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Antibacterial Activity of Cobalt Doped Zinc Oxide/ Carbon Nano Composite and Kinetics for the Photocatalytic Degradation of Acid Yellow 110

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The cobalt doped Zinc oxide/Carbon photocatalyst was prepared by solution combustion method. The prepared photocatalyst was tested for its antibacterial activity against the clinical pathogens *Escherichia coli, Klebsiella pneumaniae, Pseudomonas aeruginosa and Staphylococcus aureus*. Antibacterial activity was performed by using well diffusion method. No activity was observed *against Escherichia coli and Klebsiella pneumoniae* at all the concentrations but positive activity was observed against *Pseudomonas aeruginosa and Staphylococcus aureus*. The surface area of this nanocomposite was calculated by Brunaeur-Emmet-Teller method. The average crystallite size was evaluated using X-ray diffractometer. Elemental analysis was performed by energy dispersive X-ray spectroscopy analysis. Fourier transformation infrared spectroscopy and ultraviolet – diffuse reflectance spectroscopy were also performed. This catalyst was also tested for its photocatalytic activity, by its decolorizing effect of an azo dye namely acid yellow 110 under UV light and the influence of various parameters on degradation of the dye was investigated.

Key words: Combustion; Photocatalyst; Zinc oxide; Carbon; Cobalt; Antibacterial activity.

Advanced oxidation process (AOPs) has been initiated to meet the growing needs of an effective wastewater treatment in recent years. This process exploits the strong reactivity of hydroxyl radicals for the extensive mineralization of environmental contaminants by the oxidation process[1, 2]. Most of the studies have focused on large band gap semiconductor oxides such as TiO_2 and ZnO which provides electron-hole pairs by photoexcitation using UV light to enable initial production of hydroxyl radicals in water[3-5]. Nowadays nano materials are of great interest from research point of view because the properties of these materials change drastically when the particle size reaches to nanometer range.

Further, the use of nanoparticles exhibit higher photocatalytic activity than their counterparts, as a consequence of their increasing surface area and porosity[6-8]. Due to the superior optical, electrical, magnetic and chemical properties of highly effective semiconductor oxides with noble or transition or rare earth metal nanocomposites, their design and development are interesting. Since carbon nanostructures are attractive because of their unique and novel properties, doping ZnO with carbon or preparing a ZnO/Carbon nanocomposite can decrease the band gap and increase photocatalytic activity[9-12]. Because of these properties these nanocomposites were used in different application areas like nanoelectronic devices, catalysis, non linear optical devices, bio-medical, etc[13-15].

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Nanoparticles play a wide range of applications in biology, food industries and pharmaceuticals like anti-inflammatory, anti-hypersensitive and anti-microbial functions. Inorganic materials, in particular, metal oxides have strong antibacterial activity at low concentrations[16]. The main advantages of inorganic antibacterial agents are their good stability at high temperatures and pressure, and long shelf-life when compared to organic antibacterial agents. It has also be seen to be useful antibacterial and antifungal agents when used as a coating on materials and textiles[17-19].Transition metal doped ZnO shows maximum effect against pathogenic organisms as compared to pure nano ZnO. In earlier studies, impurity doping in semiconductor nanoparticles was investigated mainly to enhance the photocatalytic activity in the UV light region[20]. A number of investigations have focussed on transition metal doped ZnO semi conductor because of its band gap of 3.37ev, and its large excitation binding energy(60 mev)[21,22].

Nanocomposites prepared by using different semiconducting metal oxides and carbon materials are currently the active photocatalytic materials for the degradation of dyes and industrial effluents. Hence, in this present investigation an attempt was made to synthesize cobalt doped nano zinc oxide/carbon (ZnO/C/Co) composite by solution combustion method. Cobalt (Co) was chosen for its expected ease in doping due to the similar ionic radius (0.058 nm) to that of Zn (0.06 nm). Moreover cobalt seems to improve photodegradation slightly or selectively for some organic compounds[23]. The synthesized zinc oxide/carbon/cobalt (ZnO/C/Co) nano composite was characterised by various analytical techniques like BET, XRD, FESEM, EDAX and FTIR. Its photocatalytic activity is carried out in batch reactor for the degradation of the dye acid yellow 110 (AY 110). The influence of various operational parameters such as catalyst loading, initial dye concentration and effect of pH was also studied. The effect of light intensity on the photo conversion was determined by electrical energy measurements. Antibacterial activity was ascertained by performing well diffusion method in Muller Hinton Agar plates against the clinical isolates.

MATERIALS AND METHODS

$Zn(NO_3)_2.6H_2O$, $Co(NO_3)_2.6H_2O$ and dextrose were of analytical grade and were used as received. The dye, AY 110 commercially known as acid yellow 5GN was obtained from local dye suppliers and used without further purification. The absorption maximum for the dye was found at 420 nm. The solutions of desired concentrations were prepared using deionized water. The pH of the solutions was adjusted between 5.0 and 9.0 using dilute solutions of HCl or NaOH as the case may be. The structure of acid yellow 110 is given in figure 1.

Synthesis of ZnO/C/Co nano composites

ZnO/C/Co nano composite was synthesized by self propagating solution combustion method[24]. In this preparation 8g of zinc nitrate and 2g of cobalt nitrate were dissolved in deionised water. 3.6g of dextrose was dissolved in deionised water in a separate beaker and heated on a hot plate for five minutes. The mixture of zinc and cobalt nitrate solution was added drop wise to the hot solution of dextrose with constant stirring. The beaker was heated on a preheated muffle furnace kept at 400^0C for about five minutes.

Characterisation techniques

The x-ray powder diffraction patterns (XRD) were obtained using Rigaku X-ray diffractometer, Japan. The crystalline phase of ZnO was identified by comparing with JCPDS card no. 36-1451. The BET surface area measurements were carried out using Micromeritics, ASAP 2020 V3.01 G. Field emission scanning electron spectroscopy (FESEM), Energy dispersive x-ray diffraction (EDAX) photographs of ZnO/C/Co were obtained by using a high resolution scanning electron microscope (Carlzeiss, Supra 55, Germany). UV studies were carried out using SL -210 UV-visible double beam spectrophotometer. Fourier transform infrared (FT-IR) spectra were recorded on a Perkin Elmer Spectrum 1 FT-IR instrument consisting of globar and mercury vapour lamp as sources.

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/C/Co nanocomposites 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.

RESULTS AND DISCUSSION

Characterisation of the catalyst

The crystal structure of the sample was investigated using XRD which matches with the standard JCPDS No. 36-1451.The average crystallite size of ZnO/C/Co nanocomposite was found to be 10.53 nm respectively and shown in figure 2.

The specific surface area is an important micro structural parameter of ZnO/C/Co nano composite which depends on the geometrical shape and porosity of the particles and it was found to be 34.3572 m^2/g (Fig.3) and the data was given in Table 1.

The particle size and surface morphology of ZnO/C/Co nanocomposites analysed by FESEM is shown in figure 4. The FESEM image reveals that the entire product is comprised of spherical nano particles with the average size of 22 nm.

The EDAX studies of ZnO/C/Co nanocomposite confirm the presence of zinc, cobalt and oxygen as the primary components which are shown by figure 5 and its mapping is shown in figure 5a.

The FTIR spectroscopy presented in figure 6, was performed to study the absorbance properties of ZnO/C/Co nanocomposite and therefore to deduce the nature of bonds present in the nanocomposite. In the given figure on wave number axis, the absorbance peaks from wave number 3400 to 3900cm^{-1} and another one around 1600cm^{-1} were the peaks assigned to O-H stretching and O-H bending vibrations respectively. The peak at approximately 466 $cm^{-1}$is due to the typical bond between zinc and oxygen (Zn-O). For all doped and undoped ZnO samples the absorption peaks in the range of 400 - 700 cm^{-1} could be attributed to the ZnO stretching modes. The main peaks were observed in the range of 1100 - 1600 cm^{-1} corresponding to the Zn-OH bending mode, and this band could be normally reduced by calcinations process at higher temperature and to C-OH plane bending and C-OH out-of-plane bending. The peaks from 700 to 900 $cm^{-1}$are attributed to the bond between cobalt and oxygen (Co-O).

Photodegradation of Acid yellow 110

The photo degradability of the dye was investigated in a batch reactor by exposing the dye solution to UV light in the presence of ZnO/C/Co nanocomposite. The various reaction parameters such as effect of pH, catalyst loading and initial concentration have been studied. The kinetics of the dye degradation was also investigated. The dye has undergone maximum degradation in acidic pH conditions. The optimum catalyst loading was found to be 0.5 g/L. The initial rate of photo degradation of the dye increased from 1.045 to 5.346 µM / min with an increase in concentration from 20-60 µM and further increase in concentration resulted in decrease of the rate. A plot of log C_0/C vs. irradiation time t, as shown in figure 7, was found to be linear, confirming first order kinetics. It was further established by the linear plot obtained by reciprocal of initial rate 1/*r* against reciprocal of initial concentration of the dye 1/ C_0 (figure 8) and also a plot of $t_{0.5}$ versus 0.5 C_0 which yielded a straight line (figure 9).

Antibacterial Activity of ZnO/C/Co nanocomposite

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,

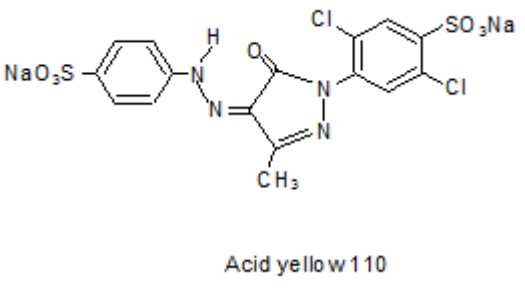

Fig. 1. Structure of acid yellow 110

50, 75 and 100 ppm of ZnO/C/Co nanocomposite against *Pseudomonas aeruginosa* and subsequently against *Staphylococcus aureus* as given in Table 2. The antibacterial activity of ZnO/C/Co nanocomposite was observed to be almost similar when compared to the positive control. The higher concentration of nanocomposite exhibited more activity which can be inferred from the larger circular zones of inhibition. These inorganic

Table 1. Surface characteristics of the catalyst. BET-specific surface area ($S_{BET} \pm 2m^2/g$), BJH-cumulative surface area ($S_C \pm 2m^2/g$), BJH-average cumulative pore volume ($V_P^C \pm 0.002cm^3/g$) and pore diameter (d_p in Å)

Catalyst	S_{BET}	V_P^C	d_P
ZnO/C/Co	34.3572	0.122487	88.077

Table 2. Antibacterial activity of ZnO/Carbon/Cobalt nanocomposite against various clinical pathogens

Microorganism	Concentration of Nanocomposite – Zone of Inhibition (mm)					
	PositiveControl	10 ppm	25 ppm	50 ppm	75 ppm	100 ppm
Staphylococcus aureus	9	-	6	4	3	11
Klebsiella pneumoniae	6	-	-	-	-	-
Pseudomonas aeruginosa	10	-	2	4	6	5
E.coli	8	-	-	-	-	-

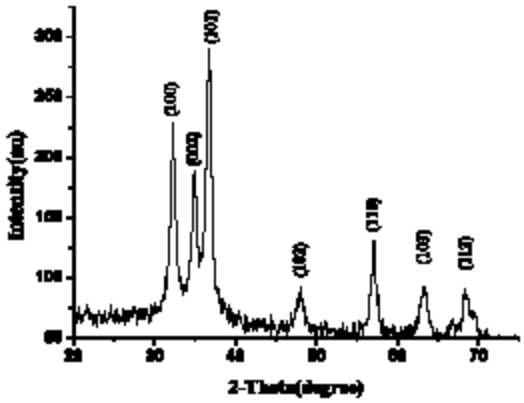

Fig. 2. XRD photograph of ZnO/Carbon/Cobalt nanocomposite

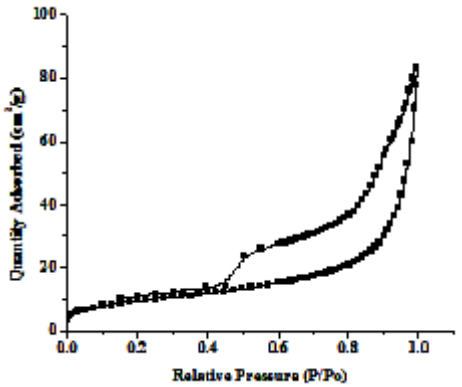

Fig. 3. BET isotherm of ZnO/carbon/cobalt nano composite

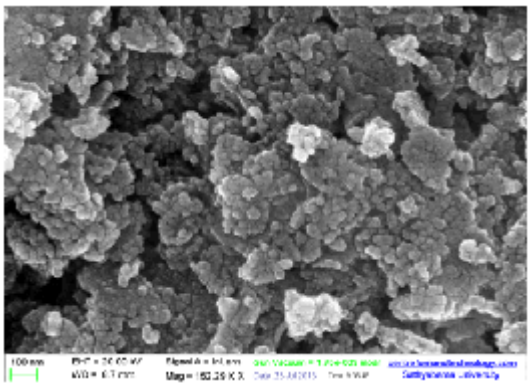

Fig. 4. FESEM image of ZnO/carbon/cobalt nano composite

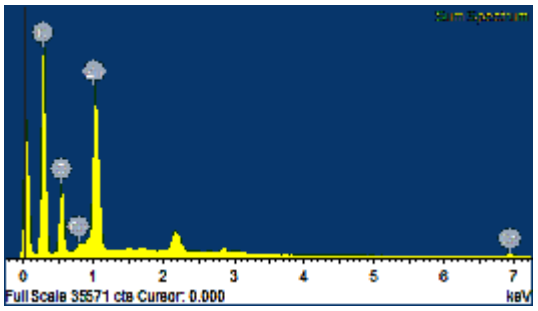

Fig. 5. EDAX image of ZnO/carbon/cobalt nano composite

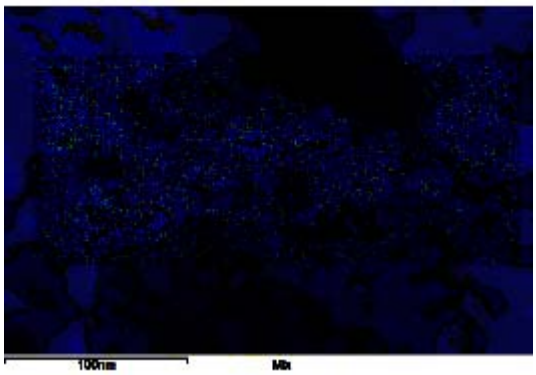

Fig. 5a. EDAX mapping image of ZnO/carbon/ cobalt nano composite

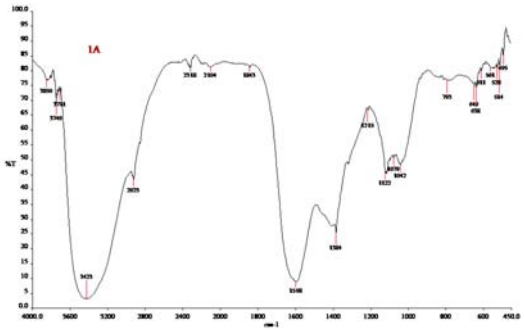

Fig. 6. FTIR image of ZnO/carbon/cobalt nano composite

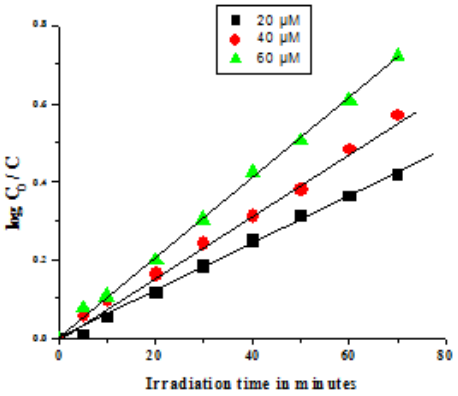

Fig. 7. Plot of log C_0/C versus time for acid yellow 110. Catalyst = ZnO /C/Co (0.5 g/L); pH = 6.2; Temperature = 30.0 ± 0.1 ºC ; Incident wavelength = 254 nm; Absorbance measured at 420 nm.

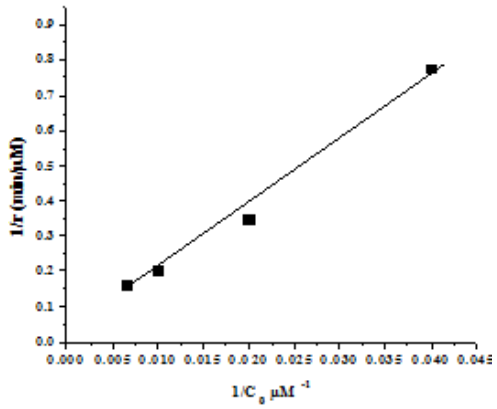

Fig.8. Plot of 1/r versus $1/C_0$ for acid yellow 110. Catalyst = ZnO /C/Co (0.5 g/L); pH = 6.2; Temperature = 30.0 ± 0.1 ºC ; Incident wavelength = 254 nm; Absorbance measured at 420nm.

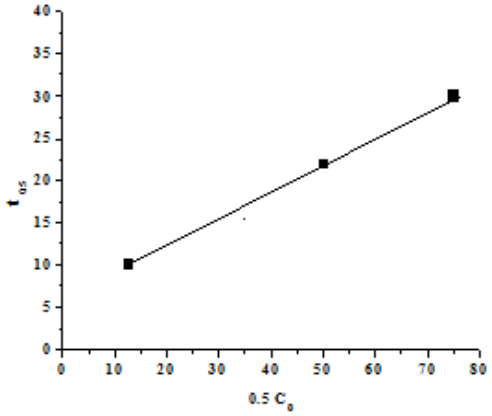

Fig.9. Plot of $t_{0.5}$ versus $0.5C_0$ for acid yellow 110. Catalyst = ZnO /C/Co (0.5 g/L); pH = 6.2; Temperature = 30.0 ± 0.1 ºC ; Incident wavelength = 254 nm; Absorbance measured at 420nm.

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].

CONCLUSIONS

The cobalt doped Zinc oxide/Carbon catalyst was prepared by solution combustion method. The Antibacterial activity of the catalyst was performed by using well diffusion method. The catalyst exhibited positive activity against *Pseudomonas aeruginosa* and *Staphylococcus*

aureus. No activity was observed *against Escherichia coli and Klebsiella pneumonia*. The surface area of nanocomposite was found to be 34.3572 m^2/g. The average crystallite size was evaluated as 10.53 nm. The elemental signature from the analysis of EDAX indicated the presence of Zn, O, C and Co. The main peaks were observed in the FTIR spectrum in the range of 1100 - 1600 cm^{-1} corresponding to the Zn-OH bending mode, C-OH plane bending and C-OH out-of-plane bending and the peaks from 700 to 900 cm^{-1} are attributed to the bond between cobalt and oxygen (Co-O). This catalyst was also tested for its photocatalytic activity, by its decolorizing effect of an azo dye namely acid yellow 110 under UV light and the influence of various parameters on degradation of the dye was investigated.

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