Effectiveness of ZnO/carbon-based material as a catalyst for photodegradation of acrolein

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ABSTRACT

Acrolein (ACR) is a metabolite of cyclophosphamide (CYP) and induces hemorrhagic cystitis (HC). Here, we investigated the effectiveness of ZnO/carbon fiber (CF) composites as catalysts for removing ACR through photodegradation. Specimens composed of CF and zinc oxide (ZnO) were prepared and annealed at 200–400 °C in air. For the ZnO/CF specimen annealed at 200 °C (CZ200), a continuous and porous ZnO film was formed on the CF surface. Field-emission scanning electron microscopy and physisorption analysis indicated that this composite had a high specific surface area. X-ray diffraction analysis and photoluminescence spectroscopy showed that the ZnO film was amorphous, exhibiting a broad emission spectrum. An ultraviolet (UV) radiation-based degradation system and methylene blue (MB) solution were used to evaluate the feasibility of using the composites as photodegradation catalysts. CZ200 exhibited the highest MB photodegradation rate (95%). The photodegradation of ACR (75 ppm) under 4 W UV light was investigated using an untreated CF sample, an active carbon fiber (ACF) fabric sample, and the CZ200 specimen. CZ200 (45%) exhibited higher ACR degradation rate than CF (8%) and ACF (28%). Hence, we confirmed that ZnO/CF composites can be used to photodegrade ACR and have potential for use in preventing CYP-induced HC in chemotherapy patients.

1. Introduction

Cyclophosphamide (CYP) is an oxazaphosphorine alkylating agent widely used in the treatment of both malignant and nonmalignant diseases such as lymphoproliferative disorders, nephritic syndrome, rheumatoid arthritis, systemic lupus erythematosus, and solid tumors. It also plays a role in bone marrow transplantation [1]. CYP can inhibit DNA synthesis and cell apoptosis in cancer cells, but in the process, it causes the byproduct acrolein (ACR) to be produced [2]. This is an urototoxic metabolite of alkylating antineoplastic agents and can induce hemorrhagic cystitis (HC). Direct contact between ACR and the urothelium can result in vesical edema, erosion, hemorrhage, inflammation, ulceration, and, in extreme cases, life-threatening HC [2]. Hemorrhage usually occurs during or immediately after treatment, both when short-term, high, or long-term, low doses are administered. Despite vigorous preventive measures, a mortality rate of 4% has been reported among patients who develop severe HC [1].

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2-mercaptoethane sodium sulfonate (mesna) have reduced the incidence of HC to 6–50%. However, there are a number of side effects of using mesna, including nausea, vomiting, headache, diarrhea, and generalized weakness. In a randomized controlled clinical study of recipients who received ifosfamide-based chemotherapy, we had found that, even after a classical prophylaxis treatment involving three doses of mesna, 66.7% of the patients presented with gross cystoscopic injuries, and all of them had urothelial issues such as edema, exocytosis, and hemorrhage [2,3].

ACR is a highly toxic, reactive, and irritating aldehyde. It is an intermediate in the industrial production of acrylic acid, DL-methionine, and numerous other agents. It is generally removed from aqueous environments by volatilization and hydration to beta-hydroxypropanal followed by biotransformation [2]. Activated carbon can also be used to adsorb ACR from solutions, but this results only in a removal of 30% of the ACR present [2]. Therefore, the removal of ACR from an in vivo environment is a significant challenge, but one that must be overcome, as the development of a method for removing the substance from the bladder, either partially or completely, would go a long way in reducing the occurrence of HC. In this paper, we report the use of photodegradation techniques for decreasing the concentration of ACR in solutions, towards the development of a method to degrade the compound in vivo and reduce damage to the bladder.

Photodegradation techniques have been applied in water and wastewater purification as well as in air purification [3]. Originally, it involved the use of a semiconductor photocatalyst to remove organic substances from solutions. During the photodegradation process, photons with an energy \( (h\nu) \) higher than the band gap energy \( (E_g) \) of the semiconductor catalyst excite electrons \( (e^{-}) \) from the valence band (VB) to the conduction band (CB), leaving a positive hole \( (H^+) \) behind [4]. Zinc oxide (ZnO) is one of the most popular photocatalysts for treating organically polluted water; Gouvea et al. report that it is more efficient than anatase TiO\(_2\) [5]. The activation of ZnO as photocatalyst in water, on irradiation with ultraviolet (UV) light, occurs as per the following steps:

\[
\text{ZnO} + h\nu (\lambda < 390 \text{ nm}) \rightarrow e^{-} + H^+ \\
O_2 + e^{-} \rightarrow O_2^- \\
H_2O + H^+ \rightarrow OH^- + H^+ 
\]

The byproducts, that is, the \( O_2^- \) (anion) and \( OH^- \) (hydroxyl) radicals can decompose a number of toxic organic compounds [4]. ZnO has not only high photocatalytic efficiency, but it has also been given the “generally recognized as safe” (GRAS) status by the US Food and Drug Administration (21CFR182.8991) [7]. It is biocompatible and has antibacterial properties [8]. Zn ions, when generated in a wet environment, can damage cell membranes by direct or electrostatic interactions and produce active oxygen species such as \( H_2O_2 \) in the cells; these oxygen species can kill bacteria. In a recent study, Zhou et al. used a solvothermal method that combined different techniques based on the use of ZnO as photodegradation catalyst and other high-adsorption materials to quickly adsorb contaminants from wastewater and decolorize it [6].

There are, however, a number of issues related to the use of ZnO as a photodegradation catalyst in the bladder. First, ZnO particles are small and thus are readily absorbed into the body through the bladder epithelial tissue and can potentially cause numerous other problems. Second, when used in large concentrations, ZnO particles aggregate and exhibit low photon efficiency; this necessitates extended treatment times. Hence, a suspension of ZnO cannot be used directly for photocatalytically removing ACR from the bladder. An additional problem is that the bladder epithelial tissue can be damaged by UV light. Aqueous solutions of ZnO are milky and allow UV light to be transmitted through them. It is therefore necessary to have some form of barrier present that can absorb the light and prevent it from reaching the bladder tissue.

In recent years, carbon fiber (CF) has been used widely as a supporting photocatalyst for boosting photoconversion efficiency [9]. It is also used in bone tissue applications, including in the manufacture of artificial joints. Moreover, owing to its chemical inertness and biocompatibility, CF can be placed in the human body for long periods without causing any problems.

Hence, in this study, we used CF as a supporting catalyst, owing its high light absorptivity, low toxicity, and low transmissivity for UV light. Most importantly, CF was used because it can potentially protect the bladder wall from damage from UV radiation. We also assumed that CF would support ZnO as a UV light-obstructing material and help boost the photodegradation efficiency of ZnO.

In this study, we simulated the phototherapeutic decomposition of ACR in the bladder using ZnO/CF composite specimens annealed at different temperatures as catalysts (Fig. 1) and evaluated the catalytic efficacy of the specimens. To do so, we fabricated a photodegradation device that mimicked the bladder (Fig. 2) and used it to determine the ZnO/CF composite that was the most effective as a photodegradation catalyst. For this, methylene blue (MB) was used as a model contaminant. We then investigated the suitability of the sample for photodegrading ACR.

2. **Experimental**

2.1. **Materials**

Oxidized polyacrylonitrile (PAN) fiber fabric was purchased from Kuo Tung Fabric Co., Ltd. (Taiwan, ROC). Active carbon fiber (ACF) fabric was purchased from Taiwan Carbon Technology Co., Ltd. (Taiwan, ROC). Zinc acetate (Zn(CH\(_3\)COO)\(_2\)), \( 2\text{H}_2\text{O} \), used as the photocatalyst source material, isopropyl alcohol (IPA), and ammonium hydroxide (\( \text{NH}_4\text{OH} \)) were purchased from Union Chemical Works Ltd. (Taiwan, ROC). Reagent-grade zinc oxide was purchased from Union Chemical Ltd. (Taiwan, ROC). Analytical-grade methylene blue was purchased from NBS Biologicals Ltd. (UK).

2.2. **Sample preparation**

The oxidized PAN fiber fabric was first carbonized at a temperature of 1000 °C to produce CF fabric. Next, the ZnO/CF composites were prepared, using a sol–gel route, as follows:
50 mL of a 0.1 M stock solution of Zn(CH₃COO)₂ in IPA was added to 3 mL of a 6 M solution of NH₄OH in IPA. The mixture was heated to 70°C and kept at this temperature for 3 h. This resulted in a milky solution with a pH of 10.1. A 5·5 cm piece of the CF fabric (0.250 g) was immersed in the sol–gel solution, incubated at 70°C for 1 h, and then dried in an oven at 70°C for 1 h. The coated piece of CF fabric was then subjected to rapid thermal annealing, resulting in the final ZnO/CF photocatalyst material (Fig. 3).

In order to determine the optimal fabrication conditions, three different annealing temperatures (200, 300, or 400°C) were tested. Each sample was annealed for 1 min in air and then allowed to cool to room temperature. The resulting samples are denoted as 0.1MCZ200, 0.1MCZ300, and 0.1MCZ400, in reference to the 0.1 M Zn(CH₃COO)₂ solution used and the different annealing temperatures.

2.3. Sample characterization

The morphologies and shapes of the ZnO/CF composite samples were observed using field-emission scanning electron microscopy (FESEM) (S-4800, Hitachi, Japan). The microstructures and crystalline natures of the samples were determined by transmission electron microscopy (TEM), performed using a system (Tecnai G2 F20, FEI, USA) with a retractable energy-dispersive X-ray analysis (EDAX) detector. The system was operated at an accelerating voltage of 200 keV. Before the TEM-based analyses, the G1 epoxy adhesive was used to bond the ZnO/CF composite samples (0.1MCZ200, 0.1MCZ300, and 0.1MCZ400), and then cured, polished and dried. After above preparation, the ZnO/CF TEM samples were finished. The elemental composition of ZnO/CF was measured using an EDAX spectrometer (EDAX company, USA). The structures of the ZnO/CF samples were identified using X-ray diffraction (XRD) analyses (D8 SSS, Bruker, USA), which were performed with Cu Kα radiation. The surface areas of the samples were determined on the
basis of their N₂ adsorption isotherms, obtained at 77 K using a physisorption analyzer (ASAP 2020, Micrometrics, USA). Prior to the analyses, the samples were degassed overnight in vacuum (10⁻³ Torr) at 120 °C. The surface areas were analysed by the Brunauer–Emmet–Teller (BET) method, and their micropore volumes along with their pore size distributions were calculated from the isotherms using the density functional theory (DFT) method [10]. X-ray photoelectron (XPS)/Auger spectroscopy (SigmaProbe, Thermo VG-Scientific, UK) was performed using a Mg Kα X-ray source at a residual gas pressure of less than 10⁻¹⁰ Pa. The UV–visible (Vis) spectra of the samples were obtained using a UV–Vis spectrometer (UV-1601, Shimadzu, Japan). Micro-Raman/photoluminescence (PL) spectroscopy was performed at room temperature using a Raman microscope (inVia, Renishaw, UK) with a 325 nm He–Cd laser.

2.4. Evaluation of photocatalytic degradation

The efficiency of the ZnO/CF composites as photodegradation catalysts was determined using MB as a model contaminant. A photodegradation reactor system with a capacity of 50 mL was developed. The system consisted of two parts: a UV light source and a photoreaction vessel. Four pairs of studs and nuts were used to assemble the equipment and to fix and control the distances at 10 cm. The UV light source was a 100 W UV mercury lamp with a peak wavelength of 365 nm (China Electric Mfg. Corp., Taiwan, ROC). The lamp was fixed at the center of a bakelite plate (15 × 15 cm), as shown in Fig. 2.

The photoreaction vessel had a five-layered sandwich structure, consisting of two acrylic panels, two pieces of quartz glass, and a 2-cm-thick square aluminum plate. The center of the aluminum plate had a 5 × 5 cm square hole and two flow sampling channels. The setup allowed the photoreaction area and sample solution to be controlled without having to turn off the UV light. Four O-rings were placed in the reserved grooves between the layers, and four groups of screws and nuts were used in the assembly in order to prevent the leakage of the MB solution. Finally, four groups of studs and nuts were used to ensure that the distance between the UV lamp and the photoreaction cell was 10 cm, as shown in Fig. 2. The initial concentration of the MB solution was set to approximately 10 ppm. Each ZnO/CF composite specimen (area of 5 cm²) was used to degrade a 50 mL sample of the MB solution. The photodegradation reactor was kept in a dark environment under a chemical hood throughout all the tests. Two milliliter samples of the MB solution were taken at 0, 5, 10, 20, and 30 min after exposure to UV radiation, and the changes in the concentration of the MB solutions were determined on the basis of their UV–Vis absorbance spectra. The percentage degradation values of the MB solutions were then calculated using Eq. (1), where \( C_0 \) and \( C_t \) are the initial and final concentrations of the MB solutions, respectively, and \( D\% \) is the percentage degradation:

\[
D\% = \frac{C_0 - C_t}{C_0} \times 100\%
\]  

2.5. In vitro photodegradation of ACR

The in vitro photodegradation of ACR was simulated by placing the ZnO/CF composite specimens in a device that mimicked the bladder. This device consisted of a reactor, a magnetic stirrer, a manual sampler, and a UV light source. The reactor was a 500 mL glass serum bottle with two manual valves to control the solution input and output. Silicone tubing linked the serum bottle valves with automatic syringes. Self-refilling manual syringes (0.5–5 mL, SOCOREX 187, Socorex Isba S.A., Switzerland) were used to transfer the ACR solution from the serum bottle to the sample bottle. A UV light source with an output of 4 W/cm² and a liquid-core light guide (OPAS XLite 300, OPAS UV Curing Corporation, Taichung, Taiwan, ROC) were used at an intensity of 3 W/cm². The wavelength of the light ranged from 250 to 450 nm (peak wavelength = 365 nm). The head of the liquid-core light guide was positioned vertically on the wall of the serum bottles.

Three different materials were investigated: powdered ACF (0.1 g); powdered CF (0.1 g); and powdered ZnO/CF composite (0.1MCZ200, 0.1 g). For each sample, 200 mL of the ACR solution (75 ppm) was placed in the serum bottle and was irradiated with UV radiation. After 15 and 30 min, 20 mL samples of the ACR solution were removed, and their degree of ACR degradation was calculated using high-performance liquid chromatography (HPLC)–UV (see Section 2.6). Each material was tested thrice.

2.6. Analysis of acrolein degradation using HPLC–UV

The initial and final ACR concentrations were measured using HPLC–UV as per the US Environmental Protection Agency’s specifications (EPA 8315). All the solvents used were HPLC grade. The analyses were performed using a benchtop Dionex UltiMate® 3000 HPLC Standard LC system (Thermo Scientific, USA), which was equipped with a gradient pump (LPG-3600), an autosampler (WPS-3000), a flow manager (FLM-3100), and a UV detector (VWD 3100). A measured volume of the aqueous ACR sample (approx. 100 mL) was buffered at a pH of 3, derivatized with 2,4-dinitrophenylhydrazine (DNPH), and then serially extracted three times with methylene chloride. The extracts were then concentrated through the appropriate procedure using a 3500 series method, and exchanged with acetonitrile prior to the HPLC analyses. The HPLC conditions permitted the separation of ACR and the measurement of its concentration in the extracts by absorbance detection at 360 nm. These analyses were commissioned by Sun Dream Environmental Technology Corporation, Taichung, Taiwan, ROC.

3. Results and discussion

3.1. Characterization of the ZnO/CF composite specimens

The raw material, PAN fiber fabric, was carbonized at 1000 °C. The thickness of the resulting CF fabric was measured and found to be 1 mm. The FESEM image in Fig. 4(A) shows that the CF fabric had a loose, unwoven structure consisting of
10–20 layers. The interfiber gaps in the horizontal plane were measured to be approximately 0.3 mm, while the vertical distance between the horizontal layers was 2 mm. This enabled the infrared light to penetrate the material (inset). Fig. 4(B) is a high-magnification image of an individual CF strand; the strand has a width of approximately 10 μm and a wrinkled surface.

The ZnO/CF composite samples were prepared by immersing pieces of the CF fabric in a Zn(CH$_3$COO)$_2$ sol–gel. The fabric pieces were subsequently dried and heat-treated at various temperatures. The FESEM images in Fig. 5(A1), (B1), and (C1) show the ZnO/CF fabric specimens that were annealed at 200, 300, and 400 °C, respectively. The higher-magnification image in Fig. 5(A1) shows that, in the case of the sample annealed at 200 °C, the CF fabric was coated with a ZnO film. Fig. 5(B1) shows that, in the case of the sample annealed at 300 °C, the CF fabric was sparsely coated with ZnO scales. Fig. 5(C1) shows that, in the case of the sample annealed at 400 °C, the CF fabric was coated with flower-like ZnO structures. Thus, annealing the ZnO/CF composite specimens at different temperatures resulted in the fabric pieces being coated with ZnO structures of different morphologies.

High-resolution TEM (HRTEM) was used to study the morphologies of the ZnO/CF composite specimens annealed at different temperatures. The image in Fig. 5(A2) shows the cross-section of the film formed on the surface of the
0.1MCZ200 sample; the thickness of the film was 30–50 nm. The image in Fig. 5(A3) shows this film was composed of ZnO grains having a width of 10 nm and length of 10 nm. The spacing between the ZnO layers was 2.65 Å. The image in Fig. 5(B2) shows the cross-section of the aggregated ZnO grains or scales formed on the surface of the 0.1MCZ300 specimen. These were bigger in size (50 nm in width and 80 nm in length) than the ZnO grains formed on the surface of the 0.1MCZ200 sample. The image in Fig. 5(B3) shows that distance between the ZnO layers was 2.57 Å. Finally, the image in Fig. 5(C2) shows the cross-section of the flower-like ZnO clusters formed on the surface of the 0.1MCZ400 specimen; these clusters were approximately 100 nm in size. The image in Fig. 5(C3) shows that the petals of the ZnO flowers were 20 nm in width and 40–80 nm in length and that distance between the ZnO layers was 2.67 Å. From the HRTEM images shown in Fig. 5(A3), (B3), and (C3), which correspond to the 0.1MCZ200, 0.1MCZ300, and 0.1MCZ400 samples, respectively, it could be determined that the average ZnO lattice spacing was approximately 0.26 nm. The results of the EDS of the samples shown in Fig. 5(A1), (B1), and (C1) demonstrated that the elements O and Zn present in the sample were in the form of ZnO.

Fig. 6(A) and Table 1 show the specific surface areas of the untreated CF sample and the 0.1MCZ200, 0.1MCZ300, and 0.1MCZ400 specimens. The specific surface area of the untreated CF sample was 0.01 m²/g, indicating that there were no pores on its surface. On the other hand, the 0.1MCZ200 sample had a specific surface area of 4.17 m²/g. This proved that the presence of the ZnO particles on the surface of the CF increased its specific surface area by approximately 417 times. The 0.1MCZ300 and 0.1MCZ400 samples had specific surface areas of 2.05 and 1.47 m²/g, respectively; these were least 205 and 147 times, respectively, higher than that of the untreated CF sample. Fig. 6(B) shows the pore size distributions of the untreated CF sample, and the 0.1MCZ200, 0.1MCZ300, and 0.1MCZ400 specimens. The ZnO/CF composite specimens contained nanopores, which ranged in size from 5 to 25 nm. This was due to the binding of ZnO to the surfaces of the CF pieces. No pores were evident in the case of the untreated CF sample; however, this is not conclusive proof that they were completely absent. The FESEM images show that the ZnO structures formed in the case of the 0.1MCZ200, 0.1MCZ300, and 0.1MCZ400 specimens were a ZnO film, a hybrid structure consisting of a ZnO film and ZnO particles, and dispersed flower-like ZnO clusters, respectively. Therefore, on the basis of the TEM images and results of the BET analyses, it could be assumed that the presence of ZnO structures on the CF pieces resulted in nanopores and that these structures increased the specific surface area.

![Fig. 6](image)

**Fig. 6** – (A) The specific surface areas of the untreated CF (■) sample and the 0.1MCZ200 (▲), 0.1MCZ300 (▲), and 0.1MCZ400 (▲) composite specimens, as calculated from their respective N₂ adsorption isotherms at 77 K. (B) Micropore volumes along with the pore distributions as determine from the N₂ adsorption isotherms at 77 K. (A colour version of this figure can be viewed online.)

**Table 1** – Porosities of the untreated CF sample and the various ZnO/CF composite specimens: BET surface areas, pore volumes, and pore diameters.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( S_{\text{BET}} ) (m²/g)(^a)</th>
<th>( V_t ) (cm³/g)(^b)</th>
<th>Mean ( D_{\text{micro}} ) (Å)(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF</td>
<td>0.012</td>
<td>0.0007</td>
<td>722.7644</td>
</tr>
<tr>
<td>0.1MCZ200</td>
<td>4.169</td>
<td>0.0221</td>
<td>131.8218</td>
</tr>
<tr>
<td>0.1MCZ300</td>
<td>2.046</td>
<td>0.0062</td>
<td>120.8111</td>
</tr>
<tr>
<td>0.1MCZ400</td>
<td>1.471</td>
<td>0.0034</td>
<td>93.6053</td>
</tr>
</tbody>
</table>

\(^a\) BET specific surface area.

\(^b\) Single-point-adsorption total pore volume of pores less than 828.977 Å in diameter at \( P/P_\infty \).

\(^c\) Adsorption average pore width.
surface area of the CF, as shown in Figs. 5(A3), 6(A) and Table 1.

3.2. XRD analyses

The XRD patterns of the untreated CF sample and the various ZnO/CF composite specimens are shown in Fig. 7(A). Because ZnO was immobilized on the surfaces of the CF pieces in the case of the composite specimens, interference between the CF signals and ZnO signals resulted, producing uneven XRD curves for all the composite samples. Therefore, we only collected the ZnO powder by ultrasonic separate and remove CF, individual. After collect ZnO powder, we adhered on silicon wafer by Vaseline, individual. So, the clearly XRD peacks was showed in Fig. 7(B). However, all the diffraction peaks in the patterns could be indexed as belonging to hexagonal ZnO and were consistent with the values in the standard card (JCPDS 36-1451). The peaks present were attributable to the (100), (002), (101), and (110) planes of ZnO. This indicated

<table>
<thead>
<tr>
<th>Region</th>
<th>Peak</th>
<th>Peak area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Untreated CF</td>
</tr>
<tr>
<td>C 1s</td>
<td>I C–C</td>
<td>68.6</td>
</tr>
<tr>
<td></td>
<td>II C–O</td>
<td>31.4</td>
</tr>
<tr>
<td></td>
<td>III COOH</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>IV C–H</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>V Carbonate group or π–π*</td>
<td>–</td>
</tr>
<tr>
<td>O 1s</td>
<td>ZnO</td>
<td>12.4</td>
</tr>
<tr>
<td></td>
<td>–OH</td>
<td>87.6</td>
</tr>
<tr>
<td>Zn 2p</td>
<td>Zn 2p 1/2</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Zn 2p 3/2</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 2 – Results of the deconvolution of the XPS spectra of the untreated CF samples and the 0.1MCZ200, 0.1MCZ300, and 0.1MCZ400 composite specimens.

<table>
<thead>
<tr>
<th>C 1s %</th>
<th>O 1s %</th>
<th>N 1s %</th>
<th>Zn 2p %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated CF</td>
<td>70.16</td>
<td>24.5</td>
<td>5.34</td>
</tr>
<tr>
<td>0.1MCZ200</td>
<td>25.86</td>
<td>15.9</td>
<td>0</td>
</tr>
<tr>
<td>0.1MCZ300</td>
<td>29.28</td>
<td>23.19</td>
<td>0</td>
</tr>
<tr>
<td>0.1MCZ400</td>
<td>11.06</td>
<td>17.93</td>
<td>0</td>
</tr>
</tbody>
</table>

Fig. 7 – (A) XRD patterns of CF, 0.1MCZ200, 0.1MCZ300, and 0.1MCZ400, (B) XRD patterns of ZnO powder of CF, 0.1MCZ200, 0.1MCZ300, and 0.1MCZ400 (which only collect ZnO powder by ultrasonic separate and remove CF, and then the collect ZnO powder was adhere on silicon wafer by vaseline). (A colour version of this figure can be viewed online.)

Fig. 8 – XPS survey scans of the untreated CF sample and the 0.1MCZ200, 0.1MCZ300, and 0.1MCZ400 composite specimens. For details, see Table 2(A). (A colour version of this figure can be viewed online.)
that the as-prepared specimens consisted of hexagonal wurtzite ZnO on the surfaces of the CF pieces.

### 3.3. XPS

The chemical bonds present in the ZnO/CF composite specimens was investigated by XPS. Fig. 8 shows the XPS spectra of the untreated CF sample and the different ZnO/CF composite specimens. Core level peaks attributable to C and O can be seen clearly in the spectrum of every sample, while an additional Zn peak is present in the spectra of the ZnO/CF specimens. The high-resolution C 1s, O 1s, and Zn 2p XPS spectra are shown in Figs. 9–11, respectively.

Fig. 9(A) shows that the high-resolution C 1s XPS spectrum of the untreated CF sample has two peaks. The strong, sharp peak at 284.5 eV is attributable to the C–C bonds (graphitic carbon), which were present in abundance, and the other peak, at 285.5 eV, is owing to the C–OH bonds. Fig. 9(B)–(D) show the high-resolution C 1s spectra of the ZnO/CF composite specimens. It can be seen that, as the annealing temperature increases, the peak corresponding to the C–C bond becomes weaker. The integrated peak area for the C–C bond decreases from 68.6% in the case of the untreated CF sample to 41.3% for the 0.1MCZ400 specimen.

Fig. 10(A) shows the high-resolution O 1s XPS spectrum for the untreated CF sample. The O 1s peak at 533.0 eV is attributable to the O–C bonds on the surface of the CF sample. Fig. 10(B)–(D) show the O 1s spectra of the ZnO/CF composite samples; peaks can be seen at 533.0 eV (O–C bonds) and 532.1 eV (O–Zn bonds, in the ZnO crystal lattice). The O–C bond peak decreases in intensity with the increase in the annealing temperature, changing in position from 533.0 to 534.5 eV. In contrast, the weak, wide O–Zn bond peak becomes sharper and stronger with the annealing temperature and also undergoes a change in position from 532.1 to 532.8 eV. Fig. 11(C)–(E) show the high-resolution Zn 2p spectra of the ZnO/CF composite specimens. Two peaks, namely, the Zn 2p 3/2 and 1/2 peaks, can be seen at 1026.0 and 1046.0 eV, respectively. Both peaks increased in intensity and became sharper as a result of the increase in the annealing temperature from 200 to 400 °C.

When viewed together, the results of the EDS, XRD, and XPS analyses clearly demonstrate the presence of ZnO on the surfaces of the CF pieces in the case of the composite specimens.

### 3.4. Photoluminescence spectroscopy

Fig. 12 shows the photoluminescence (PL) spectra of the untreated CF sample and the 0.1MCZ200, 0.1MCZ300, and 0.1MCZ400 specimens. As expected, no absorbance peak was seen in the spectrum of the CF sample; this was owing
to its organic structure. However, in the spectra of the 0.1MCZ200, 0.1MCZ300, and 0.1MCZ400 specimens, absorption peaks attributable to ZnO were present. These peaks demonstrate that the ZnO on the surfaces of the CF pieces in the composite specimens absorbs photons, which induce an energy transition at a particular wavelength. Further, a relationship between the annealing temperature and the PL exhibited by the ZnO/CF specimens was evident, with the PL peaks becoming stronger and sharper with an increase in the temperature. The 0.1MCZ200 and 0.1MCZ300 specimens exhibited broad emissions over wavelengths ranging from 325 to 465 nm; however, on increasing the annealing temperature to 400°C, the intensity of the luminescence band increased and the emission peaks became sharper and stronger. In addition, the blue shift of the emission band ranging from 425 to 380 nm became more pronounced at 400°C. This difference in the blue shift was due to the difference in the growth rates of the ZnO grains on the CF pieces; this difference led to the formation of different ZnO structures, depending on the oxygen vacancies and oxygen interstitials in the ZnO lattice. Although there were significant differences in the PL spectra of the composite specimens, the actual effectiveness of the specimens as photodegradation catalysts needed to be determined.

3.5. Use of the synthesized composite specimens as photodegradation catalysts

To determine the efficacy of the ZnO/CF composite specimens as photodegradation catalysts, a device in which a limited area (25 cm²) was irradiated with UV light was developed and MB was used as a model contaminant. Fig. 13(A) shows the rates at which MB was degraded by commercial ZnO (10 mg) and the 0.1MCZ200, 0.1MCZ300, and 0.1MCZ400 composite specimens. Houas et al. [12] have reported the pathway for the photocatalytic degradation of MB in water. This pathway is shown in Fig. 13(B).

As can be seen from the curves, in the case of the commercial ZnO powder (10 mg), the MB degradation rate was 68.6% after 30 min of UV irradiation. However, in the case of the 0.1MCZ200 specimen, 85% of the MB was degraded after 5 min of UV irradiation. On the other hand, the rates were only 40% and 15% for the 0.1MCZ300 and 0.1MCZ400 specimens, respectively. The rates corresponding to the commercial ZnO powder (10 mg) and the 0.1MCZ200 and 0.1MCZ400 specimens were lower than that for the 0.1MCZ200 specimens for irradiation periods of 15 and 30 min as well, demonstrating that the composite specimen annealed at 200°C was the most effective photodegradation catalyst.
However, the PL intensity in the case of the 0.1MCZ200 specimen was less than that of the 0.1MCZ400 specimen. The 0.1MCZ200 specimen yielded a weak but broad peak with an absorption wavelength ranging from 326 to 459 nm (Fig. 12). As the photodegradation experiment employed a 100 W UV lamp emitting radiation with wavelengths of 250–450 nm, the 0.1MCZ200 specimen could absorb energy over a wide range of wavelengths. As a result, its overall absorbance and degradation rate of MB both increased. In addition, the 0.1MCZ200 specimen also exhibited the highest specific surface area of all the composite samples (Fig. 6(A)). Therefore, a larger area was available for the degradation reaction. These were the reasons the 0.1MCZ200 composite specimen exhibited good photodegradation efficiency. This sample was evaluated further to establish its suitability for the degradation of ACR.

3.6. Simulation of in vitro photodegradation of acrolein

Gardner et al. [13] and Magneron et al. [14] have reported the mechanism for the photolysis of ACR by OH free radicals. The primary pathway for the photolysis is the following:

\[ \text{CH}_2 = \text{CHCHO} + \text{hv} \rightarrow \text{CH}_3 + \text{CO} \]

The efficiency of the 0.1MCZ200 composite specimen in the photodegradation of ACR under UV light irradiation was investigated using device shown in Fig. 14(A). The mechanism for the photodegradation of ACR is shown in Fig. 14(B). We increased the scale of the device by several times, so that it was similar to a rat bladder in size. The results of the photodegradation and kinetics study are shown in Fig. 15(A) and (B), respectively. ACF was also tested because a previous study had reported that the activated carbon can remove 30% ACR
Fig. 13 – (A) Photodegradation rates of MB when the 0.1MCZ200, 0.1MCZ300, 0.1MCZ400 composite specimens and commercial ZnO (10 mg) were used as catalysts. (B) Pathway for the photodegradation of MB under UV light using a ZnO/CF catalyst. (A colour version of this figure can be viewed online.)

Fig. 14 – (A) In vitro simulation photodegradation device with UV machine (4 W/cm²). (B) The mechanism of ACR photodegradation by ZnO/CF under UV light. (A colour version of this figure can be viewed online.)

Fig. 15 – (A) UV light-based photodegradation of ACR and (B) the photodegradation kinetics curves for the untreated CF, AC, and 0.1MCZ200 specimens. (A colour version of this figure can be viewed online.)
(maximum) from the ACR solution by physical adsorption [2]. Therefore, we wished to compare the efficiency of the synthesized composite specimens with that of ACF.

Fig. 15(A) shows rates at which ACR was photodegraded using the tested samples. After 15 min under the 100 W UV light, the 0.1MCZ200 specimen caused a degradation of 35%; this was higher than that in the case of ACF (25%). After 30 min of UV irradiation, the 0.1MCZ200 specimen had caused a degradation of 45%; this was again higher than that in the case of the ACF sample (28%) and significantly higher than that is the case of the untreated CF sample (8%).

The rate of photodegradation was assumed to obey pseudo-first-order kinetics, and the initial reaction rate constants were calculated using the following relation: \( -\ln(C/C_0) = kt \), where \( C/C_0 \) is the normalized concentration of compound in question and \( k \) is the apparent reaction rate constant [11]. Fig. 15(B) showed the rate constant in the case of the 0.1MCZ200 specimen (\( k = 0.021 \text{ min}^{-1} \)) was higher than that for ACF (\( k = 0.008 \text{ min}^{-1} \)). However, the rate constants for these two specimens were higher than that for the untreated CF sample (\( k = 0.003 \text{ min}^{-1} \)). This shows that ACR can be removed more quickly by photodegradation than by adsorption.

These results demonstrated that the 0.1MCZ200 composite specimen when used in photodegradation of 200 mL (75 ppm) ACR solution under UV light irradiation (output of 4 W/cm\(^2\) through a liquid-core light guide) was able to degrade 45% of the compound in 30 min. This shows the potential of the investigated ZnO/CF composites for removing acrolein from solutions.

4. Conclusions

The results obtained in this study demonstrate that a composite material consisting of ZnO as photocatalyst and carbon fiber can remove 45% of ACR from solutions through photodegradation. A number of different characterization techniques were used in order to optimize the synthesis conditions for the composite catalyst materials, and that formed after annealing at 200 °C was found to be the most effective. The efficacy of this catalyst system in an in vitro model that simulated the removal of ACR from the bladder suggests that it should be highly suited for preventing HC in chemotherapy patients. The next step will be to verify these promising results using an in vivo model. In addition to reducing the risk of hemorrhagic shock from HC, this technology has potential for use in the treatment of bacterial cystitis using sterilization techniques.

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