CHAPTER-3

SYNTHESIS, STRUCTURAL AND OPTICAL PROPERTIES OF Ag DOPED ZnO NANOPARTICLES WITH ENHANCED PHOTOCATALYTIC PROPERTIES BY DYE DEGRADATION OF ORGANIC DYES
3.1 Introduction

Different kind of residual organic dyes generated from different sources i.e. pharmaceutical, textile or paper industry etc., which act as organic pollutants to natural resources of water has become a big challenge to humans on earth. Since water is routine intake liquid by humans in daily life, so its pollution brings severe effects on human health as well as to its surrounding environment. In this respect, purification, management & disposal of contaminated water by advanced scientific techniques have become a demand of public interest. Some conventional method of purification of water like adsorption, reverse osmosis etc. have not proven much efficient due to their limitations [1]. Semiconductors are very good candidates in water purification due to their effective and efficient properties. Due to the prominent effect of removal of dyes from the polluted water, semiconductor based photocatalyst are most widely used by researchers [2-6].

In order to choose suitable semiconductor like TiO₂, ZnO, ZnS, WO₃, CdS etc. [2-6] as a photocatalytic candidate for water purification, their physical and chemical properties have been studied with respect to their efficiency, reactivity, photo stability and economical factors. Among different semiconductors, ZnO has been found the most suitable candidate to remove the organic dyes from water effectively. ZnO nanomaterial have wide band gap (~ 3.30 eV) which is suitable for tuning to enhance the efficiency of dye degradation mechanism. High exciton binding energy (60 meV) of ZnO also supports its activity in water purification applications [7]. In addition, ZnO is also used in many others applications such as electrodes [8], sensors [9], light emitting diodes [10], lasers [11] and photocatalytic activities [12, 13] etc. In order to improve the dye degradation efficiencies of ZnO NPs, their properties can be tuned through doping of suitable dopants. Further, out of different dopants, transition metal doping [14] or noble metal doping [15] has a favoured compatibility with ZnO nanomaterial. Their ability to absorb visible light and segregation of photo excited electron/hole pair leads to surface plasmon resonance [16]. These features will make them most suitable candidate as dopant in ZnO matrix.

Further the selection of noble metals as a dopants (Gold, Silver, Palladium etc.) in ZnO material, leads to enhancement of their photo catalytic performances [17-19]. In present work we have reported silver doped ZnO based nanomaterial synthesized by co-precipitation method [20-
21]. Silver doped ZnO nanomaterials generate electric field by optical vibration of delocalized electronic oscillation [22]. In addition, the doping of silver into ZnO matrix lead to incorporation of oxygen vacancies [23], reactive oxygen species [24] and improvement of light scattering [25] etc. features, which collectively improve and enhance the photo catalytic mechanism of ZnO NPs over dye degradation mechanism.

The purpose of this work is to find insight behind the variable dye degradation outcomes of Ag-doped ZnO NPs. The tuned structural, morphological and optical properties of Ag-doped ZnO, gives the desired results of degradation with different dyes. The basic requirement for generation of electron (e⁻)/hole (h⁺) for dye degradation mechanism is fulfilled by ZnO NPs effectively under exposure of light. Generated electron (e⁻)/hole (h⁺) will further create oxidizing or attacking species (O₂⁻, h⁺ etc.) to degrade the organic dyes to small fragments [26].

In literature, many dyes viz. methylene blue (MB), brilliant blue (BB), methylene orange, Napthol blue black, Rhodamine etc. [27-30] have been treated with Ag-doped ZnO NPs in order to find unknown facts on their degradation behavior (efficiency, structure fragments, stabilities etc.). Due to wider application of MB and BB in coloring paper, textiles industry, hair dye etc. the left of over waste or by-products accumulate in the environment [31, 32]. The presence of these dyes in environment will contaminate the aquatic life and natural resources badly. The presence of dyes in wastewater is loaded with high chemical oxygen demand (COD), biological oxygen demand (BOD) and suspended solids etc. In addition, this will also create many health problems in humans like vomiting, blood pressure, cyanosis, tissue nacrosis etc. [31]. In this respect, the effective activity of silver (Ag) doped ZnO over MB & BB dyes will help to solve the environment pollution problem by water purification.

In the present work, the dye degradation mechanism behind the two common dyes MB and BB has been studied after their interaction with Ag doped ZnO under visible light exposure.

3.2 Experimental

3.2.1 Synthesis of Zn₁₋ₓAgₓO(x =0, 0.02, 0.04, 0.06, 0.1) NPs by Co-precipitation method

Co-precipitation method has been used to synthesize the Ag doped ZnO NPs. Zinc nitrate, silver nitrate and sodium hydroxide have been used in appropriate ratio to synthesized their nanoparticles. Details of complete synthesis procedure, chemical reactions are given in chapter 2,
section 2.2. The synthesized NPs have been analyzed by different characterization techniques *viz.* XRD, UV-Vis., FESEM, TEM and EDAX.

### 3.3 Result and discussion

#### 3.3.1. Structural properties

The crystalline nature of synthesized ZnO NPs have been confirmed by XRD pattern for different samples in figure 3.1(i & ii). The observed XRD patterns matches with wurtzite structure of ZnO (JCPDS no.36-1451). The peak positions at $2\theta = 31.65, 34.47, 36.26, 47.67, 56.64, 62.90, 66.49, 68.03, 68.80, 72.45$ and $77.23$ with their corresponding (hkl) values $(100), (002), (101), (102), (110), (103), (200), (112), (201), (004)$ and $(202)$ respectively. The position and purity of diffraction peaks in XRD pattern confirms the formation of quality ZnO NPs. Increase in full width half maximum (FWHM) of peaks clearly confirm the transformation towards the formation of nano crystals. As the amount of silver (Ag) increases into ZnO matrix *i.e.* $x=0, 0.02, 0.04, 0.06, 0.1$ w.r.t. Zn$_{1-x}$Ag$_x$O, there is a clear phase of Ag in ZnO observed at $2\theta = 38.22^\circ, 44.20^\circ$ for $x =0.06, 0.1$ respectively. Due to major difference in ionic radii of Ag$^+$ (1.26Å) and Zn$^{2+}$ (0.74Å), there is a shift in the (101) peak position with incorporation of silver in ZnO as shown in figure 3.1(ii). Incorporation of silver via substitution or interstitial site further correlates with diffraction peak (101) shifting to lower or higher $2\theta$ values respectively[33, 34]. In the present case, with doping there is a decrease in $2\theta$ values to lower diffraction angle (as mentioned in table 3.1), which confirms the substitution of silver in ZnO structure.

All the parameters related to alteration in FWHM, intensity ratio between (002) to (101) peaks, peak shifting with silver incorporation into base matrix *i.e.* ZnO [33] are tabulated in table 3.1.

#### 3.3.2. Crystallite size and Strain

The average crystallite size of ZnOAg0, ZnOAg1, ZnOAg2, ZnOAg3 & ZnOAg4 with increasing concentration of silver in ZnO has been calculated by Scherrer equation 3.1 [35] and detail of values are summarized in table 3.1

$$D = \frac{k\lambda}{\beta_{hkl} \cos(\theta)}$$  \hspace{1cm} (3.1)
where $\beta_{hk\ell}$ is full width half maxima (FWHM) of diffracting peak, $k$ is constant values is 0.90, $\lambda$ is X-ray wavelength used in XRD instrument \textit{i.e.} $\lambda = 0.1540$ nm, $D$ is crystallite size and $\theta$ is Bragg’s angle respectively.

\textbf{Figure 3.1:} (i) XRD pattern for pure ZnO NPs and Ag doped ZnO nanoparticles (ZnOAg0, ZnOAg1, ZnOAg2, ZnOAg3 & ZnOAg4) and (ii) enlarged view XRD pattern from 35.6° to 37° ($2\theta$) respectively.
The calculation of micro strain for different nanoparticles has been evaluated by formula in equation (3.2) [36].

\[ \varepsilon = \frac{\beta_{1/2}}{4\tan(\theta)} \]  

where \( \beta_{1/2} \) is FWHM of diffracting peak (101) peak and \( \theta \) is the Bragg’s angle.

With reference to undoped ZnO NPs crystallite size (46.47 nm), there is a decrease in size to 44.44 nm for silver concentration \( x = 0.02 \) (ZnOAg1) in ZnO. The reason behind this decrease in crystallite size with Ag in ZnO is possibly due to some segregation of Ag on ZnO crystal surface (due to difference in ionic radii) in addition to its substitution which restrict the growth of ZnO crystal [37]. Further, with increase in silver doping in ZnO matrix \( i.e. \ x = 0.04, \ 0.06, \ 0.1(\text{ZnOAg2, ZnOAg3, ZnOAg4}) \) the crystallite size increases to 49.59 nm, 51.74 nm and 54.80 nm respectively. The same trend for micro strain variations has been observed as that of crystallite size \( i.e. \) for small crystallite size there is highest strain and the value of strain decreases with increase in crystallite size (table 3.1). This increase in strain value for small crystallite size can be attributed to the increase in surface area of the NPs as compared to the bigger ones. The change in the intensity ratio between 002 to 101 hkl peak for ZnOAg0, ZnOAg1, ZnOAg2, ZnOAg3 and ZnOAg4 is 0.4553, 0.4750, 0.4441, 0.4461 & 0.4891 respectively.

**Table 3.1:** Crystallite size, micro-strain, position and FWHM (101 peak) of Ag doped ZnO nanocomposite

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>D(nm)</th>
<th>Strain (( \varepsilon ) (10(^{-4}) ))</th>
<th>Position of 101 peak with FWHM (deg.)</th>
<th>Intensity ratio of 002 peak to 101 peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnOAg0</td>
<td>46.47</td>
<td>23.90</td>
<td>36.26(0.18)</td>
<td>0.4553</td>
</tr>
<tr>
<td>ZnOAg1</td>
<td>44.44</td>
<td>27.85</td>
<td>36.20(0.21)</td>
<td>0.4750</td>
</tr>
<tr>
<td>ZnOAg2</td>
<td>49.59</td>
<td>22.57</td>
<td>36.22(0.17)</td>
<td>0.4441</td>
</tr>
<tr>
<td>ZnOAg3</td>
<td>51.74</td>
<td>22.40</td>
<td>36.22(0.16)</td>
<td>0.4461</td>
</tr>
<tr>
<td>ZnOAg4</td>
<td>54.80</td>
<td>22.36</td>
<td>36.25(0.15)</td>
<td>0.4891</td>
</tr>
</tbody>
</table>

The variation pattern in the intensity ratio of diffraction peaks (table 3.1) predicts the structural alteration after the doping of silver into ZnO matrix. In figure 3.2, the relation between
crystallite size (D) and strain (ε) with silver doping have been depicted. This relation also confirms the presence of silver in ZnO matrix [37].

**Figure 3.2:** Plot of crystallite size and strain of un-doped and Ag doped ZnO NPs.

### 3.3.3 Optical Study

The absorption spectra and optical band gap study of silver doped ZnO nanoparticles have been investigated using UV-Vis spectroscopy and is depicted in figure 3.3. It is observed that with incorporation of silver into ZnO matrix, there is a shift in the absorption edge from 373.2 nm for ZnO (ZnOAg0) to 377 nm for ZnOAg4 (figure 3.3(i)). The corresponding values are listed in table 3.2. The narrowing of optical band gap with silver doping to ZnO has been observed and shown in table 3.2. There are some reports which suggest that the red shift of $E_{opt}$ with doping is explained on the basis of induced band gap renormalization effect [38]. The sp-d exchange interaction between band electrons of ZnO and localized d-electrons of Ag$^+$ may be responsible for the renormalization effect, which tunes the band gap with respect to pure ZnO. The possible exchange interaction(s-d & p-d) in nanomaterial will lead to correction in valance and conduction band edges to give final shrinked band gap [39].
Figure 3.3: (i) Absorption spectra of ZnOAg0, ZnOAg1, ZnOAg2, ZnOAg3, ZnOAg4 and (ii) optical band gap for corresponding absorption spectra.

Different parameters related to optical properties (i.e. optical band gap, absorption coefficient) of synthesized ZnO NPs have been calculated using equation 3.3 [10]

$$\alpha h\nu = [A(h\nu - E_{opt})]^{1/2} \tag{3.3}$$

where terms A, h\nu, and E_{opt} are called as a constant, photon energy and optical band gap respectively.

In addition, the possible reason for this decrease in E_{opt} is may be due to the existence of oxygen vacancies which leads to an easy transport of electrons in band structure of ZnO NPs [10]. The values of calculated optical band gap (E_{opt}) are summarized in table 3.2.

Table 3.2: Absorption maxima and optical band gap values E_{opt} for ZnOAg0, ZnOAg1, ZnOAg2 and ZnOAg3 & ZnOAg4 respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ZnOAg0</th>
<th>ZnOAg1</th>
<th>ZnOAg2</th>
<th>ZnOAg3</th>
<th>ZnOAg4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption maxima(nm)</td>
<td>373.2</td>
<td>374.2</td>
<td>374.5</td>
<td>374.9</td>
<td>377</td>
</tr>
<tr>
<td>Optical band gap(eV) E_{opt}</td>
<td>3.13</td>
<td>3.07</td>
<td>2.98</td>
<td>2.88</td>
<td>2.75</td>
</tr>
</tbody>
</table>
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The availability of oxygen related defects in nanomaterial will further transform into oxygen vacancies by electrons which get excited from valence band (VB) to conduction band (CB), further narrowing $E_{\text{opt}}$ [39]. The electrons get excited from VB to CB through fermi level of Ag cluster. The excitation of electrons from VB to CB through Ag will proceed until fermi level of Ag and conduction band of ZnO reaches the same level. With the higher concentration of Ag in ZnO will lead to generate more oxygen vacancy and decrease the $E_{\text{opt}}$ values [40,41]. Conclusively, the incorporation of silver in ZnO and possible oxygen vacancies is responsible for narrowing the optical band gap ($E_{\text{opt}}$) of ZnO NPs.

3.3.4 FESEM Study

The surface morphology of ZnO NPs has been investigated by FESEM study and results are shown in figure 3.4.

![FESEM images](image1)

**Figure 3.4:** FESEM images (a) ZnOAg0 (b) ZnOAg1 (c) ZnOAg4.
The addition of silver to ZnO matrix shows decrease in agglomeration and improves the shape of NPs (figure 3.4(b & c)) as compared to the pure ZnO nanoparticles in figure 3.4(a).

### 3.3.5 EDAX and Mapping Study

The elemental presence of components in Ag doped ZnO NPs has been investigated through EDAX measurements and are shown in figure 3.5. Figure 3.5(a) shows the presence of zinc (Zn), oxygen (O) for ZnOAg0. The presence of silver have been confirmed by figure 3.5(b) for ZnOAg4, in addition to presence of zinc (Zn), oxygen (O) elements.

![EDAX spectrum of (a) ZnOAg0 (b) ZnOAg4.](image)

*Figure 3.5: EDAX spectrum of (a) ZnOAg0 (b) ZnOAg4.*
Mapping mode of EDAX used to study the homogeneity of the synthesized NPs content for ZnOAg0 and ZnOAg4 and details are shown in figure 3.6 & 3.7.

**Figure 3.6:** EDAX mapping of ZnOAg0 (a) Mapped area (b) Zinc (c) Oxygen.

**Figure 3.7:** EDAX mapping of ZnOAg4 (a) Mapped area (b) Zinc (c) Oxygen & (d) Silver.
3.3.6 TEM study

The ultra structural morphological information of synthesized ZnO nanomaterials has been analyzed with TEM Hitachi H-7500 (figure 3.8). TEM study confirms the uniform and regular size of nanoparticles. In figure 3.8 (b & c), enhancement in contrast with respect to figure 3.8(a) has been found. The increase in the contrast of TEM images is due to the presence of silver in ZnO matrix. The average particle size observed by TEM study for ZnOAg0, ZnOAg1 and ZnOAg4 are 47 nm, 46 nm and 58 nm, which matches with the XRD results.

![TEM images](image)

**Figure 3.8:** TEM images (a) ZnOAg0 (b) ZnOAg1 (c) ZnOAg4 respectively.
3.3.7 Photo catalytic degradation Study

The dye degradation efficiency of different ZnO NPs has been studied over methylene blue (MB) and brilliant blue (BB) dyes. The optimum concentration of dye solution i.e. 20 ppm and 25 mg of different ZnO NPs were added in degradation reaction under specific condition. The UV-Visible spectroscopy technique has been used to study the effect of synthesized NPs on the absorption maxima of MB and BB dyes. The % dye degradation values have been calculated from equation 3.4 [42, 43]:

\[ \text{% dye degradation} = \frac{C_0 - C}{C_0} \times 100 = \frac{A_0 - A}{A_0} \times 100 \]

where \( C_0, C, A_0, A \) are concentration and absorbance of dye at reaction condition time (0) and (t) minute respectively.

The intensity of absorption peak of MB dye has been found to diminish on interaction of NPs with visible light exposure. The detail of all the dye degradation absorption spectra for MB and BB dyes were summarized in figures 3.9 & 3.10 and all concerned values have been tabulated in table 3.3 and table 3.4 respectively.

MB dye absorbance peak get diminished with respect to its wavelength maxima (662 nm) after 180 minutes interaction of different ZnO NPs with dye solution. The percentage dye degradation efficiency increases for silver doped ZnO from 41.55 to 96.78, 43.70 to 97.59, 44.24 to 97.72, 44.77 to 97.83 & 45.58 to 98.66 % for 20 to 180 minute irradiation time exposure w.r.t. pure ZnO(table 3.3). Under similar condition, changes in degradation of BB dye with pure and silver doped ZnO NPs show the same trend as for MB dye and the respected change in values are 17.95 to 82.15, 32.76 to 94.12, 58.62 to 95.23, 59.43 to 94.62 & 55.38 to 97.36% for same time span. BB dyes have shown drastic dye degradation effect (~ 20% degradation) after 20 minutes of exposure of light. The details of these values are given in table 3.4. The % degradation of MB and BB dyes from 80 min to 120 min is enhanced by ~ 30% and ~ 5 % respectively (tables 3.3 & 3.4). The agglomeration of NPs may lead to the saturation of dye degradation values at 180 min. time period, possibly due to combination of electron/hole mechanism [44, 45]. The saturation of dye degradation values after certain time span is explained on the basis of agglomeration of NPs in dye solution which hinders the transport of active species [46]. This reason may have diluted the basic requirement for dye degradation mechanism. The doping of silver to ZnO may bring
inhomogeneity on the NPs surface making it less available for adsorption of incident light and reactants to react after certain time span of reaction [47]. Figure 3.11 and 3.12 illustrate the pictorial representation of MB and BB dye degradation behavior with different ZnO NPs at different reaction time under visible light exposure.

The doping of silver into ZnO have tuned the optical band gap of ZnO from 3.13 to 2.75 eV and increases the absorption efficiency of incident visible light, which leads to the generation of electron/hole pairs and enhances the dye degradation efficiency [48]. The presence of Ag$^+$ ions in ZnO matrix increase the entrapment of electrons and ultimately enhances the separation of electron/hole from each other. Further, maximum time separation of charge carriers in dye degradation reaction generate more reactive oxygen sites (ROS), which makes further fragmentation of dye.

**Figure 3.9:** Absorption spectral changes of MB with (a) ZnOAg0 (b) ZnOAg1 (c) ZnOAg2 (d) ZnOAg3 (e) ZnOAg4.
Figure 3.10: Absorption spectral changes of BB with (a) ZnOAg0 (b) ZnOAg1 (c) ZnOAg2 (d) ZnOAg3 (e) ZnOAg4.
Figure 3.11: Physical appearance of different samples at different timings for MB dye with ZnO NPs.

Figure 3.12: Physical appearance of different samples at different timings for BB dye with ZnO NPs.
Table 3.3: % Dye degradation of MB with ZnOAg0, ZnOAg1, ZnOAg2, ZnOAg3 and ZnOAg4 with irradiation time & their corresponding rate constant respectively.

<table>
<thead>
<tr>
<th>Name of Sample</th>
<th>Irradiation Time (Min)</th>
<th>Rate Constant (Min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20 Min</td>
<td>40 Min</td>
</tr>
<tr>
<td>ZnOAg0</td>
<td>41.55</td>
<td>42.63</td>
</tr>
<tr>
<td>ZnOAg1</td>
<td>43.70</td>
<td>45.31</td>
</tr>
<tr>
<td>ZnOAg2</td>
<td>44.24</td>
<td>46.65</td>
</tr>
<tr>
<td>ZnOAg3</td>
<td>44.77</td>
<td>46.54</td>
</tr>
<tr>
<td>ZnOAg4</td>
<td>45.58</td>
<td>64.08</td>
</tr>
</tbody>
</table>

Degradation Efficiency (%) for MB

Table 3.4: % Dye degradation of BB with ZnOAg0, ZnOAg1, ZnOAg2, ZnOAg3 and ZnOAg4 with irradiation time & their corresponding rate constant respectively.

<table>
<thead>
<tr>
<th>Name of Sample</th>
<th>Irradiation Time (Min)</th>
<th>Rate Constant (Min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20 Min</td>
<td>40 Min</td>
</tr>
<tr>
<td>ZnOAg0</td>
<td>17.95</td>
<td>39.15</td>
</tr>
<tr>
<td>ZnOAg1</td>
<td>32.76</td>
<td>68.76</td>
</tr>
<tr>
<td>ZnOAg2</td>
<td>58.62</td>
<td>71.50</td>
</tr>
<tr>
<td>ZnOAg3</td>
<td>59.43</td>
<td>71.60</td>
</tr>
<tr>
<td>ZnOAg4</td>
<td>55.38</td>
<td>66.43</td>
</tr>
</tbody>
</table>
The detail values of % dye degradation for MB and BB dyes in pictorial form has been depicted in figure 3.13(a & b).

![Figure 3.13: (a) Pictorial representation of % dye removal for MB and (b) BB dye.](image)

The enhanced crystallinity of different ZnO NPs can be correlated with their decrease in FWHM values for 101 peak as tabulated in table 3.1 [49]. The increased crystallinity of ZnO NPs improves the generation of electron/hole with their least recombination, which enhances the dye degradation efficiency [50].
The ZnO NPs adsorption effect with both dyes has also been examined under dark environment. In this study no prominent effects have been found which affect the overall photocatalytic behavior of NPs with dye.

The first order rate constant ($k_{obs}$) for MB and BB with different ZnO NPs is calculated by plotting graph between $\ln(C/C_0)$ and irradiation time as shown in Figure 3.14(a & b). The inset view in figure 3.14(a & b) gives the linear fit of MB and BB observed plots. The values of rate constant for MB and BB increases from 0.022 to 0.026 and 0.013 to 0.019 for ZnOAg0 to ZnOAg4 respectively.

![Figure 3.14](image)

**Figure 3.14:** (a & b) Plots of $\ln(C/C_0)$ versus irradiation time for photo degradation of MB & BB under visible light.

The higher values of rate constant (0.022 to 0.026 min$^{-1}$) for MB dye clearly justify the observed higher dye degradation efficiency values in comparison to BB dyes values (0.013 to 0.019 min$^{-1}$). All related observed values are summarized in table 3.3 & 3.4.

### 3.3.8 Mechanism of Photo-catalytic reaction

The mechanism behind the dye degradation of ZnO NPs with dyes may have two possible reasons. The first one is explained with the generation of electron/hole by ZnO under exposure of suitable light source. The limited recombination of electron/hole and their maximum separation [18] maintained by presence of silver particles and oxygen defects leads to effective dye degradation behavior. Second factor is; the dye itself which under exposure of incident light goes...
to excited state (sensitizer) and transfer electrons to electron acceptor species. Dye after giving electrons, exists as a cationic free radical as shown in figure 3.15. Further, the ionic form of dye gets easily degraded due to the presence of different oxidizing species generated during degradation mechanism shown in figure 3.15.

**Figure 3.15:** Schematic representation of dye degradation in presence of ZnO NPs (catalyst) and its proposed photo-catalytic reaction mechanism for same.

The generated electron and hole from conduction and valence band under photo excitation get separated on the surface of ZnO NPs. The photo generated electron with reacting species in dye degradation mechanism produce super oxide anion radical $O_2^-$, creates $H_2O_2$ and $OH^-$ radical [51]. The already generated hole will further generate active hydroxyl ion from water. The presence of oxygen vacancies on the photo catalyst surface avoid the combination of electron/hole by trapping the electrons on the NPs surface. The dye mineralization also helps in efficient dye degradation mechanism by photo generated electrons which follows the creation of superoxide anion and hydroxyl ion [52]. The different bondings which exist in dye structure like C-N, C=O, C-S, N=N, C=C etc., get fragmented by hydroxyl ion(OH$^-$) and are finally converted into $CO_2$ and other inorganic species like $NH_4^+$, $NO_3^-$, $SO_4^{2-}$ etc. The proper and appropriate exposure of incident light energy on the photocatalyst surface enhances the reaction with $O_2^-$ & $OH$ ions increasing the dye degradation efficiency.

The schematic representation of dye degradation mechanism is given in figure 3.15, from which following conclusions can be drawn: (a) under exposure of visible light, ZnO NPs act as
the source of electron / hole as shown by eq.(i); (b) the enrichment of electrons on ZnO surface is contributed by transfer of delocalized n-electrons to conduction band of photocatalyst surface (schematic representation in figure 3.15); (c) generation of oxygen related defects (eq.iv) and trapping of electrons on photocatalyst surface managed by availability of oxygen vacancy and silver on the their surface which delays the recombination of electron/hole; (d) induced holes attack the hydroxyl ion (OH\(^-\)) and convert it into its radical form (‘OH) (eq.iii); (e) trapping of photo induced electrons become possible after interaction of species like adsorbed oxygen converted into super oxide radical anion(O\(_2^–\)) (eq.iv); (f) the presence of hydroxyl (‘OH) radical and super oxide radical anion (O\(_2^–\)) plays a crucial role in dye degradation mechanism (eq.v)[53].

3.3.9 Comparison of degradation ability between MB and BB

In order to explain the reason behind the dye degradation behavior of any dye can be correlated with the presence of chromophoric group in dye structure. In the present study, MB and BB dyes have different behavior from each other with respect to their molecular structure, functional group and ionization state in solution. The number of chromphores present on the MB and BB dye decides their stabilization on interaction with reducing species in degradation reaction. The MB dyes have possibly four chromophoric groups (highlighted by arrow) and four methyl groups (highlighted by arrow) in figure 3.16, whereas the BB dyes have seven active sites and no methyl group. The destabilization of chromophoric sites present in dyes may be due the reaction with the species i.e. ‘OH or O\(_2^–\) etc. generated from ZnO surfaces [54]. The presence of four methyl groups in MB dyes as compared to BB dye will make +I (inductive) effect on the structure of MB and stabilizes it as compared to BB dye. Due to this reason, initially there is slow degradation effect in MB dyes in comparison to BB dye from 20 minute to 40 minute irradiation exposure time. In continuation, for 80 to 120 minute interaction time, % degradation of MB dye drastically increases by ~ 20% in comparison to BB dye (~ 10%).

The possible reason behind the enhanced degradation effect for MB dyes may be due to sufficient availability of attacking sites on dye structure compared to BB dye. The improved and enhanced dye degradation ability of MB dye in comparison to BB dye with Ag doped ZnO NPs is mainly due to presence of less chromophoric sites (group) on its structure as compare to BB dye structure.
3.4 Conclusion

In present study the preparation of silver doped ZnO NPs through co-precipitation method is reported. The structural purity of synthesized ZnO NPs has been confirmed by XRD technique. The crystallite size changed from 46.67 nm to 54.80 nm and lattice strain changed from 23.90 x10^{-4} to 22.36 x 10^{-4} for pure ZnO to maximum silver doped ZnO NPs respectively. XRD, EDAX and UV-Visible spectroscopy studies have indicated the presence of silver in ZnO matrix. The morphological information of synthesised nanoparticles is obtained from FESEM and TEM study. The dye degradation capabilities of different silver doped ZnO NPs have been studied under visible light exposure. The % degradation efficiency for ZnOAg0, ZnOAg1, ZnOAg2, ZnOAg3 and ZnOAg4 of MB increased from 41.55 to 96.78, 43.70 to 97.59, 44.24 to 97.72, 44.77 to 97.83, and 45.58 to 98.66% respectively. Similar trend has been observed for BB dye. The improved dye degradation efficiency of MB dye also has been confirmed by its higher rate constant (0.022 to 0.026 min^{-1}) values in comparison to BB dye (0.013 to 0.019 min^{-1}). The initial degradation efficiency of MB have slow propagation due to + I effect by –CH\(_3\) (methyl group) on its structure. These factors render the MB dye adherence from attack of oxidizing species generated in photo catalysis mechanism. Further, with increase in reaction time of dye and photocatalyst, the MB degradation efficiency increases in comparison to BB dye because of less chromophoric sites in MB dye compared to BB dye. Finally, the silver doped ZnO NPs synthesized by co precipitation method has been proposed as useful, economical with effective application based treatment of polluted water coming from textile, pharmaceutical industry etc.
REFERENCES


