



Exploration of Pristine ZnO and Cobalt Doped ZnO for the Solar Photocatalytic Degradation of Methylene Blue Dye

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ABSTRACT

The ZnO and Co-doped ZnO were prepared by eco-friendly and modest route, including thermal disintegration of zinc oxalate (ZnOx) and cobalt-zinc oxalate (CoZnOx) powders, respectively, from a mechano-chemical method. The process of conversion of metal/s oxalate dihydrate to the pristine ZnO and cobalt-doped ZnO was studied with TG-DTG and FTIR spectroscopy. ZnO and Co-doped ZnO crystallites were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), Energy dispersive X-ray (EDX), UV-visible and photoluminescence (PL) spectroscopies. Hexagonal Wurtzite crystallite structures of the aforementioned materials were illustrated from XRD data. The surface morphological investigation was done with SEM. EDX study confirms the elemental purity of materials. Chemical bonding information was obtained from FTIR spectra. Optical properties were studied from UV-visible and photoluminescence spectroscopy. Exploration of pristine ZnO and cobalt-doped ZnO for the solar photocatalytic degradation (PCD) of methylene blue dye has been done in a batch photoreactor. The various related parameters such as photocatalyst amount, initial concentration of dye and pH were also examined for maximum degradation efficiency for mentioned dye.

Keywords: ZnO, Co-doped ZnO, photocatalytic degradation, methylene blue.

INTRODUCTION

Complex and nonbiodegradable organic compounds can be efficiently converted to simpler form by heterogeneous photocatalysis.^[1] ZnO is extensively studied for solar photocatalytic applications than TiO₂.^[2] The solar PCD of organic pollutants over TiO₂ is less economical since it requires UV radiation. ZnO is non-toxic, chemically stable, biosafe, biocompatible and wide band gap material.^[3] ZnO can operate under totally free and inexhaustible solar light irradiation containing 43% visible light as it reaches to earth's surface.

The solar photocatalytic activity of ZnO can be improved with metal (Transition/Rare earths) doping^[4,5] and non-metal doping.^[6,7] Among the mentioned routes for the modification of ZnO for solar photocatalysis, its doping with transition metals is generally more suitable since transition metal sources are cheap (in comparison to rare earth sources), easily available and their doping into ZnO relatively simple to perform as compared to non-metal doping.^[8] Some of the researchers also have highlighted the importance of doping ZnO with transition metals for their photocatalytic applications.^[8] A suitable dopant and its quantity can reduce electron-hole pair recombination, hence raising the photocatalytic activity. Doping of ZnO with cobalt (Co) will be an efficient method for narrowing the band gap and shifting the threshold wavelength to the visible light region. This could be helpful to utilize solar energy for the photocatalytic elimination of organic hazards.^[9] Mechano-

chemical doping is one of the convenient methods employed for the incorporation of metals into ZnO.^[10,11]

Current work summarizing the eco-friendly and modest route, including thermal disintegration of zinc oxalate (ZnOx) and cobalt-zinc oxalate (CoZnOx) powders obtained by a simple mechanochemical method for getting pure ZnO and Co-doped ZnO, respectively.^[12,13] The Co-doped ZnO synthesized by this method shows enhanced solar photocatalytic degradation efficiency for methylene blue dye than that of pristine ZnO. Parameters such as the amount of photocatalyst, the concentration of dye, pH, irradiation time, etc., on photocatalytic degradation of methylene blue dye are also studied.

MATERIALS AND METHODS

Materials

In the said study, zinc acetate dihydrate (assay $\geq 98\%$), oxalic acid dihydrate (assay 99.5%), cobalt acetate tetrahydrate (assay $\geq 98\%$), Methylene Blue (assay 99%) and other required chemicals were of analytical grade, obtained from S. D. Fine Chemicals Pune, India and were used as it received. The methylene blue dye solutions of suitable concentrations were prepared by using double distilled water. The pH of the solutions was adjusted to the desired values from 6 to 12 with H₂SO₄ (0.025N) and NaOH (0.025N).

Table 1: Characterization techniques used

Sr. No.	Characterization Technique Used	Specification of instrument	Information earned about samples
1	Thermogravimetric analysis (TGA)	Thermogravimetric analysis machine (Shimadzu, TG - DTG - 60H)	Optimum calcination for samples
2	Fourier transform infrared spectroscopy	FTIR spectrometer. (PerkinElmer UATR spectrum Two)	Bonding and purity of samples
3	X-ray diffraction (XRD)	X-ray diffractometer (Rikagu Miniflex-600) using Cu K α radiation ($\lambda = 1.5418\text{\AA}$)	Phase purity and the average crystallite size (D) of the particles.
4	Field emission scanning electron microscopy (FESEM)	FEI (Thermo Fisher) Nova NanoSEM 450 – Microscope	Morphological information like size and shape of particles
5	Energy dispersive X-ray (EDX) spectroscopy	Bruker XFlash 6130 energy dispersive spectrometer	Elemental composition and chemical purity
6	UV-visible spectrophotometry	UV-visible spectrophotometer (PerkinElmer Lambda 365)	Optical band gap and type of emissions.

Synthesis of photocatalyst

A two-step process prepared co-doped ZnO, involves mechanochemical synthesis of cobalt zinc oxalate (CoZnOx) powder followed by its thermal decomposition. In this synthesis, 5.21 gm of zinc acetate dihydrate and 3.78gm of oxalic acid dihydrate were hand-ground for 10 to 15 min at room temperature in agate mortar to obtain zinc oxalate dihydrate. Then 0.31gm of cobalt acetate tetrahydrate was added to the same and hand grinding process was continued for next 20-25 min with subsequent drying under IR lamp till the evolution of acetic acid vapors to give the formation of cobalt zinc oxalate (CoZnOx) precursor. Calcination of CoZnOx at 500^oC ends with the formation of Co-doped ZnO. The same procedure was repeated without adding cobalt acetate tetrahydrate to obtain zinc oxalate (ZnOx) and pure ZnO for comparison.^[13]

Equipments and experimental arrangements

The synthetic progress of pure ZnO and Co-doped ZnO and its characterizations was studied with various instrumental techniques, which are summarized in Table 1.

Furthermore, the PCD reactions were carried out at room temperature in a batch reactor with a glass cool trap mounted on a magnetic stirrer under solar light irradiation from 10.00 am to 4.00 pm. A known quantity photocatalyst was added and the mixture was agitated in an ultrasonic bath for 5 minutes to obtain uniform suspension. The pH of the suspension was adjusted with the assistance of a pH meter (LABTRONICS LT-11) and it was placed under solar light for PCD. Colorimetric absorbance measurement with a digital colorimeter (EQUIP-TRONICS EQ-353) is used for determining PCD efficiency. The percent degradation (%D) was calculated from the expression $\%D = \{(A_0 - A_t) / A_0\} \left[\frac{A_0 - A_t}{A_0} \right] \times 100$ where %D – Percent Degradation, A_0 - Initial absorbance, A_t - Absorbance at time t . A Lux meter (HTC LX-100) is used to measure the light intensity.

RESULT AND DISCUSSION

The optimum calcination temperature for the metal oxalate precursors was determined from the TG-DTA analysis. After calcination at the optimum temperature, the FTIR spectroscopic study is carried out to obtain the frequency changes involved therein as a primary tool to ensure the formation of pure ZnO and Co-doped ZnO. These samples were then subjected to further advanced characterization techniques as mentioned in the following subsections.

Thermal analysis of Metal Oxalate Dihydrate Precursors (ZnOx&CoZnOx)

TG-DTA has examined the thermal change in metal oxalate dihydrate precursor powders indicated in Fig. 1. The thermal decomposition process of both these occurred with several endothermal effects. There are two major weight losses from 30 to 400^oC in TG. The first endothermal peak situated at 30 to 170^oC in the case of both these thermograms is weight losses collectively corresponding to the loss of residual acetic acid and residual water and is nearly equal to the theoretical weight loss of 19, whereas second endothermal peak 350 to 440^oC in case of both these thermograms is weight losses collectively corresponding to the loss of oxalate entity and is nearly equal to the theoretical weight loss of 38. These thermograms clearly suggested that the optimum calcination temperature for getting the pure and Co-doped ZnO should be $\geq 450^{\circ}\text{C}$. Hence for the present study metal oxalate dihydrate precursors was calcined at 500^oC.

FTIR Spectroscopic Study

The FTIR spectra of metal oxalate dihydrate precursors synthesized by mechanochemical method are shown in Fig. 2. The pristine ZnO and Co-doped ZnO were obtained by thermal decomposition of ZnOx and CoZnOx precursor, respectively. In the case of both FTIR spectra of the samples, precursor moiety contains the band corresponding to the stretching vibration of O-H in crystal water nearly at $3410 \pm 20 \text{ cm}^{-1}$. Another band at $1623 \pm 5 \text{ cm}^{-1}$ is due to C=O stretching vibration. The band at $421/422 \text{ cm}^{-1}$ is for Zn-O bonding. When metal oxalate dihydrate precursors were calcined at 500^oC, all bands disappeared except those at 433 cm^{-1} in the case of pristine ZnO and that is at 423 cm^{-1} in the case of Co-doped ZnO. Hence, FTIR spectra confirm the formation of Co-doped ZnO. XRD and EDX also confirm this.

XRD Analysis

Fig. 3 shows X-ray diffractograms collected over 2θ range 20 to 80^o of synthesized ZnO and Co-doped ZnO samples.

The sample gained have a hexagonal wurtzite structure with peaks centered at $2\theta = 31.70^{\circ}, 34.36^{\circ}, 36.20^{\circ}, 47.50^{\circ}, 56.60^{\circ}, 62.80^{\circ}, 66.40^{\circ}, 67.94^{\circ}, 69.08^{\circ}, 72.54^{\circ}, 76.90^{\circ}$ for pristine ZnO and at $2\theta = 31.58^{\circ}, 34.24^{\circ}, 36.06^{\circ}, 47.40^{\circ}, 56.44^{\circ}, 62.72^{\circ}, 66.30^{\circ}, 67.82^{\circ}, 68.96^{\circ}, 72.46^{\circ}, 76.86^{\circ}$ for Co-doped ZnO, belonging to crystal planes (100), (002), (101), (102), (110), (103), (200), (112),

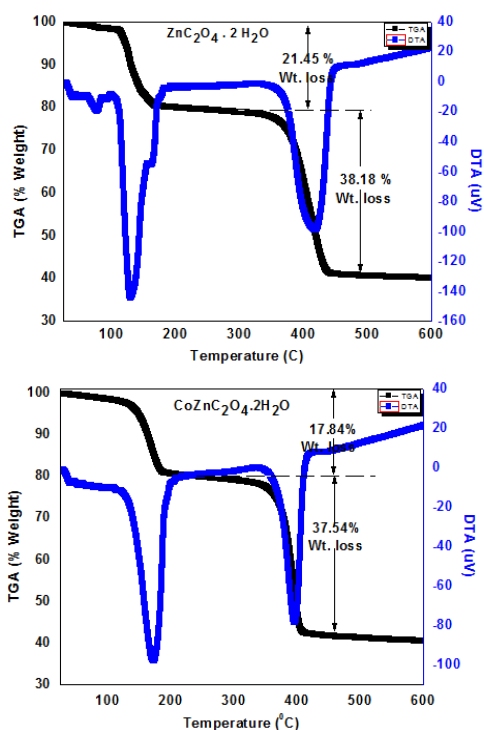


Fig. 1: TG-DTA of metal oxalate dihydrate precursors

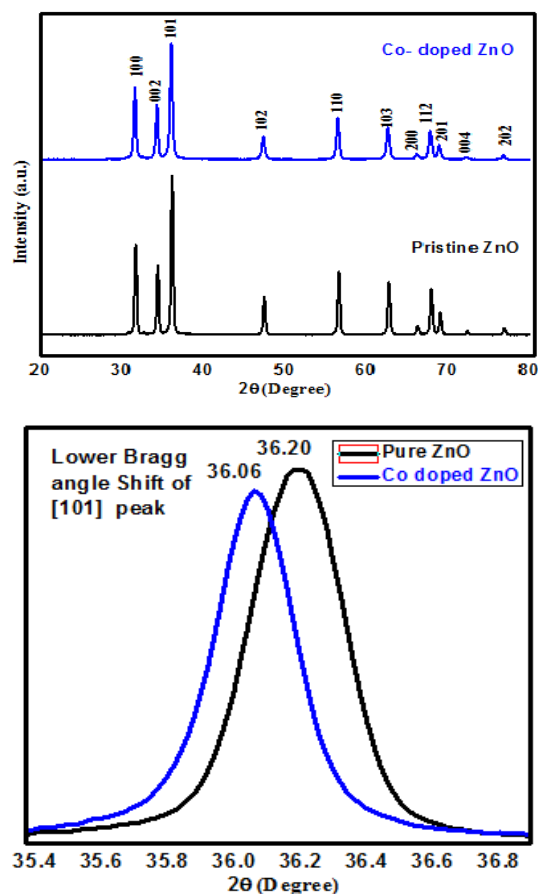


Fig. 3: XRD pattern of pristine ZnO and Co-doped ZnO

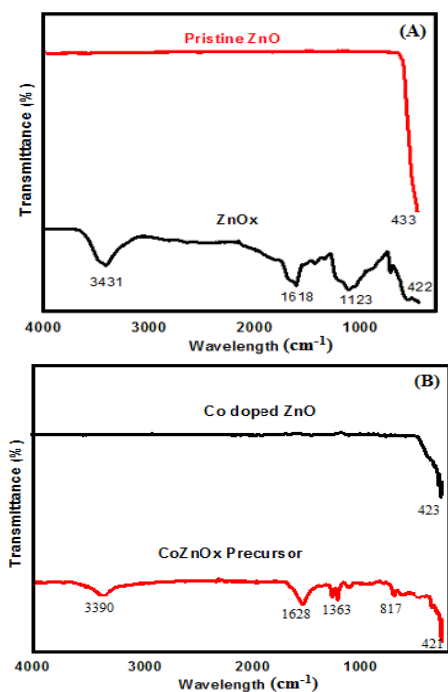


Fig. 2: FTIR changes in the thermal decomposition metal oxalate dihydrate precursors

(201), (004), and (202) respectively. The obtained data is in very fine agreement with the JCPDS card 36-1451 for ZnO.^[14] The crystallite size of ZnO and Co-doped ZnO was 28 ± 0.2 and 25 ± 0.5 nm, respectively as calculated by Scherer's formula.^[15] The specific surface

areas deliberated for the ZnO and Co-doped ZnO samples using Sauter Formula^[16] were 38.30 ± 0.25 m²/gm and 42.80 ± 0.86 m²/gm, respectively. Incorporation of Co in the ZnO crystal produces distortion of its structure with shrinkage of some crystallite planes of ZnO as reflected in the lower Bragg angle shift and peak broadening for Co-doped ZnO than that of ZnO.^[17]

FESEM analysis of Pure ZnO and Co-doped ZnO

The surface morphology of ZnO and Co-doped ZnO samples were studied with SEM (Fig. 4). The SEM photograph of ZnO shows the agglomerated particles with hexagonal morphology. In contrast, the SEM photograph of Co-doped ZnO shows non-agglomerated particles with mixed morphology and some particles have distinct hexagonal shape.

EDX analysis of Pristine ZnO and Co-doped ZnO

For synthesized ZnO and Co-doped ZnO samples energy dispersive X-ray spectra (EDX) obtained is shown in Fig. 5.

EDX spectra of ZnO shows peaks corresponding to Zn and O only and that of Co-doped ZnO shows peaks corresponding to Zn, O and Co, which clearly support the elemental purity of these samples. Additional unlabeled peaks in the EDX spectra of samples are due to the elements presents in conducting material like Al, Au and C used to record the EDX spectra.

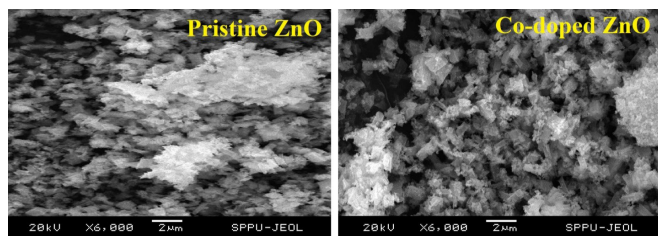


Fig. 4: FESEM analysis of pure ZnO and Co-doped ZnO

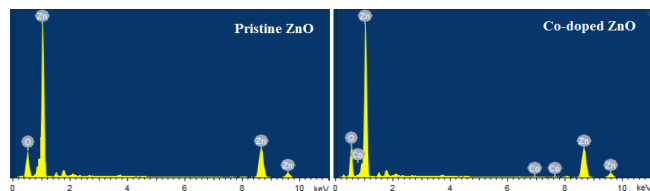


Fig. 5: EDX spectra of pristine ZnO (left) and Co-doped ZnO (right)

UV-visible Spectra of Pristine ZnO and Co-doped ZnO

UV-visible spectra of pristine ZnO and Co-doped ZnO samples are shown in Fig. 6. For both samples, it shows distinctly situated extinction bands in the range of 390 to 410 nm. It implies that the incorporation of Cobalt ions in ZnO shifts the absorption wavelength (λ_{max}) of ZnO towards a longer wavelength (393.03–408.6 nm). A decrease in the band gap energy of ZnO from 3.155 to 3.035 eV on Co-doping suggests the presence of more absorption states in Co-doped ZnO than in pristine ZnO.

Photoluminescence (PL) Spectra of Pristine ZnO and Co-doped ZnO

Photoluminescence (PL) spectra of pristine ZnO and Co-doped ZnO are shown in Fig. 7, which is recorded with excitation wavelength 320 nm over the range 340 to 630 nm.

The strong peaks centered at 282 nm in the case of both the samples correspond to the contribution of excitonic recombination matching with near band edge emissions (NBE) and those centered at 505 nm correspond to the green emission, which is attributed to the singly ionized oxygen vacancy in these samples and the emission due to the radiative recombination of a photogenerated hole with an electron occupying the oxygen vacancy^[13] by the crystals of these samples. The lowering of the intensity of NBE band in the case of Co-doped ZnO over pristine ZnO indicates the presence of additional electronic levels in this sample.

Photocatalytic activity of Co-doped ZnO

Exploration of pristine ZnO and cobalt-doped ZnO for the solar photocatalytic degradation (PCD) of methylene blue dye has been done in a batch photoreactor. The various related parameters such as photocatalyst amount, initial concentration of dye and pH were also examined for maximum degradation efficiency for mentioned dye. The observed results are discussed in the following subsections.

Effect of initial pH of suspension

The effect of the initial pH of suspension on PCD of methylene blue was studied from 6 to 12 with arbitrarily chosen 50 ppm dye

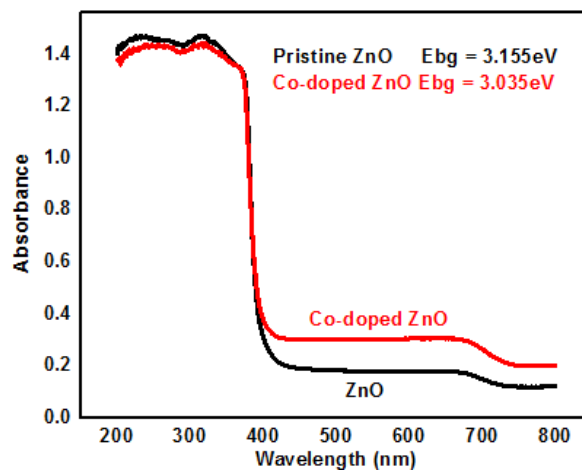


Fig. 6: UV-visible spectra of pristine ZnO and Co-doped ZnO

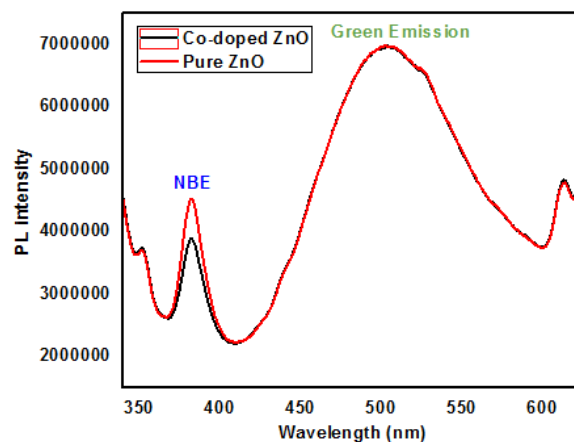


Fig. 7: Photoluminescence (PL) spectra of pristine ZnO and Co-doped ZnO

solution and 150 mg/100 mL photocatalyst loading with 6 hours of solar light irradiation. The pH of the suspension was adjusted only prior to sunlight irradiation and was not controlled during the course of a reaction. All other parameters were kept constant. As ZnO material is slightly soluble in the acidic pH therefore, pristine ZnO and Co-doped ZnO showed lower PCD. The extent PCD was found to increase with an increase in initial pH of suspension (Fig.8). In alkaline medium, additional hydroxyl anions promote photogeneration of active radical species involved in the PCD. The PCD efficiency of ZnO and Co-doped ZnO declined for higher pH (11-12) of the suspension due to increased turbidity. So for the PCD of methylene blue the optimal initial pH of suspension was found to be 11 over pure ZnO and Co-doped ZnO.

Effect of amount of photocatalyst

Fig. 9 shows PCD of 50 ppm methylene blue taken at pH 11 containing 100 to 300 mg/100 mL amount of photocatalyst loading in sunlight irradiation for 6 hours. The degradation efficiency was gradually increased up to 200 mg/100 mL and then it declined. At a lower amount than the optimum amount of photocatalyst due to the limited

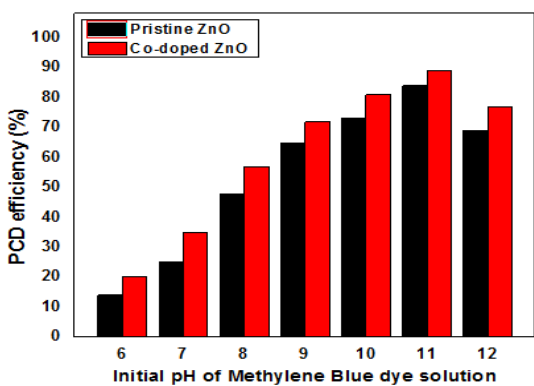


Fig. 8: Effect of initial pH of suspension

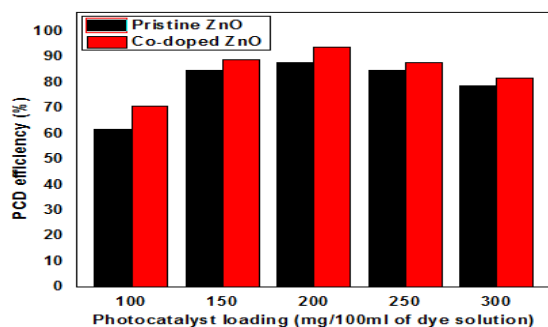


Fig. 9: Effect of amount of photocatalyst (mg/100 mL)

surface area of photocatalyst, the photonic absorption and catalyst activation is limited so PCD efficiency was less. With an increase in the amount of photocatalyst, the number of surficial active sites and hence the PCD efficiency increases upto optimum amount of photocatalyst. Beyond the optimum level of photocatalyst loading due to the shadowing effect and turbidity of the solution, PCD decreases. Hence, the optimal photocatalyst loading is 200 mg/100 mL in this case.

Effect of initial concentration of substrate

The PCD efficiency of methylene blue over pristine ZnO and Co-doped ZnO at diverse initial concentrations in the range 25 to 100 ppm was inspected with respect to irradiation time at optimum pH and catalyst loading. The PCD efficiency is measured as decrease in the absorbance of the dye solutions and results are illustrated in Fig. 10.

The 50 ppm methylene blue was 94% mineralized by using 200 mg/100 mL of Co-doped ZnO upon 6 hours of irradiation at pH 11 and it was more PCD than that over pristine ZnO. Overall PCD of methylene blue was inversely affected by its concentration beyond 25 ppm. This might be due to the fact that the dye solution becomes more intensely colored; hence light photons cannot reach the surface of the photocatalyst easily for its activation.

Effect of irradiation time

The PCD efficiency of pristine ZnO and Co-doped ZnO in sunlight gradually increases with an increase in irradiation time (Fig. 11). 50 ppm methylene blue solution was 94% mineralized over 200 mg Co-doped ZnO/100 mL at pH 11. It is observed that with an increase

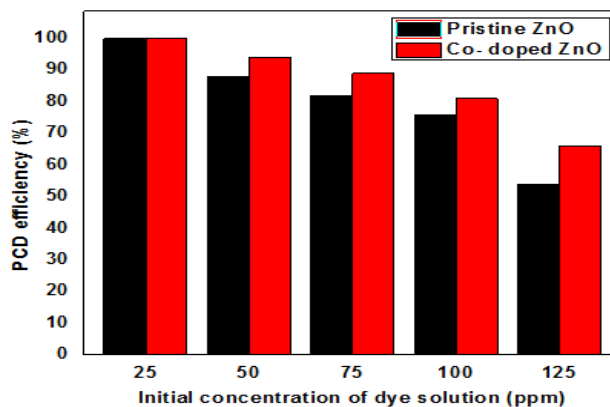


Fig. 10: Effect of initial concentration of substrate

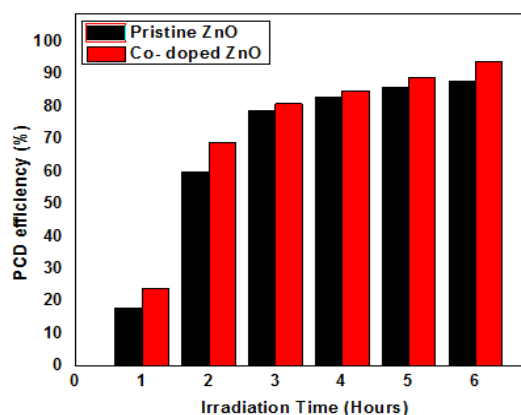


Fig. 11: Effect of irradiation time

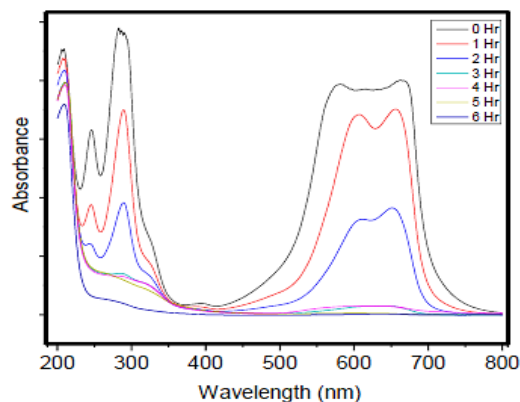


Fig. 12: UV-visible spectra showing photocatalytic degradation

in irradiation time, the absorbance of methylene blue was found to decrease (Fig. 12).

CONCLUSION

In this study pristine ZnO and Co-doped ZnO was synthesized by simple, solvent-free and eco-friendly mechanochemical methods. When ZnOx and CoZnOx powders was calcined at 500°C it gave pristine ZnO and Co-doped ZnO, respectively, as confirmed by

FTIR, UV-visible and PL spectroscopies and additionally with XRD, SEM and EDX studies. In case XRD of Co-doped ZnO peak broadening and shifting to lower Bragg angle as compared to pristine ZnO clearly confirms insertion of Co into ZnO crystals. Insertion of Co into ZnO crystal was also confirmed from the absence of additional peaks in the XRD corresponding to any mix phase material. The elemental purity of the synthesized samples was easily identified from the EDX study. The enhancement in the optical properties of Co-doped ZnO over pristine ZnO can be clearly studied from the UV-visible and PL spectra of these samples. The 94% PCD of 50 ppm methylene blue was achieved over 200 mg/100ml loading of Co-doped ZnO at pH 11 within 6 hours of irradiation of sunlight. Also the PCD efficiency of Co-doped ZnO was found to be greater than that of pristine ZnO.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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