A simple co-precipitation method at normal temperature was used to prepare Mg and Al co-doped ZnO nanoparticles. The structure and chemical properties of synthesized nanoparticles were characterized by various techniques such as XRD, FTIR, SEM-EDX, UV-Visible Spectroscopy and AFM, whereas the photo-catalysis study of congo red (CR) was performed by UV/VIS spectrophotometry. The XRD results exhibited that Mg, Al co-doped ZnO nanoparticles possess hexagonal wurtzite structure. The SEM analysis suggested varying nano morphology of synthesized nanoparticles and the purity of the sample was checked by EDX analysis. Mg, Al co-doped ZnO nanoparticles were subjected for the photo-degradation of congo red dye (CR) in aqueous medium under UV-light irradiation. The photo-degradation study revealed that the Mg, Al co-doped ZnO nanoparticles is a promising substance for the hazardous ecological remediation.

**Keywords:** ZnO nanoparticles, Soft-chemical method, Congored, Photodegradation.

### Introduction

In the past few decades, dyes are significantly used additive or colorant in many industries like textile, leather, paper, printing, ink, pharmaceutical, cosmetics, and food industries. The application of synthetic dye over natural dye has been increased in recent years due to its performance and low cost. As per the reports, over 10000 tons of dyes were produced annually which ultimately resulted in increasing public interest about the dyeing waste water treatment. The waste water containing high concentration of dyes is highly toxic to the environment and adds colour to the water that prevents the penetration of sunlight. In addition to this, chemicals also cause carcinogenic and mutagenic effects to the life around it.

The predominant dye Congo red (CR) used by the textile industries is the sodium salt of 3, 3′-(1, 1′-biphenyl)-4, 4′-dihyl) bis 4-aminonaphthalene-1-sulfonic acid (C_{32}H_{22}N_{6}Na_{2}O_{6}S_{2}). Inefficient decolourisation because of fading resistance and persistence to biological degradation was the complication occurred. To overcome these complications, endless development of advanced water treatments has been progressed. Many numbers of studies have been reported in the development of dye removal in water. The major removal methods are physical (Precipitation, adsorption, filtration, flocculation), chemical (Photochemical decolourisation, ozonation, Chlorination) and biological methods (Biological oxidation). About 95% of CR removal by adsorption after 24 hr of contact time was achieved earlier by researchers. Despite the CR removal, adsorption separates dyes from waste water and thus it is not a destructive process. Further, acid functional group in CR dye inhibits them being attached by the low cost adsorbents. Activated carbon is highly effective and that can bind acid dyes like CR but high cost minimizes its usage. All other treatments needed...
to treat the waste stream resulted in inefficient
decolorization. Subsequently, much of attention
has been required for the degradation of dyes.
Earlier reports suggested that advance oxidation
processes showcased high efficiency in dye
degradation processes. Equally, photocatalytic
degradation has also attracted researchers to treat
organic pollutant. Photocatalysis is proficient to
treat wide range of organic pollutant at ambient
temperature and pressure to degradable product.

Zinc oxide (ZnO) mediated based
photodegradation has attracted extensive interest
owing to its great advantages in the complete
removal of organic pollutants from wastewater.
This is mainly because of its various merits
such as optical-electronic properties, low-cost,
chemical stability and nontoxicity9. The main
aim of this paper is to produce a condensed
and coherent overview on the photocatalytic
degradation of azo dyes in the presence of ZnO
doped with selective transition metals, which can
serve as a ready reference for future scientific
endeavors in this area. Photodegradation of azo
dyes using transition metal doped ZnO has been
found to be very effective for the treatment of
dye-contaminated solutions. The basis of the
reaction is photoredox process. In this process,
an important role is played by molecular oxygen
and other active species, such as O2•-, H2O2, and
•OH, which are generated in a sequence
of reactions10. They make the photocatalytic
processes more efficient resulting in enhanced dye
degradation via the formation of intermediates
such as aromatic amines, phenolic compounds
and several organic acids. Although azo dyes
are one of the most commonly used class of
dyes in industrial applications, limited literature
is available on their remediation from effluents
using ZnO doped with transition metals.

Materials and Methods

The essential chemicals for the preparation of
ZnO nanoparticles by soft chemical method were
purchased from Merck and used as a precursors
and double distilled water was used as solvent.

Synthesis of Mg and Al Codoped ZnO
Nanoparticles

Zinc nitrate hexahydrate (1M), Magnesium
nitrate hexahydrate (0.05 M) and Aluminium
nona hydrate (0.05 M) were used as precursors
and methods as mentioned in the earlier reports11.
The salts were dissolved in 100 ml distilled water
in magnetic stirrer for 30 mins. A solution of
NaOH (2M) was mixed with starting solution
to get a large amount of white precipitate under
constant stirring at 45°C. By using distilled water,
the precipitates were filtered and washed; then
dried in hot air oven at 120°C for 4 hours, and the
precipitates were powdered in an aggar mortar.
The final powder was calcined at 450°C for 3 hours
and allowed for cooling in furnace. The nanomaterials
were collected for further characterization studies.
Mg and Al co-doped ZnO obtained by above-
mentioned procedure was collected and assigned
as Z, ZA, ZB, ZC and ZD (Table 1).

Photodegradation analysis

About 10 mg/L of conored dye and 50 ml
of distilled water with 40 mg of Mg and Alco-
doped ZnO nanomaterials were placed under
UV irradiation for the degradation of dye in
different time interval (0, 30, 60, 90, 120,150
and 180 minutes). The influence of UV light
sources on photo-degradation of conored dye
was supported with a 30 W mercury lamp and
the decomposition effect was measured by UV-
absorption measurement.

Results and Discussion

XRD Analysis

Figure 1. shows the X-ray diffraction pattern
of un-doped ZnO in comparison with different
concentrations of Mg & Al co-doped ZnO
nanoparticles synthesized by soft chemical
method at 450°C using X-ray diffractometer
(BRUKER, Germany, Model-D8-Advance)
with Cu Kα radiation source (λ = 1.54060
A°). All diffraction peaks corresponded to
hexagonal wurtzite structure of ZnO with (JCPDS
No.800075)12. The peaks of co-doped ZnO had
high intensity compared with un-doped ZnO and
diffraction intensity increased with magnesium
concentration. The average particle size was
calculated by Debye Scherrer’s formula13,

\[
D = \frac{0.9\lambda}{\beta\cos\theta}
\]

Where, D is average particle size,
λ is incident wavelength of X-ray beam,
β - full-width at half-maximum (FWHM) and
θ is Bragg’s diffraction angle respectively.

The calculated particle sizes were 52 nm
for un-doped ZnO and 40 nm, 38 nm, 34 nm,
37 nm for samples ZA, ZB, ZC and ZD of Mg, Al co-doped ZnO nanomaterials respectively. The nanoparticles size of sample ZC was decreased when compared with un-doped ZnO and samples ZA, ZB & ZD of Mg & Al co-doped ZnO.

**FT-IR spectrum analysis**

Figure 2. shows the FTIR spectra of prepared un-doped ZnO and Mg & Al co-doped ZnO (ZA, ZB, ZC and ZD) nanoparticles on KBr pellets using SHIMADZU FTIR 8400S, Europe in the range 4000-500 cm⁻¹. The bands perceived at 481.17 cm⁻¹ for un-doped ZnO, and 480.90 cm⁻¹, 460.88 cm⁻¹, 490.90 cm⁻¹ and 470.89 cm⁻¹ for samples ZA, ZB, ZC and ZD of Mg & Al co-doped ZnO nanoparticles were associated to metal oxide. It was admitted that the peaks range of 410 – 735 cm⁻¹ corresponded to ZnO as reported earlier.14 Peaks at 1384.26 cm⁻¹ for Un-doped ZnO and samples ZA, ZB, ZC and ZD were attributed to the bending frequency of oxygen stretching mode.15 The presence of peak around 3445.12 cm⁻¹ for un-doped ZnO and the band at 3445.73, 3446.32 and 3444.41 cm⁻¹ for ZA, ZB, ZC and ZD of Mg & Al co-doped ZnO due to O-H stretching vibrations.16

**SEM Analysis**

Figure 3. indicates the pictures of Un-doped ZnO (Z) and Mg and Al co-doped ZnO (ZB) nanoparticles obtained in JEOL JSM 6390LV, Japan, a high performance, low cost scanning electron microscope with a high resolution of 3.0nm. The SEM images revealed that prepared nanoparticles were non-uniform in size and almost in spherical morphology.17 The surface agglomeration was large in un-doped ZnO compared to co-doped ZnO.18 The nanoparticle size of un-doped ZnO and Mg, Al co-doped ZnO nanoparticles were calculated to be around 85 nm (0.085µm).

**UV-Visible Spectroscopy**

Figure 5. shows the optical absorption spectra of un-doped ZnO and Mg, Al co-doped ZnO (ZA, ZB, ZC and ZD) nanoparticles using JASCO (V-530), UV-Vis spectrophotometer, USA in the absorption range of 190-1000nm. The wavelength of prepared nanomaterials optical absorption spectra was 379 nm for un-doped ZnO and 374 nm, 369 nm, 371 nm and 374 nm for ZA, ZB, ZC and ZD of Mg, Al co-doped ZnO nanoparticles respectively. The absorption peak towards the lower wavelength with a blue shift and compared with un-doped ZnO, the absorption peak of doped nanomaterials towards the longer wavelength with red shift, it was ascribed to the small changes in the particle size with rising Mg and Al concentration. The band gap energy values were calculated using the following equation,

\[ E = \frac{(hc)}{(\lambda)} \]  

Where h is Planck’s constant, c is the velocity of light and \( \lambda \) is the wavelength of light and the obtained values were 3.27eV for un-doped ZnO and 3.32eV, 3.36eV, 3.34eV, 3.32eV for samples ZA, ZB, ZC and ZD of Mg, Alco-doped ZnO nanoparticles. The difference in absorption was established by the presence of doping agents.22

**AFM Analysis**

Figure 6. shows the AFM analysis of synthesized Un-doped ZnO (Z) and ZB nanoparticles by soft chemical method using AFM instrument made in USA (Model-PicoSPM-2100). The average size of the particles was detected as 61 nm for Un-doped ZnO and 37nm for Mg and Al co-doped ZnO which was in good agreement with XRD analysis. The appearance of AFM images with regular shape and random arrangement was observed.23

**Investigation of Photodegradation of Un-doped ZnO and Mg, Al Co-doped ZnO Np’S**

Figure 7. exhibits the photodegradation spectra of Un-doped ZnO (Z) and ZB nanocomposites. The prepared nanoparticles were absorbed by UV light, and electrons were stimulated from the valence band to the conduction band. The light energy caused holes and reacted with water and hydroxyl radical was created. The hydroxyl radical was extremely strong, non-selective oxidant and oxidizing agent which leads to the degradation of organic chemicals. The light energy caused electrons and reacted with molecular oxygen, then superoxide radical anions were generated which was responsible for degradation of dye solution.
TABLE 1. The composition of prepared Nanoparticles.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Nanoparticles</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Z</td>
<td>Undoped ZnO</td>
</tr>
<tr>
<td>2</td>
<td>Z_A</td>
<td>Mg_{0.04}Al_{0.01} co-doped ZnO</td>
</tr>
<tr>
<td>3</td>
<td>Z_B</td>
<td>Mg_{0.03}Al_{0.02} co-doped ZnO</td>
</tr>
<tr>
<td>4</td>
<td>Z_C</td>
<td>Mg_{0.02}Al_{0.03} co-doped ZnO</td>
</tr>
<tr>
<td>5</td>
<td>Z_D</td>
<td>Mg_{0.01}Al_{0.04} co-doped ZnO</td>
</tr>
</tbody>
</table>

Fig. 1. XRD patterns of (i) Z (ii) Z_A (iii) Z_B (iv) Z_C and (v) Z_D.
Fig. 2. FT-IR Spectrum of (i) $Z$ and (ii) $Z_A$ (iii) $Z_B$ (iv) $Z_C$ (v) $Z_D$

Fig. 3. SEM analysis of (i) $Z$ and (ii) $Z_A$ 3.4 EDAX Analysis
Fig. 4. EDAX analysis of SEM analysis of (i) Z and (ii) ZB

Fig. 5. UV-Vis spectra analysis of (i) Z and (ii) ZA (iii) ZB (iv) ZC (v) ZD
The photo-degradation reaction can be schematically represented as follows:

![Diagram of photo-degradation reaction](image)

**Fig. 6.** AFM images of SEM analysis of (i) Z and (ii) $Z_n$

**Fig. 7.** Absorbance spectra of (i) Z and (ii) $Z_n$

The photodegradation efficiency of nanomaterials was calculated by following formula:

\[ D(\%) = \left( \frac{A_0 - A_t}{A_0} \right) \times 100 \]  

(3)

Where, \( D \) is the degradation efficiency (in \%). \( A_0 \) is the UV absorption of dye with sun light irradiation time (0 min) and \( A_t \) is the UV absorption of dye after UV-light irradiation (t-min).

Figure 7 (i) and (ii) shows the UV-Vis absorption spectra of congored dye solution in the presence of Un-doped ZnO and Mg, Al doped ZnO nanocomposites with UV irradiation in different time intervals (30, 60, 90, 120, 150 and 180 mins). The photo-degradation efficiency calculated using equation (3) and the values were 55% for Un-doped ZnO and 83.6% for Mg and Al co-doped ZnO nanoparticles. The result of Photodegradation analysis of congo red dye with Un-doped and doped ZnO photocatalyst clearly presented a higher dye removal efficiency of the Mg and Alco-doped ZnO nanoparticles. Therefore, the experimental results concluded that the Mg and Alco-doped ZnO nanoparticles was a respectable dye removal catalyst compared to Un-doped ZnO nanoparticles. This route could be suitable for sewage and industrial water treatment.

Conclusion

Un-doped ZnO and Mg, Al co-doped ZnO nanoparticles were prepared successfully using soft chemical method at room temperature. The synthesized samples were carefully characterized with XRD, FTIR, SEM-EDX, UV-Visible Spectroscopy and AFM and investigated different properties such as structural, morphological and optical. The hexagonal wurtzite structure of Un-doped ZnO and Mg, Al co-doped ZnO nanoparticles were confirmed by XRD analysis. SEM images exhibited the formation of nanoparticles and surface agglomeration. EDAX analysis results clearly indicated the percentage presence of material and its purity. AFM study indicated the surface morphology and average particle size of nanoparticles. The photo-degradation efficiency of Mg and Al co-doped ZnO (83.6%) nanoparticles owed superior performance than un-doped ZnO (55%) nanoparticles against congo red dye solution under UV irradiation. Ultimately, prepared nanoparticles will show a promising effect in waste water treatment for many industries.

References


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