

Research Article

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Synthesis and characterization of ZnO/ β -cyclodextrin/nicotinic acid nanocomposite and its biological and environmental application

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Abstract: In the present work, the disk-shaped zinc oxide (ZnO) nanoparticles were synthesized and functionalized with β -cyclodextrin (β -CD) and nicotinic acid (vitamin B3) using the wet co-precipitation method. The functionalized ZnO/ β -CD/nicotinic acid nanocomposite materials were characterized using UV-visible spectroscopy (UV-Vis), Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), energy dispersive spectroscopy (EDS), field emission electron microscopy (FESEM), and band-gap energy analysis. The band gap value (E_g) was 4.3 eV. The average XRD crystallite size was determined using the Scherrer formula and was found to be 50 nm. The ZnO/ β -CD/nicotinic acid nanocomposite material showed a photocatalytic effect for dye-polluted wastewater. It also showed an antibacterial effect against the Gram-positive bacterial strain *Streptococcus aureus* (*S. aureus*) but did not show any antibacterial activity with Gram-negative *Escherichia coli* (*E. coli*). The ZnO/ β -CD/nicotinic acid nanocomposite also showed antifungal activity with *Aspergillus niger* (*A. niger*). It was noticed that ZnO/ β -CD/nicotinic acid nanocomposite showed efficient anticancer activity with $IC_{50} = 14.95 \mu\text{g}\cdot\text{mL}^{-1}$ in MCF-7 cell lines. Because of the formation of singlet oxygen ($O_2^{\cdot-}$) and hydrogen oxide radical ($\cdot\text{OH}$), the composite material showed a photodegradation reaction against aq. solution of methylene blue dye. After 190 min, the blue colour of aq. solution methylene blue was decolourized at 6 pH at a constant time interval.

Keywords: ZnO/ β -cyclodextrin/nicotinic acid nanocomposite material, wastewater, antibacterial property, antifungal activity, anticancer

1 Introduction

In the last few years, nanomaterials are used in almost every field including drug delivery [1], sensors and photonic devices [1], electro-catalytic degradation of dyes, removal of metal ions [2–4], energy storage, etc. Because of environmental friendliness as well as unique electrical, optoelectronic, photochemical, catalytic, and biomedical [5] properties, zinc oxide (ZnO) nanomaterials were extensively used [6–9]. ZnO, one of the earliest materials, was used as a gas sensor because of the high mobility of conduction electrons in the material and good chemical and thermal stability [10,11]. ZnO nanomaterials also attract interest because of their wide range of applications [12,13]. They had a wide band energy gap and are used in electronics, semiconductors, and sensor technology [14,15]. Recently, Cu–ZnO nanocomposite materials played an important role under reduced reaction conditions [16].

The ZnO nanomaterials were synthesized by different synthetic methods like sol–gel technique [17,18], micro-emulsion process [19], mechano-chemical process [20], spray pyrolysis and drying process [21], plasma synthesis [22], hydrothermal process [23], sonochemical or microwave synthesis [24,25], direct precipitation process [26], etc. However, due to the presence of water, the formation of Zn–O–Zn bonds and hard agglomerates in the nanomaterial impede applications of ZnO nanomaterials. Thus, the reduction of water from the nanomaterial is an important process for reducing hard agglomerates. Nowadays, water pollution has increased due to the contamination of non-biodegradable pollutants from many industries [27].

Today, the most common water pollutants are organic dyes, which affect the photosynthesis process and also cause medical conditions like skin irritation, allergy,

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cancer, etc., in humans [28]. For the treatment of dyes, various physicochemical and biological processes have been developed; each of them has some advantages and disadvantages [29]. The most useful and important method is semiconductor photocatalysis. It is cheap, easy to synthesize, and also has high removal efficiency of dyes [30]. Numerous metal oxides such as Fe_2O_3 , ZnO , TiO_2 , and Co_3O_4 are used as photocatalysts for dye degradation [31–33]. Zinc oxide nanoparticles (ZnO NPs) are able to remove both cationic and anionic dyes and also have good adsorption capacity, reusability, selectivity, and antibacterial properties [34]. There were two ways to modify the metal oxide nanoparticles: the first is doping with other metals, non-metals, and metal oxides; and the second method is the synthesis of the composite of metal oxides with macromolecules or polymers [35]. β -Cyclodextrin (β -CD) is a common host molecule and possesses photocatalyst, energy transfer, drug carrier, and photoelectric activities [36]. β -CD is a biodegradable oligosaccharide and its modified form is used in photocatalytic degradation [37], cell imaging [38], decolouration of ethyl violet dye [39], oil spill remediation [40], antiseptic to avoid skin diseases [41] as well as the removal of persistent organic pollutants like perfluorooctanoic acid, perfluorooctane sulphonate and Cr(VI) [42]. It is also used as a mediator between the surface of the photocatalyst and guest molecules. β -CD with metal oxide (like ZnO) composites acts as an electron-donating and hole-capturing species and enhances the photocatalytic activity via reduced charge hole recombination. β -CD used solar energy and extended up to visible light, whereas metal oxides usually used only UV rays [43].

On the other hand, nicotinic acid, also known as vitamin B3, received great attention because of its pharmaceutical use. Every year, around 20,000 tons of vitamin B3 are produced worldwide. These days, chromic acid commonly used as an oxidizing agent for the formation of vitamin B3 is characterized as corrosive. The development of an efficient catalytic system is very important to minimize the inorganic wastes and obtain vitamin B3 in high yield [44]. Owing to biological importance [45], vitamin B3 is produced by the catalytic oxidation of 3-pyridinemethanol [45], 3-pyridinecarboxyaldehyde [46], or picoline [47]. Nanostructured catalysts attract the interest of scientists because of their heterogeneous catalytic properties with improved characteristics [48,49]. Today, the use of recyclable nanocatalysts in oxidation reactions get more attention because of their eco-friendly nature [50,51].

Therefore, we described here a recyclable, eco-friendly, and efficient $\text{ZnO}/\beta\text{-CD}/\text{nicotinic acid}$ nanocatalytic composite material, with a short reaction time. It is morphologically characterized by X-ray diffraction (XRD) and field

emission electron microscopy (FESEM). It is also characterized by UV-visible (UV-Vis) spectroscopy, band gap energy analysis, Fourier transform infrared (FTIR) spectroscopy, and weight percentage of elements determined via energy dispersive spectroscopy (EDS). We also explore the biological and photocatalytic applications of the functionalized $\text{ZnO}/\beta\text{-CD}/\text{nicotinic acid}$ nanocomposite material.

2 Experimental

2.1 Chemical and reagents

Methylene blue (MB) and β -CD were obtained from Merck (99.8%). Zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, 99%) and other chemicals used were of analytical grade and received from Merck. Nicotinic acid and tetramethylethylenediamine (TMED) were purchased from Sigma Aldrich. All reagents and solvents were of commercial grade and used without purification. *Escherichia coli* (*E. coli*) and *Streptococcus aureus* (*S. aureus*) pure culture, agar media (Hi-Media), and PDA were used; deionized distilled water was used as a solvent.

2.2 Instrumentation

In the absorbance mode, UV-Vis spectra were acquired using a UV-1900i Double beam spectrophotometer. Samples were dispersed in ethanol to determine the absorbance. X-ray diffraction of the composite material was analysed using an Advanced D8 Bruker X-ray diffractometer with Ni-filtered Cu-K (1.5405) ($2\text{--}10\text{--}80^\circ$ and step size of 0.02°). The vibration spectra were recorded using an Avtar 370, Thermo Nicolet, Fourier transform infrared (FT-IR) spectrophotometer equipped with a DTGS detector with 4 cm^{-1} resolution and samples were prepared with KBr discs for this study. For the FESEM study, a CARL ZEISS UHR FESEM MODEL GEMINI SEM 500 KMAT with 0.8 nm resolution and probe current of 3 pA to 100 nA was used.

2.3 Synthesis

2.3.1 Synthesis of ZnO nanoparticles

ZnO nanoparticles were synthesized by modifying the method of Royer et al. [28]. About 2.195 g of zinc acetate dihydrate was dissolved in 90 mL of ethanol under

vigorous stirring for 15 min on a magnetic stirrer at ambient conditions. After that, 1.122 g of KOH was dissolved in 30 mL of distilled water, and it was added to the zinc acetate solution dropwise. A viscous milky white precipitate was obtained which was then heated at 90°C up to 3 h. Then, the suspension was centrifuged and the resultant product was washed 3–5 times with ethanol for removing impurities. Finally, the dried solid product was heated in a furnace at 70°C up to 24 h to obtain the ZnO nanoparticles powder.

2.3.2 Synthesis of the ZnO/ β -CD nanocomposite material

For the synthesis of the ZnO/ β -CD nanocomposite material, 30 mg of ZnO nanoparticles was dispersed in 10 mL of deionized water and sonicated for 15 min. After that, 30 mg of β -CD was dissolved in 10 mL of deionized water and stirred at 600 rpm for 10 min to obtain a transparent solution. Both solutions were mixed and continuously stirred at 600 rpm. After 6 h, the ZnO/ β -CD nanocomposite was separated via centrifugation and washed three times with deionized water. The supernatant was freeze-dried, and the residue was weighed. Finally, the residue was dried in an oven below 80°C.

2.3.3 Synthesis of the ZnO/ β -CD/nicotinic acid nanocomposite

For the synthesis of the ZnO/ β -CD/nicotinic acid composite, 0.32 g of nicotinic acid was dissolved in 50 cm³ of hot water (80°C) and then cooled at room temperature. Then, 0.23 g of ZnO/ β -CD was dissolved in a 1:1 ratio of methanol/water solution. This was added to aq. solution of nicotinic acid. The reaction mixture was stirred for up to 10 min. After that, 0.39 mL of TMED was added dropwise to the reaction mixture. Then, the whole reaction mixture was stirred for up to 30 min. The resultant white crystalline material was obtained and washed with distilled water and methanol. The solid crystalline material obtained was dried under a vacuum.

2.4 Antibacterial activity

To determine the antibacterial activity, we used the well diffusion system on a nutrient agar medium. First, the agar medium was put into two different Petri dishes under sterile conditions and kept for 1 h for solidification. After

that, fresh, overnight-cultured *E. coli* and *S. aureus* (100 $\mu\text{g}\cdot\text{mL}^{-1}$) bacterial strains were spread onto both solidified agar media. Then, both the dishes were left up to 15–20 min for complete absorption of bacterial cultures. After that, three wells were prepared in each Petri dish by the gel puncture (6 mm) procedure under aseptic conditions. Samples of the ZnO/ β -CD/nicotinic acid nanocomposite material were introduced in those wells at different concentrations of 10, 20, and 30 $\mu\text{g}\cdot\text{mL}^{-1}$. After that, for the diffusion of the extract, both treated dishes were kept at room temperature for 30 min. Later, they were incubated at 37°C up to 24 h for maximum growth of microorganisms. After incubation, the ZnO/ β -CD/nicotinic acid composite material showed inhibition of bacterial growth via a clear zone of inhibition (ZOI) around the well.

2.5 Antifungal activity

For antifungal activity, we used the well diffusion system on a PDA medium. First, the PDA medium was into a Petri dish under sterile conditions and kept for 1 h for solidification. The antifungal activity of the ZnO/ β -CD/nicotinic acid nanocomposite was examined against cultured and tested fungal species *Aspergillus niger* (*A. niger*). A 5-day-old *A. niger* fungus was used for antifungal activity against the ZnO/ β -CD/nicotinic acid nanocomposite. In this process, 3–4 mL of sterile normal saline was used for the fungal growth and gently scraped to collect the conidia. About 100 μL of the liquid spore suspension was spread evenly on the PDA dish. A sterile cork-borer was used to puncture two 6 mm-diameter circular wells on the PDA medium. Both wells of the Petri dish were filled with 20 and 40 μL of concentrated ZnO/ β -CD/nicotinic acid nanocomposite to check for antifungal activity. Then, the petri dish was incubated at 25°C for 2–3 days and the zone of inhibition was measured [52].

2.6 Dye remediation

The MB adsorption experiment was used for photocatalysis via the ZnO/ β -CD/nicotinic acid nanocomposite material. First, the standard stock solution of MB was made. Then, it was diluted with deionized water at various concentrations. The obtained MB solution was kept in a fixed volume flask (10 mL of 5 ppm) to which was added the ZnO/ β -CD/nicotinic acid nanocomposite material. At room temperature, the whole solution (pH = 6) was placed in a sonicator for up to 170 min. The upper layer of the

solution was analysed at 600 nm wavelength using a UV-Vis spectrometer (UV-Visible 1900i, Shimadzu, Japan). The ZnO/ β -CD/nicotinic acid was removed by centrifugation when the experiment was completed. The removal ($R\%$) was calculated by Eq. 1:

$$R\% = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where C_0 is the initial concentration of MB ($\text{mg}\cdot\text{L}^{-1}$) and C_e is the equilibrium concentration of MB ($\text{mg}\cdot\text{L}^{-1}$).

2.7 Cytotoxicity study

The cytotoxic action of various cell lines toward different oncology products was determined using the high-throughput cell-based 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) assay. Cytotoxicity evaluation of the ZnO/ β -CD/nicotinic acid nanocomposite was performed using MCF-7 cell lines collected from the cryopreservation cells that were thawed properly. They were initially grown in Dulbecco's modified Eagle's medium (DMEM) in a 50 mL flask with 5% fetal bovine serum and antibiotics in a 5% CO_2 incubator. After incubation, the affluent cells were counted with a Neubauer chamber, and different concentrations of cells were seeded in 96 well plates. The twofold serially diluted ZnO/ β -CD/nicotinic acid nanocomposite was added to the 96 well plates and incubated at 37°C for 2 h in a 5% CO_2 incubator. After incubation, 96-well plates were washed and 100 μL of the MTT reagent was added to each well. After incubation for 4 h, the plates were washed with PBS buffer, and 100 μL of dimethyl sulphoxide was added to solubilize the unbounded formazan, followed by measuring the absorbance of the plate at 570 nm using a plate reader (Biotek, USA). The complete evaluation was carried out in triplicate, and it was based on the formazan dye's colour intensity, which was assumed to be directly proportional to the number of live cells.

3 Results and discussion

3.1 Characterization of nanocomposite materials

3.1.1 UV-Vis absorption

The UV-Vis spectra of the functionalized ZnO/ β -CD/nicotinic acid nanocomposite material showed an absorption peak at 217 and 353 nm with one hump at 304 nm (Figure 1).

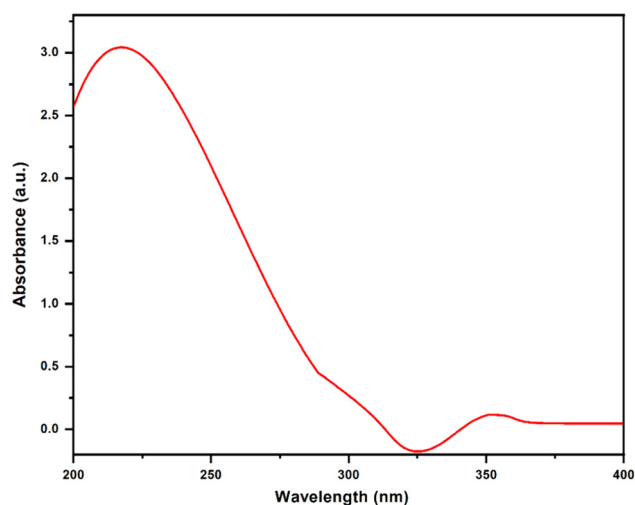


Figure 1: The UV-Vis absorption spectrum of the ZnO/ β -CD/nicotinic acid nanocomposite.

The characteristic absorption spectra of the ZnO composite material in the quantum size regime absorption observed blue shift [53].

The optical bandgap (E_g) of the nanomaterial can be determined using the classical Tauc approach [54], which shows a relationship between the incident photoenergy ($h\nu$) and the absorption coefficient (α) near the absorption edge, as follows (Eq. 2):

$$\alpha h\nu = A_0(h\nu - E_g)^n \quad (2)$$

It depends on the interband transition (e.g. $n = 1/2$ for direct transitions and $n = 2$ for indirect transitions). A_0 is a constant, band tailing parameter and E_g is the intercept of the extrapolated line, when $(\alpha h\nu)^{1/n}$ vs $h\nu$ is plotted. Figure 2

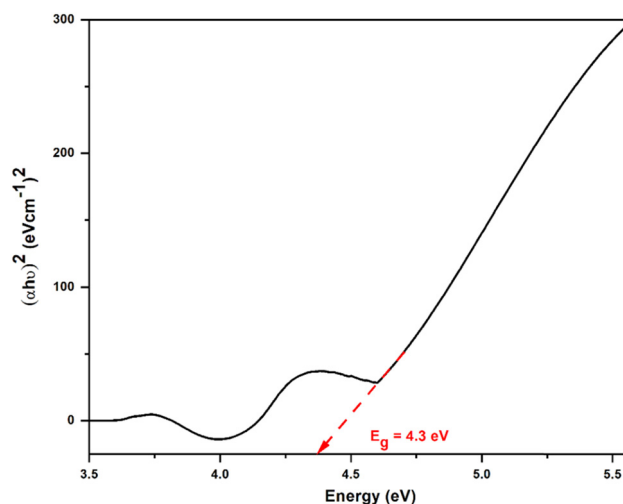


Figure 2: The Tauc plot of the ZnO/ β -CD/nicotinic acid composite material, which was derived from UV-Vis absorption, where the band gap value (E_g) was 4.3 eV.

shows a Tauc plot of ZnO/ β -CD/nicotinic acid nanocomposite and the band gap value was 4.3 eV.

3.1.2 FTIR spectra

The FTIR spectrum (Figure 3) shows that water molecules and organic moieties are present in the precursor of the nanocomposite material. The FTIR spectrum of the ZnO/ β -CD/nicotinic acid nanocomposite material showed a broad peak at $3,153.38\text{ cm}^{-1}$, which is a characteristic peak of the O–H group. The H–O–H bond of β -CD has a prominent absorption peak at $1,639.09\text{ cm}^{-1}$. The peak at $1,581.78\text{ cm}^{-1}$ is attributed to $\nu_{as}(\text{COO}^-)$ (asymmetric stretches). The peaks at $1,472.45$ and $1,426.19\text{ cm}^{-1}$ are attributed to $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{N})$ of nicotinic acid. The peak at $1,400.53\text{ cm}^{-1}$ is assigned for $\nu_s(\text{COO}^-)$ (symmetric stretch) of the carboxyl group (18-009). The peaks at $1,315.09$ and $1,189.85\text{ cm}^{-1}$ correspond to the bending signals of the imidazole ring and C–N stretching vibrations [55,56]. The peak at $1,156.94$, $1,099.05$, $1,045.08$, and $1,016\text{ cm}^{-1}$ correspond to $\nu(\text{C}-\text{O})$, C–O–C of β -CD attached to ZnO. The peaks observed at 906.75 , 816.86 , 762.14 , 749.76 , 704.93 , 995 , and 760 cm^{-1} can be assigned to C–N and C–H bending vibrations, respectively. Most characteristic peaks occur at $500\text{--}400\text{ cm}^{-1}$, which correspond to the Zn–O bond [38,57]. The Zn–O and Zn–N bonding vibration

exhibited peaks at 421.31 and 571.87 cm^{-1} for Zn–O and the Zn–N stretching mode, respectively.

3.1.3 XRD

The XRD pattern of hexagonal ZnO/ β -CD/nicotinic acid composite nanomaterials is described in Figure 4. It has a similarity with the ZnO wurtzite structure [58]. The XRD peak values relate to diffraction peaks such as 2θ , $(h\ k\ l)$, and inter-planar spacing d_{hkl} as described in Table 1. In the XRD pattern, a few peaks different, in comparison with the pure ZnO structure are observed, which indicates that the synthesized nanomaterial was the composite of ZnO/ β -CD/nicotinic acid. With the increase in the calcination temperature, the intensity of XRD peaks and the average crystallite size increased [59]. At high temperatures, small grains aggregate to form large particles, and migration of molecules is observed.

The XRD of the ZnO/ β -CD/nicotinic acid nanocomposites was analysed using the following formula [60]:

$$\frac{1}{d_{hkl}^2} = \frac{4}{3} \left[\frac{h^2 + hk + k^2}{a^2} \right] + \frac{l^2}{c^2} \quad (3)$$

where d is the inter-planar spacing; h , k , l are Miller indices; a and c are lattice constants with $a = 3.2554\text{ \AA}$, $c = 4.9569\text{ \AA}$, and $c/a = 1.5227\text{ \AA}$.

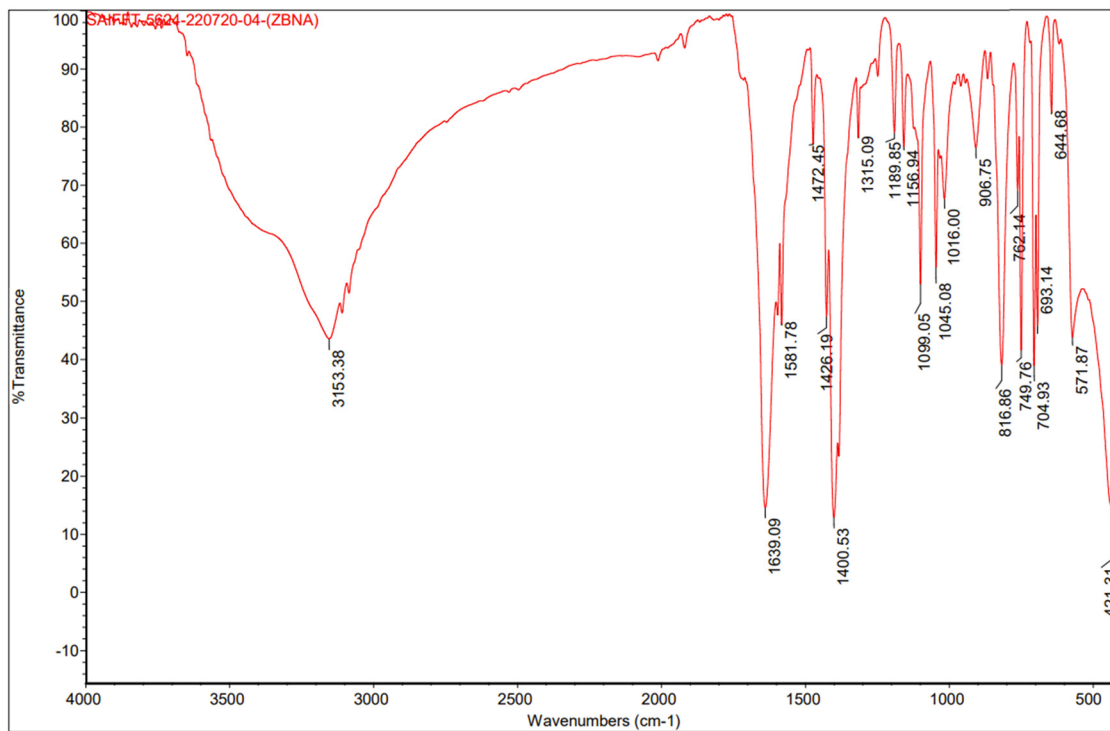


Figure 3: The FTIR spectrum of the ZnO/ β -CD/nicotinic acid nanocomposite material.

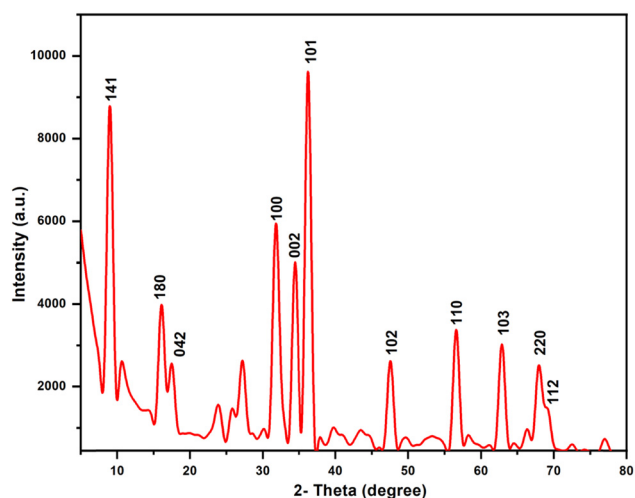


Figure 4: The XRD spectrum of the ZnO/β-CD/nicotinic acid (ZnO/β-CD/nicotinic acid) nanocomposite material.

Table 1: Recycling of the used nanocatalyst ZnO/β-CD/nicotinic acid composite material

Sl. no.	Recycling	Time of reaction (min)	Yield after wash (%)
1.	1st	190	95.4
2.	2nd	190	94.0
3.	3rd	190	93.1
4.	4th	190	91.7
5.	5th	190	90.0

The presence of finite broadening in the XRD diffraction peaks showed that the ZnO composite material had a nanometre range. The average crystallite size of the synthesized ZnO/β-CD/nicotinic acid nanocomposite material was calculated using the Debye–Scherrer’s formula [61] as follows:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (4)$$

where λ is the wavelength of the source Cu K α (0.15406); β is full width at half-maximum of the XRD peak; and θ is the diffraction angle of the peak.

The crystallinity of the functionalized ZnO/β-CD/nicotinic acid composite material was confirmed by XRD analysis (Figure 4). The XRD pattern of the functionalized ZnO nanocomposite material exhibited peaks at $2\theta = 8.95^\circ$, 16.02° , 17.53° , 31.74° , 34.38° , 36.11° , 47.46° , 56.57° , 62.82° , 67.85° , and 69.05° corresponding to (141), (180), (042), (002), (101), (102), (110), (103), (220), and (112) planes of the hexagonal ZnO/β-CD/nicotinic acid nanocomposite, respectively (Figure 4 and Table 1). Also, we calculated the average

particle sizes using the first three prominent peaks at $2\theta = 31.74^\circ$, 34.38° , and 36.11° , which are indexed as (100), (002), and (101) peaks of the X-ray diffraction, respectively. The grain sizes were calculated to be 45.87, 51.21, and 55.28 nm, respectively. Thus, the average size of nanoparticles was around 50 nm.

3.1.4 FESEM

The morphological analysis of the ZnO/β-CD/nicotinic acid (ZnO/β-CD/nicotinic acid) nanocomposite material was done using FESEM (Figure 5). The FESEM images of the functionalized ZnO/β-CD/nicotinic acid nanocomposite material on a graphite surface are shown in Figure 5. As clearly shown in Figure 5, the ZnO nanocomposite sample was uniformly dispersed on the surface. The incorporation of functionalized ZnO composite promoted the migration of vacancies from the pores of the grain of the nanocomposite, which ultimately creates voids in the electrode. These voids provided a path for the ionic movement.

Here, the surface of the ZnO/β-CD/nicotinic acid nanomaterial composite was loosely packed and was hexagonal disk-shaped, which was more active. Thus, its photocatalytic activity is increased due to the aggregation of the composite on surfaces. It provided a superior adsorption environment and more active sites for the photocatalytic reaction.

3.1.5 EDS

The elemental composition and the purity of ZnO/β-CD/nicotinic acid nanocomposite material were determined

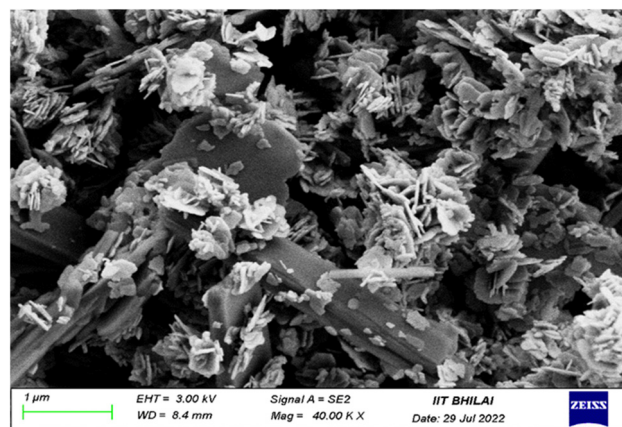


Figure 5: The FESEM image of the ZnO/β-CD/nicotinic acid nanocomposite material.

by EDS analysis (Figure 7). A uniform distribution of C, N, O, and Zn on the matrix was observed in the EDS spectrum and mapping (Figures 6 and 7). No other corresponding peak of impurity was observed. It contained a smooth surface, which was associated with heterogenous mixing of C, N, O, and Zn, resulting in a single-phase surface morphology as observed (Figure 7).

3.2 Photocatalysis

The photocatalytic experiment of ZnO/ β -CD/nicotinic acid nanocomposite samples was analysed via the degradation of MB dye in aqueous solution under UV and visible irradiation. The photodegradation experiment was followed

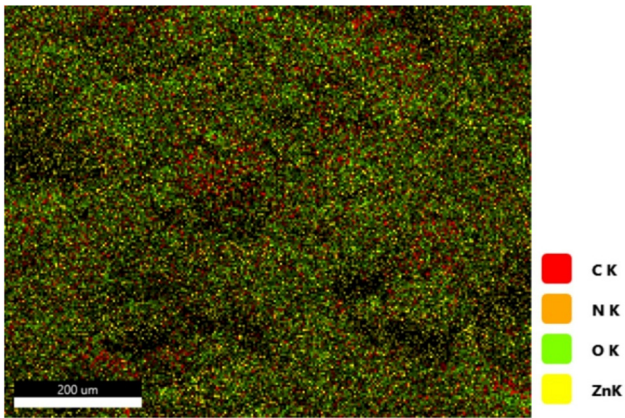


Figure 6: EDS mapping for the ZnO/ β -CD/nicotinic acid nanocomposite material.

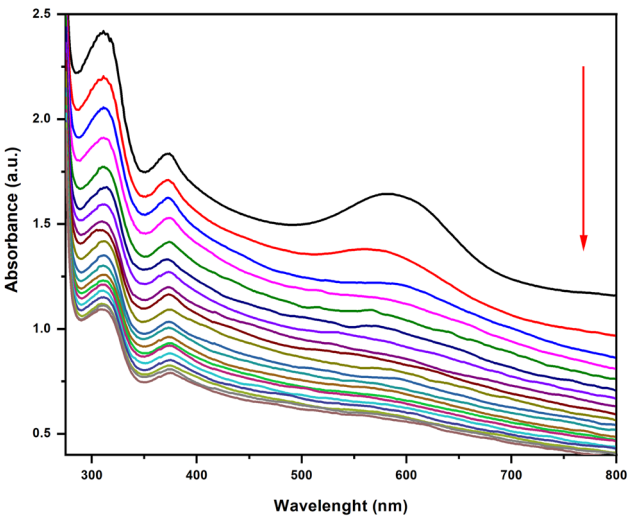


Figure 8: The photocatalysis experiment via the absorption spectra of MB dye with the ZnO/ β -CD/nicotinic acid nanocomposite material under UV-Vis irradiation.

by UV-Vis absorption spectroscopy at different irradiation times (Figure 8) [62].

In this photocatalysis process, the MB dye was degraded under light irradiation, where UV-Vis light was used as an irradiation source. We described here the photocatalysis reaction of ZnO/ β -CD/nicotinic acid nanocomposite with MB. In the presence of light and air, 40.0 mg of the ZnO/ β -CD/nicotinic acid nanocomposite material was added to 10.0 mL aq. solution of MB (1.0×10^{-4} M) (pH = 6). After 10 min, the degradation of blue colour starts. At a constant time (10 min) interval, the ZnO/ β -CD/nicotinic acid nanocomposite degrades the blue colour of the solution (Figure 8).

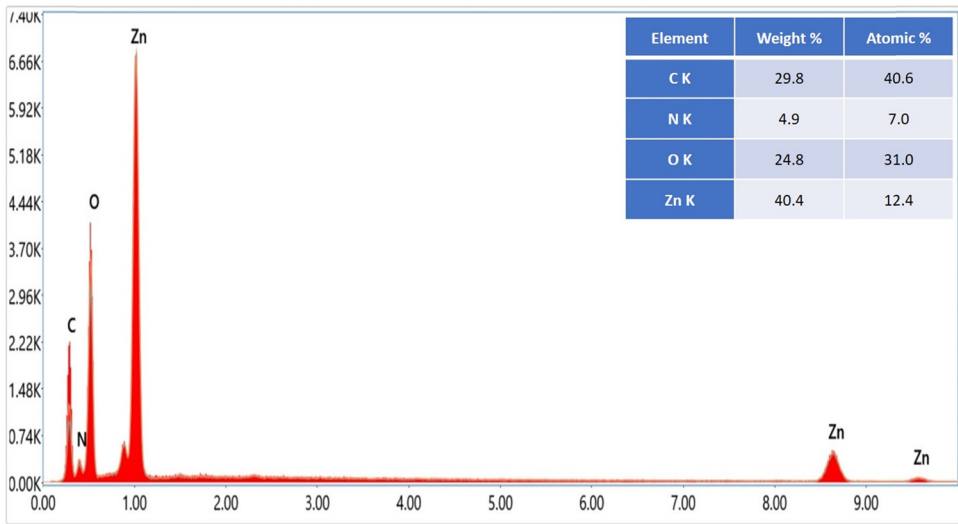


Figure 7: The EDS spectrum with a weight percentage table of ZnO- β -CD.

A scanning range between 200 and 800 nm was used for the MB solution. According to previous studies, the absorption peak of MB was observed at 650 nm. After adding 40.0 mg of the ZnO/ β -CD/nicotinic acid nanocomposite, the absorption peak shifted and λ_{max} was obtained at 587 nm because of the formation of tetramer, which is responsible for the blue shift [63].

In the presence of visible light, the ZnO/ β -CD/nicotinic acid nanocomposite material formed OH^- in the presence of water (H_2O). The whole reaction was monitored via MB

degradation at 587 nm wavelength in an aq. solution by a decrease in the absorbance (Figure 9).

According to Figure 9, in the presence of the ZnO/ β -CD/nicotinic acid nanocomposite, the blue colour of aq. MB dye decreased with time, and it was clearly observed at a wavelength of 587 nm. At a constant time interval (10 min), the blue colour decreased and the peak at 587 nm also decreased. After 190 min, the peak converted into a straight line and the blue colour of the aq. solution of MB became transparent and colourless.

According to Figure 10, at 587 nm wavelength, the absorption decreased at a constant time interval (10 min). After 10 min, the absorption was decreased and as time increased, the absorption of blue dye decreased. Resultant force of optical density, get a straight line with constant time interval (10 min). After the completion of the photo-degradation process, the absorption was constant and the blue colour of the solution also turned colourless.

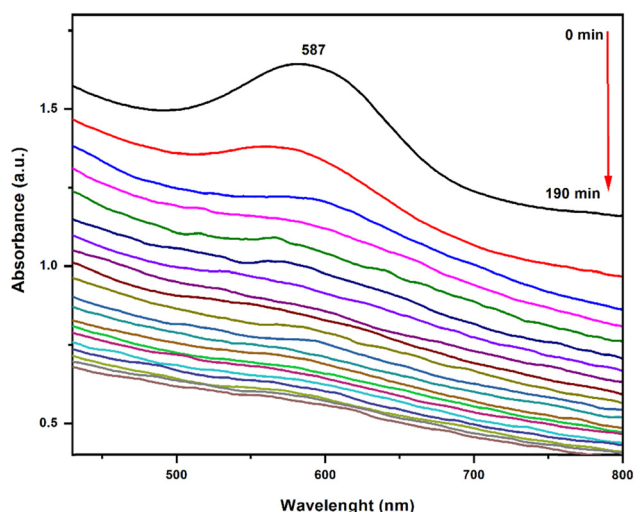


Figure 9: Demonstration of the photodegradation process of MB in the presence of ZnO/ β -CD/nicotinic acid nanocomposite at a 587 nm wavelength up to 190 min.

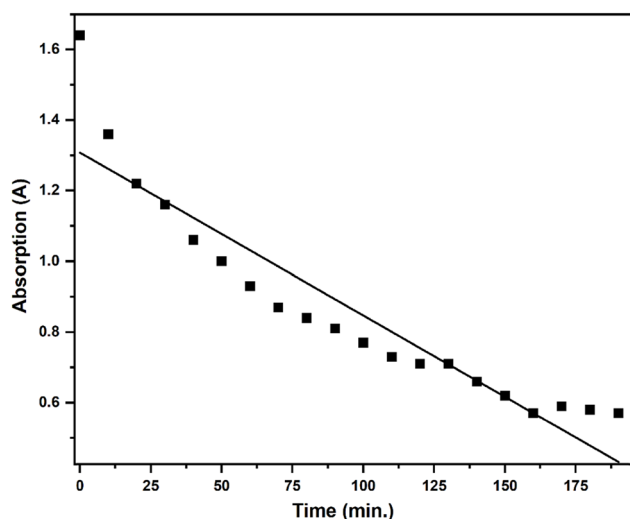


Figure 10: The addition of the ZnO/ β -CD/nicotinic acid nanocomposite material (40.0 mg), at 587 nm wavelength. The time increased, the absorption decreased up to 190 min at a constant time interval (10 min) and the blue colour of the solution was decolourized.

3.3 Cytotoxicity test (MTT assay)

The MTT assay is a high-throughput cell-based assay and is used to evaluate the cytotoxic response of different cell lines to different oncology products. In the present work, the MTT assay was reformed as a chemosensitivity test and its potential was examined. This technique also has numerous benefits regarding speed, quantitation, managing various samples, and cell number. The application of this assay for chemosensitivity testing appears to be valuable and advantageous. MTT examines cell respiration, and the amount of formazan formed is proportional to the number of living cells present in the culture. An increase or reduction in the cell number results in a concomitant change in the quantity of formazan formed, demonstrating the degree of cytotoxicity initiated by the drug. The IC_{50} (concentration) value of the tested drug determines the ability of the drug to cause the death of 50% of the cells and can predict the degree of its cytotoxic effect. The lower the value, the more cytotoxic the substance will be. Figure 11 shows the comparative graph of the IC_{50} values of as-synthesized ZnO/ β -CD/nicotinic acid nanocomposites against MCF-7 cancer cell lines. The percentage cell viability of cancer cells response to various doses of ZnO/ β -CD/nicotinic acid nanocomposite is shown. The ZnO/ β -CD/nicotinic acid nanocomposite ability to promote cell proliferation was tested at concentrations between 0.7 and 200 $\mu\text{g}\cdot\text{mL}^{-1}$; the IC_{50} value was 14.95 $\mu\text{g}\cdot\text{mL}^{-1}$ after 24 h. The cytotoxicity results clearly indicate that the ZnO/ β -CD/nicotinic acid nanocomposite has the best ability to be used as an anticancer agent in oncology

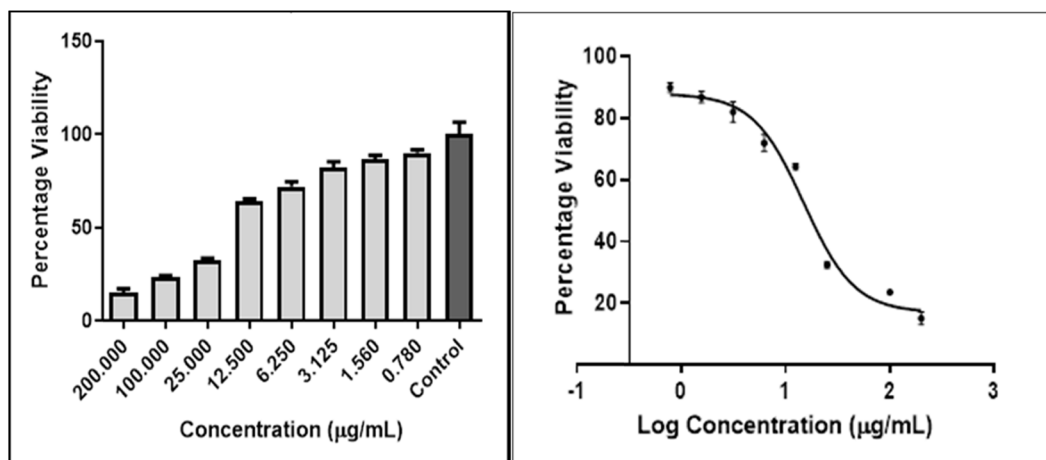


Figure 11: The MTT assay using the ZnO/ β -CD/nicotinic acid nanocomposite in MCF-7 cell lines.

treatment. ZnO nanoparticles are known to be a potential anti-cancer agent, which was proven by many previous studies [64].

3.4 Reuse of the catalyst

For the reuse of the catalyst, the stability of the catalyst is highly important. We use the Fenton reaction to evaluate the stability of the ZnO/ β -CD/nicotinic acid nanocomposite material; we used it many times for several consecutive MB removal cycles. At each cycle, the solid nanocomposite catalyst was separated by centrifugation from the solution and washed with ethanol and distilled water. After that, it was dried in a vacuum and was ready to be reused as a catalyst in the next reaction. In the whole process, we also

observed a slight weight loss of the catalyst after every cycle (190 min). As shown in Figure 12, it is clear that the weight of ZnO/ β -CD/nicotinic acid nanocomposite material decreased in each cycle from 95.4%, 94.0%, 93.1%, and 91.7%, and retained up to 90.0% of its catalytic activity after 5th cycle (Table 1). The small decrease in its catalytic activity after each cycle might be attributed to its incomplete removal during washing. This showed that the ZnO/ β -CD/nicotinic acid nanocomposite was highly stable in an aqueous solution during the photocatalysis process.

3.5 Antimicrobial activity

The antibacterial properties of the ZnO- β -CD nanocomposite material prevented further growth of two bacterial strains *E. coli* and *S. aureus*. Figure 13 shows that the different ZOI (zones of inhibition) for antibacterial activity obtained with different concentrations (10, 50, and 100 $\mu\text{g}\cdot\text{mL}^{-1}$) of the ZnO/ β -CD/nicotinic acid (ZnO/ β -CD/nicotinic acid) nanocomposite. It is clear that the ZnO/ β -CD/nicotinic acid (ZnO/ β -CD/nicotinic acid) nanocomposite produced a good ZOI for the *S. aureus* bacterial strain (Figure 13a) with a clear area around the sample showing complete inhibition. But with *E. coli* it did not show the ZOI area (Figure 13b). The probable antimicrobial action of the nanocomposite is due to the inhibition of microbial proteins causing eventual cell damage and the death of microbes [65].

The antifungal activity was studied with different concentrations (20 and 40 μL) of the ZnO/ β -CD/nicotinic acid (ZnO/ β -CD/nicotinic acid) nanocomposite. It clearly showed that ZnO/ β -CD/nicotinic acid (ZnO/ β -CD/nicotinic acid) produced a minimum ZOI for *A. niger* (Figure 14b). The clear area around the sample showed a complete inhibition

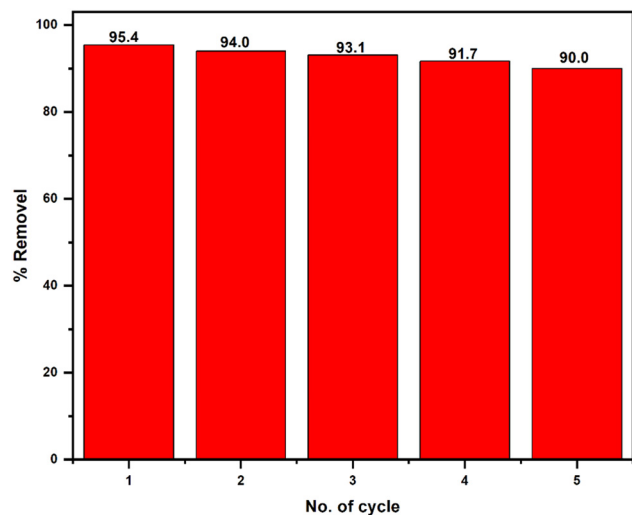


Figure 12: Recycling experiment of ZnO/ β -CD/nicotinic acid nanocomposite materials for the MB degradation process.

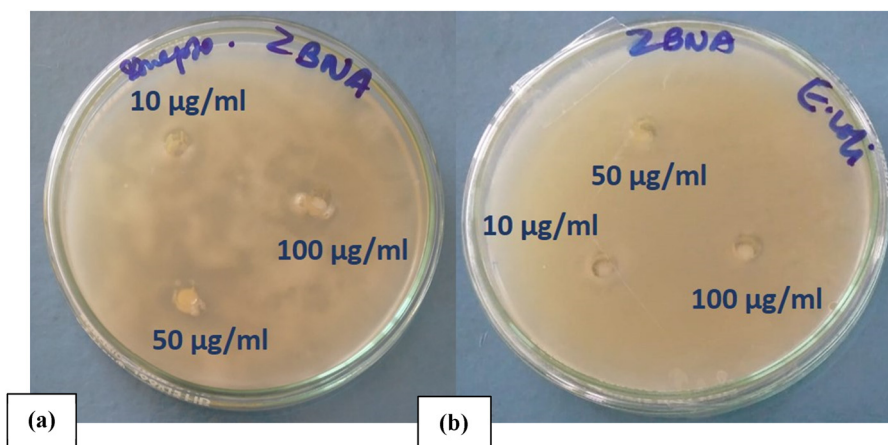


Figure 13: (a) *S. aureus*- and (b) *E. coli*-treated with the ZnO/β-CD/nicotinic acid nanocomposite material at different concentrations in methanol (10, 50, and 100 μg·mL⁻¹).

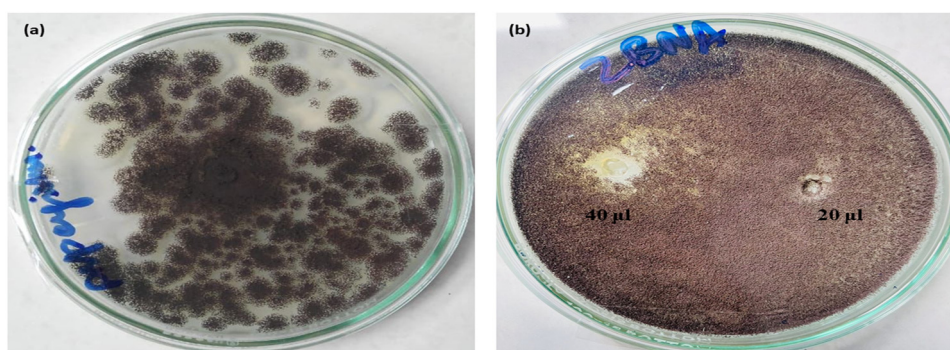


Figure 14: (a) The colony of cultured *Aspergillus niger* fungal strain; (b) *Aspergillus niger*-treated with the ZnO/β-CD/nicotinic acid nanocomposite material at different concentrations in methanol (20 and 40 μL).

zone. Figure 14 shows that increased concentrations of the ZnO/β-CD/nicotinic acid nanocomposite result in the decreased growth rate of *Aspergillus niger*. On comparison of both wells, the well with 40 μL of the ZnO composite sample showed good activity than the well with 20 μL of the sample. When *A. niger* was treated with the Zn/β-CD/nicotinic acid nanocomposite, it released proteins, carbohydrates, and lipids by damaging the cell membranes. As a result, decreased amounts of proteins, carbohydrates, and lipids were observed in the fungal cells, which leads to the death of the cells [66,67].

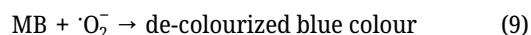
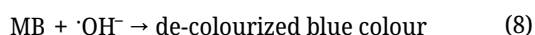
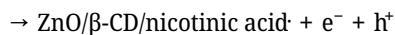
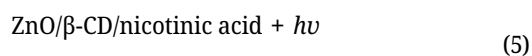
3.6 Photocatalytic degradation mechanism

The photocatalysis mechanisms are described via the photodegradation of MB by the ZnO/β-CD/nicotinic acid nanocomposite material in the presence of UV-Vis light and air [59,68–73]. It can be explained as follows: In the photocatalysis process at a 587 nm wavelength, 1.0×10^{-4} M

MB dye was mixed with 40.0 mg of the ZnO/β-CD/nicotinic acid nanocomposite material. The solution mixture of MB and the ZnO/β-CD/nicotinic acid nanocomposite vessel was photo-irradiated under UV/visible light; the ZnO composite is excited. Due to the excitation of the composite material, photo-induced pairs of electrons and holes ($e^- + h^+$) are formed. These electrons or holes are captured by the aqueous solution of MB dye and radicals like $OH^{\cdot}$ and $O_2^{\cdot-}$ are generated, which decolorized the blue colour of MB [73,74]. The active sites of the ZnO composite catalyst are covered by the MB dye and degradation products, which compete with the H_2O and $OH^{\cdot}$ to be adsorbed on the same sites; as a result fewer $OH^{\cdot}$ radicals are formed and high degradation efficiency is observed [75]. A specific amount of light radiation is used by the MB dye molecules and less amount of photons reach the surface of the catalyst to generate $OH^{\cdot}$ radicals [74,76].

The MB dye enters into the holes of the ZnO/β-CD/nicotinic acid composite (which binds with ZnO centrally) surface and absorbs radiation of light for excitation. An electron rapidly

excites the MB dye to the conduction band of ZnO. Along with the $\text{OH}^\cdot$ radical, another important radical, the superoxide anion radical ($\text{O}_2^\cdot$), is illuminated from the ZnO nanocomposite. Thus, the excited MB dye with the ZnO/ β -CD/nicotinic acid composite material undergoes the photocatalytic degradation reaction [77,78]. The mechanism reaction is as follows:



In summary, in the presence of light and air, the ZnO/ β -CD/nicotinic acid nanocomposite material generates holes and electrons. They react with water and form $\text{O}_2^\cdot$ and $\text{OH}^\cdot$ radicals, which are used in the photocatalysis or in the photodegradation process of MB at pH 6 of the solution. In an acidic medium, the rate of degradation was high in comparison with the basic medium because the negatively charged hydroxyl radicals easily degrade the cationic dye. At a constant time interval, the activity of the ZnO/ β -CD/nicotinic acid nanocomposite material decreases because of the formation of a layer of OH that coats the surface of the catalyst, which could be washed with ethanol and distilled water. After drying the solid nanocomposite, it can again be reused for the next catalysis reaction cycle. After each cycle, the activity of the catalyst for degradation is slightly decreased and after the 5th cycle, it would be around 90%. These ZnO/ β -CD/nicotinic acid nanocomposites are also used as antibacterial or growth inhibitors against *E. coli* and *S. aureus* bacterial strains. At high optical density, the nanocomposites damaged the cell membranes of *S. aureus*. As a result, at high optical density, colony growth was not observed; for *E. coli* it did not show any result. The ZnO/ β -CD/nicotinic acid nanocomposite produced a clear ZOI for *S. aureus* but for *E. coli*, no clear region was observed around the wells. Similar to antibacterial activity, the Zn/ β -CD/nicotinic acid nanocomposite showed antifungal activity for the *A. niger* fungal strain.

4 Conclusion

Here, we synthesized ZnO/ β -CD/nicotinic acid nanocomposites using the co-precipitation method with aq. solvent. The reaction between both precursors in the presence of water generated OH^- ions for precipitation. The

synthesized ZnO/ β -CD/nicotinic acid nanocomposite was characterized, and the average XRD crystallite size was 50 nm as calculated using the Scherrer formula. It also showed a remarkable photocatalytic property with MB. The ZnO/ β -CD/nicotinic acid composite showed good catalytic efficiency in the degradation of MB at pH 6 in comparison with ZnO. The blue colour of MB was decolourized at a constant time interval. After 190 min, the blue colour of the solution became colourless. This process provided easy recovery of the nanocomposite catalyst by centrifugation and separation. The catalytic activity was again regained in consecutive steps. The degradation efficiency was around 90%. Due to the generation of $\text{O}_2^\cdot$ and $\text{OH}^\cdot$ radicals by the ZnO/ β -CD/nicotinic acid nanocomposite material, it was also used as antibacterial or growth inhibitors against *S. aureus* bacterial strains, but it did not show any antibacterial effect against *E. coli*. It was also used as an antifungal growth inhibitor for *A. niger* fungal strains. The prepared materials also showed the efficacy of anticancer activity towards MCF-7 cell lines.

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