5. ZnO based coupled oxides for photocatalytic degradation of textile effluent under visible light

5.1 Introduction

The photodegradation efficiency of ZnO can be improved by different techniques like doping with a metal or a nonmetal; or forming composites such as ZnO/metal, ZnO/semiconductor or coupled oxides [1-6]. The prevention of electron-hole recombination process is considered as one of the most important factors that enhance the photocatalytic activity. The coupled semiconductor materials have two different energy-level systems which play an important role in achieving charge separation. Coupling of different semiconductor oxides can reduce the band gap, extending the absorbance range to visible light region and consequently achieving a higher photocatalytic activity [7-10]. These systems also exhibit higher degradation of organic pollutants. The CuO/TiO$_2$ [11], WO$_3$/TiO$_2$ [12], ZnO/TiO$_2$ [13], ZnO/SnO$_2$ [7] and TiO$_2$/MgO [14] are the types of coupled semiconductors that were successfully synthesized. These composite materials are used for other applications such as sensors, solar cells, antibacterial activity and so on.

In the discussion of the previous chapter, it is noted that modification of ZnO with Ag effectively shifted the photocatalytic activity from UV to visible light. The main aim of this chapter represents the photocatalytic performance of ZnO with the use of metal oxides. Nanocomposites comprises of ZnO along with metal oxides (CdO, CuO, Mn$_2$O$_3$ and CeO$_2$). These ZnO-X nanocomposites (99:1, 97:3, 95:5, 90:10, 80:20, 70:30, 60:40 and 50:50) were prepared by varying the weight percentage of ZnO and metal oxide (X). These materials were characterized by various techniques and the performances of photodegradation efficiency were studied. The best catalyst from each nanocomposite was chosen and the degradation of real effluent was done under visible light.

5.2 Coupling of ZnO/CdO semiconductors

Cadmium oxide (CdO) is an important semiconductor with a bandgap of ~2.2 eV [15, 16]. This is a promising catalyst for opto-electronic applications viz transparent electrodes, solar cells, phototransistors, photodiodes and gas sensors. In literature, successful preparation of titanium dioxide coupled with cadmium oxide by electro-spinning method and its application in photocatalytic degradation under UV-light has been reported [17]. There are very few reports on the coupling of zinc oxide with
cadmium oxide [18-20]. The present work discusses the synthesis of ZnO coupled with CdO (99:1, 97:3, 95:5, 90:10, 80:20, 70:30, 60:40 and 50:50) by thermal decomposition method. The prepared samples are characterized by different techniques and used for the photodegradation of organic dyes under visible light.

5.2.1 Experimental procedure

5.2.1.1 Materials

Zinc acetate dihydrate (Rankem) and cadmium acetate (Rankem) used in the present study were of analytical reagent grade. Methylene blue (MB) and methyl orange (MO) were from Aldrich chemicals. All aqueous solutions were prepared using double distilled water.

5.2.1.2 Synthesis of ZnO/CdO composites

Before the actual synthesis of catalysts, thermogravimetric analyses were carried out in order to determine the decomposition temperatures of zinc acetate dihydrate and zinc acetate dihydrate with cadmium acetate mixture (figure 5.1).

![TGA curve of (a) Zinc acetate dihydrate and (b) Zinc acetate dihydrate mixed with cadmium acetate (95:5).](image)

Figure 5.1 TGA curve of (a) Zinc acetate dihydrate and (b) Zinc acetate dihydrate mixed with cadmium acetate (95:5).
Various weight percentages of ZnO/CdO nanocomposites were synthesized by taking zinc acetate dihydrate and cadmium acetate (in the weight ratios of 99:1, 97:3, 95:5, 90:10, 80:20, 70:30, 60:40 and 50:50) and were mixed together. The mixtures were ground for 60 minutes and then calcined at 350 °C for 3 hours in a muffle furnace. During this process, the temperature was raised at a uniform rate of 4 °C/min. After the heat treatment, the sample was cooled to room temperature naturally.

5.2.2 Results and discussion

5.2.2.1 XRD analysis

The powder X-ray diffraction patterns were carried out in order to get the structural information of ZnO, CdO and ZnO/CdO samples. The XRD pattern of ZnO is shown in figure 5.2 (a) and the diffraction patterns are indexed. The ZnO exhibits hexagonal structure (JCPDS No: 79-0208) and the lattice constant values are given in table 5.1. The diffraction pattern of the CdO sample is depicted in figure 5.2 (b). The peaks (111), (200) and (220) indicate the cubic structure with lattice constant value a=4.709(6) Å which coincides with the JCPDS No: 73-2245. The figures 5.2 (c) and (d) show the XRD pattern of 1% and 3% of CdO. Since the CdO percentage is very low, the CdO peaks were not visible in the above samples.

When the weight percentage of cadmium oxide is increased in the sample, the CdO peaks were visible in the XRD pattern (figures 5.2 (e) to (j)). It is clearly observed from the figures 5.2 (e) to (j) that the intensity of ZnO peaks decrease with increasing cadmium oxide weight percentage. Compared with ZnO peaks, the composite peaks are shifted to lower angle. The shift in the peaks was reasonable because the ionic radius of Cd$^{2+}$ is larger than that of Zn$^{2+}$. This observation is similar to the previous report by Ziabari et.al [21]. The crystallite size of the prepared samples was calculated using Scherrer formula. The lattice parameters and the crystallite sizes (D) are tabulated in table 5.1. Hence, the XRD results describe the formation of ZnO/CdO and no other impurity peak was detected.
Chapter 5

Figure 5.2 The XRD pattern of a) ZnO, b) CdO, c) ZnO/CdO (99:1), d) ZnO/CdO (97:3), e) ZnO/CdO (95:5), f) ZnO/CdO (90:10), g) ZnO/CdO (80:20), h) ZnO/CdO (70:30), i) ZnO/CdO (60:40) and j) ZnO/CdO (50:50)

Table 5.1 Lattice parameter and crystallite size (D) of all the prepared samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>ZnO Hexagonal 79-0208</th>
<th>CdO Cubic 73-2245</th>
<th>ZnO D (nm)</th>
<th>CdO D (nm)</th>
</tr>
</thead>
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<tr>
<td>ZnO</td>
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<td></td>
<td>24</td>
<td>-----</td>
</tr>
<tr>
<td>CdO</td>
<td></td>
<td>4.709(6)</td>
<td>49</td>
<td>-----</td>
</tr>
<tr>
<td>ZnO/CdO(1)</td>
<td>3.265(7)</td>
<td>5.214(3)</td>
<td>-----</td>
<td>39</td>
</tr>
<tr>
<td>ZnO/CdO(3)</td>
<td>3.263(6)</td>
<td>5.211(3)</td>
<td>-----</td>
<td>38</td>
</tr>
<tr>
<td>ZnO/ CdO(5)</td>
<td>3.264(6)</td>
<td>5.213(2)</td>
<td>4.696(2)</td>
<td>30</td>
</tr>
<tr>
<td>ZnO/CdO(10)</td>
<td>3.263(3)</td>
<td>5.221(2)</td>
<td>4.698(2)</td>
<td>26</td>
</tr>
<tr>
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<td>3.269(6)</td>
<td>5.221(3)</td>
<td>4.707(6)</td>
<td>30</td>
</tr>
<tr>
<td>ZnO/CdO(30)</td>
<td>3.266(6)</td>
<td>5.222(3)</td>
<td>4.709(4)</td>
<td>32</td>
</tr>
<tr>
<td>ZnO/CdO(40)</td>
<td>3.266(1)</td>
<td>5.218(3)</td>
<td>4.706(6)</td>
<td>33</td>
</tr>
<tr>
<td>ZnO/CdO(50)</td>
<td>3.267(6)</td>
<td>5.219(2)</td>
<td>4.706(6)</td>
<td>35</td>
</tr>
</tbody>
</table>
5.2.2.2 FE-SEM analysis

The FE-SEM images of ZnO, CdO and ZnO/CdO (99:1, 97:3, 95:5, 90:10, 80:20, 70:30, 60:40 and 50:50) samples were shown in figure 5.3. The ZnO image (figure 5.3 (a)) indicates the randomly dispersed nanorods which show irregular sizes. Figure 5.3 (b) represents the pyramid shaped CdO. Figures 5.3 (c to h) show that the length of the nanorods decreases with the increasing wt% of CdO upto 30 wt%. Close observation of the images shows the nanorods along with some spherical shaped particles. With the increase in CdO content upto 50 wt%, the image represent agglomerated nanoparticles as shown in the figures 5.3 (i) and (j). Thus, the addition of CdO influences the size and morphology of ZnO by its involvement in the nucleation and growth [22]

Figure 5.3 The FE-SEM images of (a) ZnO, (b) CdO, (c) ZnO/CdO (99:1) and (d) ZnO/CdO (97:3)
Figure 5.3 The FE-SEM images of (e) ZnO/CdO (95:05), (f) ZnO/CdO (90:10), (g) ZnO/CdO (80:20), (h) ZnO/CdO (70:30), (i) ZnO/CdO (60:40) and (j) ZnO/CdO (50:50)
5.2.2.3 EDX spectroscopy

The samples were analyzed through energy dispersive X-ray spectroscopy for identifying the presence of elements. The EDX spectra of ZnO, CdO and ZnO/CdO (90:10 and 70:30) samples were displayed in figure 5.4. It was visibly seen from the figure 5.4 (a), the ZnO samples composed of Zn and O. The EDX spectrum of CdO shown in figure 5.4 (b) confirms the existence of cadmium and oxygen. Figures 5.4 (c) and (d) shows 10 wt% and 30 wt% of CdO along with ZnO samples and this clearly indicates the presence Zn, Cd and O. Therefore, the EDX spectra have confirmed the elemental composition of ZnO/CdO without any impurities.

![Figure 5.4](image)

Figure 5.4 The EDX spectra of (a) ZnO, (b) CdO, (c) ZnO/CdO (90:10) and (d) ZnO/CdO(70:30)
5.2.2.4 TEM analysis

The shape and size of the synthesized nanocomposite ZnO/CdO (95:5) were determined by TEM analysis. The TEM image has exposed that the ZnO/CdO nanocomposites are composed of nanorods seen in figure 5.5 (a). The diameters of ZnO/CdO nanorods range between 40-50 nm and the lengths are between 300-500 nm.

Figure 5.5 (a) The TEM image of ZnO/CdO (95:5)

The EDX spectrum of ZnO/CdO (95:5) sample is presented in figure 5.5 (b). This spectrum signifies that the elements zinc, cadmium and oxygen were present in the sample and no other impurities are detected in the EDX spectrum.

Figure 5.5 (b) The EDX spectrum of ZnO/CdO (95:5)
5.2.2.5 UV-Vis absorption spectra

The room temperature UV–Vis absorption spectrum of the ZnO, CdO and ZnO/CdO (99:1, 97:3, 95:5, 90:10, 80:20, 70:30, 60:40 and 50:50) are shown in figure 5.6. It is clearly observed that the ZnO absorption edge is \(~360\) nm and the corresponding wavelength exists in the UV region. The absorption edge of pure CdO is \(~490\) nm which is in the visible region. The ZnO/CdO nanocomposites show the absorption wavelength in the range from 400 to 500 nm. The absorption bands of composite materials are wider and have extended to the red region as compared to ZnO which is in the blue region. The absorption edge of ZnO/CdO nanocomposites lies in the visible region. Therefore, the photocatalytic reaction under visible light will increase the number of photogenerated electrons and holes.

**Figure 5.6** UV-vis absorption spectra of a) ZnO, b) CdO, c) ZnO/CdO (99:1), d) ZnO/CdO (97:3), e) ZnO)/CdO (95:5), f) ZnO/CdO (90:10), g) ZnO/CdO (80:20), h)ZnO/CdO (70:30), i) ZnO/CdO (60:40) and j) ZnO/CdO (50:50)
5.2.2.6 XPS analysis

The oxidation states and the element present in the surface were examined by X-ray photoelectron spectroscopy (XPS) analysis. All binding energies were calibrated using carbon C 1s (284.6 eV) as the reference. The presence of C comes from the hydrocarbon contaminants which is a common feature of XPS analysis. Figure 5.7 (a) shows the XPS survey spectrum. It confirms ZnO/CdO (80:20) nanocomposite material which are composed of Zn, Cd and O. Figures 5.7 (b) and (c) exhibit the high resolution XPS spectra of Zn 2p, and Cd 3d respectively. As shown in figure 5.7 (b), it is observed that the binding energy of zinc is 1021.2 eV and 1044.2 eV for 2p\textsubscript{3/2} and 2p\textsubscript{1/2} states. These values agree well with the literatures [23]. Figure 5.7 (c) shows the high resolution XPS spectrum of cadmium. It consists of 3d\textsubscript{5/2} and 3d\textsubscript{3/2} states of cadmium and the corresponding binding energies 405.3 eV and 412.1 eV, respectively. These values are well coincide with the previously reported values [24-27]. There is no evidence for the formation of metallic Zn and Cd. The three types of oxygen are represented in figure 5.7 (d). The binding energy values at 529.8 eV, 532.4 eV and 534.9 eV are associated with CdO, ZnO and the surface hydroxyl group respectively [24]. Hence, XPS spectra have confirmed that the sample was composed of 2+ states of ZnO and CdO.

![Figure 5.7 (a) XPS survey spectrum of ZnO/CdO (80:20) sample](image-url)
Figure 5.7 (b) High resolution scanning XPS spectrum of Zinc

Figure 5.7 (c) High resolution scanning XPS spectrum of Cadmium
5.2.2.7 BET analysis

The surface area of the nanocomposite material was determined through BET analysis. The specific surface area of pure ZnO is compared with ZnO/CdO (90:10 and 50:50) composites and the values are 8.7 m² g⁻¹, 13.2 m² g⁻¹ and 7.4 m² g⁻¹ respectively. The 10 wt% of CdO sample shows higher surface area and the surface area decreases for 50 wt% of CdO. The decrease in surface area is due to the deposition of excess crystalline CdO on the surface of ZnO. These results are similar to Michalow et al. [28].

5.2.3 Photocatalytic degradation under visible light illumination

5.2.3.1 MB and MO degradation

The photocatalytic activity of ZnO, CdO and ZnO/CdO (99:1, 97:3, 95:5, 90:10, 80:20, 70:30, 60:40 and 50:50) samples were tested to degrade the model organic dyes. The preparation of model dyes and the self designed photocatalytic reactor were described in chapter 3. The change in optical absorption spectra of MB and MO by ZnO/CdO (90:10) catalyst under visible light irradiation for different time intervals was shown in figures 5.8 ((a) and (b)). The disappearance of the band at 664 nm/464 nm indicates that MB/MO has been photodegraded by ZnO/CdO within 3 hours of irradiation time. Time course degradation curves for MB and MO were shown in figures 5.9 and
5.10. The de-colouration of MB and MO takes place with CdO and ZnO/CdO samples. From the figures, it is observed that there is no decolouration in the presence of pure ZnO due to its larger bandgap and the pure CdO sample indicates 13% and 11% degradation of MB and MO. The ZnO/CdO (90:10) sample shows higher degradation efficiency (98% of MB and 93% of MO) compared with other prepared samples during 3 hours irradiation time.

**Figure 5.8 (a)** The change in absorption spectra of MB using ZnO/CdO (90:10) catalyst for different irradiation periods under visible light.

**Figure 5.8 (b)** The change in absorption spectra of MO using ZnO/CdO (90:10) catalyst for different irradiation periods under visible light.
Figure 5.9 Time dependent degradation curve of MB at 664 nm using a) ZnO, b) CdO, c) ZnO/CdO (99:1), d) ZnO/CdO (97:3), e) ZnO/CdO (95:5), f) ZnO/CdO (90:10), g) ZnO/CdO (80:20) h) ZnO/CdO (70:30), i) ZnO/CdO (60:40) and j) ZnO/CdO (50:50) catalysts

Figure 5.10 Time dependent degradation curve of MO at 464 nm using a) ZnO, b) CdO, c) ZnO/CdO (99:1), d) ZnO/CdO (97:3), e) ZnO/CdO (95:5), f) ZnO/CdO (90:10), g) ZnO/CdO (80:20) h) ZnO/CdO (70:30), i) ZnO/CdO (60:40) and j) ZnO/CdO (50:50) catalysts
5.2.3.2 Photocatalytic mechanism

The schematic diagram (Figure 5.11) represents the photocatalytic mechanism of the composite material. The conduction and valence band positions of CdO and ZnO are determined using the following formula [10]

\[ E_{vb} = X - E_e + 0.5 E_g \] (5.1)

Where \( E_{vb} \) is the valence band potential, \( X \) is the electronegativity of the semiconductor, which is the geometric mean of the electronegativity of the constituent atoms. The electronegativity value for CdO and ZnO are 5.71 eV and 5.79 eV respectively [29]. \( E_e \) is the energy of free electrons on the hydrogen scale (~4.5 eV) and \( E_g \) is band gap energy of the semiconductor. The conduction band of CdO and ZnO are very close to each other. The injection of electrons from the conduction band of CdO into conduction band of ZnO particles is expected to retard the back reaction between the photogenerated charge carriers. This process of the hole trapping which is facilitated in the mixed semiconductor system would increase the efficiency. Thus, the efficiency of photogenerated electron-hole in ZnO/CdO could be higher than those of pure ZnO and CdO [5]. Also ZnO/CdO photocatalyst shows red shift in the absorption wavelength range (Figure 5.6) compared to ZnO, which would improve its photocatalytic activity in the visible light.

![Diagram of Photocatalytic Mechanism](image)

**Figure 5.11** The schematic diagram represents the photocatalytic mechanism of ZnO/CdO composite
5.2.3.3 Degradation of textile effluent

The high efficiency catalyst ZnO/CdO (90:10) was further used to study the decolouration of industrial effluent under visible light irradiation. The preparation of textile effluent was described in chapter 4 and the self designed photocatalytic reactor was discussed in chapter 3. Figure 5.12 represents the change in absorption of industrial effluent solution. The decrease in the absorption band with increase in irradiation time was evidently shown in the figure 5.12. Most of the textile effluent has been degraded within 7 hours using ZnO/CdO (90:10) as a catalyst under visible light irradiation. It was found that more than 85% of the selected catalyst (ZnO/CdO (90:10)) was achieved during the photocatalytic activity of textile effluent.

![Figure 5.12](image.png)

Fig 5.12 The change in absorption spectra of textile effluent using ZnO/CdO (90:10) catalyst for different exposure time under visible light irradiation

Among the prepared samples, the ZnO/CdO (90:10) has shown the best photocatalytic degradation efficiency for the two common dyes under visible light irradiation. Further, the high efficiency catalyst effectively degrades the textile effluent with the achievement of 85% decolouration in 7 hours under visible light irradiation.
5.3 Coupling of ZnO/CuO semiconductors

Copper oxide (CuO) is a semiconductor material with a narrow band gap (1.7 eV). It is non-toxic and its constituents are available in abundance. CuO has received widespread attention because of its various applications in electronic and optoelectronic devices such as lithium ion electrode materials, heterogeneous catalysts, gas sensors and solar cells [30-33]. ZnO coupled with CuO has already been proposed for various applications such as conductivity studies, photocatalytic activity, magnetic properties and gas sensors [34-38] by researchers. The ZnO coupled with CuO (99:1, 97:3, 95:5, 90:10, 80:20, 70:30, 60:40 and 50:50) samples were prepared by thermal decomposition method. The prepared samples were characterized by various techniques; the results are discussed in detail. The catalysts were used for the photocatalytic degradation of methylene blue and methyl orange under visible light irradiation. Further the sample exhibiting the best photocatalytic activity was employed for the degradation of textile effluent.

5.3.1 Experimental procedure

5.3.1.1 Materials

The precursors involved in the preparation of ZnO/CuO nanocomposites, Zinc acetate dihydrate (Rankem) and copper (II) acetate monohydrate (Rankem) were of analytical reagent grade.

5.3.1.2 Synthesis of ZnO/CuO composites

To prepare ZnO/CuO, different weight percentages of zinc acetate dihydrate and copper (II) acetate monohydrate (in the weight ratios of 99:1, 97:3, 95:5, 90:10, 80:20, 70:30, 60:40 and 50:50) were mixed and ground for 1 h. This was calcined in an alumina crucible at 350 °C for 3 h using a muffle furnace in air atmosphere. During this process, the temperature was raised at a uniform rate of 4 °C/min. After the heat treatment, the sample was cooled to room temperature naturally. Before the actual synthesis of catalysts, thermogravimetric analyses were carried out in order to determine the decomposition temperatures of zinc acetate dihydrate and zinc acetate dihydrate mixed with copper (II) acetate monohydrate (figure 5.13). Figure 5.13 (b) shows the TGA graph of zinc acetate dihydrate mixed with copper (II) acetate monohydrate nanocomposite (95:5) system in the same temperature range. A weight loss of 51.5%, in the range of 160–320 °C indicates the decomposition of acetates and the formation of oxides.

108
5.3.2 Result and discussion

5.3.2.1 XRD analysis

The Powder X-ray diffraction patterns of ZnO, CuO and ZnO/CuO samples were shown in figure 5.14. The XRD pattern of ZnO is shown in figure 5.14 (a), which exhibits (100), (002), (101), (102), (110), (103), (200), (112) and (201) characteristic peaks of ZnO with hexagonal structure. The lattice parameter values are shown in table. 5.2. The lattice parameters of pure ZnO sample match well with the JCPDS file no: 79-0208. For the comparison purpose, CuO is prepared by the same method at the same temperature and the XRD result is shown in figure 5.14 (b). The characteristic peaks of the prepared CuO were indexed to monoclinic structure and the lattice constant values are similar to JCPDS file no: 89-5899. Figures 5.14 (c, d and e) represent the samples in which CuO (1%, 3% and 5%) is coupled with ZnO. When the CuO content is ≤5 wt% the reflection peaks (CuO) have very low intensity. So we cannot find out the lattice parameters in the XRD pattern (Figures 5.14 c, d and e) for these samples. The pattern of samples containing 10% to 50% CuO coupled with ZnO are shown in figures 5.14 (f) to (j), which clearly indicates the formation of composite ZnO/CuO. No other segregation of phases was detected in the XRD pattern and lattice parameter values of all prepared samples are shown in Table 5.2. Hence the XRD results indicate the formation of ZnO/CuO composite.
Figure 5.14: The XRD pattern of a) ZnO, b) CuO, c) ZnO/CuO (99:1), d) ZnO/CuO (97:3), e) ZnO/CuO (95:5), f) ZnO/CuO (90:10), g) ZnO/CuO (80:20) h) ZnO/CuO (70:30), i) ZnO/CuO (60:40) and j) ZnO/CuO (50:50).

Table 5.2: Lattice parameter and crystallite sizes (D) for prepared samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ZnO Hexagonal 79-0208</th>
<th>CuO Monoclinic 89-5899</th>
<th>ZnO D (nm)</th>
<th>CuO D (nm)</th>
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<td>a(Å)</td>
<td>c(Å)</td>
<td>a(Å)</td>
<td>b(Å)</td>
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<tr>
<td>ZnO</td>
<td>3.262(9)</td>
<td>5.206(3)</td>
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<td>----</td>
</tr>
<tr>
<td>CuO</td>
<td>-</td>
<td>-</td>
<td>4.701(2)</td>
<td>3.430(4)</td>
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<td>ZnO/CuO(3)</td>
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</table>
5.3.2.2 FE-SEM and BET analysis

The field emission scanning electron microscopy (FE-SEM) images of ZnO, CuO and 1 wt% CuO were shown in figures 5.15 (a), (b) and (c) respectively. The FE-SEM image of CuO sample is shown in figure 5.15 (b) revealed a large number of aggregated spherical shaped nanoparticles. Figures 5.15 (a) and (c) indicate that the particles are randomly distributed nanorods with an average diameter of ~35 nm and a length of 500 nm. Figures 5.15 (c) and (d) show 3 wt% and 5 wt% CuO doped samples. The length of the rod decreases to 200 nm. For the samples 10 wt% to 50 wt% CuO the FE-SEM images are shown in figures 5.15 (e) to (j) and the length is found to be around 50 -100 nm. Thus, addition of CuO may influence the size and morphology of ZnO by its involvement in the nucleation and growth [22]. It is evident from the observed FE-SEM images that the size of the nanorods decreases with an increase in the percentage of CuO.

Figure 5.15 The FE-SEM images of (a) ZnO, (b) CuO, (c) ZnO/CuO (99:1) and (d) ZnO/CuO (97:3)
The BET surface area of 5 wt.% of CuO (15.4 m$^2$/g) sample is comparatively higher than ZnO (8.7 m$^2$/g) due to the lower particle size. The surface area of 50 wt.% CuO (9.7 m$^2$/g) decreases which might be due to the deposition of excess crystalline CuO on the surface of ZnO. A similar observation has been recently reported by Leghari et al. [39].

**Figure 5.15** The FE-SEM images of (e) ZnO/CuO (95:5), (f) ZnO/CuO (90:10), (g) ZnO/CuO (80:20), (h) ZnO/CuO (70:30), (i) ZnO/CuO (60:40) and (j) ZnO/CuO (50:50)
5.3.2.3 EDX spectroscopy

The presence of elements in the ZnO, CuO and ZnO/CuO (95:5 and 80:20) nanocomposites were analyzed using energy dispersive X-ray spectroscopy and were displayed in figure 5.16. It can be seen from the figure 5.16 (a), the ZnO samples are composed of Zn and O. The EDX spectra of CuO shown in figure 5.16 (b) indicates the presence of copper and oxygen. Figures 5.16 (c) and (d) shows 5 wt% and 20 wt% for CuO along with ZnO samples and this clearly indicates the presence of Zn, Cu and O without any impurities.

Figure 5.16 The EDX spectrum of (a) ZnO, (b) CuO, (c) ZnO/CuO(95:5) and (d) ZnO/CuO(80:20)
5.3.2.4 TEM analysis

TEM analysis were carried out to identify the shape and size of the synthesized ZnO/CuO(95:5) nanocomposites. As shown in figure 5.17, the TEM image of ZnO/CuO (95:5) symbolizes nanorod-shaped particle. The ZnO/CuO nanorods have diameters ranging between 30-40 nm and the length ranging between 150-200 nm.

![TEM image of ZnO/CuO (95:5)](image)

**Figure 5.17** The TEM image of ZnO/CuO (95:5)

5.3.2.5 XPS analysis

XPS analysis is performed to analyze the chemical composition and oxidation states of ZnO/CuO (95:5) nanocomposites. The XPS survey spectrum is shown in figure 5.18. The figure indicates the presence of Zn, Cu, O and a small amount of carbon. The presence of C comes from the hydrocarbon contaminants which is a common feature of XPS analysis. The binding energy of C 1s (284.6 eV) is used to calibrate the XPS spectra. The high resolution XPS spectra for Zn, Cu and O elements are shown in figures 5.18 (b), (c) and (d) respectively. Figure 5.18 (b) shows the core level of Zn 2p XPS spectrum and the corresponding binding energies are 1021.5 eV and 1044.2 eV for 2p_{3/2} and 2p_{1/2} states.
Figure 5.18 (a) XPS survey spectrum of ZnO/CuO (95:5)

Figure 5.18 (b) High resolution XPS spectrum of Zinc
Figure 5.18 (c) High resolution XPS spectrum of Copper

Figure 5.18 (d) High resolution XPS spectrum of Oxygen
The high resolution XPS spectrum of Cu is shown in figure 5.18 (c). The spectrum reveals the core level of Cu 2p3/2 and Cu 2p1/2 transitions along with the satellite peak and the corresponding binding energies are 932.7 and 952.8 eV respectively. Thus, it clearly indicates the existence of Cu in 2+ states and this was confirmed by earlier reports [40- 41]. The satellite peaks may occur when the outgoing photoelectron simultaneously interacts with a valence electron and excites it (shakes it up) to a higher-energy level; the energy of the core electron is then reduced slightly giving a satellite structure a few electron volts below (but above on a binding-energy scale) the core level position [42]. There was no evidence for the formation of metallic Zn and Cu. The high resolution spectrum of oxygen is shown in figure 5.18 (d). The figure depicted three types of oxygen species represented in the ZnO/CuO composite surfaces. The binding energies of oxygen peaks at 529.9 eV, 531.4 eV and 532.4 eV are associated with CuO, ZnO and the surface hydroxyl group [24]. Hence, the XPS result confirmed that the ZnO/CuO sample is composed of Zn$^{2+}$, Cu$^{2+}$ and O, which is in good agreement with the XRD result.

### 5.3.2.6 FT-IR analysis

The characteristic functional groups of the particles were investigated using FTIR spectra. In figure 5.19, the broad absorption band observed at $\sim$3428 cm$^{-1}$ corresponds to the O-H stretching vibrations of water present in ZnO and CuO. The absorbance band found at $\sim$2923 cm$^{-1}$ is assigned to the residual organic component. The band at $\sim$1645 cm$^{-1}$ can be associated with the bending vibrations of H$_2$O molecules. The absorption bands at $\sim$1570 cm$^{-1}$ and $\sim$1412 cm$^{-1}$ in both the samples were due to the carbonyl groups of the carboxylate ions which might remain adsorbed on the surface of ZnO and CuO. The peaks appearing between 400 cm$^{-1}$ and 600 cm$^{-1}$ are assigned to the metal-oxygen (M-O) stretching mode [43]. In figure 5.19 (a), the stretching mode of ZnO nanorod appears at 546 cm$^{-1}$. Figures 5.19 (b, c and d) indicate that there is not much variation upto 5% CuO incorporation, new peaks or shift in the peak at 546 cm$^{-1}$ is observed for 10 wt.% and 50 wt.% CuO incorporation as shown in figures 5.19 (e and f). This shift is due to the formation of separate CuO crystals as proved by the XRD. The broad peak observed in the range 460-560 cm$^{-1}$ is the combination of Cu-O and Zn-O vibrations.
Figure 5.19 The FT-IR spectra of a) ZnO, b) ZnO/CuO (99:1), c) ZnO/CuO (97:3),
d) ZnO/CuO (95:5), e) ZnO/CuO (90:10) and f) ZnO/CuO (50:50)
5.3.2.7 UV-Vis absorption spectra

The room temperature UV–Vis absorption spectra for ZnO, CuO and ZnO/CuO (99:1, 97:3, 95:5, 90:10, 80:20, 70:30, 60:40 and 50:50) are shown in figure 5.20. It is evidently observed that the absorption wavelength of ZnO lies in the UV region. The absorption edge of pure CuO is ~730 nm. The absorption band for composite materials is wider and has extended to the red region as compared to ZnO which is in the blue region. The absorption edge of ZnO/CuO nanocomposites lies in the visible region. These results suggest that the photocatalytic efficiency of the ZnO/CuO composites will be higher than that of the pure ZnO nanorods.

![UV-Vis absorption spectra](image_url)

**Figure 5.20** The UV-Vis absorption spectra of a) ZnO, b) CuO, c) ZnO/CuO (99:1), d) ZnO/CuO (97:3), e) ZnO/CuO (95:5), f) ZnO/CuO (90:10), g) ZnO/CuO (80:20), h) ZnO/CuO (70:30), i) ZnO/CuO (60:40) and j) ZnO/CuO (50:50)
5.3.3 Photocatalytic degradation under visible light illumination

5.3.3.1 MB and MO degradation

The preparation of model dyes and the self designed photocatalytic reactor were described in chapter 3. The change in optical absorption spectra of MB & MO by ZnO/CuO (95:5) catalyst under visible light irradiation for different time intervals was shown in figures 5.21 (a) & (b). The disappearance of the band at 664 nm indicates that MB has been photodegraded as shown in figure 5.21 (a). In the case of methyl orange, the disappearance of the band at 464 nm is shown in figure 5.21 (b). The time course degradation curves of MB and MO for all prepared samples are shown in figures 5.22 and 5.23 respectively. The maximum photocatalytic activity is obtained for five percentage of CuO coupled with ZnO sample as compared with all other prepared samples due to their large surface area. It is known that the photocatalytic redox reaction mainly takes place on the surface of the photocatalysts, so the surface properties significantly influence the efficiency of photocatalysts.

Figure 5.21 (a) The change in absorption spectra of MB using ZnO/CuO (95:05) catalyst under visible light for different irradiation periods
Figure 5.21 (b) The change in absorption spectra of MO using ZnO/CuO (95:05) catalyst under visible light for different irradiation periods.

Figure 5.22 Time dependent degradation curve of MB at 664 nm using (a) ZnO, (b) CuO, (c) ZnO/CuO (99:1), (d) ZnO/CuO (97:3), (e) ZnO/CuO (95:5), (f) ZnO/CuO (90:10), (g) ZnO/CuO (80:20), (h) ZnO/CuO (70:30), (i) ZnO/CuO (60:40) and (j) ZnO/CuO (50:50) catalysts.
Few research groups have used ZnO/CuO for the degradation of various dyes (RhB, Acid red88, Cr(VI), Acid Orange 7 and Methyl Orange) in the recent past under UV and visible light irradiation [2, 36, 44-46]. Among them, two research groups have explained the degradation of methyl orange under visible light. ZnO/CuO (different weight percentages) synthesized by thermal decomposition method provided an effective way for cost-effective, simple and fast process compared with all other previous reports. These ZnO/CuO (95:5 weight ratio) sample shows higher degradation efficiency when compared with the data reported in the literature [44-45]. This variation in degradation time is due the difference in synthesis method, the particle size, crystallinity of the catalyst and the dopant concentration.
5.3.3.2 Degradation of textile effluent

The degradation of colour from waste water is often more significant than the degradation of other organic colourless chemicals because the waste water contains a lot of colour and has toxic odour. The self designed photocatalytic reactor and the preparation of textile effluent were described in the chapters 3 and 4. Change in the colour of the textile dye by ZnO/CuO (95:5) catalyst under visible light irradiation for different time intervals is shown in figure 5.24. It indicates that with increase in irradiation time, the colour disappears steadily and the corresponding UV- absorption spectra are shown in figure 5.25. Decolourization efficiency is inversely related to the dye concentration. The colour degradation is closely related to TOC (Total Organic Carbon) data [47-48]. Figure 5.26 shows TOC, COD (Chemical Oxygen Demand) and BOD (Biological Oxygen Demand) results for the degradation of textile dye for different intervals of time and the data are shown in table 5.3. The TOC, COD and BOD results exhibit that the concentration of textile dye decreases significantly with increasing visible light irradiation. The results demonstrate that ZnO/CuO (99:5) degrade the textile water under visible light. The catalyst exhibits high photocatalytic activity not only in the decolourization but also in mineralization of colourless organic pollutants. The TOC, COD and BOD results represent more than 90% of the initial waste water degradation using coupled semiconductor ZnO/CuO (99:5) as a catalyst.

![Figure 5.24](image)

**Figure 5.24** Photography image represents change in colour of textile dyes using ZnO/CuO (95:5) catalyst for different exposure time under visible light irradiation
Figure 5.25 The change in absorption spectra of textile effluent using ZnO/CuO (95:5) catalyst under visible light for different irradiation periods.

Figure 5.26 TOC, COD and BOD results for catalyst (5 wt.% CuO) loading on the photocatalytic degradation of textile waste water under visible light irradiation.
Table 5.3 TOC, COD and BOD data for degradation of textile pollutant

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>COD mg/L</th>
<th>COD/COD₀</th>
<th>TOC mg/L</th>
<th>TOC/TOC₀</th>
<th>BOD Mg/L</th>
<th>BOD/BOD₀</th>
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<td>462</td>
<td>1</td>
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<td>1</td>
<td>213</td>
<td>1</td>
</tr>
<tr>
<td>30</td>
<td>320</td>
<td>0.69</td>
<td>153</td>
<td>0.68</td>
<td>140</td>
<td>0.65</td>
</tr>
<tr>
<td>60</td>
<td>210</td>
<td>0.45</td>
<td>105</td>
<td>0.47</td>
<td>101</td>
<td>0.48</td>
</tr>
<tr>
<td>90</td>
<td>185</td>
<td>0.40</td>
<td>97</td>
<td>0.43</td>
<td>93</td>
<td>0.44</td>
</tr>
<tr>
<td>120</td>
<td>158</td>
<td>0.34</td>
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<td>0.37</td>
<td>80</td>
<td>0.38</td>
</tr>
<tr>
<td>150</td>
<td>123</td>
<td>0.26</td>
<td>53</td>
<td>0.24</td>
<td>62</td>
<td>0.29</td>
</tr>
<tr>
<td>180</td>
<td>100</td>
<td>0.22</td>
<td>41</td>
<td>0.18</td>
<td>45</td>
<td>0.21</td>
</tr>
<tr>
<td>210</td>
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<td>0.19</td>
<td>33</td>
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<td>30</td>
<td>0.14</td>
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<tr>
<td>240</td>
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<td>0.16</td>
<td>29</td>
<td>0.12</td>
<td>24</td>
<td>0.11</td>
</tr>
<tr>
<td>270</td>
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<td>0.11</td>
<td>25</td>
<td>0.11</td>
<td>20</td>
<td>0.09</td>
</tr>
<tr>
<td>300</td>
<td>38</td>
<td>0.08</td>
<td>20</td>
<td>0.09</td>
<td>18</td>
<td>0.08</td>
</tr>
</tbody>
</table>

5.3.3.3 Photocatalytic mechanism

The conduction and valence band positions of the two semiconductors at the point of zero charge can be calculated using equation 5.1. The electronegativity values for CuO and ZnO are 5.81 eV and 5.79 eV respectively [5, 22, 28-29]. The photocatalytic mechanism of composite material is shown in figure 5.27 and the following equation expressed the reaction mechanism based on earlier reports [49-51].

\[
\text{ZnO}(e^- + h^+) / \text{CuO}(e^- + h^+) \xrightarrow{\text{visible light}} \text{ZnO}(e^- + e^-) / \text{CuO}(h^+ + h^+) \quad (5.2)
\]

\[
h^+ + OH^- \rightarrowHO^+ \quad (5.3)
\]

\[
e^- + O_2 \rightarrow O_2^- \quad (5.4)
\]

\[
H_2O + O_2^- \rightarrow OO^- + OH^- \quad (5.5)
\]

\[
200H^+ \rightarrow O_2 + H_2O_2 \quad (5.6)
\]

\[
H_2O_2 + O_2^- \rightarrow OH^- + OH^- + O_2 \quad (5.7)
\]

\[
OH^+ + O_2^- + h^+_b + \text{pollutants} \rightarrow \text{degraded pollutants} \quad (5.8)
\]

\[
OH^+ + .O_2^- + h^+_b + \text{degraded pollutants} \rightarrow CO_2 \uparrow + H_2O \quad (5.9)
\]
When the effluent is irradiated with visible light, the electron transfer may occur from the conduction band of CuO (p-type) to the conduction band of ZnO (n-type). This is possible due to the work function of CuO being similar to that of ZnO (5.3 eV). On the other hand, transfer of holes may occur from the more anodic valence band of ZnO to the cathodic valence band of CuO [45]. At the same time, the ZnO/CuO materials exhibit red shift in the absorption wavelength range compared with that of pure ZnO, which might also benefit the improvement of photocatalytic performance. The UV- absorbance data suggests that ZnO/CuO nanocomposite has improved the photocatalytic activity. At higher percentages (10% to 50%) of CuO, the photocatalytic activity decreases.

Figure 5.27 The schematic diagram represents the photocatalytic mechanism of ZnO/CuO composite

This is due to the presence of CuO that improves charge recombination rate. The same behaviour has already been reported for CuO-TiO$_2$ [52] and TiO$_2$/WO$_3$ [12]. At the same time, the absorption value at higher percentages (10% to 50%) decreases compared to lower percentages (1%, 3% and 5%) of CuO samples. Hence the photocatalytic activity efficiency has improved for composite material (ZnO/CuO) to decomposition of organic dyes under visible light.
The coupled semiconductor ZnO/CuO possesses higher photocatalytic degradation of MB and MO when compared to ZnO under visible light since the coupling of ZnO/CuO reduces the band gap, extending the wavelength range to visible light region leading to electron-hole pair separation under visible light irradiation and consequently, achieving a higher photocatalytic activity. The maximum efficiency is observed for 5% CuO loaded on ZnO. This environmental friendly composite material was used for the degradation of real textile dye effluent under visible light illumination. The catalyst exhibits high photocatalytic activity not only in decolourization but also in mineralization of colourless organic pollutants.
5.4 Coupling of ZnO/Mn$_2$O$_3$ semiconductors

Many researchers have focused on synthesis manganese oxides because of its magnetic, electrical, and catalytic properties [53-57]. Among the oxides of manganese (MnO, MnO$_2$ Mn$_2$O$_3$ and Mn$_3$O$_4$), Mn$_2$O$_3$ has higher activity for the decomposition kinetics of N$_2$O and NO because of its stability [55]. Mn$_2$O$_3$ has lot of advantages including cost effective and eco-friendly catalyst for the decomposition of nitrogen oxide, carbon monoxide and organic pollutants; it also act as an electrode for lithium batteries. Recently, successful preparation of Mn$_2$O$_3$/TiO$_2$ and its application in photocatalytic degradation of various dyes under visible light has been reported [58]. The ZnO/Mn$_2$O$_3$ nanocomposites (99:1, 97:3, 95:5, 90:10, 80:20, 70:30, 60:40 and 50:50) were prepared by thermal decomposition method. The prepared samples are characterized by different techniques and used for the photodegradation of organic dyes under visible light.

5.4.1 Experimental procedure
5.4.1.1 Materials

Zinc acetate dihydrate (Rankem) and manganese (II) acetate tetrahydrate (Aldrich) used in the present study were of analytical reagent grade.

5.4.1.2 Synthesis of ZnO/Mn$_2$O$_3$ composites

Thermogravimetric analyses were carried out to study the decomposition temperatures of zinc acetate dihydrate and zinc acetate dehydrate with manganese (II) acetate tetrahydrate mixture which is represented in figure 5.28.

![Figure 5.28 TGA curve of (a) Zinc acetate dihydrate and (b) Zinc acetate dihydrate mixed with manganese (II) acetate tetrahydrate (95:5)](image)
Various weight percentages of ZnO/Mn$_2$O$_3$ nanocomposites were synthesized by taking zinc acetate dihydrate and manganese (II) acetate tetrahydrate (in the weight ratios of 99:1, 97:3, 95:5, 90:10, 80:20, 70:30, 60:40 and 50:50) and were mixed together. The mixtures were ground for 60 minutes and then calcined at 350 °C for 3 hours in a muffle furnace. During this process, the temperature was raised at a uniform rate of 4 °C/min. After the heat treatment, the sample was cooled to room temperature naturally.

5.4.2 Result and discussion

5.4.2.1 XRD analysis

The powder X-ray diffraction pattern of the synthesized ZnO, Mn$_2$O$_3$ and ZnO/Mn$_2$O$_3$ (99:1, 97:3, 95:5, 90:10, 80:20, 70:30, 60:40 and 50:50) nanocomposites are presented in figure 5.29. All the diffraction peaks of ZnO are indexed and it exhibits the hexagonal structure which coincides with JCPDS No: 79-0208. In the case of Mn$_2$O$_3$, the characteristic peaks (111), (202), (221), (203) and (213) were observed and indexed. As a result, it confirms the tetragonal structure of γ-Mn$_2$O$_3$ (JCPDS 06-0540). The wt% ≤ 20 of Mn$_2$O$_3$ along with ZnO composites is shown in the figures 5.29 (c to g) and the diffraction peak of Mn$_2$O$_3$ is undetectable. This is due to the dispersion of Mn species and/or the incorporation of Mn ions in the ZnO [63]. Moreover, increase in the wt% of Mn$_2$O$_3$ along with ZnO is represented in the figures 5.29 (h to j). From the figures it is clearly seen that Mn$_2$O$_3$ peak exists along with ZnO peaks. Compared with the intensity of ZnO peaks, Mn$_2$O$_3$ intensity peaks are very small. This is due to the scattering factor of an atom that depends on sin θ/λ and atomic number Z (θ = scattering angle and λ = wavelength of X-ray). Therefore in a crystal structure, it is difficult to identify lighter atoms due to its weak diffraction in presence of heavier atoms [59]. All the peaks are indexed and the results revealed two types of phases. One of the phases is the hexagonal structure of ZnO and the other matches with the tetragonal structure of Mn$_2$O$_3$. The crystallite sizes of ZnO/Mn$_2$O$_3$ samples were calculated by Scherrer equation using the (101) diffraction peak of ZnO and the (203) diffraction peak of Mn$_2$O$_3$. 

129
Figure 5.29 The XRD pattern of a) ZnO, b) Mn$_2$O$_3$, c) ZnO/Mn$_2$O$_3$ (99:1), d) ZnO/Mn$_2$O$_3$ (97:3), e) ZnO/Mn$_2$O$_3$ (95:5), f) ZnO/Mn$_2$O$_3$ (90:10), g) ZnO/Mn$_2$O$_3$ (80:20), h) ZnO/Mn$_2$O$_3$ (70:30), i) ZnO/Mn$_2$O$_3$ (60:40) and j) ZnO/Mn$_2$O$_3$ (50:50)

Table 5.4 Lattice parameter and Crystallite size (D) for prepared samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ZnO Hexagonal 79-0208</th>
<th>Mn$_2$O$_3$ Tetragonal 06-0540</th>
<th>ZnO D (nm)</th>
<th>Mn$_2$O$_3$ D (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a(Å)</td>
<td>c(Å)</td>
<td>a(Å)</td>
<td>c(Å)</td>
</tr>
<tr>
<td>ZnO</td>
<td>3.262(9)</td>
<td>5.206(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn$_2$O$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnO/Mn$_2$O$_3$(1)</td>
<td>3.245(5)</td>
<td>5.194(2)</td>
<td>8.244(2)</td>
<td>9.326(2)</td>
</tr>
<tr>
<td>ZnO/Mn$_2$O$_3$(3)</td>
<td>3.250(3)</td>
<td>5.209(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnO/Mn$_2$O$_3$(5)</td>
<td>3.276(6)</td>
<td>5.230(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnO/Mn$_2$O$_3$(10)</td>
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<td>5.202(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnO/Mn$_2$O$_3$(20)</td>
<td>3.248(3)</td>
<td>5.206(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnO/Mn$_2$O$_3$(30)</td>
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<td>5.205(2)</td>
<td>8.011(1)</td>
<td>9.893(2)</td>
</tr>
<tr>
<td>ZnO/Mn$_2$O$_3$(40)</td>
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<td>5.201(2)</td>
<td>8.005(6)</td>
<td>9.240(1)</td>
</tr>
<tr>
<td>ZnO/Mn$_2$O$_3$(50)</td>
<td>3.253(3)</td>
<td>5.207(2)</td>
<td>7.834(3)</td>
<td>9.678(3)</td>
</tr>
</tbody>
</table>
5.4.2.2 FE-SEM analysis

The FE-SEM images of ZnO, Mn$_2$O$_3$ and ZnO/Mn$_2$O$_3$ (99:1, 97:3, 95:5, 90:10, 80:20, 70:30, 60:40 and 50:50) samples were represented in figure 5.30. The randomly dispersed rod shaped ZnO was exposed in the figure 5.30 (a). The Mn$_2$O$_3$ sample is aggregated with more number of sphere shaped nanoparticles. The length of the nanorods decreases for the samples synthesized with upto 10 wt% of Mn$_2$O$_3$ and further increase for the samples upto 50% of Mn$_2$O$_3$ which results in the huge number of agglomerated nanoparticles; it is clearly seen in figure 5.30. The size and morphology of ZnO/Mn$_2$O$_3$ was influenced by increasing the wt.% of Mn$_2$O$_3$ because of its involvement in the nucleation and growth [22].

![FE-SEM images](image_url)

**Figure 5.30** The FE-SEM images of (a) ZnO and (b) Mn$_2$O$_3$, (c) ZnO/Mn$_2$O$_3$ (99:1) and (d) ZnO/Mn$_2$O$_3$ (97:3)
Figure 5.30 The FE-SEM images of (e) ZnO/Mn$_2$O$_3$ (95:5), (f) ZnO/Mn$_2$O$_3$ (90:10), (g) ZnO/Mn$_2$O$_3$ (80:20), (h) ZnO/Mn$_2$O$_3$ (70:30), (i) ZnO/Mn$_2$O$_3$ (60:40) and (j) ZnO/Mn$_2$O$_3$ (50:50)
5.4.2.3 BET analysis

The BET analysis was carried out to determine the surface area of the nanoparticles. The surface area values are 8.7 m²g⁻¹, 12.8 m²g⁻¹ and 10.2 m²g⁻¹ respectively for the samples ZnO, ZnO with 10 wt% and 50 wt% of Mn₂O₃. The 10% of Mn₂O₃ samples show the higher surface area and a subsequent decrease were observed for 50 wt% Mn₂O₃. The 50 wt% of Mn₂O₃ sample shows the decrease in surface area which might be due to the deposition of excess crystalline Mn₂O₃ on the surface of ZnO [39].

5.4.2.4 EDX spectroscopy

The quantitative analysis of the ZnO, Mn₂O₃ and ZnO/Mn₂O₃ (90:10 and 70:30) nanocomposites were carried out by using energy dispersive X-ray spectroscopy and are displayed in figure 5.31.

![Figure 5.31](image.png) The EDX spectrum of a) ZnO, b) Mn₂O₃, c) ZnO/Mn₂O₃ (90:10) and ZnO/Mn₂O₃ (70:30)
It was observed from the figure 5.31 (a), the Zn and O elements were present in ZnO samples. Figure 5.31 (b) indicates the EDX spectra of Mn$_2$O$_3$ which shows the existence of Mn and O. The 10 wt% and 30 wt% of Mn$_2$O$_3$ along with ZnO samples are shown in the figures 5.31 (c) and (d) which clearly exhibits the presence of ZnO/Mn$_2$O$_3$ without any impurities.

5.4.2.3 TEM analysis

The size and shape of the nanocomposites ZnO/Mn$_2$O$_3$ (95:5) was confirmed by TEM analysis. The TEM image of ZnO/Mn$_2$O$_3$ (95:5) sample denotes nanorod-shaped particle as shown in figure 5.32 (a). However some nanospheres are also seen in the image. From the observation of TEM image, it was confirmed that the prepared ZnO/Mn$_2$O$_3$ (95:5) nanocomposites exhibit nanorod shaped particles. Figure 5.32 (b) indicates the EDX spectrum of ZnO/Mn$_2$O$_3$ (95:5) sample. This spectrum shows that the sample contains the elements zinc, cadmium and oxygen and no other impurities are observed in the EDX spectrum.

Figure 5.32 (a) The TEM image of ZnO/Mn$_2$O$_3$ (95:5)
5.4.2.6 XPS analysis

The presence of elements and their oxidation states of the synthesized ZnO/Mn$_2$O$_3$ (90:10) nanocomposites were analyzed by XPS. The surface of ZnO/Mn$_2$O$_3$ (90:10) nanocomposite is composed of Zn, Mn, O and C. It is evidently shown in the XPS survey spectrum. Small amount of C is present in the XPS survey spectrum due to the hydrocarbon contaminants which is a common feature of XPS analysis. The high resolution spectrum of each element was corrected using the standard correction factor C 1s (284.6 eV). The high resolution XPS spectrum of Zn is represented in figure 5.33 (b). The binding energies are at 1021.1 and 1044.1 eV for 2p$_{3/2}$ and 2p$_{1/2}$ of Zn$^{2+}$ states. Figure 5.33 (c) shows that the high resolution XPS spectrum of Mn indicates Mn 2p$_{3/2}$ and Mn 2p$_{1/2}$ peaks and the corresponding binding energy values are 641.2 and 653.5 eV. It is a clear evidence for Mn$^{3+}$ present in the ZnO/Mn$_2$O$_3$ sample. The binding energy values of Mn$_2$O$_3$ are well matched with the previous reports [60-61]. Figure 5.33 (d) shows the high resolution XPS spectrum of oxygen and the curve fitting patterns which indicate the presence of three types of oxygen in the nanocomposite sample. The binding energy values observed at 528.4, 530.1 and 531.7 eV are attributed to Mn$_2$O$_3$, ZnO and surface hydroxyl group [24]. Hence the XPS analysis gives the direct
proof of Zn (II) and Mn (III) present in the ZnO/Mn$_2$O$_3$ nanocomposite surface which is in good agreement with the XRD result.

Figure 5.33 (a) XPS survey spectrum of ZnO/Mn$_2$O$_3$ (90:10)

Figure 5.33 (b) High resolution XPS spectrum of Zinc
Figure 5.33 (c) High resolution XPS spectrum of $\text{Mn}_2\text{O}_3$

Figure 5.33 (d) High resolution XPS spectrum of Oxygen
5.4.2.7 UV-Vis absorption spectra

The optical properties of ZnO, Mn$_2$O$_3$ and ZnO/Mn$_2$O$_3$ (99:1, 97:3, 95:5, 90:10, 80:20, 70:30, 60:40 and 50:50) were monitored by UV-Vis absorption spectrophotometer and are shown in figure 5.34. The absorption edge of ZnO lies in the blue region and the corresponding wavelength is $\sim$ 360 nm. The absorption edge of the synthesized Mn$_2$O$_3$ sample is $\sim$ 570 nm which is in the red region [61]. The composite materials (ZnO/Mn$_2$O$_3$) wavelength exists between 400-500 nm which is in the red region. Therefore the photocatalytic activity of ZnO/Mn$_2$O$_3$ nanocomposites might be good under visible light condition because its absorption edge in the red region generates more number of electrons and holes. These results show that the photodegradation efficiency of nanocomposite system is higher than that of pure ZnO.

![Figure 5.34](image)

*Figure 5.34* The UV-vis absorption spectra of a) ZnO, b) Mn$_2$O$_3$, c) ZnO/Mn$_2$O$_3$ (99:1), d) ZnO/Mn$_2$O$_3$ (97:3), e) ZnO/Mn$_2$O$_3$ (95:5), f) ZnO/Mn$_2$O$_3$ (90:10), g) ZnO/Mn$_2$O$_3$ (80:20), h) ZnO/Mn$_2$O$_3$ (70:30), i) ZnO/Mn$_2$O$_3$ (60:40) and j) ZnO/Mn$_2$O$_3$ (50:50)
5.4.3 Photocatalytic degradation under visible light illumination

5.4.3.1 MB and MO degradation

The preparation of model dyes and the self designed photocatalytic reactor were described in chapter 3. The catalytic efficiency was determined for the degradation of the organic dyes such as MB and MO. Figures 5.35 (a) and (b) represents the change in absorption curves of MB and MO with uniform irradiation time using ZnO/Mn$_2$O$_3$ (90:10) as a catalyst. From the figure, the maximum wavelength of MB and MO is shown at 664 nm and 464 nm respectively. When the irradiation time is increased, the absorbance band at 664 nm and 464 nm decreases which indicates that MB and MO undergoes photodegradation. The different concentrations of MB and MO (C/C$_0$) with irradiation time are presented in figures 5.36 (a) & (b) respectively. From the figure, ZnO/Mn$_2$O$_3$ (90:10) shows higher degradation rate of MB and MO dyes about 95% and 90% respectively after 210 min irradiation. This is due to synergetic coupling effect between ZnO and Mn$_2$O$_3$ and the high specific surface area of the particular ZnO/Mn$_2$O$_3$ (90:10) nanocomposite system.

![Figure 5.35](a) The Change in absorption spectra of MB using ZnO/Mn$_2$O$_3$ (90:10) catalyst under visible light for different period of irradiation
Figure 5.35 (b) The Change in absorption spectra of MO using ZnO/Mn$_2$O$_3$ (90:10) catalyst under visible light for different period of irradiation.

Figure 5.36 (a) Time dependent degradation curve of MB at 664 nm using (a) ZnO, b) Mn$_2$O$_3$, c) ZnO/Mn$_2$O$_3$ (99:1), d) ZnO/Mn$_2$O$_3$ (97:3), e) ZnO/Mn$_2$O$_3$ (95:5), f) ZnO/Mn$_2$O$_3$ (90:10), g) ZnO/Mn$_2$O$_3$ (80:20), h) ZnO/Mn$_2$O$_3$ (70:30), i) ZnO/Mn$_2$O$_3$ (60:40) and j) ZnO/Mn$_2$O$_3$ (50:50) catalysts.
Figure 5.36 (b) Time dependent degradation curve of MO at 464 nm using a) ZnO, b) Mn$_2$O$_3$, c) ZnO/Mn$_2$O$_3$ (99:1), d) ZnO/Mn$_2$O$_3$ (97:3), e) ZnO/Mn$_2$O$_3$ (95:5), f) ZnO/Mn$_2$O$_3$ (90:10), g) ZnO/Mn$_2$O$_3$ (80:20), h) ZnO/Mn$_2$O$_3$ (70:30), i) ZnO/Mn$_2$O$_3$ (60:40) and j) ZnO/Mn$_2$O$_3$ (50:50) catalysts

### 5.4.3.2 Photocatalytic mechanism

The schematic diagram shown in figure 5.37 represents the photocatalytic reaction mechanism of the nanocomposite ZnO/Mn$_2$O$_3$ system. The conduction band and valence band positions of ZnO and Mn$_2$O$_3$ were followed by previous reports [5, 62]. The conduction band of Mn$_2$O$_3$ and ZnO are very close to each other and the values are -0.31 eV and -0.35 eV respectively. When Mn$_2$O$_3$ is excited by the visible light, holes will be formed in the valence band of Mn$_2$O$_3$ and the electrons in the valence band of ZnO can move to that of Mn$_2$O$_3$. The excited electrons at the conduction band of Mn$_2$O$_3$ are transferred to the conduction band of ZnO. This process of the hole trapping which is facilitated in the mixed semiconductor system would increase the efficiency. Thus, the degradation efficiency of ZnO/Mn$_2$O$_3$ could be higher than those of pure ZnO and Mn$_2$O$_3$. This is due to synergetic coupling effect between ZnO and Mn$_2$O$_3$ and the high specific surface area of the nanocomposite system.
5.4.3.3 Degradation of textile effluent

The higher degradation efficiency of the sample ZnO/Mn$_2$O$_3$ (90:10) was further employed in the photodecolouration of industrial effluent under visible light irradiation. The self-designed photocatalytic reactor and the preparation of textile effluent were described in the chapters 3 and 4. The irradiated sample was collected at uniform interval of time and the absorption spectra were monitored by UV-Vis spectrophotometer. Figure 5.38 represents the change in absorption of industrial effluent solution. As the irradiation time is increased, the absorption band decreases and this was evidently observed from the figure 5.37. Most of the textile effluent has been degraded within 8 hours using ZnO/Mn$_2$O$_3$ (90:10) as a catalyst under visible light irradiation. It was found that more than 85% of the textile effluent has been photodegraded and it was achieved within 8 hours irradiation time.
Figure 5.38 The change in absorption spectra of textile effluent using ZnO/Mn$_2$O$_3$ (90:10) catalyst under visible light for different period of irradiation

Among the prepared samples, the present system ZnO/Mn$_2$O$_3$ (90:10) has shown the best photocatalytic efficiency of two common dyes under visible light. Further the higher efficiency catalyst successfully degrades the textile effluents.
5.5 Coupling of ZnO/CeO$_2$ semiconductors

The rare earth oxides have been used for various fields. Among them, cerium oxide (CeO$_2$) is an important rare earth semiconducting material; it is used in various fields such as catalysts, sensors, solar cells and fuel cells due to thermal stability, mild synthesis condition, low cost when compared with other rare-earth materials and easy scale-up [63-64]. The present nanocomposite system deals with the preparation of ZnO coupled with CeO$_2$ (99:1, 97:3, 95:5, 90:10, 80:20, 70:30, 60:40 and 50:50) by thermal decomposition method. The synthesized catalysts were characterized by different techniques. The catalysts were used for the photodegradation of methylene blue and methyl orange under visible light irradiation. In addition, the sample exhibiting the best photocatalytic activity was employed for the degradation of textile effluent.

5.5.1 Experimental procedure

5.5.1.1 Materials

Zinc acetate dihydrate (Rankem) and cerium (III) acetate hydrate (Aldrich) used in the present study were of analytical reagent grade.

5.5.1.2 Synthesis of ZnO/CeO$_2$ composites

Different weight percentages of ZnO/CdO nanocomposites were synthesized by taking zinc acetate dihydrate and cerium (III) acetate hydrate (in the weight ratios of 99:1, 97:3, 95:5, 90:10, 80:20, 70:30, 60:40 and 50:50) and were mixed together. The mixtures were ground for 60 minutes and then calcined at 350 °C for 3 hours in a muffle furnace. During this process, the temperature was raised at a uniform rate of 4 °C/min. After the heat treatment, the sample was cooled to room temperature naturally. Before the actual synthesis of catalysts, thermogravimetric analyses were carried out in order to determine the decomposition temperatures of zinc acetate dihydrate and zinc acetate dihydrate mixed with cerium (III) acetate hydrate (figure 5.39).
5.5.2 Result and discussion

5.5.2.1 XRD analysis

The structure of the prepared samples and its crystallinity were confirmed by X-ray diffraction. The ZnO/CeO$_2$ nanocomposite materials were compared with pure ZnO and pure CeO$_2$. The X-ray diffraction pattern of ZnO is shown in figure 5.40 (a). All the diffraction peaks are indexed and it exhibits the hexagonal structure of ZnO which coincides well with the JCPDS No: 79-0208. The XRD pattern of pure CeO$_2$ is presented in figure 5.40 (b) which revealed the cubic structure related to (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes with the JCPDS No: 65-2975. The lower wt.% of CeO$_2$ (1 wt.%, 3 wt.% and 5 wt.%) along with ZnO is shown in the figures 5.40 (c to e). The CeO$_2$ content ≤ 5 wt.% shows that the reflection peaks (CeO$_2$) have very low intensity. So we cannot find out the lattice parameters in the XRD pattern.

When the wt.% of CeO$_2$ is increased from 10 to 50 wt.% in the nanocomposite samples, there is a decrease in the intensity of ZnO whereas the CeO$_2$ intensity increases. It is visibly seen in the figures 5.40 (f to j). The variation of intensity is due to the scattering factor. The Ce$^{4+}$ ions show higher scattering factor compared with Zn$^{2+}$ ions in the ZnO/CeO$_2$ composite catalysts. This similar observation is also explained by Mishra et.al [59]. The scattering factor of an atom depends on sin $\theta$/\lambda ($\theta =$ scattering
angle and \( \lambda = \) wavelength of X-ray) and atomic number \( Z \). The XRD pattern of CeO\(_2\) wt% \( \geq 10 \) along with ZnO is shown in the figures 5.40 (f to j) which exhibit the presence of both CeO\(_2\) and ZnO peaks. From the figure, the entire diffraction patterns are indexed and it reveals two types of phases. One is the hexagonal structure of ZnO and the other phase resembles with the cubic structure of CeO\(_2\). The lattice parameters of all the prepared samples were determined and tabulated in table 5.5.

The crystallite sizes of ZnO, CeO\(_2\) and ZnO/CeO\(_2\) nanocomposite materials were calculated by Scherrer equation using the (101) diffraction peak of ZnO and the (111) diffraction peak of CeO\(_2\). The results are summarized in table 5.5. The diffraction peaks of the composite materials are compared with pure ZnO and CeO\(_2\). The composite oxides have both the phases of ZnO and CeO\(_2\) and also it contain the doping of small amount of ZnO in CeO\(_2\) and vice versa. Hence, the XRD pattern confirmed the formation of ZnO/CeO\(_2\) nanocomposite systems without any impurities.

![Figure 5.40](image)

**Figure 5.40** The XRD pattern of a) ZnO, b) CeO\(_2\), c) ZnO/CeO\(_2\) (99:1), d) ZnO/CeO\(_2\) (97:3), e) ZnO/CeO\(_2\) (95:5), f) ZnO/CeO\(_2\) (90:10), g) ZnO/CeO\(_2\) (80:20) h)ZnO/CeO\(_2\) (70:30),i) ZnO/CeO\(_2\) (60:40) and j) ZnO/CeO\(_2\) (50:50)
### Table 5.5 Lattice parameter and crystallite size (D) values for prepared samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>ZnO Hexagonal 79-0208</th>
<th>CeO$_2$ Cubic 65-2975</th>
<th>ZnO D (nm)</th>
<th>CeO$_2$ D (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>3.26 5.21</td>
<td></td>
<td>---- 24</td>
<td>----</td>
</tr>
<tr>
<td>CeO$_2$</td>
<td></td>
<td>5.439(1)</td>
<td>---- 9</td>
<td></td>
</tr>
<tr>
<td>ZnO/CeO$_2$(1)</td>
<td>3.273(9) 5.221(4)</td>
<td></td>
<td>---- 34</td>
<td>----</td>
</tr>
<tr>
<td>ZnO/CeO$_2$(3)</td>
<td>3.268(8) 5.220(3)</td>
<td></td>
<td>---- 33</td>
<td>----</td>
</tr>
<tr>
<td>ZnO/CeO$_2$(5)</td>
<td>3.273(9) 5.219(3)</td>
<td></td>
<td>---- 35</td>
<td>----</td>
</tr>
<tr>
<td>ZnO/CeO$_2$(10)</td>
<td>3.270(9) 5.215(3)</td>
<td></td>
<td>5.411(2) 29</td>
<td>6</td>
</tr>
<tr>
<td>ZnO/CeO$_2$(20)</td>
<td>3.271(9) 5.219(3)</td>
<td></td>
<td>5.398(2) 31</td>
<td>7</td>
</tr>
<tr>
<td>ZnO/CeO$_2$(30)</td>
<td>3.266(1) 5.215(3)</td>
<td></td>
<td>5.403(1) 32</td>
<td>9</td>
</tr>
<tr>
<td>ZnO/CeO$_2$(40)</td>
<td>3.267(3) 5.216(3)</td>
<td></td>
<td>5.423(2) 34</td>
<td>8</td>
</tr>
<tr>
<td>ZnO/CeO$_2$(50)</td>
<td>3.262(2) 5.220(2)</td>
<td></td>
<td>5.413(1) 33</td>
<td>9</td>
</tr>
</tbody>
</table>

#### 5.5.2.2 FE-SEM analysis

The FE-SEM images of ZnO, CeO$_2$ and ZnO/CeO$_2$ (99:1, 97:3, 95:5, 90:10, 80:20, 70:30, 60:40 and 50:50) samples were represented in figure 5.41. The image of ZnO powder is shown in the figure 5.41(a). The images show that ZnO samples are visibly appeared as nanorods in shape. The CeO$_2$ sample shows agglomerated huge number of spherical shaped nanoparticles (Figure 5.41 (b)). The addition of CeO$_2$ into ZnO seems to influence the morphology and the size of composite materials. It is evidently observed from the FE-SEM images (figures 5.41 c to j).

![Figure 5.41](image-url) The FE-SEM images of (a) ZnO and (b) CeO$_2$
Figure 5.41 The FE-SEM images of (c) ZnO/CeO$_2$ (99:1), (d) ZnO/CeO$_2$ (97:3), (e) ZnO/CeO$_2$ (95:5), (f) ZnO/CeO$_2$ (90:10), (g) ZnO/CeO$_2$ (80:20) and (h) ZnO/CeO$_2$ (70:30)
5.5.2.3 BET analysis

The surface area values of ZnO, ZnO(90)/CeO2(10) and ZnO(50)/CeO2(50) were found to be 8.7 m²/g, 13.4 m²/g and 11.4 m²/g from BET analysis. The surface area of 10 wt.% CeO2 sample is comparatively higher than pure ZnO due to lower particle size. The surface area of 50 wt.% ZnO/CeO2 decreases which might be due to the deposition of excess crystalline CeO2 on the surface of ZnO. A similar observation has been recently reported by Leghari et al. [39].

5.5.2.4 EDX spectroscopy

The presence of elements and their quantitative values of the ZnO, CeO2 and ZnO/CeO2 (90:10 and 70:30) nanocomposites were carried out by using energy dispersive X-ray spectroscopy and are displayed in figure 5.42. Figure 5.42 (a) shows that the ZnO samples contain only Zn and O. Figure 5.42 (b) shows the existence of only cerium and oxygen in CeO2 sample. The composites 10 wt% and 30 wt% of CeO2 along with ZnO samples have Zn, Ce and O. This is visibly seen in the figures 5.42 (c) and (d). Hence, the EDX spectra have confirmed the presence of ZnO, CeO2 and ZnO/CeO2 samples without any impurities.

Figure 5.41 The FE-SEM images of (i) ZnO/CeO2 (60:40) and (j) ZnO/CeO2 (50:50)
5.5.2.5 TEM analysis

TEM analysis was carried out to identify the shape and size of the synthesized ZnO/CeO$_2$ (95:5) nanocomposites. As shown in figure 5.43 (a), the TEM image of ZnO/CeO$_2$ (95:5) symbolizes nanorod-shaped particle. The ZnO/CeO$_2$ nanorods have diameters ranging between 30-40 nm and in the length ranging between 150-200 nm. The EDX spectrum of ZnO/CeO$_2$ (95:5) sample is presented in figure 5.43 (b). This spectrum indicates that zinc, cerium and oxygen were present in the sample and no other impurities are detected in the EDX spectrum.
Figure 5.43 (a) The TEM image of ZnO/ CeO$_2$ (95:5)

Figure 5.43 (b) The EDX spectrum of ZnO/CeO$_2$ (95:5)
5.5.2.6 XPS analysis

The elemental composition and chemical state of the synthesized ZnO/CeO$_2$ (90:10) nanocomposites were characterized using XPS. The XPS survey spectrum is shown in figure 5.44 (a). It can be seen that the ZnO/CeO$_2$ surface is composed of Zn, O, Ce, and C elements without any other elements. The binding energy values at 1021.6 eV and 1044.7 eV represent Zn 2p$_{3/2}$ and Zn 2p$_{1/2}$ in the samples ZnO/CeO$_2$ shown in the figure 5.44 (b). This indicates that the Zn exists in Zn$^{2+}$ oxidation states. The high resolution scanning XPS spectrum of cerium along with satellite peaks are presented in the figure 5.44 (c). The binding energies of Ce 3d$_{5/2}$ and Ce 3d$_{3/2}$ are located at 882.7 and 906.6 eV. This value was confirmed by the previous report [65-66]. Three kinds of oxygen (531.2, 532.9 and 534.4 eV) on the sample surface are associated with ZnO, CeO$_2$ and surface hydroxyl groups [24]. Hence, the XPS results have confirmed that the ZnO/CeO$_2$ sample is composed of Zn$^{2+}$, Ce$^{4+}$ and O$^2-$, which is in good agreement with the XRD result.

![Figure 5.44 (a) XPS survey spectrum of ZnO/CeO$_2$ (95:5)](a)
Figure 5.44 (b) High resolution XPS spectrum of Zinc

Figure 5.44 (c) High resolution XPS spectrum of Cerium
5.5.2.7 UV-Vis absorption spectra

The optical property of the catalysts is one of the important parameters for the estimation of its photocatalytic activity. Thus, the optical properties of the prepared ZnO/CeO$_2$ (99:1, 97:3, 95:5, 90:10, 80:20, 70:30, 60:40 and 50:50) nanocomposites along with ZnO and CeO$_2$ were observed by UV-Vis absorption spectrophotometer and were shown in figure 5.45. The ZnO absorption edge is in blue region and the corresponding wavelength is ~360 nm. The prepared ceria exhibits the absorption edge in the red region and the bandgap value is ~2.8 eV which coincides with the literature bandgap value [67]. The composite materials (ZnO/CeO$_2$) wavelength is wider when compared to ZnO sample. Hence the UV-Vis absorption result has confirmed that the composite materials generate more number of electrons and holes under visible light. These results may suggest that during the photocatalytic reaction, the holes and electrons were actively participated in the oxidation and reduction reactions.
Figure 5.45 The UV-vis absorption spectra of (a) ZnO, (b) CeO$_2$, (c) ZnO/CeO$_2$ (99:1),
d) ZnO/CeO$_2$ (97:3), e) ZnO/CeO$_2$ (95:5), f) ZnO/CeO$_2$ (90:10), g) ZnO/CeO$_2$ (80:20)
h) ZnO/CeO$_2$ (70:30), i) ZnO/CeO$_2$ (60:40) and j) ZnO/CeO$_2$ (50:50)

5.5.3 Photocatalytic degradation under visible light illumination

5.5.3.1 MB and MO degradation

The photocatalytic activity of the synthesized ZnO/CeO$_2$ (99:1, 97:3, 95:5, 90:10,
80:20, 70:30, 60:40 and 50:50) samples were evaluated for the degradation of two
different organic dyes: methylene blue (MB) and methyl orange (MO) in aqueous
solution under visible light irradiation. The preparation of model dyes and the self
designed photocatalytic reactor were described in chapter 3. The degradation of MB and
MO using pure ZnO and pure CeO$_2$ were also performed under the identical conditions
for comparative studies. Figures 5.46 (a) and (b) shows the change in absorption spectra
for the photocatalytic degradation of MB and MO as a function of irradiation time. The
absorption intensity of aqueous suspensions of MB and MO dyes in the presence of
ZnO/CeO$_2$ decreases with increase in the irradiation time. The disappearance of the band
at 664 and 464 nm indicates that MB/MO has been photodegraded as shown in figures
5.46 (a) and (b).
Figure 5.46 (a) The Change in absorption spectra of MB using ZnO/CeO\(_2\) (90:10) catalyst under visible light for different period of irradiation.

Figure 5.46 (b) The Change in absorption spectra of MO using ZnO/CeO\(_2\) (90:10) catalyst under visible light for different period of irradiation.
Figure 5.47 (a) Time dependent degradation curve of MB at 664 nm using a) ZnO, b) CeO₂, c) ZnO/CeO₂ (99:1), d) ZnO/CeO₂ (97:3), e) ZnO/CeO₂ (95:5), f) ZnO/CeO₂ (90:10), g) ZnO/CeO₂ (80:20) h) ZnO/CeO₂ (70:30), i) ZnO/CeO₂ (60:40) and j) ZnO/CeO₂ (50:50) catalysts

Figure 5.47 (b) Time dependent degradation curve of MO using at 464 nm a) ZnO, b) CeO₂, c) ZnO/CeO₂ (99:1), d) ZnO/CeO₂ (97:3), e) ZnO/CeO₂ (95:5), f) ZnO/CeO₂ (90:10), g) ZnO/CeO₂ (80:20) h) ZnO/CeO₂ (70:30), i) ZnO/CeO₂ (60:40) and j) ZnO/CeO₂ (50:50) catalysts
For the photodegradation of MB and MO under visible light condition, 10 wt% of CeO$_2$ along with ZnO provided the highest photocatalytic activity when compared to pure ZnO, CeO$_2$ and other wt% nanocomposite system and the results are shown in the figures 5.47 (a) and (b). The 10 wt% of CeO$_2$ along with ZnO shows that 97% of methylene blue and 94% of methyl orange is degraded after 150 minutes of visible light irradiation time.

5.5.3.2 Photocatalytic mechanism

The conduction and valence band positions of the ZnO and CeO$_2$ semiconductors were calculated using equation 3.1. The electronegativity values for CeO$_2$ and ZnO were 5.56 eV and 5.79 eV respectively [5, 29, 67]. Figure 5.48 shows the photocatalytic mechanism of nanocomposite (ZnO/CeO$_2$) system. The conduction band of CeO$_2$ and ZnO are very close to each other. When CeO$_2$ is excited by the visible light, holes will be formed in the valence band of CeO$_2$ and the electrons in the valence band of ZnO can move to that of CeO$_2$. The excited electrons at the conduction band of CeO$_2$ are transferred to the conduction band of ZnO.

![Figure 5.48](image)

**Figure 5.48** The schematic diagram represents the photocatalytic mechanism of ZnO/CeO$_2$ composite.
The electrons will then react with oxygen molecules finally to form hydroxyl radicals. The holes react with water and generate OH radical, which can subsequently oxidize the organic pollutants. This oxidation and reduction processes were capable to degrade MB and MO molecules under visible light. The ZnO/CeO$_2$ (90:10) materials exhibit red shift in the absorption wavelength range compared with that of ZnO and also had the largest specific surface area due to their extremely small sizes, which benefit the improvement of photocatalytic performance.

### 5.5.3.3 Degradation of textile effluent

The catalyst ZnO/CeO$_2$ (90:10) which shows the higher efficiency was further used to study the decolouration of industrial effluent under visible light irradiation. The self designed photocatalytic reactor and the preparation of textile effluent were described in the chapters 3 and 4. The change in absorption of industrial effluent is shown in figure 5.49 with respective irradiation time. The figure clearly indicates that the absorption band decreases with increase in irradiation time.

![Figure 5.49](image)

**Figure 5.49** The change in absorption spectra of textile effluent using ZnO/CeO$_2$ (90:10) catalyst under visible light for different period of irradiation.

The absorption spectra seem to be completely flat after 6 hours of irradiation time which represent that most of the textile effluent has been degraded using ZnO/CeO$_2$ (90:10) as a catalyst under visible light irradiation. It was found that more than 90% degradation was achieved within 6 hours.
Conclusion

In this chapter, different nanocomposites (ZnO/CdO, ZnO/CuO, ZnO/Mn$_2$O$_3$ and ZnO/CeO$_2$) were examined and the characterization results are discussed. All the prepared samples were used to degrade the organic dyes such as methylene blue and methyl orange under visible light and the degradation efficiency was calculated. The higher degradation catalyst for each nanocomposites are ZnO/CdO (90:10), ZnO/CuO (95:5), ZnO/Mn$_2$O$_3$ (90:10) and ZnO/CeO$_2$ (90:10). Further the best catalyst of each nanocomposites were employed to degrade the real textile effluent. These catalysts not only degrade the model organic dyes, but also the textile effluents. The degradation efficiency is in the order of ZnO/CuO (95:5) > ZnO/CeO$_2$ (90:10) > ZnO/CdO (90:10) > ZnO/Mn$_2$O$_3$ (90:10) with respective irradiation time. Among all other prepared samples, the maximum efficiency was observed for 5% CuO loaded on ZnO. The ZnO/CuO (95:5) exhibits high photocatalytic activity not only in decolourization but also in mineralization of textile pollutant which was confirmed through TOC, COD and BOD analysis.
References:


