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Synthesis of Biocompatible ZnO/β-CD Nanocomposite and Photocatalytic Degradation Study with Methylene Blue Dye

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ABSTRACT

In this present work zinc oxide/ β-cyclodextrin nanocomposite was successfully synthesized by a simple precipitation method using zinc nitrate hexa hydrate and sodium carbonate as precursors. The prepared ZnO nanoparticles were mixed with β-cyclodextrin solution under proper proportions and formed nanocomposite then annealed at 150 °C for 2 h. The prepared samples were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), UV- visible spectroscopy and AFM. The XRD results indicate that the ZnO crystal has a hexagonal wurtzite structure. The optical properties of the samples are investigated by measuring the UV-VIS absorption at room temperature. FTIR results prove the functional groups present. Photocatalytic degradation of methylene blue (MB) dye was studied using the synthesized nanocomposites applied as photocatalyst.

1. Introduction

Nanotechnology is the manipulation of matter on an atomic, molecular, and supramolecular scale. In its original sense, nanotechnology refers to the projected ability to construct items from the bottom up, using techniques and tools being developed today to make complete, high performance products. The two approaches for nanomaterials synthesis are (i) top down and (ii) bottom up approaches. The present state of nanoscience can be viewed as an amalgamation of bottom-up chemistry and top-down engineering techniques. Recently, ZnO nanomaterials have been observed to have important application in improved photocatalytic degradation of dyes. Many researchers have reported their achievements in preparing ZnO nanomaterials and its composites through different methods and their improved application in photocatalytic degradation of organic dyes. The uses of ZnO as a photocatalytic degradation material has been extensively studied [1]. The extensive properties of β-cyclodextrin (β-CD) derived in useful for solubilizing and stabilizing highly hydrophobic molecules in solvents such as water [2-7]. These properties can be used with nanoparticle to destroy the organic dyes in the industrial wastes. Methylene blue (MB) is a heterocyclic aromatic chemical compound used as a dye and pharmaceutical drug. It enters water bodies through effluents from textile, paper, and pharmaceutical industries and adversely affects eco-system and aquatic life. Presence of methylene blue in drinking water is a health hazard as it causes eye and skin irritation, hemolytic anaemia, nausea, vomiting, and abdominal pain. Therefore, its removal from the polluted water is of significant importance. In the present work zinc oxide/β-CD nanocomposites were prepared and studied their dye degradation properties against MB.

2. Experimental Methods

2.1 Materials

Zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$), 99% Sigma-Aldrich, sodium carbonate (Na_2CO_3), 99% Sigma-Aldrich and ethanol (C_2H_5OH), 95%, Biochem were used as received.

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2.2 Preparation of ZnO NPs

ZnO NPs were prepared by a precipitation method as follows [8]: Briefly, two solutions were prepared: Solution A (0.1 M $Zn(NO_3)_2.6H_2O$) was prepared by dissolving 2.9747 g of zinc nitrate hexahydrate in 100 mL distilled water; and solution B (0.12 M Na_2CO_3) was prepared by dissolving 12.7188 g of sodium carbonate in 120 mL distilled water. After that, the ZnO NPs was prepared by adding solution A to solution B drop wise under vigorous stirring. The white precipitate was collected by filtration and rinsed with distilled water three times. The solid was then washed with ethanol and dried at 100 °C for 2 h. Finally, ZnO NPs were obtained after annealing of the precursor in muffle furnace at 600 °C for 2 h.

2.3 Preparation of β-Cyclodextrin/ZnO Nanocomposites

The β-cyclodextrin/ZnO nanocomposites were prepared by addition of β-cyclodextrin and prepared ZnO nanoparticles in water (2:1 molar ratio) for 4 hours constant stirring. The ZnO nanocomposite obtained from this method annealed at 150 °C.

2.4 Photocatalytic Degradation Study

Aqueous solution of methylene blue (100 mL) was mixed with known amount of photocatalyst in a reactor. The reaction mixture was kept under dark for 30 min to attain sorption-desorption equilibrium. A UV lamp (Philips, 12 W) was placed 10 cm above the reactor tube. The reaction mixture was irradiated while continuously being stirred and simultaneously purged with air. Five milliliter of reaction mixture was collected at a regular interval of 20 min. The suspension was centrifuged at 3000 rpm for 10 min, and absorbance of the clear supernatant was recorded at 665 nm using a UV-Vis spectrophotometer [9].

3. Results and Discussion

The purity, phase, average particle size and over all crystallinity of the synthesized nanocomposites were confirm through X-ray diffraction pattern. From Fig. 1, the peaks at 2θ values 31.8°, 34.66°, 36.42°, 34.77°, 56.87°, 62.91° and 67.96° of ZnO/β-cyclodextrin nanocomposites are corresponding to (100), (002), (101), (102), (110), (103), (112) and (201) in the JCPDS data card 89-0510. Hexagonal structure was confirmed by the (1 0 1) crystalline peak and the average crystal size of synthesized ZnO

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nanoparticle is in the range 39.3 nm, calculated using Debye- Scherrer formula. The presence of β-cyclodextrin as well as ZnO characteristic reflections indicated the maintenance of the β-cyclodextrin and ZnO nanoparticles in crystallographic organization of the nanocomposites. The presence of high and narrow shaped peaks is highlighting that ZnO nanoparticles possess high crystallinity and low surface defects and were of ultrapure phase.

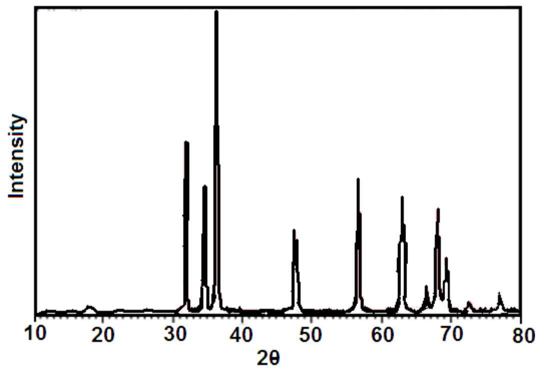

Fig. 1 XRD pattern of ZnO/β-cyclodextrin nanocomposites

Fourier transform infrared spectroscopy (FTIR) data of the ZnO/ β-cyclodextrin nanocomposite is presented in Fig. 2. The transmittance band characteristics of alginate were obtained at 3434 cm^{-1} corresponding to OH group and the peaks near 1626 cm^{-1} and 1459 cm^{-1} are assigned to symmetric and asymmetric stretching vibration of COO^- groups. The band around 1019 cm^{-1} (C-O-C) stretching was attributed to its saccharide structure. The absorption band around 2924 cm^{-1} may be due to the C-H stretching of the CH_2 group. The peak around 435 cm^{-1} is the characteristic absorption of Zn-O bond.

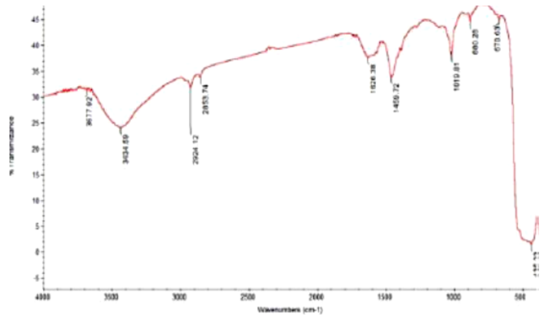

Fig. 2 The FTIR image of the ZnO/β-cyclodextrin nanocomposite

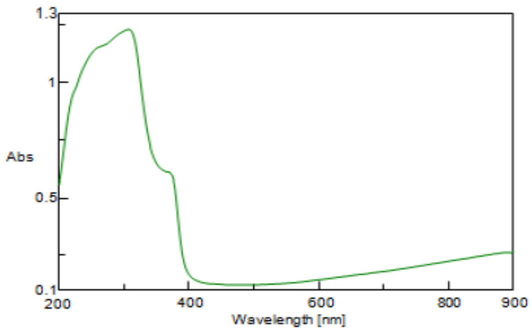

Fig. 3 UV-Vis spectra of the ZnO/ β-cyclodextrin nanocomposite

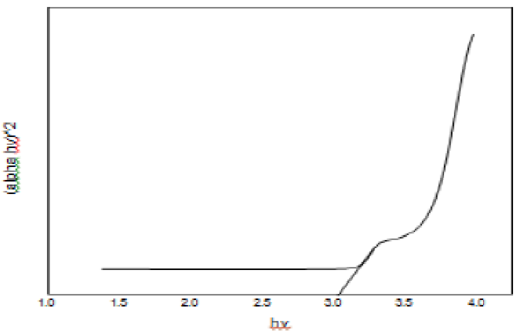

Fig. 4 The band gap calculated from the UV-vis spectra of ZnO/β-cyclodextrin

The absorption spectrum of the synthesized nanocompositie is shown in Fig. 3. The excitation of a strong absorption peak at around 320 nm can be assigned to the intrinsic band-gap absorption of ZnO. An excitonic absorption peak is found at about 258 nm due to the ZnO nanoparticles which lie much below the band gap wavelength of 358 nm. The band gap was calculated (Fig. 4) from the UV-vis spectra of ZnO/β-cyclodextrin and the value is found as 3.0 eV.

Surface topology of the synthesized ZnO/β-cyclodextrin nanocomposite was studied by atomic force microscope (AFM) analysis as given in Fig. 5. The results showed a uniform surface and indicated that the particles have uniform dimensions.

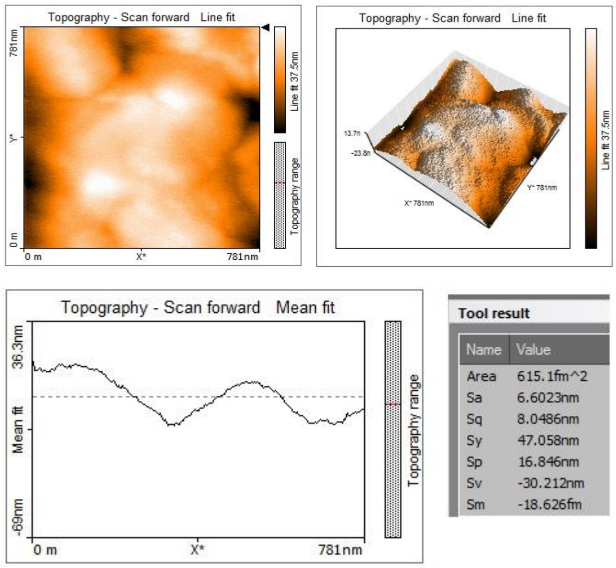

Fig. 5 AFM image of ZnO/ β-cyclodextrin nanocomposite

3.1 Photodegradation Studies

During the photocatalytic degradation of MB, the conduction band electrons (e^-) and valence band holes (h^+) are generated when aqueous ZnO/β-cyclodextrin suspension irradiated with light energy greater than its band gap energy (Eg = 3.2 eV). The photo generated electrons could reduce the dye or react with electron acceptors such as O_2 absorbed on the Zn (II) surface reducing it to super oxide radical anion $O^{\bullet -}$. The holes generated by photochemical reactions can oxidize the organic molecule to form $R^\bullet$ or react with $OH^\bullet$ or H_2O oxidizing them into $OH^\bullet$ radicals. Together with other highly oxidant species (peroxide radicals) they are reported to be responsible for the heterogeneous ZnO/ β-cyclodextrin photodecomposition of dyes. The photochemical reactions at the semiconductor surface which results the degradation of dyes can be demonstrated as follows.

$$ZnO + h\upsilon(\mathrm{UV}) \rightarrow \mathrm{ZnO}(\mathrm{eCB}^- + hVB^+)$$

$$ZnO(hVB^+) + H_2O \rightarrow ZnO + H^+ + OH\_$$

$$ZnO(hVB^+) + OH^- \rightarrow ZnO + OH^-$$

$$ZnO(eCB^-) + O_2 \rightarrow ZnO + O_2^{\,-}$$

$$O_2^- + H^+ \rightarrow HO^{\cdot}$$

$$Dye + OH^{\cdot} \rightarrow Degradation\ products$$

The resulting $OH^\bullet$ radical, being a very strong oxidizing agent (standard redox potential +2.8 V) can oxidize most of MB dye, the mineral end-products substrates not reactive toward hydroxyl radicals, are degraded employing ZnO/β-cyclodextrin photocatalysis with rates of decay, and highly influenced by the semiconductor valence band edge position [10].

Plots of photocatalyst load (100 mg/L) and different initial concentration of dye, i.e., MB, the plots of percent photocatalytic degradation of the dye as a function of time are presented in Fig. 7. Such plots under UV radiation are shown in Fig. 6.

About 90% degradation was achieved with an initial dye concentration of 20 mg/L and a catalyst dose of 100 mg/L; 80% achieved with an initial dye concentration of 40 mg/L and a catalyst dose of 100 mg/L; 60% achieved with an initial dye concentration of 60 mg/L and a catalyst dose of 100 mg/L and 40% achieved with an initial dye concentration of 80 mg/L and a catalyst dose of 100 mg/L.

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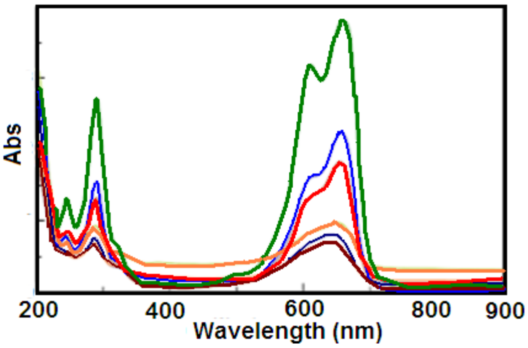

Fig. 6 UV-Vis spectra of methylene blue treated with the photocatalytic reaction in presence of as prepared ZnO/β -cyclodextrin nanocompositie

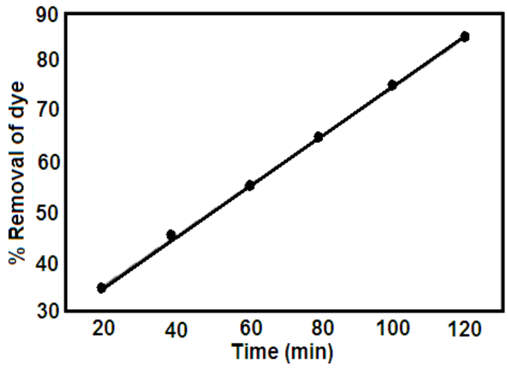

Fig. 7 Plots of percentage degradation of MB dye under UV radiation

4. Conclusion

The ZnO/β-cyclodextrin nanocomposite was prepared by a facile process. The synthesized nanocomposite shows that the size was approximately 39.3 nm calculated through XRD. The band gap is calculated from the UV-vis spectra of ZnO/β-cyclodextrin and the value is found as 3.0 eV. The FTIR spectrum confirms the functional groups of β-cyclodextrin and ZnO. The prepared ZnO nanomaterials have been utilized for the photocatalytic degradation of methylene blue in aqueous medium. The photocatalytic degradation of methylene blue in ZnO/β-cyclodextrin suspension was carried out using UV irradiation. Photocatalytic degradation of MB increased with increasing in catalyst load up to a limiting value (100 mg/L) and then decreases at higher catalyst concentrations. However, at a fixed catalyst load, the degradation of MB decreases with increase of dye concentration. Using dye initial concentration of 20 mg/L, maximum degradations of MB under UV radiation photocatalysts by prepared ZnO/β-cyclodextrin is achieved to 90% efficiency.

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