence of un-doped and co-doped ZnO solutions were measured at their optimum degradation efficiencies. The optimum degradation efficiency was obtained at pH 8, dye concentration of 5 ppm and a catalyst loading of 0.2g in the presence of co-doped ZnO. The chemical oxygen demand obtained was 94 mg/l after solar irradiation of 120 mins, The maximum efficiency, in the presence of un-doped ZnO, was obtained at pH 7, dye concentration 5 ppm and a catalyst loading of 0.3g. The COD obtained was 183 mg/l.

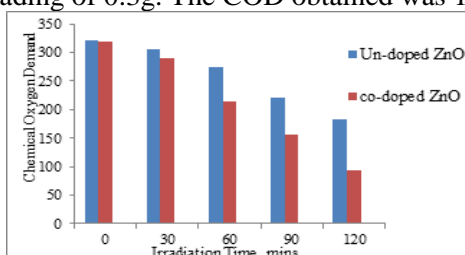


Fig.7.Reduction in COD during solar photocatalytic degradation of Acid Blue 113

4. CONCLUSION

In the present study, synthesized Co-doped ZnO was found to be a better photocatalyst compared to un-doped ZnO. Nickel ions and Silver ions were successfully doped on ZnO nanoparticles. This was confirmed by certain characterization techniques such as FTIR, XRD and SEM-EDAX. Acid blue 113 solutions of lower concentrations was completely mineralized by co-doped ZnO under solar radiation compared to un-doped ZnO particles. The co-doped (Ni^{2+} , Ag^{2+}) ZnO nanoparticles show twice as potent in degrading acid blue 113 in the presence of sunlight compared to un-doped ZnO. The co-doped ZnO particles were more efficient because the synthesized photocatalyst was a rich source of oxygen which results in the production of hydroxyl radicals. Thus the degradation efficiency was twice to that of un-doped ZnO particles. Hence the study proved that the Co-doped ZnO particles could treat textile effluent.

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