Zinc Oxide Decorated Carbon Nanotubes Composites for Photocatalysis and Antifungal Application

Snehal S. Wagh, Dipak B. Salunkhe, Shashikant P. Patole, Sandesh Jadkar and Rajendra S. Patil

Abstract

Zinc oxide decorated carbon nanotube composites are synthesized using reflux chemical method. Structural, morphological and optical properties were investigated using x-ray diffraction, scanning electron microscope; electron dispersion spectroscopy, UV-visible absorption spectroscopy, and Fourier transform infrared spectroscopy. In current efforts, we have explored the impact of using different zinc precursors on the morphology, structural and optical properties of zinc oxide decorated carbon nanotube (ZnO/CNT) composite. The outcome of using zinc precursors, variation in degradation time and pH has been evaluated. The dye degradation activity of as prepared composites was studied for Methylene Blue (MB) and Rose Bengal (RB) dyes under visible spectrum shows rapid decline in effective degradation time with slight surge in pH of the dye sample. The ZnO:CNT catalyst exhibits higher photo catalytic performance in comparison with the pristine ZnO when exposed to visible spectrum. The optimum efficiency achieved here is 99% in 15 min. at pH 10 and 96% in 50 min at pH 5 against MB and RB dye respectively. Further, for the first time we report the antifungal activity of the as synthesized nanoparticles against Bipolaris sorokiniana which demonstrates optimum efficiency of 34%.

Keywords: ZnO:CNT; composites; Methylene blue; Rose Bengal; Photocatalysis; Antifungal.

1. Introduction

Organic contaminants such as synthetic dyes are commonly utilized in wide range of industry including textile, pulp, letterpress, leather, body beautification, plastic and food. Therefore, eradicating them is very challenging and important. Such dyes show properties like toxicity, mutagenicity and carcinogenicity due to creation of aromatic structure by their decomposition, creating harm to the life on planet earth. Dyes also possess ability to arrest path of light penetrating through aquatic environment creating negative effect on the aquatic life. The elimination of dyes from waste and sewage water is critical to protect the environment. In contemporary times, a variety of techniques, such as membrane separation processes, adsorption processes, chemical precipitation, sono-oxidation, and photocatalysis, have been employed to eliminate organic pollutants from wastewater. There are many attempts to find viable solutions to handle the dangerous impurities. Heterogeneous photocatalysis is another such technology contributing to the total mineralization of utmost organic pollutants to carbon dioxide, water and other mineral acids. Zinc oxide (ZnO) is a prominent semiconductor material with a wide band gap of 3.37 eV and n-type conductivity, which has become a popular choice as a photocatalyst due to its unique optical and electrical properties. In addition to its photocatalytic activity, ZnO also boasts small toxicity, good stability, and cost-effectiveness, making it a promising candidate for various applications. The photocatalytic performance of ZnO is limited by the high recombination rate of charge carriers and the narrow spectrum range caused by its wide band gap. Therefore, adding substantial element to zinc oxide is an advantageous method. This addition of an element can work as an electron storage facility or steadying the catalysts on ingredients that have an extensive surface to facilitate electron transfer in resulted composite. Carbon nanotubes (CNTs) turned the world attention towards them since their inception. They can be either semiconducting, semi metallic or metallic, depending on the helicity and the
diameter of the tube. multi walled CNTs (MWCNTs) possess remarkable characteristics such as good electrical and thermal conductivity, large mechanical strength, elasticity, good catalytic activity, strong adsorptive ability, large surface area and high aspect ratio. They are assumed to be rolled graphene sheets. CNTs based composites have fascinated researchers because they alter or enhance the properties of material by adding the carbon nanotubes into the host material. CNTs are non-polar in nature making them hydrophobic. A very strong bond is formed due to π electrons present on the exteriors of carbon nanotubes. The hydrophobic property of CNTs can be altered by functionalization process. Functionalization of CNTs is a process of attachment of individual atoms, molecules to CNTs. Such Functionalized MWCNTs are broadly used in synthesis of catalysts. Zeo et al proposed that the dye degradation performance of CNT loaded ZnO blends are better than pristine ZnO.

ZnO:CNT composite were synthesized by thermal method to degrade carcinogenic acetaldehyde under Laser irradiation for 60 min. Samadi et al reported fabrication of MWCNT-doped ZnO nanofibers by electro-spinning method. The band gap concentrated to 2.94 eV and photo catalytic activity for methylene blue dye raised 7 folds. ZnO/N-CNT were synthesized via chemical precipitation approach to degrade methylene blue and benzoic acid shown enhanced results. ZnO:CNT composite prepared using facile sol method shown highest degradation of rhodamine B (RhB) via sono photocatalysis method for 10wt% CNT on ZnO. Thorn-like ZnO-MWCNT was prepared by hydrothermal method shown removal of RhB in 90 min under the influence of ultra violet light. ZnO/Co-Ni-Al layered CNT hybrid known as ZNO/MMO/CNT composite synthesized to degrade Acid red at pH 5.5 shown efficiency of 96.2% under irradiation of visible light for 120 min.

Recently it has been proven that functionalized multi walled carbon nano tubes decrease their immunity distresses with mice and macrophages, also it shown improved colloidal properties without altering their characteristic antibiosis performance. Therefore surface modifications in MWCNTs were found to be more effective against Fusarium graminearum. CNT along with Toyocamycin shown selective toxicity against Candida albicans. Thus, making CNTs a good candidate against fungal growth. The fungal species Bipolaris sorokiniana (formerly known as Helminthosporium sativum and also called Cochliobolus sativus in its sexual form) is responsible for inducing spot blotch disease in wheat, which can result in severe damage to the crop and economy.

In this study we have synthesised functionalized CNT modified ZnO via zinc chloride, zinc nitrate and zinc acetate resources to understand its effect on variation in precursor, dyes and its pH. Also we are first time reporting antifungal activity on the spot blotch of wheat using ZnO:CNT composites.

2. Experimental

2.1 Materials and methods

All the chemicals utilized in current effort were of AR grade and utilized as purchased excluding any further refinement. Zinc acetate (Sisco Research Lab (SRL), India), zinc nitrate hexahydrate (Merck life sciences pvt. ltd., India), zinc Chloride (Thomas Baker (Chemicals) Pvt. Ltd., India), diethylene glycol (Sisco Research Lab (SRL), India), Sodium Hydroxide pellets (ACROS organics, India), multi walled Carbon Nano Tube (Monad Nano Tech Pvt. Ltd, India), Sodium Lauryl Sulphate (Loba Chemicals Pvt. Ltd., India), Methylene Blue (HPLC ltd, India) and Rose Bengal (Molychem ltd., India) commercially purchased. Potato dextrose agar medium (Himedia, Mumbai, India) was commercially purchased. The preparation of solutions was carried out with double distilled water (DDW).

2.2 Functionalization of CNT surface

10 mg sodium lauryl sulphate (SLS) was suspended in 50 ml of ethanol, with the addition of 10 mg CNT followed by sonication of 2 hours. To form functionalized CNTs, the blend was repeatedly splashed with ethanol and centrifuged to eliminate any extra surfactant, after which it was dried at 70 °C for 24 hours.

2.3 Synthesis of ZnO:CNT composite

Zinc oxide carbon nano tube composites samples were obtained by simple reflux method as reported earlier using zinc chloride, zinc nitrate and zinc acetate as precursor sources. Each of 1M zinc precursor solutions were prepared in 100 ml double distilled water (DDW) by adding 10 ml diethylene glycol and stirring for additional 2 h at 80 °C. Subsequently, 10 mg of functionalized MWCNTs were sonicated for two hours in 10 mL of DDW and mixed with the zinc precursor solution. A solution of zinc hydroxide was prepared using 100 mL of double distilled water and slowly added to the above mixture at a rate of one drop per second for 2 hrs. at 80 °C. The prepared solution was allowed to cool overnight which appeared blackish brown in colour. The outcome of the reaction was washed and centrifuged multiple times with ethanol at 2000 rpm with drying at 70 °C for 36 hrs. The powder was dried followed by grinding and then annealed for 2 hrs. at 400 °C to obtain ZnO:CNT composite. The ZnO:CNT composite samples prepared with zinc chloride, zinc nitrate and zinc acetate precursor were named as ZC-C1, ZC-N and ZC-Ac respectively.

2.4 Characterization methods

The crystallite structure, phase and average crystallite size of zinc oxide nanoparticle were determined by x-ray diffraction (XRD) method on a Rigaku diffractometer (D/B max-2400, CuKα15406 nm, Rigaku, USA). Morphology analysis was performed field emission scanning electron microscopy (FESEM) (NOVA Nano SEM NPEP303, USA), Optical studies were carried using UV–vis spectrophotometer.
(JASCO V-670, Germany) and FTIR spectroscopy (Bruker Alpha, USA). Photo catalytic activities of the ZnO:CNT composites were performed in aqueous medium of methylene blue and rose bengal under OSRAM ultra vitalax 300 W halogen lamp as the source of visible light (emission range ~400–800 nm) at room temperature.

3. Results and discussion
3.1 Structural properties

We have investigated the XRD pattern of ZC-Cl, ZC-N and ZC-Ac as displayed in Fig. 1. The validation of nanocrystal development is demonstrated by observing the broadened peaks of pure ZnO in the corresponding XRD pattern.[22] The incorporation of CNTs into ZnO prevents the formation of secondary phases in the XRD pattern of ZnO:CNT composite materials. Fig. 1 displays XRD pattern of pristine CNT, ZC-Cl, ZC-N and ZC-Ac respectively. The XRD peaks corresponding to diffractions of the (100), (002), (101), (102), (110), (103), (200), and (112) planes were detected as the hexagonal phase of ZnO (JCPDS Card No. 653411) for all samples.[22] The pristine CNT shows sharp diffraction peak at (002) and low intensity peaks at (100), (004) planes.[23] In addition to measuring micro strain and dislocation density, the Scherrer formula was used to determine the average crystallite size.[22,24] Table 1 shows average crystallite size of 29 nm, 36 nm and 24 nm for ZC-Cl, ZC-N and ZC-Ac respectively, corresponding to prominent orientations of (100), (002) and (101) peaks. Table 1 demonstrates that the micro strain and dislocation density of the ZnO:CNT composite are inversely proportional to its crystallite size.[22] Here ZnO displays hexagonal structure with $\alpha=\beta=90^\circ$ and $\gamma=120^\circ$ for all samples.[25]

Table 1. Parameters calculated from XRD analysis.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Crystal structure</th>
<th>Average Crystallite size (D) nm</th>
<th>Micro strain ($\varepsilon$) $\times 10^{-3}$</th>
<th>Dislocation density $\delta$ $\times 10^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZC-Cl</td>
<td>Hexagonal</td>
<td>26</td>
<td>3.4</td>
<td>1.6</td>
</tr>
<tr>
<td>ZC-N</td>
<td>Hexagonal</td>
<td>34</td>
<td>1.1</td>
<td>0.9</td>
</tr>
<tr>
<td>ZC-Ac</td>
<td>Hexagonal</td>
<td>23</td>
<td>1.7</td>
<td>2.1</td>
</tr>
</tbody>
</table>

3.2 Optical studies

The UV-visible spectra in absorbance mode for ZnO:CNT composite nanoparticles were shown in Fig. 2(a). This indicates that the absorption of charges, as they move from the valence band (VB) to the conduction band (CB) of ZnO, results in a strong absorption edge in the UV region (200–420 nm).[26,27] Fig. 2 displays a plot of $(Ah\nu)^{2}$ versus photon energy (h\nu), which was used to determine the band gap energy (Eg) of the powder samples collected by extending the intercept of its linear region on the x-axis. Band gap Energies for ZC-Cl, ZC-N and ZC-Ac were observed to be 3.29 eV, 3.22 eV and 3.20 eV respectively. The absorbance maxima obtained this study are 359 nm, 365 nm and 365 nm for ZC-Cl, ZC-N and ZC-Ac samples respectively.

Fig. 1 XRD of Pristine CNT, ZC-Cl, ZC-N, and ZC-Ac.

Fig. 2 (a) UV-visible spectra (b) FTIR spectra of ZC-Cl, ZC-N and ZC-Ac respectively.
The FT-IR spectrums illustrate the information of a particular compound, functional groups, molecular geometry, and inter/intra-molecular interactions. Fig. 2(b) displays the FT-IR spectra of as prepared (i) ZC-Cl, (ii) ZC-N, and (iii) ZC-Ac nano composite respectively, performed in the wave number range 400–4000 cm\(^{-1}\) using the KBr pellet method at room temperature. All FT-IR spectra display a broad absorption band at around 3400–3600 cm\(^{-1}\) due to the presence of the O–H stretching mode of the hydroxyl groups. The absorption band around 2800–2900 cm\(^{-1}\) was identified as a stretching mode for the C–H bond of residues of SLS. The absorption band around 2320–2350 cm\(^{-1}\) was identified as a stretching mode for the C≡N bond. The band positioned at 1530 cm\(^{-1}\) characterizes the H–O–H bending vibration of water and the band near 1400 cm\(^{-1}\) corresponds to asymmetric stretch of C=C=C. The bands in the low wave number region, 426 cm\(^{-1}\), correspond to the vibration modes of Zn–O. It was observed that seen the hydroxyl and carboxylic groups have their prominent presence on the surface of the catalysts, it enhances the photocatalytic activity.

### 3.3 Morphological and compositional properties

The FESEM images of ZC-Cl, ZC-N and ZC-Ac respectively at 500 nm magnification were displayed in Fig. 3. It was found that there is agglomeration of ZnO particles on CNT, displaying cauliflower like morphology. Each FESEM micrographs shows varying particle size which also differs with change in zinc precursor’s material having small to large size range. The bigger size particles were occurring due to agglomeration effect. Here the average sizes of particle and diameter of CNT calculated using FESEM images were approximately 56 nm and 80 nm respectively.

Figure 3(d) shows EDS spectrum for ZC-Cl, ZC-N, ZC-Ac. The composition and distribution of ZnO:CNT composite nanoparticles is indicated by EDS mapping which shows the even distribution of CNTs in ZnO array. The distribution of zinc and oxygen peaks in EDS mapping confirms the purity of ZnO nanoparticles. The occurrence of Carbon peak in ZnO:CNT array adds to the composite formation in the matrix. The Atomic % of ZnO:CNT is shown in Table 2 for ZC-Cl, ZC-N and ZC-Ac samples.

<table>
<thead>
<tr>
<th>Sample/</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zn</td>
</tr>
<tr>
<td>ZC-Cl</td>
<td>58</td>
</tr>
<tr>
<td>ZC-N</td>
<td>42</td>
</tr>
<tr>
<td>ZC-Ac</td>
<td>67</td>
</tr>
</tbody>
</table>

Fig. 3 FESEM micrograph of (a) ZC-Cl, (b) ZC-N, (c) ZC-Ac, and (d) EDS spectra.
3.4 Photocatalytic study
Photocatalytic activity studies of ZnO:CNT were performed under the irradiation of sunlight with methylene blue and rose Bengal as a representative pollutant. In current work we have explored the photocatalytic effect of the as prepared composites on methylene blue and rose Bengal dye. 10 ppm each of MB and RB dye solutions were prepared by dissolving 10 mg each of methylene blue dye and rose Bengal dye in 1000 ml double distilled water separately. The photo catalytic performance was initially examined in dark environment to see the consequence of adsorption. Both, MB and RB dyes do not display any noticeable result by adsorption in photo catalytic reaction.

Initially, for MB dye, three beakers set, each containing 100 ml as prepared MB dye solution having pH value 6 were added with 0.1 g ZC-Cl, ZC-N and ZC-Ac catalysts separately under visible light irradiation of intensity 1 sun. At fixed time interval, 2 mL of the dye solution were taken during the experiment, which are then centrifuged and their absorption spectra are carried out using UV–vis spectroscopy. The study shows that as irradiation time increases, the intensity of absorption decreases. The degradation of MB dyes at pH 6 is as shown in Fig. 4. Percentage photocatalytic efficiency was measured using Beer–Lambert law as presented in Equation (1).\[^{32,33}\]

\[
R = \left(1 - \frac{C_f}{C_0}\right) \times 100 = \left(1 - \frac{A_f}{A_0}\right) \times 100
\]  

(1)

The percentage dye degradation of all samples was calculated using Equation (1).

The photo catalytic activity of given samples with respect to time, can be explained using the pseudo-first-order-equation in Equation (2).\[^{34}\]

\[
\ln \left(\frac{C_f}{C_0}\right) = -kt
\]  

(2)

where \(C_1\) is concentration of dye (mg/L) at an instant ‘\(t\)’, ‘\(t\)’ is the time for which irradiation of sample takes place and \(k\) is adsorption constant of dye on nanoparticles.\[^{22}\]

Also, calculation of the half-life, \(t_{1/2}\), is performed using following Equation (3).

\[
t_{1/2} = \frac{\ln 2}{k}
\]  

(3)

Table 3 summarizes values of rate constant, half-life, relative concentration and photocatalytic efficiency of degradation of MB dye using ZC-Cl, ZC-N and ZC-Ac under visible light irradiation for 15 minutes for pH varying from 6 to 12.

The surface alteration of CNTs might have a substantial impact on the enhanced photocatalytic performance. The photocatalytic degradation outcome of the ZnO:CNT composites may be reasonably elucidated in a mechanism built on two measures. In the first scenario the catalysis is due to adsorption capability of CNTs which indeed has impact on the catalytic annihilation of impurities. While in the another case is the electron transmission from ZnO to the CNTs performs the electron injection.\[^{35,36}\] When ZnO was irradiated with photons of sufficient energy, equal to or greater than its band gap energy, electrons from its valence band (VB) are raised to its conduction band (CB). As a result, holes are created in the valence band of ZnO, which react with hydroxyl to form hydroxyl radicals.

Additionally, the reaction of excited CB electrons with dissolved oxygen also produces superoxide anion radicals. These generated hydroxyl radical and superoxide anion radicals destruct the dye molecule. Thus the conduction band electron of ZnO may directly get involved with oxygen molecules which were adsorbed on the surface of CNTs, forming a superoxide radical. Hence there is an abundance of reactive radicals to disintegrate the dye. Also CNTs are capable of adsorbing the dye considered as well-thought-out principal phase in the efficient photo-degradation of dye.\[^{37}\] The OH⁺ radical that is produced is capable of breaking the various bonds present in the dye, causing it to break down into carbon dioxide and other inorganic ions (such as NH₄⁺, NO₃⁻, SO₄²⁻ etc.). Ultimately, the hydroxyl radicals degrade the MB dye through hydrogen abstraction and subsequent oxidation processes [Equations (4–10)].\[^{38,39}\]

\[
\begin{align*}
\text{ZnO} + \text{hv} \rightarrow & \text{hole} (h^+) + (e') \quad (4) \\
\text{ZnO} (e') + \text{CNT} \rightarrow & \text{CNT(eCB)} + \text{ZnO} (h^+) \quad (5) \\
\text{CNT} (e_{\text{CB}}) + \text{O}_2 \rightarrow & \text{ZnO} + \text{O}_2^{-} \quad (6) \\
\text{H}_2\text{O} \rightarrow & \text{OH} + \text{H}^+ \quad (7) \\
\text{O}_2^{-} + \text{H}^+ \rightarrow & 2\text{HO}_2 \rightarrow \text{H}_2\text{O}_2 \rightarrow \text{OH} + \text{OH}^- + \text{O}_2 \quad (8) \\
\text{ZnO} (h^+) + \text{OH} \rightarrow & \text{ZnO} + \text{OH}^- \quad (9) \\
\text{MB} + \text{OH} \rightarrow & \text{H}_2\text{O} + \text{MB}^- \rightarrow \text{degradation products} \quad (10) \\
\end{align*}
\]

Alternatively, the durable collaboration and development of ester bonds among the zinc with CNTs heading to a handy interaction, this provides an operative path for electron shift from the CB in to the CNT’s reducing the recombination of photo generated electron-hole pairs resulting in disintegration of dye into constituent elements as described in Equation (11–17). Thus there is observably higher activity of the ZnO:CNT composites because CNTs are being comparatively more electron acceptors while semiconductors are decent electron donor under illumination of light [Equations (11–17)].\[^{40,41}\]

\[
\begin{align*}
\text{CNT} + \text{hv} \rightarrow & \text{hole} (h^+) + (e') \quad (11) \\
\text{CNT} (e') + \text{ZnO} \rightarrow & \text{ZnO} (e_{\text{CB}}) + \text{CNT} (h^+) \quad (12) \\
\text{H}_2\text{O} \rightarrow & \text{OH} + \text{H}^+ \quad (13) \\
\text{ZnO} (e_{\text{CB}}) + \text{O}_2 \rightarrow & \text{ZnO} + \text{O}_2^- \quad (14) \\
\text{O}_2^- + \text{H}^+ \rightarrow & 2\text{HO}_2 \rightarrow \text{H}_2\text{O}_2 \rightarrow \text{OH} + \text{OH}^- + \text{O}_2 \quad (15) \\
\text{CNT} (h^+) + \text{OH} \rightarrow & \text{CNT} + \text{OH}^- \quad (16) \\
\text{MB} + \text{OH} \rightarrow & \text{H}_2\text{O} + \text{MB}^- \rightarrow \text{degradation products} \quad (17) \\
\end{align*}
\]

Similarly, 10 ppm of rose Bengal (RB) dye solutions was formed by adding 10 mg of RB dye with 1000 ml double distilled water. To perform photocatalysis experiment, initially three beaker set, each containing 200 ml as arranged RB dye solution were mixed with 0.1 g ZC-Cl, ZC-N and ZC-Ac catalysts separately under visible light irradiation of intensity 1 sun at pH value 5. Samples of 2 mL of the dye solution were collected at fixed time intervals during the experiment. These samples were centrifuged and absorption spectra are carried out using UV–vis spectroscopy. Fig. 5(f) represents the photocatalytic degradation efficiency of RB dye for ZC-Cl, ZC-N and ZC-Ac at pH 5.
Fig. 4 Photocatalytic degradation of methylene blue dye for (a) ZC-Cl, (b) ZC-N, (c) ZC-Ac at pH 6 and rose Bengal dye for (d) ZC-Cl, (e) ZC-N, (f) ZC-Ac at pH 5.

Table 3. MB dye degradation parameters for ZC-Cl, ZC-N and ZC-Ac under visible light irradiation at pH 6 to 12.

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH of sample</th>
<th>Rate constant</th>
<th>Half life (min)</th>
<th>Relative concentration ((x 10^2))</th>
<th>Degradation efficiency in 15 min (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZC-Cl</td>
<td>06</td>
<td>0.06</td>
<td>15</td>
<td>46</td>
<td>53</td>
</tr>
<tr>
<td>ZC-N</td>
<td>06</td>
<td>0.06</td>
<td>15</td>
<td>43</td>
<td>56</td>
</tr>
<tr>
<td>ZC-Ac</td>
<td>06</td>
<td>0.07</td>
<td>13</td>
<td>40</td>
<td>60</td>
</tr>
<tr>
<td>ZC-Cl</td>
<td>08</td>
<td>0.07</td>
<td>10</td>
<td>31</td>
<td>69</td>
</tr>
<tr>
<td>ZC-N</td>
<td>08</td>
<td>0.07</td>
<td>10</td>
<td>27</td>
<td>73</td>
</tr>
<tr>
<td>ZC-Ac</td>
<td>08</td>
<td>0.07</td>
<td>9</td>
<td>24</td>
<td>76</td>
</tr>
<tr>
<td>ZC-Cl</td>
<td>08</td>
<td>0.38</td>
<td>1.8</td>
<td>4</td>
<td>96</td>
</tr>
<tr>
<td>ZC-N</td>
<td>10</td>
<td>0.59</td>
<td>1.2</td>
<td>3</td>
<td>96</td>
</tr>
<tr>
<td>ZC-Ac</td>
<td>10</td>
<td>0.46</td>
<td>1.5</td>
<td>1</td>
<td>99</td>
</tr>
<tr>
<td>ZC-Cl</td>
<td>12</td>
<td>0.356</td>
<td>1.94</td>
<td>8</td>
<td>93</td>
</tr>
<tr>
<td>ZC-N</td>
<td>12</td>
<td>0.378</td>
<td>1.83</td>
<td>7</td>
<td>94</td>
</tr>
<tr>
<td>ZC-Ac</td>
<td>12</td>
<td>0.373</td>
<td>1.85</td>
<td>6</td>
<td>95</td>
</tr>
</tbody>
</table>
3.5 Effect of pH

Studying the effect of pH on the efficiency of photo catalytic progress is an intriguing task, as processes such as hydroxyl radical attack, direct oxidation by the positive hole, and direct reduction by CB electrons can influence the photo catalytic process.\[42\] When the pH of the dye system was reduced, the photo catalytic performance reduces due to lack of oxygen and hydroxyl radicals. When the pH of the dye solution was increased, the OH\(^{-}\) ions generate a negatively charged surface on the catalyst, leading to a decrease in the surface concentration of the dye and an increase in that of OH radicals. Thus in alkaline medium, the OH\(^{-}\) ions enhances the rate of photo assisted degradation reaction.\[4\]

The pH of the dye solution is a significant factor that affects the rate of photocatalysis during the photo catalytic study. Hence in understanding its effect, we have varied the pH of MB dye solutions from 6 to 12 by accumulation of fitting volumes of 0.01M NaOH solution. In alkaline environment, the concentration of OH\(^{-}\) ions is higher, thus the surface of catalyst powder sample becomes negatively charged by virtue of the attachment of OH\(^{-}\) and the zinc atom, helps to increase the rate of photocatalysis.\[4\] From literature it was observed that, in the acidic environment ZnO tend to get away with its oxygen to the hydrogen ion becoming water-soluble, (Equation (18)) in turn losing its photo catalytic property.\[43–45\]

\[\text{ZnO} + 2\text{H}^{+} \rightarrow \text{Zn}^{2+} + \text{H}_{2}\text{O}\]  
(18)

![Fig. 5](image-url)  
Fig. 5 Photocatalytic efficiency of MB dye for ZC-Cl, ZC-N and ZC-Ac catalysts at pH (a) 6, (b) 8, (c) 10, and (d) 12. (e) Photocatalytic efficiency with variation in pH for MB. (f) Photocatalytic efficiency of RB dye at pH 5.
Here, we have studied the effect of variation in pH of MB dye only. The dye degradation experimentation was by repeated keeping pH of dye solution at 6, 8, 10 and 12. Fig. 5 shows the photocatalytic degradation efficiency of MB dye for ZC-Cl, ZC-N and ZC-Ac for pH varying from 6 to 12. From our observations, initially the degradation performance increases with the rise in pH value of dye solution from 6 to 10 and then decreases as pH further raised up to 12. This might be attributed to chemical stability of dye structure at high pH values even after irradiation of light. Similar results were reported in the literature for variation in degradation performance with change in pH. The distinction in the photocatalytic performance of MB of with irradiation time and pH by ZC-Cl, ZC-N and ZC-Ac catalysts is illustrated in Fig. 5.

### 3.6 Antifungal Activity

In this study, we have evaluated the antifungal activity of ZnO:CNT against a phytopathogenic fungi namely Bipolaris sorokiniana which is causing spot blotch disease in wheat. Potato dextrose agar (PDA) is a regularly used medium for the culture of fungi, making it an appropriate substrate for testing the antifungal activity of catalysts. PDA is made up of potato infusion and dextrose, both of which supply nutrients for fungal development. The ZnO:CNT catalyst is added into the media at a specified concentration to test antifungal activity. The medium is subsequently injected with fungal spores, and the development of the fungi is tracked over time. The antifungal activity of the substance under test is determined by the suppression of fungal growth, which is manifested by a lack of apparent growth or a reduction in the number of fungal colonies. Our findings suggest that ZnO has significant potential as an alternative to synthetic fungicides for the management of plant diseases. The photo induced generation of ROS and a poisoning effect because to Zn$^{2+}$ releases are the two key suppliers to the antifungal performance of ZnO nanoparticles. The mechanism of action for ZnO:CNT against fungi involves the production and accumulation of ROS and free radicals, which mainly affect the cell wall, surface protein, and nucleic acid of the fungi. Additionally, they block proton pumps. This suggests that ZnO:CNT has the potential to be an effective treatment for fungal infections. The antifungal activity of ZnO:CNT was evaluated using the Poisoned food method. The diameter are measured using Kirby Bauer method (Equation 19).

\[
\% \text{ Antifungal Activity} = \frac{(D_c - D_s)}{D_c} \times 100
\]  

where, $D_c$ is the diameter of growth in the control plate, and $D_s$ is the diameter in the plate containing ZnO:CNT nanoparticles. The % antifungal activity of the ZC-Cl, ZC-N and ZC-Ac are 34%, 25% and 24% respectively. Fig. 6 shows inhibition of fungus against ZC-Cl, ZC-N and ZC-Ac composites.

**Fig. 6** Antifungal activity of ZnO/CNT against Bipolaris sorokiniana for (a) control (b) ZC-Cl, (c) ZC-N and (d) ZC-Ac.
4. Conclusions
In this study, ZnO:CNT nano composites were formed by refluxed chemical method. XRD analysis shows the structural clarity of ZnO:CNT nano composites. The XRD investigation has revealed non presence of carbon peaks and the average crystallite sizes of the Nano composites were ranging from 23 nm to 26 nm. The micro strain for ZnO:CNT slightly changes with change in precursors. Lattice parameters, crystal structure and band gap energy of ZnO:CNT crystal structures for all ZC-Cl, ZC-N and ZC-Ac were found to be of very nearing values. FE-SEM and EDS analysis confirms the occurrence of ZnO on the exteriors of CNT. The FESEM micrograph shows agglomerated nano flower like morphology. The photo catalytic activity of MB and RB dyes were found to be higher for ZnO:CNT composite in comparison with pristine ZnO as reported in our earlier work. There was increase in photo catalytic efficiency with increase in pH of dye solution up to optimum value. The optimum result for MB dye was observed for ZC-Ac at pH 10 showing 99% photo catalytic efficiency in 15 minutes. While the RB dye showed 96 % photo catalytic efficiency in 50 minutes at pH 5. Also we have investigated first time the usage of ZnO:CNT as an antifungal agent against Bipolaris sorokiniana. It was observed that Zn-Cl shows better inhibition of Bipolaris sorokiniana fungus showing 34 % efficiency.

Acknowledgement
Authors are thankful to the members of Advanced Physics Laboratory for experimental facilities and fruitful discussion.

Conflict of Interest
There is no conflict of interest.

Supporting Information
Not applicable.

References


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