SYNTHESIS CHARACTERISATION AND APPLICATION OF NOVEL COMPOSITE Mn\(^{6+}\): ZNO NANOCRYSTALS

H R Ravi\(^1\), P Naveen Kumar\(^2\), C P Sajan\(^3\), N Pavan\(^4\), S Chandramma\(^2\), H C Devarajegowda\(^4\)

ABSTRACT

The hydrothermally synthesis of Mn\(^{6+}\) doped ZnO nanocrystals at 150\(^0\)C with an autogenous pressure and experimental duration of 40 hrs has been reported. A control over the particle size, morphology and crystallinity of the as prepared compound has been studied with respect to the experimental parameters like nutrient composition, solvent, experimental duration, temperature, pressure and so on. The products synthesized were characterized using XRD, SEM, FTIR and DLS. The photodegradation of textile effluent using these composite was investigated under both solar and UV irradiation. The degradation of textile effluent was checked by the following parameters like COD, %T, irradiation time and duration. The preliminary results are highly encouraging and further work is being carried out for the use of these photocatalytic compounds for other organic decomposition.

Keywords: Photocatalytic, Hydrothermal, Textile Effluent, Chemical Oxygen Demand.

INTRODUCTION

The properties of ZnO make it an attractive candidate for UV light-emitters, varistors, transparent high power electronics, surface acoustic wave devices, piezoelectric Transducers, gas sensing, window material for flat panel displays, and more efficient solar cells [1-12]. Recently, a lot of studies have been concentrated on the degradation of toxic organic compounds in waste water via photocatalysis of various semiconductors [13]. Especially, TiO\(_2\) with anatase phase has been most widely investigated due to its photocatalytic activity and chemical stability. However, it is generally known that TiO\(_2\) can barely absorb visible light due to its wide band-gap energy (3.2 eV) and this is one of the most acceptable serious obstacles associated with its further application [14]. As a contrast ZnO, a kind of semiconductor that has the similar band gap as TiO\(_2\), is not thoroughly investigated. However, the greatest advantage of ZnO is that it absorb large fraction of solar spectrum and more light quanta than TiO\(_2\) [15].
There is also interest in developing the use of ion implantation of ZnO for device doping and isolation [8], as well as investigating the effectiveness of different transition metals for magnetic doping, model by Dietl et al [16, 17]. The Mn–Zn–O system has attracted much attention because of the controversial magnetic properties reported, but their basic origins remain unclear. Both the existence and absence of FM have been reported in Mn-doped ZnO thin films. However, in the present article the authors report the hydrothermal synthesis of Mn doped ZnO under mild PT condition and their application in the photocatalytic degradation of textile effluent to know the photodegradation efficiency of the synthesised compound.

MATERIALS AND METHODS

In the synthesis of Mn$^{6+}$: ZnO a known amount of commercially available ZnO was taken in the in a Teflon liner to which MnO$_3$ was doped from 1 to 10 % respectively. The chemical ingredients were weighed in stoichiometric proportions and a required amount of suitable mineralizer (double distilled water) was added into this teflon liner maintaining 40% of % fill. The teflon liner was then placed inside the autoclave. The autoclave was then placed inside the oven and the temperature of the oven was set to 150°C for 40 hrs. After the experimental run, the autoclave was quenched and the sample was taken out. The sample inside the liner was separated from the solution and washed with the double distilled water, and then ultrasonicated. The product extracted was centrifuged to remove undesired components and dried at a temperature of 35-40°C in a dust free environment.

The synthesized Mn$^{6+}$: ZnO was characterised using a high resolution SEM. The XRD pattern was obtained using MXP3, MAC Science Co., Ltd, Tokyo, Japan, with Cu Kα radiation (wavelength =0.154nm). The scanning range was 10-80 °C (2θ). The crystallinity of the compound was identified by comparison with JCPDS files (PCPDF WIN-2.01). The FTIR result was obtained using JASCO-460 Plus, Japan. The DLS study was carried out in order to know the population of the crystal synthesized. In order to know the photodegradation efficiency of the synthesized compound the photodegradation of textile effluent was carried out under both sunlight and UV light. In the photocatalytic degradation of the textile effluent a known volume of the effluent (50ml) was taken in a beaker. To this a known amount of catalyst was added. The experiment was carried out under both UV and sunlight. For UV source the sample was kept in UV chamber (Sankyo, Denki, Japan, 8W) the distance between the UV and effluent was 18 cm. The intensity of sunlight and UV was estimated by photolysis of Uranil Oxalate (Steven1973). It was estimated that the intensity of sunlight was 6.722 X 10$^{16}$ quanta/sec, and the intensity of UV was 2.375 X 10$^{15}$ quanta/s. 2-3 ml of the sample exposed to light was taken and centrifuged for 4-5 min at 1000rpm and then used to measure the percentage transmission (%T) at 540nm using spectrophotometer (Model: Minispec SL 171, Elico, India). Chemical oxygen demand (COD) was estimated before and after the treatment (using the K$_2$Cr$_2$O$_7$ oxidation method). The photodegradation of the Textile effluent was calculated using the equation,

\[ \text{Photodegradation} = \frac{\text{Initial COD} - \text{Final COD}}{\text{Initial COD}} \times 100 \]

RESULTS AND DISCUSSION

Characterisation of Mn: ZnO photocatalyst

The XRD powder diffraction pattern of Mn$^{6+}$: ZnO is shown in Figure 1. The peaks were compared with standard patterns of JCPDS data bank. The crystalline phase of ZnO matches with JCPDS 800075 respectively. The cell parameter and indexing of the prepared Mn$^{6+}$: ZnO compound was done using chek cells software. Table 1 gives the cell parameters of Mn$^{6+}$: ZnO photocatalyst.
obtained in the present work. The cell parameters obtained matches with the space group P63MC. The crystal system of the synthesized Mn$^{6+}$: ZnO is identified as hexagonal system. However, (010), (020) and (011) peak positions shows a slight shift to the smaller angles due to the addition of doping material which clearly depicts that the doping has effectively taken place. The reduction in the unit volume of the cell when doped with Mn$^{6+}$ is due to the smaller ionic radii of the dopants (ionic radii of Mn$^{6+}$ is 0.69 Å). A high resolution SEM study was done to know the size and morphology of the crystals obtained. Figure 2 represents the morphology and size of the particles obtained. The SEM study clearly reveals that the product obtained is monodispersed. Figure 3 represents the FTIR spectra of Mn$^{6+}$:ZnO. The bands at 574 cm$^{-1}$ is assigned to the stretching vibrations of Zn-O. The broad absorption peak centered 3418 cm$^{-1}$ correspond to O–H group, indicating the existence of water absorbed on the surface of synthesized compound. The bands in the region 523 cm$^{-1}$ represents the presence of manganese. In the present study the population and particle size distribution of the prepared compounds were carried out using HORIBA, LB-550. The histograms were plotted by analyzing the correlation function and the calculation were done based on the assumed distribution. Figure 4 represents the DLS results obtained. The histogram clearly shows that among the synthesized compound 70% of the crystals are in the size of 8.225 and 9.85 nm, and the rest 30% of the crystals are in the size of 11.475 and 15 nm.
Effect of Mn: ZnO on photodegradation of textile effluent

In order to obtain an optimum condition with respect to the amount of catalyst used at which photodegradation is maximum the experiment was carried out for the degradation of textile effluent using different amount of Mn$^{6+}$: ZnO. Figure 4 illustrates the effect of different amount of catalyst (10-30 mg) on the degradation of the textile effluent. Figure 4 clearly shows that when the degradation was carried under sunlight and UV light, using 30 mg of the photocatalyst the % decomposition rate of the effluent is high.

**Fig 4,** Graphical representation of increase in % decomposition ($\eta$) under UV light and sunlight using Mn$^{6+}$: ZnO

Effect of Mn$^{6+}$: ZnO on the chemical oxygen demand (COD) of the textile effluent

The COD of the effluent was estimated before and after the treatment. The reduction in the COD value of the effluent depicts the destruction of the organics present in the effluent. A maximum of 87.5% of degradation efficiency was obtained with in the duration of 5hrs in the present study. Figure 5 represents the reduction of COD using Mn$^{6+}$: ZnO under both sunlight and UV light. The COD of the effluent was reduced from 256 to 64 mg/L. Tables 2 and 3 represent the effect of Mn$^{6+}$: ZnO weight on COD, decomposition ($\eta$) and % transmission (%T) of textile effluent under both sunlight and UV light.
Effect of Mn$^{6+}$: ZnO on % transmission of the textile effluent

The % transmission (T) of the effluent was analyzed before and after the treatment of the textile effluent using spectrophotometer. As the duration of exposure of the effluent containing Mn$^{6+}$: ZnO photocatalyst to light increases, the %T increases. The increase of %T clearly depicts the destruction of dye molecules present in the textile effluent, Figure 6, represents the graphical representation of increase in %T under both UV and sunlight with respect to time. Tables 2 and 3 represent the effect of Mn$^{6+}$: ZnO weight on COD, decomposition ($\eta$) and % transmission (%T) of textile effluent under both sunlight and UV light.

![Graphical representation of decrease in COD under UV and sunlight using Mn$^{6+}$: ZnO](image1)

**Fig .5.** Graphical representation of decrease in COD under UV and sunlight using Mn$^{6+}$: ZnO

![Graphical representation of increase in %T under UV and sunlight using Mn$^{6+}$: ZnO](image2)

**Fig .6.** Graphical representation of increase in %T under UV and sunlight using Mn$^{6+}$: ZnO.

**Table 2.** Effect of Photocatalytic degradation efficiency ($\eta$) and Decolorization (%T) on Textile effluent under UV using Mn$^{6+}$:ZnO

<table>
<thead>
<tr>
<th>Time in Hrs</th>
<th>10 mg</th>
<th>20 mg</th>
<th>30 mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD</td>
<td>$\eta$</td>
<td>%T</td>
<td>COD</td>
</tr>
<tr>
<td>1</td>
<td>248</td>
<td>3.125</td>
<td>45.2</td>
</tr>
<tr>
<td>2</td>
<td>232</td>
<td>9.375</td>
<td>49.1</td>
</tr>
<tr>
<td>3</td>
<td>200</td>
<td>21.87</td>
<td>56.8</td>
</tr>
<tr>
<td>4</td>
<td>176</td>
<td>31.25</td>
<td>58.5</td>
</tr>
<tr>
<td>5</td>
<td>144</td>
<td>43.75</td>
<td>67.3</td>
</tr>
</tbody>
</table>
Table 3. Effect of Photocatalytic degradation efficiency (ƞ) and Decolorization (%T) on Textile effluent under sunlight using Mn\(^{6+}\):ZnO.

<table>
<thead>
<tr>
<th>Time in Hrs</th>
<th>COD 10 mg</th>
<th>ƞ</th>
<th>%T</th>
<th>COD 20 mg</th>
<th>ƞ</th>
<th>%T</th>
<th>COD 30 mg</th>
<th>ƞ</th>
<th>%T</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>232</td>
<td>9.37</td>
<td>49.2</td>
<td>216</td>
<td>15.62</td>
<td>51</td>
<td>208</td>
<td>18.75</td>
<td>53.1</td>
</tr>
<tr>
<td>2</td>
<td>216</td>
<td>15.62</td>
<td>51.4</td>
<td>184</td>
<td>28.125</td>
<td>55.4</td>
<td>168</td>
<td>34.37</td>
<td>61.4</td>
</tr>
<tr>
<td>3</td>
<td>168</td>
<td>34.37</td>
<td>61.4</td>
<td>136</td>
<td>46.875</td>
<td>69.3</td>
<td>120</td>
<td>53.12</td>
<td>72.5</td>
</tr>
<tr>
<td>4</td>
<td>128</td>
<td>50.00</td>
<td>71.2</td>
<td>96</td>
<td>62.25</td>
<td>84.4</td>
<td>72</td>
<td>71.87</td>
<td>84.5</td>
</tr>
<tr>
<td>5</td>
<td>88</td>
<td>65.62</td>
<td>85.2</td>
<td>56</td>
<td>78.12</td>
<td>89.7</td>
<td>32</td>
<td>87.5</td>
<td>94.4</td>
</tr>
</tbody>
</table>

CONCLUSION

The synthesis of Mn\(^{6+}\): ZnO was achieved under mild hydrothermal conditions. The crystallinity, crystal structure and surface morphology were revealed by XRD, SEM and FTIR. The XRD result of the synthesized compound reveals that the doping of manganese has decreased the cell volume of the ZnO particles. The DLS study gives the population density of the synthesized compound, the results of the DLS clearly reveals that among the crystals synthesized 70 % of the crystals are in the range of 8.22-9.85nm size. The decrease in crystal size increases the surface area thereby enhancing the photodegradation efficiency of the compound. The photo-catalytic degradation of textile effluent using the prepared composite materials is an efficient and environmentally benign technique, because it facilitates the complete mineralization of the complex organics into simpler non-toxic products. The study of various kinetic parameters like initial concentration of the organics, catalyst amount, %T and COD test has helped in finding out the optimum reaction conditions. Moreover the use of sunlight as the source of illumination in the photodegradation reaction could be a safe and highly cost effective source. The textile effluent was treated successfully using the prepared compound. The decrease in the COD values from 256 to 64 demonstrated the destruction of the organics present in the effluent and increase in the % transmittance. COD reduces and degradation efficiency increases as the time increases. The proposed degradation mechanisms showed that the final products of the degradation are less toxic and environmental friendly.

REFERENCE