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Journal of Advanced Scientific Research

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ISSN 0976-9595

Research Article

SYNTHESIS OF SILVER (Ag) DOPED ZINC OXIDE (ZnO) NANOPARTICLES AS EFFICIENT PHOTOCATALYTIC ACTIVITY FOR DEGRADATION METHYLENE BLUE DYE

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Received: 29-01-2022; Revised: 14-02-2022; Re-revised: 21-02-2022; Accepted: 25-02-2022; Published: 31-03-2022

 https://doi.org/10.55218/JASR.202213217

ABSTRACT

Zinc oxide (ZnO) and silver doped zinc oxide (Ag-ZnO) nanoparticles were prepared using zinc nitrates as oxidizers, glycine and citric acid as fuels as solution combustion synthesis (SCS) at 500°C. X-ray diffraction (XRD) pattern demonstrates the presence of Ag^{+} in the hexagonal zincite structure of ZnO. The average crystalline size of the particles of ZnO and Ag-ZnO were found to 47 nm and 74 nm respectively. From the Fourier transform infrared (FTIR) spectrum, the composition of Ag doped ZnO confirmed Ag-Zn-O stretching vibration at 510 cm^{-1}. The UV-Visible absorption spectra results showed that synthesized ZnO and Ag-ZnO nanoparticles exhibited UV-visible absorption peaks at 370 nm, corresponds to a band gap of 3.24 eVand 3.08 eV respectively. Based on the above characterization techniques, the incorporation of silver affects the structural and optical behaviour of ZnO nanoparticles. The ZnO nanoparticles were observed that the particles are spherical morphologies. EDAX spectrum indicates no other elemental presence in the synthesized nanoparticle. The present work illustrate the Ag-ZnO nanoparticles as a photo-catalyst to decompose contaminants in the presence of UV light. The photo-catalytic activity of ZnO samples were investigated by UV- irradiation of methylene blue solution in a photocatalytic setup. The resulting mixtures were irradiated with UV light for a period of 45 mins. Based on results, the photocatalytic activity of Ag-ZnO nanoparticles were enhanced by the addition of Ag in pure ZnO nanoparticles. Ag doped ZnO nanoparticles showed higher photocatalytic activity efficiency than pure ZnO nanoparticles.

Keywords: Combustion method, Photocatalytic activity, ZnO, Nanoparticles, Methylene blue.

1. INTRODUCTION

An increase in industries leads to severe environmental problems, and one among these is the dye industry. The waste from the dye industry disturbs the water ecosystem by entering the soil and natural water body. Compared to all other industries' wastages, methylene blue (MB) dye from the textile industry is the most common effluent and is highly damaging to humans. It leads to increased heart rates, cyanosis, gangrene, skin related diseases, and intestinal problems [1].

For the dye degradation progression, nano sized semiconductor materials such as TiO_2, SnO_2, and ZnO are used recently [2, 3]. Co-precipitation method, hydrothermal method, sol- gel method, biosynthesis method, and sono-chemical method are used for the preparation of ZnO NPs [4, 5]. To rectify the above-mentioned problems, considerable researches have been focused on the upgrading of the photocatalytic activity employing semiconductor combination, [6] transition metal doping [7] or noble metal deposition [8].

Recently, preparation of silver-doped ZnO nano-particles has developed as an electrifying area in research and different photocatalytic mechanisms for Ag doped ZnO nanoparticles have been planned [9]. In addition, higher light scattering of Ag improves the photocatalytic properties of ZnO nanoparticles [10, 11]. A variety of methods have been oppressed to synthesize Ag- ZnO nanostructures like sol-gel [12], hydrothermal [13], microwave [14], flame spray pyrolysis [15] and solution combustion method [16]. Among all the

preparation techniques solution combustion method is prominent one because is a simple, quick, energy saving and inexpensive [17, 18]. In this study, the photo degradation of MB using ZnO doped with Silver was investigated. Silver affects the crystalline structure and optical behaviour of ZnO, which enhance the photocatalytic activity of pure ZnO nanoparticle. We have analysed MB dye degradations with ZnO and silver doped ZnO nanoparticles on photocatalytic activity. Fig. 1 shows structure of methylene blue dye.

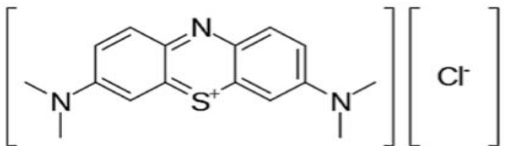

Fig. 1: Structure of methylene blue

2. EXPERIMENTAL PROCEDURE

2.1. Material

Zinc Nitrate (Zn $(NO_3)_2$ $6H_2O$), Glycine ($C_2H_5NO_2$), Citric acid (C_6 H_8 O_7), Silver Nitrate ($AgNO_3$), methylene blue (C_{16} H_{18} ClN_3 SxH_2O) and Distilled water was used all over the experiment.

2.2. Preparation of ZnONanoparticles

Preparation of ZnO nanoparticles was achieved by combustion method using zinc nitrate (Zn $(NO_3)_2 \cdot 6H_2O$) as oxidizer, Glycine $C_2H_5NO_2$) and Citric acid (C_6 H_8 O_7) as fuel. Stochiometric ratio 1:4 of zinc nitrate acted as oxidant and fuel (Glycine, Citric acid) are taken with 30 ml of water in the 100 mL beaker and stirred to form homogeneous mixture. The mixture solution was transferred to 1000 ml beaker and kept on hot plate for boiling. After few minutes the solution was changed to pale yellow foam and the water molecules evaporated. Combustion occurred instantaneously leading to explosion. After, few minutes it was burnt and turned to ash. After the 5-15 min ZnO nanoparticles are formed. Final product is calcined at, 500°C for 4 hour.

2.3. Synthesis of Silver Doped Zinc Oxide (Ag-ZnO) Nanoparticles

Ag doped ZnO nanoparticles were synthesized by combustion method using zinc nitrate (Zn $(NO_3)_2 \cdot 6H_2O$), glycine ($C_2H_5NO_2$) and Citric acid (C_6 H_8 O_7) as starting materials and (Silver nitrate ($AgNO_3$) as doping source. Remaining procedure is same as ZnO nanoparticles synthesis.

2.4. Photocatalytic Experiment

A 0.001 M methylene blue stock solution was prepared by taking 0.032 g of methylene blue in 100 ml distilled water. For the photocatalytic degradation, methylene blue was taken as the sample as it has been extensively used as an indicator for the photocatalytic activities. 0.1 g of Silver doped and undoped photocatalyst was added to 50 mL of 10 µM methylene blue solution and kept in dark condition. The solutions were subjected to irradiation of UV lamp (Philips TUV 15 W/G15 T8 (UV-C,λ_{max}=253.7nm)) under continuous stirring. The experiment was continued for 45 minutes to acquire the equilibrium of adsorption-desorption in dispersed solutions and were irradiated by radiation and in regular time interval, 0.5 ml sample was collected and absorbance was measured. The solution was taken every 5 minutes and centrifuged, the sample was analysed by double beam UV Visible spectrophotometer, and the absorbance was measured at 665 nm. The percentage of dye degradation can be estimated from the following equation, [19]

$$\% \text{ of degradation} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

Where C_i represents absorbance of first peak, C_f represents changed absorbance peak

3. RESULTS AND DISCUSSION

3.1. XRD Analysis

The XRD analysis was used to detect the phase structure and the purity of the photo catalysts. Fig.3 indicates the XRD patterns of prepared pure ZnO and Ag doped ZnO nanoparticles. All the prepared samples have the typical hexagonal zincite structure with lattice constant a = b = 3.254 Å and c = 5.206 Å (space group P63mc, JCPDS card no. 65-3411). No extra peaks due to impurities were observed indicating the high purity of commercial ZnO. Upon consolidation of metallic Ag on ZnO, three small additional diffraction peaks at 2θ = 38.2, 44.2 and 64.3 were observed in the XRD pattern of Ag/ZnO that correspond to (111), (200) and (220) crystal planes of Ag, respectively, confirming the presence of metallic silver FCC phase (JCPDS04-0783) in the sample [20]. The crystallite size of un-doped ZnO and Ag doped samples calculated from the average high intensity (100), (002), (101) peak was 47 nm and for the modified samples were 74 nm. The crystallite size D of the samples was calculated by using the Scherer's formula [21], which is shown in equation (2).

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (2)$$

Here, D and λ, are the crystallite size and the wavelength (1.54 Å), of the x-ray source, β is the full width at half maximum; θ is the Braggs diffracting angle. K is Scherrer constant (0.9 Å).

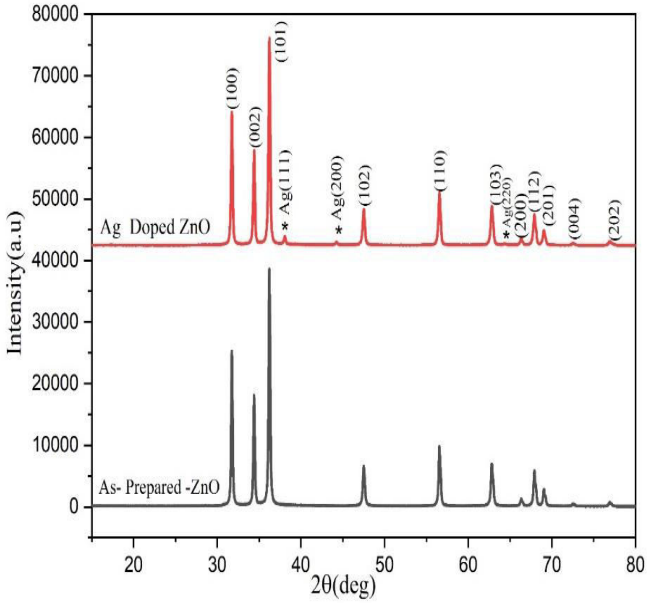

Fig. 2: XRD Patterns of ZnO and Ag- ZnO nano-particles

3.2. Thermogravimetric Analysis

The absorbed water content was determined from the weight difference measured at 0°C -800°C from thermogravimetric data. From Fig. 3, TGA curves shows ZnO nanoparticles doped silver. It shows a continuous weight loss on heating. The first weight loss is observed above 100°C. This weight loss is due to removal of water from the samples. The net weight loss (22%) was observed beyond 700°C in ZnO and Ag doped ZnO 12% was observed beyond 400°C, a thermal decomposition stage related to the total combustion of organic waste and consequent crystallization of the crystalline phases.

3.3. UV-Visible absorption Analysis

Optical behaviour of the prepared pure ZnO and Ag doped ZnO nanoparticles were determined from UV-Vis spectroscopy. Fig. 4 indicates the UV-Vis spectra of the ZnO and Ag doped ZnO nanoparticles. The prepared ZnO nanoparticles show wurtzite crystal structure of ZnO, which was confirmed by the presence of UV absorption edge at 364 nm. The red shift was occurred due to the presence of Ag in ZnO lattice, which affect the structure of pure ZnO.

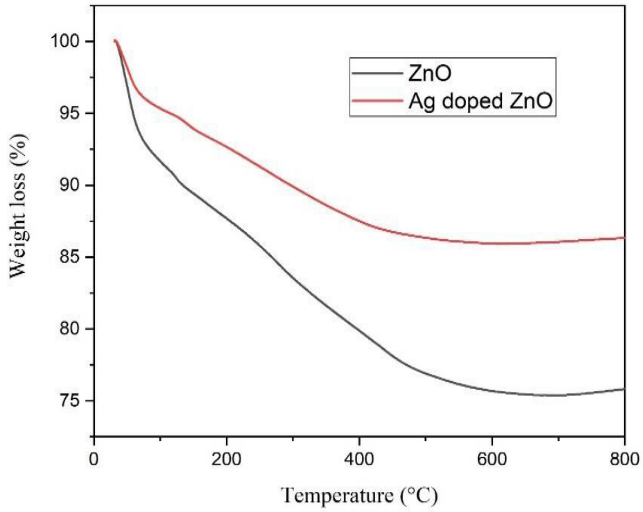

Fig. 3: Thermogravimetric analysis of ZnO and Ag- ZnO nanoparticles

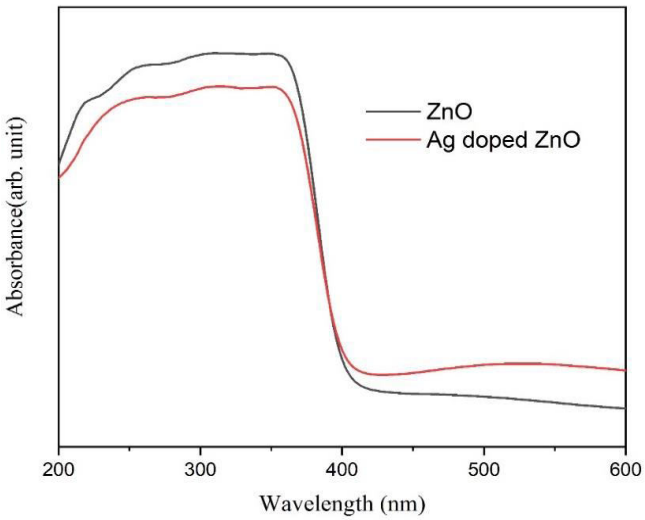

Fig. 4: UV -Visible spectrum of ZnO and Ag-ZnO nanoparticles

3.4. Band gap determination

The optical band-gap of the prepared pure ZnO and Ag doped ZnO nano particles can be calculated by Tauc's model. From the Mott and Davis relation

$$\alpha h\upsilon \sim (h\upsilon - Eg)^{\frac{1}{2}} \quad (3)$$

Where, Eg is energy band gap which is shown in fig.6. Also the band gap energy was determined using Tauc's formula which shows the relationship among absorption coefficient as follows (Eq. (4)):

$$(\alpha h\upsilon)^2 = B\,(h\upsilon - Eg) \quad (4)$$

Where α is the absorption coefficient, h is Planck's constant and υ is the frequency (υ = c/$\boldsymbol{\lambda}$, $\boldsymbol{\lambda}$ is wavelength, c is light speed) [40]. B is a constant called

band tailing parameter. Hence, the band gap energy was acquired graphically from $(\alpha h\upsilon)^2$ vs. $h\upsilon$ for direct transition, extrapolating the linear part according to Eq. (4) (Fig. 5). The band gap energy reduces from pure ZnO nanoparticle (3.36 eV at 369 nm) to Ag doped ZnO nanoparticles (3.34 eV at 371 nm).

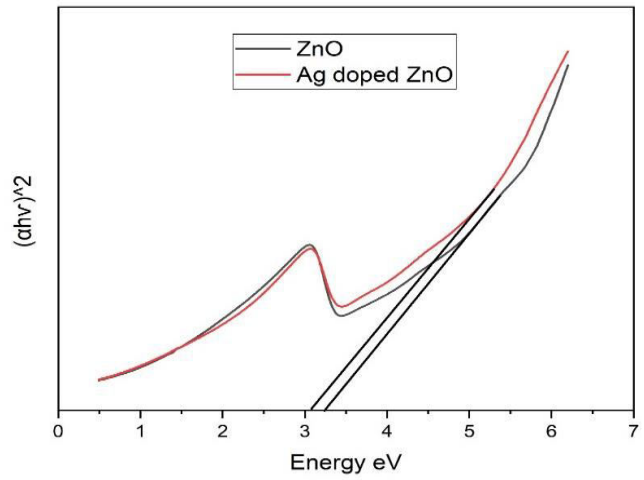

Fig. 5: UV -Band gap spectrum of ZnO and Ag-ZnO nanoparticles

3.5. Diffuse- reflectancespectrum Analysis

Fig. 6 explains the diffuse-reflectance spectra of prepared ZnO and Ag doped ZnO nanoparticles. It revealed characteristic absorption edge near 370 nm.

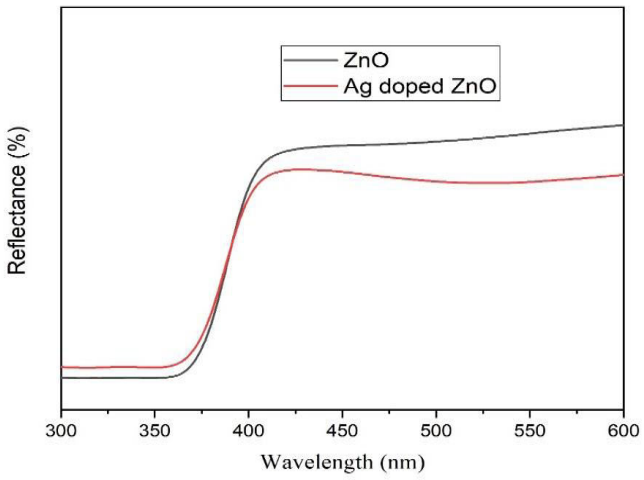

Fig. 6: UV -Band gap spectrum of ZnO and Ag-ZnO nanoparticles

The ZnO nanoparticles exposed high reflectance in the visible region comparing the Reflectance of the Ag-doped ZnO samples. Reflectance of the Ag-doped ZnO samples decreased. From the Figure, the reflectance at wavelengths larger than 370 nm can be connected to the direct bandgap of pure ZnO and Ag:ZnO due to the transition of an electron from the valence band to the conduction band.

3.6. FTIR Analysis

Fig. 7 depicts the FTIR spectra of prepared pure and ZnO nanoparticles in the range of 400-4000 cm^{-1}. Form the figure, sharp peak was observed in 480 cm^{-1}, 510 cm^{-1}, which could be attributed to the Zn-O and Ag-Zn-O stretching vibration mode [22]. A wide peak was in the range of 3020cm^{-1}-3650cm^{-1} that was accredited to the presence of hydroxyl ions (OH) in the Ag- ZnO system. The symmetric and asymmetric bending modes of C=O bonds were in 1580cm^{-1} and 1410 cm^{-1}cm. The vibration peak located at 2860cm^{-1} and 2950cm^{-1} is connected to the symmetric and asymmetric C-H stretching bonds, respectively [23]. The absorption band at 885 cm^{-1} could be attributed to bending vibrational modes [24]. According to Fig. 7, a small shift with increasing silver (Ag) is visible. The presence of Ag^+ ion in the ZnO lattice was confirmed by the blue shift of Ag:ZnO sample. This blue shift is corresponds to the changes in bond length due to the partial substitution of Ag^+ ion at the ZnO lattice [25].

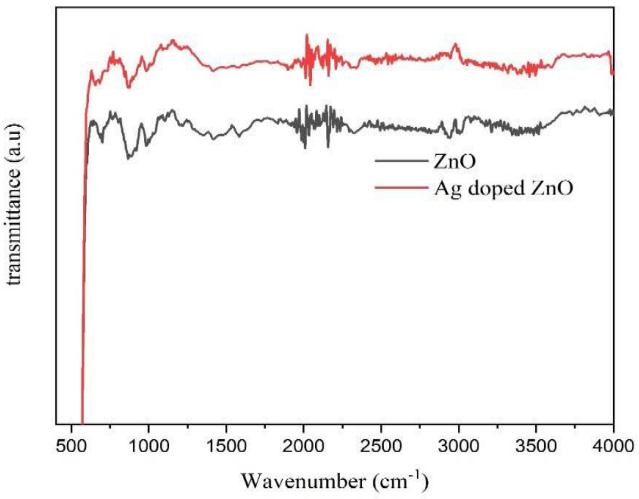

Fig. 7: FTIR Spectrum of ZnO and Ag- ZnO nanoparticles

3.7. SEM and EDX analysis

The surface morphology and elemental composition of the prepared nanoparticles were examined by scanning electron microscopy and energy dispersive X-ray spectroscopy. Fig. 8(a) shows the SEM image of the ZnO. The morphology of Ag-ZnO indicates mostly spherical particles and few are irregular shaped particles. The average particle size of the bare ZnO was

observed as 68 nm from the size distribution of the particles and the particle size distribution is shown as inset in Fig. 8(a). As seen from Fig. 8(c), the morphology of ZnO-Ag indicates the particles are much more agglomerated with the formation of small particles on the larger clusters. The size distribution of the particles is larger than that of the ZnO photocatalyst, which is shown in inset of Fig. 8(c). The average diameter of ZnO-Ag is observed as 7 μm. Further, determination of the elemental composition of nanoparticles was analysed from the EDX spectra, the recorded EDX spectrum of ZnO photocatalyst is shown in Fig. 8(b) and it shows the presence of Zn and O indicating the formation of Zinc oxide. No other elementals are observed in the EDX spectrum, which confirms that the synthesized samples were very pure. Fig. 8(d) represents the EDX spectrum of ZnO-Ag photocatalyst and it reveals the existence of silver in addition to Zn and O.

3.8. Photocatalytic study

The photocatalytic activities of the samples were evaluated by the photocatalytic degradation of methylene blue (MB) dye under UV irradiation. The ZnO and Ag doped ZnO nanoparticle UV-vis absorption spectrum is shown Fig.9. Both nano particles are subjected to the 500°C calcination. The photocatalytic activity of ZnO and Ag-ZnO nanoparticles is shown in Fig.9, Moreover, it was found that ZnO had little ability to mineralize MB under UV light irradiation. The samples prepared with Silver doped ZnO exhibit higher photocatalytic activity.

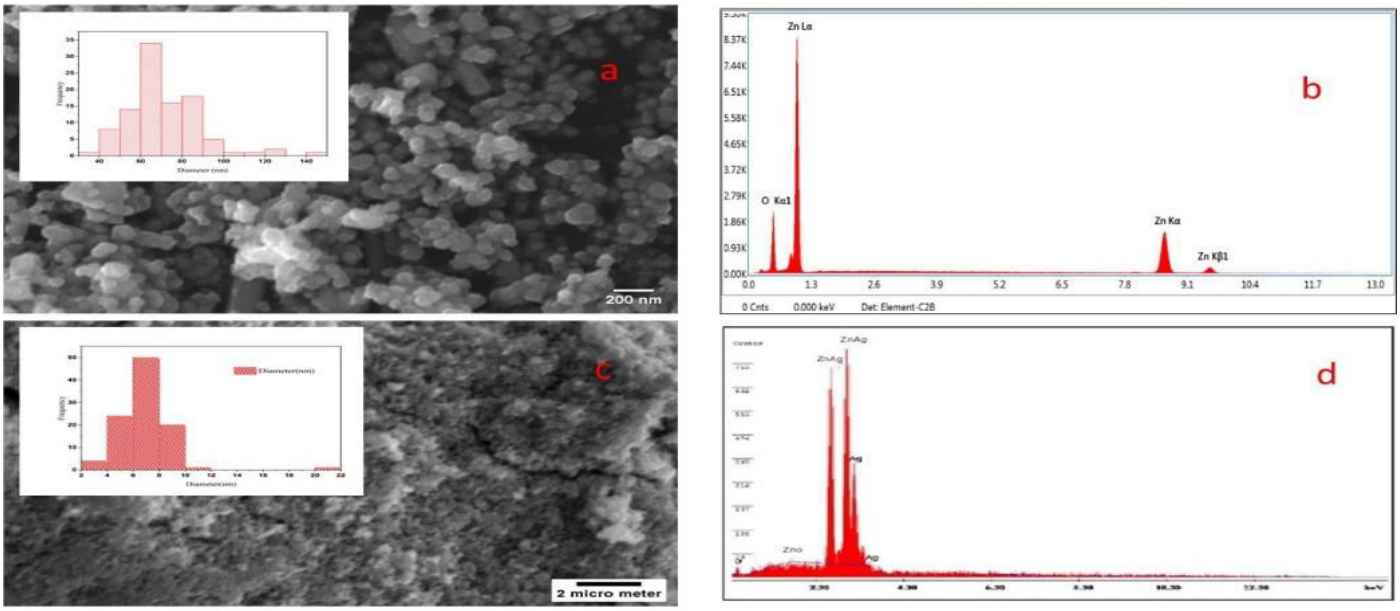

Fig. 8: SEM and EDAX spectrum of ZnO and Ag- ZnO nanoparticles

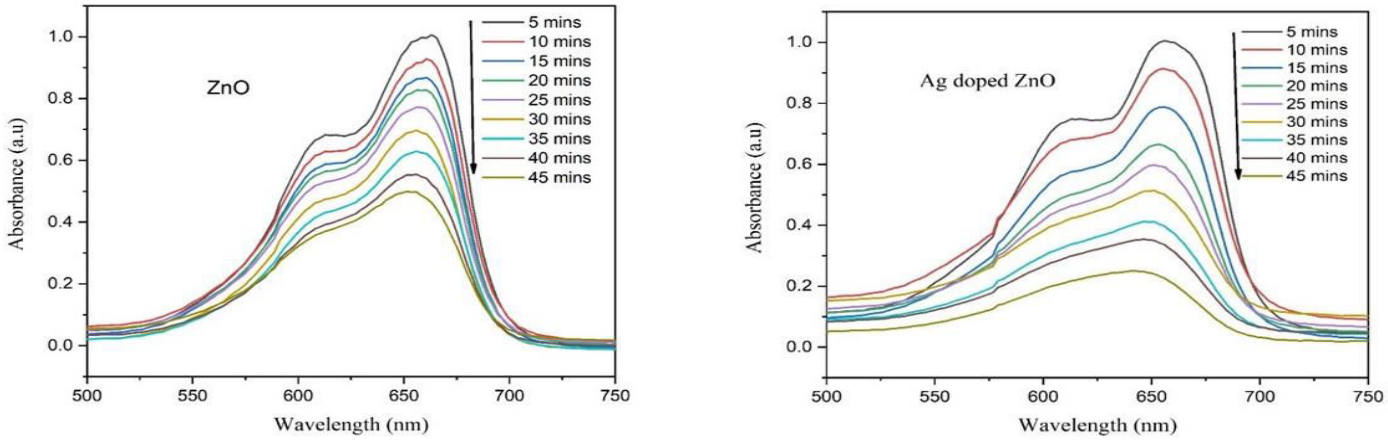

Fig. 9: Photocatalytic Activity of ZnO and Ag- ZnO nanoparticles.

3.9. Degradation Efficiency

Fig.10 illustrates prepared ZnO and Ag:ZnO nanoparticles photo degradation efficiency (%) at 45 minutes irradiation time. The photo degradation efficiency was achieved by 83% at 1% wt of Ag doped ZnO sample. This is higher than the pure ZnO, which was around 50%. Based on above-results, it is observed that un-doped ZnO comparatively has slower activity about 33%, and dye was decolorized after 45 min of light irradiation. It clearly indicates that Ag doped ZnO degrades the dye more efficiently than pure ZnO. This behaviour confirmed the doping of ZnO with noble metal Ag enhances photocatalytic activities of ZnO. The enhanced activity endorsed that incorporation of Ag with the ZnO leads to the efficient production of highly reactive hydroxyl (OH^{-1}) and superoxide anion (O_2^-) for the breakdown of dye into simple organic compounds [26]. Thus, doping of the metal oxide with noble metals increases the photocatalytic activity. This paper provides a new insight for the synthesis of various doped metal oxides properties towards a sustainable clean energy environment due to their excelled photo degradation properties.

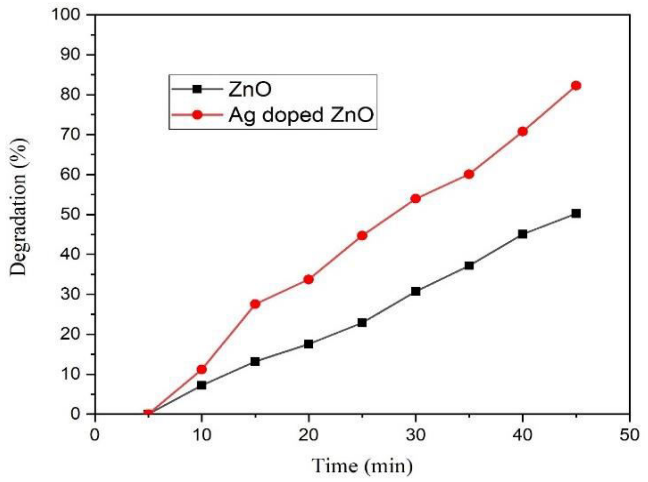

Fig. 10: Degradation Efficiency of ZnO and Ag-ZnO nanoparticles

4. CONCLUSION

We have successfully synthesized ZnO and ZnO:Ag nanoparticles by facile solution combustion method. TGA, UV-DRS, XRD, EDX and SEM. characterized the prepared nanoparticles. We have successfully prepared ZnO and Ag-doped ZnO nanoparticles with particle size of 47 nmand 74nm respectively. XRD pattern of doped ZnO clearly shows the presence of Ag in the ZnO matrix, which is only, composed the Zincite-type ZnO. The UV-DRS displayed the optical properties and FTIR shows a band at 405 cm^{-1} and 510 cm^{-1} due to Zn-O and Ag-ZnO vibrational stretching.The morphology of the Ag-ZnO nanoparticle photocatalyst is altered upon the silver inclusion and an enhanced particle size was detected compared to the ZnO. The prepared pure ZnO and Ag:ZnO nanoparticles exhibited UV-visible absorption peaks at 370 nm, corresponds to a band gap of 3.24 eV and 3.08 eV respectively. The photocatalytic activity of (ZnO-Ag) was investigated by the decomposition of Methylene blue under UV irradiation. The Ag doped ZnO, the removal of MB reaches 86% at 45 min, which improve more 33% than that of the pure ZnO, the improvement of photocatalytic activity. In future Photo catalyst study of ZnO will be carried out with other doped material.

Conflict of interest

None declared

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