



Article

Enhanced Photocatalytic Degradation and Photocorrosion Inhibition of CNC-Supported Ag–ZnO Nanocomposites: Structural Evolution and Intermediate Identification

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Abstract

In this study, a cellulose nanocrystal (CNC)-supported Ag–ZnO nanocomposite was synthesized via a hydrothermal route as a polymeric photocatalyst for efficient UV-A light-driven dye degradation. The renewable CNC framework provides abundant hydroxyl functional groups for nanoparticle anchoring, enhancing dispersion and interfacial charge transfer. Structural (XRD, FTIR, TEM, PL, and XPS) and thermal (TGA and DTG) analyses confirm successful incorporation of Ag nanoparticles and retention of CNC crystallinity. The composite exhibits a reduced optical bandgap (3.02 eV) and demonstrates superior photocatalytic activity, achieving 96% methylene blue (MB) degradation within 120 min. Enhanced performance is attributed to the synergistic effect of Ag-induced plasmonic excitation and CNC-facilitated charge migration, effectively suppressing ZnO photocorrosion. Moreover, the optimization of the parameters was conducted and found to be pH 7, a catalyst dose of 0.3 g L^{−1}, and an initial MB concentration of 10 ppm, which shows the best photocatalytic degradation reaction. The CNC/Ag–ZnO catalyst maintains 87% activity after five reuse cycles, showing good stability and reusability. The photostability of the CNC/Ag–ZnO catalyst was evaluated by ICP-MS, which measured Zn²⁺ concentration in the aqueous solution. Additionally, the degraded MB compounds were identified using GC-MS/MS analysis. This work highlights the potential of polymer-based biogenic supports for sustainable photocatalyst design and bridges polymer science with environmental remediation technology.



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Keywords: cellulose nanocrystals; zinc oxide; silver; methylene blue; photocatalytic degradation; photocorrosion; ICP-MS; GC-MS/MS

1. Introduction

Textile industries, one of the largest global sectors, significantly contribute to the economies of many nations, including Bangladesh, by providing employment without requiring specialized training [1]. Chemical-laden textile effluents discharged into key

water sources pose serious health risks, including dermatitis and hemorrhage, while also blocking sunlight and increasing biological oxygen demand (BOD), which harms aquatic ecosystems [2]. To address the high costs and inefficiencies of traditional textile wastewater treatment, advanced oxidation processes (AOPs) have emerged as a viable solution, employing highly reactive hydroxyl radicals to effectively mineralize persistent organic pollutants (POPs), such as dyes, pharmaceutical wastes, and heavy metals [3]. Photocatalysis has emerged as a sophisticated method for removing these harmful chemicals due to its low cost, environmental friendliness, high reactivity, and the availability of raw materials [4]. Photocatalysis employs metal oxide semiconductors as light-active materials that accelerate the degradation of organic pollutants under illumination. ZnO and TiO₂ are popular photocatalysts for this purpose [5]. Recent research has explored various combinations of metal oxides, including ZnO, TiO₂, CuO, Fe₂O₃, Fe₃O₄, MnO₂, BiOBr, Ag₃PO₄, graphene oxide, and graphitic carbon nitride (g-C₃N₄), to enhance pollutant degradation [5]. While ZnO and TiO₂ are active in the UV region of the electromagnetic spectrum, others, such as CuO, Cu₂O, Ag₃PO₄, Fe₃O₄, Fe₂O₃, and MnO₂, are active in the visible region, enabling the utilization of solar energy for pollutant degradation [6–9]. ZnO is particularly promising due to its low cost, environmental friendliness, ease of preparation, and superior quantum efficiency. However, its activity is limited to the UV-C region, reducing its ability to utilize solar energy. Various studies have attempted to tune the photoactivity of ZnO to the UV-A to visible range [10–12]. One limitation of ZnO is its photocorrosive behavior, which can be mitigated by combining it with Ag nanoparticles. Thermodynamically, Ag acts as an electron sink, increasing charge separation and mitigating hole formation at the ZnO surface, thereby kinetically inhibiting photocorrosion, boosting photocatalytic activity, and simultaneously enhancing the mechanical robustness of the composite [13,14]. A key indicator of photocorrosion is the amount of zinc ions leached into the solution. Techniques like ICP-MS, researchers have demonstrated a dramatic reduction in Zn²⁺ leaching for Ag/ZnO composites [15]. While pristine ZnO shows a substantial increase in dissolved Zn²⁺ after prolonged irradiation, Ag/ZnO composites exhibit a much lower concentration, often remaining stable over multiple cycles [15,16]. The collective evidence from thermodynamic and kinetic studies strongly supports the role of Ag in enhancing the photostability of ZnO.

Ag-ZnO nanocomposites not only reduce photocorrosion but also enhance redox reactions and adjust the energy band gap of ZnO to be active in UV-A light [17–19]. Another issue with ZnO is its tendency to agglomerate in aqueous media, which decreases its photocatalytic activity. Immobilizing ZnO on a matrix is one effective way to prevent this aggregation [5]. Several support matrices have been studied for immobilizing ZnO to enhance its photocatalytic performance, with a focus on green materials that significantly boost photoactivity. These include clay minerals, cellulose, chitosan, and other bio-based materials [20]. Bio-based materials are environmentally friendly, cheap, and readily available. Nanohybrids of bio-based materials and ZnO have proven to be sustainable and effective in removing POPs [21,22]. Because of its large surface area and pollutant-binding capacity, cellulose is an excellent low-cost support for water cleanup [23,24]. It is also abundant and biodegradable. Nanocellulose amplifies these advantages by providing improved mechanical properties and abundant surface hydroxyl groups that facilitate the anchoring of metal cations [25]. While mineral acid hydrolysis often yields thermally unstable compounds, sustainable synthesis with organic acids is preferred to improve both yield and surface functionalization [26]. In this context, Shi et al. successfully synthesized Ag-ZnO/cellulose nanohybrids by mechanically grinding the composite to optimize its structural and photocatalytic activities [27]. Increasing the grinding time polished the cellulose fibrils, resulting in a greater surface area of 40.64 m² g^{−1}, a more uniform

nanoparticle dispersion, and a morphological change in ZnO from a flower-like to a flaky structure. The optimized 3D network achieved 90% degradation of methyl orange under sunlight and demonstrated outstanding stability over 10 cycles, indicating a scalable strategy for customizing nanoparticle morphology via biopolymer modification. Using organic acids to synthesize cellulose nanocrystals (CNCs) offers several advantages over the traditional method with strong mineral acids [28]. Since organic acids are milder and less corrosive, this approach is more environmentally friendly, safer, and leads to higher quality CNCs with enhanced thermal stability and useful surface functionalization [29]. Immobilizing silver on zinc oxide for photocatalysis improves its activity and stability [13]. It boosts photocatalytic activity by reducing electron–hole recombination and broadening light absorption through the localized surface plasmon resonance of silver [14,15]. It also enhances stability by preventing photocorrosion and makes the catalyst easier to recover and reuse [15,16].

The objective of this study is to design a catalyst with reduced band gap energy, slower recombination of electron–hole pairs, high surface area, and reduced aggregation of particles that effectively removes organic dyes from wastewater by the irradiation of natural sunlight. In this study, we synthesize CNCs via organic acid hydrolysis, synthesize Ag-ZnO and CNC/Ag-ZnO nanocomposites via the solvothermal method, characterize CNCs, Ag-ZnO, and CNC/Ag-ZnO nanocomposites, and investigate their photocatalytic degradation activity using MB as a model organic pollutant. As ZnO is a powerful photocatalyst, its practical applications are limited by rapid charge recombination and susceptibility to photocorrosion. This study overcomes these restrictions by using CNCs as a renewable, high-surface-area support. The novelty lies in the synergistic integration of Ag-induced plasmonic excitation and CNC-facilitated charge transfer, which not only extends the photocatalytic activity into the UV-A range but also significantly enhances the structural stability of materials, as evidenced by ICP-MS analysis. Another key contribution of this study is the reporting of new MB degradation intermediates identified through GC-MS/MS, uncovering intermediate steps in the mineralization pathway that have not been previously reported.

2. Materials and Methods

2.1. Materials

Bleached kraft pulp of *Trema orientalis* L. (Nalita or Gunpowder tree) was provided by the Pulp and Paper Research Division, BCSIR, Bangladesh, and was denoted as BNKP. Both glacial acetic acid and sulfuric acid were obtained from Sigma-Aldrich (Germany; purities ~99.80% and ~95%, respectively). Silver nitrate (99%), zinc nitrate hexahydrate (98%), sodium hydroxide pellets (assay $\geq 98.0\%$), and ethanol were supplied by Merck, Germany, and used as received. The methylene blue (MB) dye used in this study was sourced from Janssen Chimica, Belgium, and was of analytical purity, requiring no additional purification. De-Ionized (DI) water with a conductivity of $0.055 \mu\text{S cm}^{-1}$ at 25°C , obtained from an HPLC-grade water purification system (BOECO, Germany), was used throughout the experiments.

2.2. Preparation of CNCs Using Acetic Acid Catalyzed by Sulfuric Acid

To obtain CNCs, bleached non-wood kraft pulp (BNKP) with 70% moisture was first processed in a disintegrator. For the hydrolysis step, a mixture of sulfuric acid, glacial acetic acid, and DI water in a 1:7:2 ratio (total 200 g) was prepared in a three-necked round-bottom flask [30,31]. The BNKP was then added to the acid mixture at a 3:100 ratio and allowed to swell for 24 h to ensure thorough, even hydrolysis. After swelling, the mixture was heated to 80°C in an oil bath and stirred vigorously at 900 rpm for 7 h to complete the hydrolysis.

After cooling, the mixture was centrifuged at 8000 rpm for 10 min to separate the CNCs (residue) from the acidic supernatant, which contained byproducts like glucose, xylan, and furfural. The CNC residue was repeatedly washed with DI water using centrifugation. To remove any remaining acid, the resulting suspension was dialyzed against DI water using a cellulose dialysis membrane (molecular weight cut-off of 12,500 Da) until the conductivity of the suspension matched that of pure DI water ($0.055 \mu\text{S cm}^{-1}$). Finally, the CNC suspension was freeze-dried to obtain the solid CNCs, with a reported yield of approximately 75%.

2.3. Synthesis of ZnO NRs, Ag/ZnO, and CNC/Ag-ZnO Nanocomposites

Ag-ZnO composites were synthesized in a facile solvothermal method, avoiding the use of a strong reducing agent [32,33]. The reduction process involves a spontaneous redox reaction in which ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) acts as the reducing agent, converting silver ions (Ag^+) into solid elemental silver (Ag^0). In total, 3 mmol of zinc nitrate hexahydrate and 0.15 mmol of silver nitrate were dissolved in absolute ethanol for the synthesis of Ag-ZnO [34,35]. For the preparation of ZnO nanoparticles, the synthesis was performed without adding silver nitrate in this step. The ratio of Ag:ZnO in the Ag-ZnO composite was 1:20. The solution was stirred vigorously at room temperature for 10 min, then 30 mmol of sodium hydroxide was added. This precursor solution was kept in the dark and stirred for about 1 h at 35°C , after which it turned dark gray. The solution obtained in the previous step was then placed in a sealed stainless-steel container lined with Teflon (an autoclave with a 100 mL capacity) and heated to 120°C for 12 h. After the heating process, the resulting suspension was filtered, washed with ethanol to remove impurities, and subsequently dried in an oven at 65°C for 12 h.

CNC/Ag-ZnO composites were prepared following the same procedure as Ag-ZnO, except for an additional step of adding CNC into the precursor solution. A certain amount of dried CNC was dispersed in 80 mL of absolute ethanol using an ultrasonic bath for 1 h at 35°C . Similar amounts of zinc nitrate hexahydrate and silver nitrate, as mentioned in the synthesis of Ag-ZnO, were dissolved in the CNC dispersion, and the precursor solution was stirred for 10 min at room temperature. The precursors were added to maintain a 1:1 mass ratio of Ag-ZnO to CNC. Subsequently, sodium hydroxide was added to the dispersion, which was vigorously stirred in the dark for 1 h at 35°C . This precursor dispersion was then transferred to the autoclave and heated under the same conditions as before. The summary of ratios with reaction conditions of the preparation of ZnO, Ag-ZnO, and CNC/Ag-ZnO is given in Table 1.

Table 1. Preparation of ZnO, Ag-ZnO, and CNC/Ag-ZnO nanomaterials.

Materials	Ratio	Reaction Condition
ZnO	1	Heated to 120°C for 12 h in a sealed stainless-steel container lined with Teflon autoclave
Ag-ZnO	1:20	
CNC/Ag-ZnO	1:1	

2.4. Characterization of the Prepared Nanocomposite

The crystalline properties of the nanocomposites were analyzed by a powder X-ray diffraction (XRD) diffractometer. Diffractograms were performed over a 2θ range of 5° to 80° at a scan speed of 4° min^{-1} . The molecular characterization of the nanocomposites was conducted by a Fourier Transform Infrared (FTIR) spectrophotometer (Frontier, PerkinElmer, UK). A small amount of the sample was thoroughly mixed and ground with potassium bromide (KBr, Alfa Aesar, 99+%, UK) into a fine powder, with KBr being 200 times the mass of the sample. Subsequently, the samples were scanned by FTIR at

25 °C over 400–4000 cm^{-1} , with 16 scans. Optical properties of the nanocomposites were analyzed using a UV-Visible absorption spectrophotometer (LAMBDA 35, PerkinElmer, USA). The samples were dispersed in DI water, and the measurements were taken in a quartz cuvette with a 1 cm path length. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of the prepared materials were performed using a Hitachi TG/DTA 7200 instrument under a nitrogen (N_2) atmosphere at a flow rate of 100 mL min^{-1} . Alumina (Al_2O_3 , 99% alumina porcelain) crucibles were used for preparing samples. The sensitivities of TG analysis and DTA were 0.2 μg and 0.06 μV , respectively.

The shape and structure of the synthesized nanocomposite materials were examined using a transmission electron microscope (TEM; specifically a Technai F30 from FEI, operating in bright-field (BF) mode). The microscope used an accelerating voltage of 300 keV and featured a field-emission gun (FEG) with SuperTwin[®] lens technology, enabling a resolution of 1.9 Å. To prepare samples for imaging, a diluted nanoparticle solution was dropped onto a copper (Cu) grid and allowed to dry. Throughout the compositional analysis, samples were mounted on aluminum stages using conductive carbon tape.

To analyze the elements present on the material surfaces, X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Scientific instrument manufactured in China. The spectrometer used an aluminum K-alpha ($\text{Al K}\alpha$) X-ray source, emitting photons with an energy of 1486.68 eV. To provide a general overview of the elements present, survey scans were performed at a pass energy of 200 eV. More detailed information about specific elements was obtained through high-resolution scans conducted with a pass energy of 50 eV using the Hemispherical Capacitor Analyzer. This setup provided a full-width at half-maximum (FWHM) of the Ag 3d_{5/2} peak of less than 1 eV and measured intensity above a linear baseline from a binding energy (BE) of 365 to 371 eV, with a 1 eV background averaging range.

The photoluminescence (PL) properties of the CNC, ZnO, Ag-ZnO, and CNC/Ag-ZnO nanocomposites were examined using an RF-6000 Spectrofluorophotometer (Shimadzu, Japan) under solid-state conditions at room temperature. Powdered samples were uniformly spread on a clean quartz sample holder without the use of any solvent to avoid interference from dispersion media. PL excitation and emission spectra were recorded over appropriate wavelength ranges based on the optical response of ZnO. The excitation and emission slit widths were fixed at 5 nm, and all measurements were performed with optimized scanning parameters to ensure an adequate signal-to-noise ratio. Background correction was applied prior to data acquisition. The obtained solid-state fluorescence spectra were analyzed to observe variations in emission intensity, peak position, and spectral broadening. These changes were used to evaluate the synergistic interaction between cellulose nanocrystals, Ag particles, and ZnO, as well as charge transfer and recombination behavior. The suppression of fluorescence intensity in the CNC/Ag-ZnO composite relative to pristine ZnO was interpreted as evidence of enhanced charge separation, which is beneficial for photocatalytic performance.

2.5. Photocatalytic Degradation Experiment

The photocatalytic activity of the prepared materials was evaluated in a typical photocatalysis procedure [36]. MB dye has been utilized as a model pollutant for the photodegradation experiments. The degradation parameters were optimized, and the optimal values were found to be a catalyst dose of 0.3 g L^{-1} , a solution pH of 7, and a dye concentration of 10 ppm. For that, 30 mg of catalyst was added to 100 mL of a 10 ppm MB aqueous solution. This solution was kept in the dark, stirring for 30 min in an inactive UV-A chamber (homemade) (Figure S1) to reach adsorption–desorption equilibrium. Subsequently, an aliquot was taken from the solution and centrifuged to prevent any interference from

suspended catalyst particles that could scatter light during measurements. The solution concentration was determined by UV-visible absorption spectroscopy. The solution was then returned to the UV chamber, and the UV-A lamp (Philips 8 W UV-A light, 365 nm) (Figure S2) was activated to initiate MB photodegradation. UV-A lamps are designed to emit a narrow band of light, often with a peak near 365 nm. Immersed Lamp Reactor: This common design (Figure S1) features a UV-A lamp placed inside a quartz sleeve, which is then submerged in the solution. This geometry provides a uniform, 360-degree light penetration angle, maximizing the amount of light reaching the catalyst particles in the slurry. During the reaction, aliquots of the solution were taken at different time points, and their concentrations were determined by the former method. Percent removal of MB at different time intervals was measured by the following formula:

$$\% \text{ Removal} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where C_0 is the initial concentration of the MB prior to the photodegradation reaction, and C_t is the concentration of the MB at time t .

2.6. Gas Chromatography–Mass Spectrometry (GC–MS/MS) Analysis

The degradation products of MB in aqueous solution were extracted into chloroform using a separating funnel. This process allowed for the separation of the organic compounds from the water phase for further analysis. The degradation products were analyzed using a Perkin-Elmer Clarus 680 GC-MS/MS system equipped with an Elite-5MS capillary column (30 m × 250 μm × 0.25 μm). Helium (99.99%) was used as the carrier gas at a flow rate of 1 mL min^{−1}. A 1 μL sample was injected (split ratio 10:1) at an injector temperature of 250 °C. The oven program started at 50 °C (3 min), ramped at 10 °C min^{−1} to 280 °C, and concluded at 300 °C (10 min). Both the sample and the standard were analyzed using electron ionization (EI) in the same mode, with an electron energy of 70 eV over the range 40–600 m/z . To ensure analytical rigor, compound assignments were cross-validated by integrating NIST library match factors (maintaining a minimum match quality of 80%) with the relative peak area (%) and the calculated concentration of each constituent. This multi-parameter approach ensures that the reported identities represent the most chemically significant components within the sample matrix.

2.7. Determination of Zinc Ion (Zn²⁺) Leaching by ICP-MS

The concentration of Zn²⁺ ions in the aqueous solutions of degraded MB, obtained during degradation cycles 1–4 using the CNC/Ag–ZnO composite, was determined using an inductively coupled plasma mass spectrometer (ICP-MS, NexION®, Perkin-Elmer, USA). Prior to analysis, the aqueous solutions were passed through a 0.2 μm filter to remove any suspended solids. The instrument was equipped with an ST-PFA MicroFlow nebulizer, a quartz cyclonic spray chamber, and a one-piece quartz torch with a 2 mm i.d. injector. A nickel sampler cone was used for ion extraction. Sample introduction was carried out at a sample uptake rate of 0.2 mL min^{−1}, and an internal standard with an internal diameter of 0.38 mm was applied to correct for instrumental drift and matrix interferences. The ICP-MS operating conditions were optimized prior to analysis. The RF power was set to 1600 W, with plasma gas flow rate of 15 L min^{−1} and auxiliary gas flow rate of 1.2 L min^{−1}. Oxygen and helium were employed as collision/reaction cell gases to reduce spectral interferences. The air/acetylene flame provided a stable environment for ionizing metal atoms, ensuring precise and reproducible measurements. Calibration curves (Figure S3) were constructed using standard Zn²⁺ solutions (prepared in DI water. The concentration of Zn²⁺ ions in the calibration curve ranges from 0 to 100 ppb (Figure S3). A five-point

calibration ($R^2 = 0.9961$) was established using the concentration of Zn^{2+} ions 0, 10, 20, 50, and 100 ppb, with triplicate analyses ensuring the relative standard deviation (RSD) within 5–8%. Instrument detection limits (DL) and quantification limits (QL) were determined based on signal responses that were three and ten times higher than the background noise, respectively. Analytical accuracy was verified using standard reference materials (SRM), yielding recoveries of 95.97–104.21%. Rigorous quality assurance and control (QA/QC) protocols, including procedural blanks and spike recoveries, were implemented to minimize errors, with Zn^{2+} ion concentrations adjusted based on blank and recovery analysis to maintain data integrity.

3. Results and Discussion

3.1. Characterization of Catalysts

3.1.1. FTIR Spectroscopic Analysis

Fourier Transform Infrared (FTIR) Spectroscopy was employed to identify the specific chemical bonds and functional groups present in CNC, ZnO, Ag/ZnO, and CNC/Ag-ZnO nanocomposites. The resulting spectra, shown in Figure 1, exhibit characteristic absorption peaks corresponding to the molecular vibrations of each material. For pure CNC, a broad peak in the $3300\text{--}3500\text{ cm}^{-1}$ range indicates O-H stretching, revealing that the surface of the cellulose contains hydroxyl groups and adsorbed water molecules. A peak around 2900 cm^{-1} is due to C-H stretching in aliphatic chains. The peak around 1650 cm^{-1} is the antisymmetric bending mode (scissoring), which belongs only to water (two H needs for scissoring) and not to single OH groups. Peaks in the range of $1430\text{--}1315\text{ cm}^{-1}$ are associated with C-H and O-H symmetric bending vibrations. Furthermore, the absorption bands between 1020 and 1170 cm^{-1} are attributed to C-O-C stretching, confirming the polysaccharide structure of CNC [37]. The FTIR spectrum of ZnO nanoparticles shows characteristic Zn-O stretching vibrations at 545 and 1101 cm^{-1} [38]. Peaks at 1383 and 1645 cm^{-1} represent C=O stretching vibrations, while a broad band at 3450 cm^{-1} indicates O-H stretching, possibly due to impurities and adsorbed moisture [39]. In the Ag/ZnO sample, similar ZnO peaks are observed, along with minor shifts in the fingerprint region, suggesting interactions between silver and ZnO nanoparticles. The main feature is the strong peak below 600 cm^{-1} corresponding to the Zn-O bond. The Ag is likely dispersed on the surface of the ZnO because there were no Ag-O or bonded silver peaks found. Moreover, elemental Ag is not possible to detect via IR spectroscopy [40]. The intensities of the Zn-O vibrations were slightly reduced compared to pristine ZnO (545 cm^{-1}), signifying potential interactions between the metal oxides and the hydroxyl groups of CNC [41]. The peaks at 1393 and 1645 cm^{-1} in the composite spectrum are attributed to symmetric and asymmetric stretching of carboxyl groups, which may arise from interactions between CNC and metal oxide species. Overall, the FTIR analysis confirms the incorporation of ZnO and Ag/ZnO within the CNC matrix. The successful synthesis of the CNC/Ag-ZnO composite is further confirmed by the simultaneous presence of characteristic peaks for both CNCs and ZnO, with subtle changes in peak positions and shapes indicating strong interactions between the CNC functional groups and the metal oxide components.

3.1.2. XPS Analysis

The successful formation of the CNC/Ag-ZnO composite was further verified by the elemental composition analysis of CNC, Ag-ZnO, and CNC/Ag-ZnO via XPS. Figure 2 shows the typical XPS scanning spectrum for CNC, Ag-ZnO, and CNC/Ag-ZnO composites. As shown in Figure 3, the XPS spectrum of CNC shows only C1s (Figure 3A) and O1s (Figure 3B) peaks. Four distinct peaks observed at 287.7 , 286.3 , 284.6 , and 284.4 eV in the high-resolution C1s spectra, obtained through deconvolution, correspond to the

chemical bonds C=O, C–O–C, C–O, and C–C/C–H, respectively [42]. Based on the deconvolution of the O1s peak (Figure 3B), two distinct components were identified: one at 533.3 eV, attributed to C–O–H/C–O–C bonds, and another at 532.7 eV, corresponding to C=O bonds [43,44].

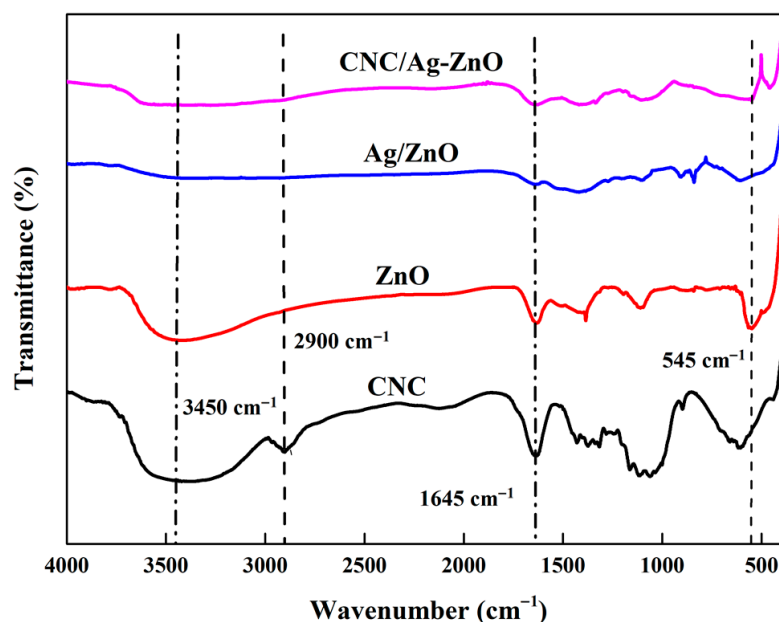


Figure 1. FTIR spectra of CNC, ZnO, Ag/ZnO, and CNC/Ag-ZnO nanocomposites.

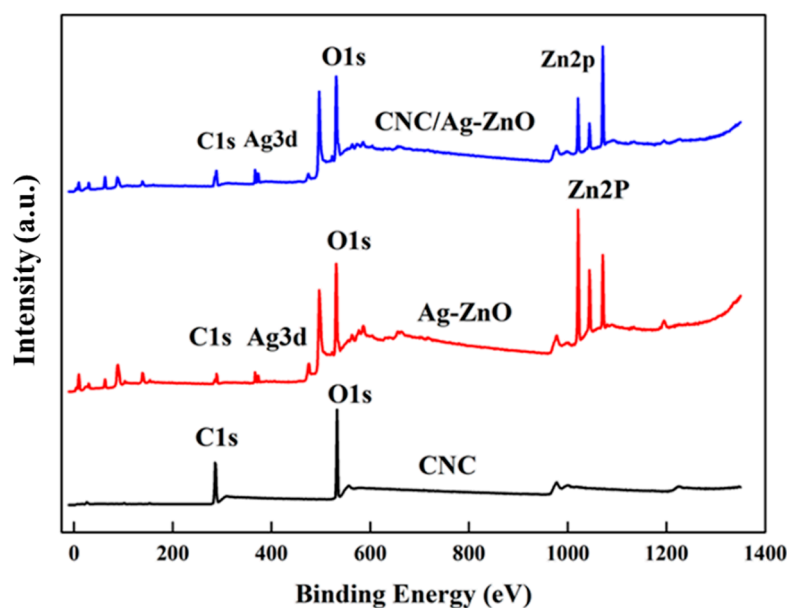


Figure 2. X-ray photoelectron survey spectra for CNC, Ag-ZnO, and CNC/Ag-ZnO composites.

Figure 3C,D displays the wide-range XPS spectra for Ag-ZnO nanoparticles. Specifically, Figure 3C shows a peak corresponding to Ag 3d, confirming the presence of silver on the nanoparticles' surfaces. Furthermore, the high-resolution Zn 2p spectra in Figure 3D exhibit two prominent peaks at 1044.3 and 1021.3 eV, which are assigned to the Zn ($2p_{1/2}$) and Zn ($2p_{3/2}$) core levels, respectively.

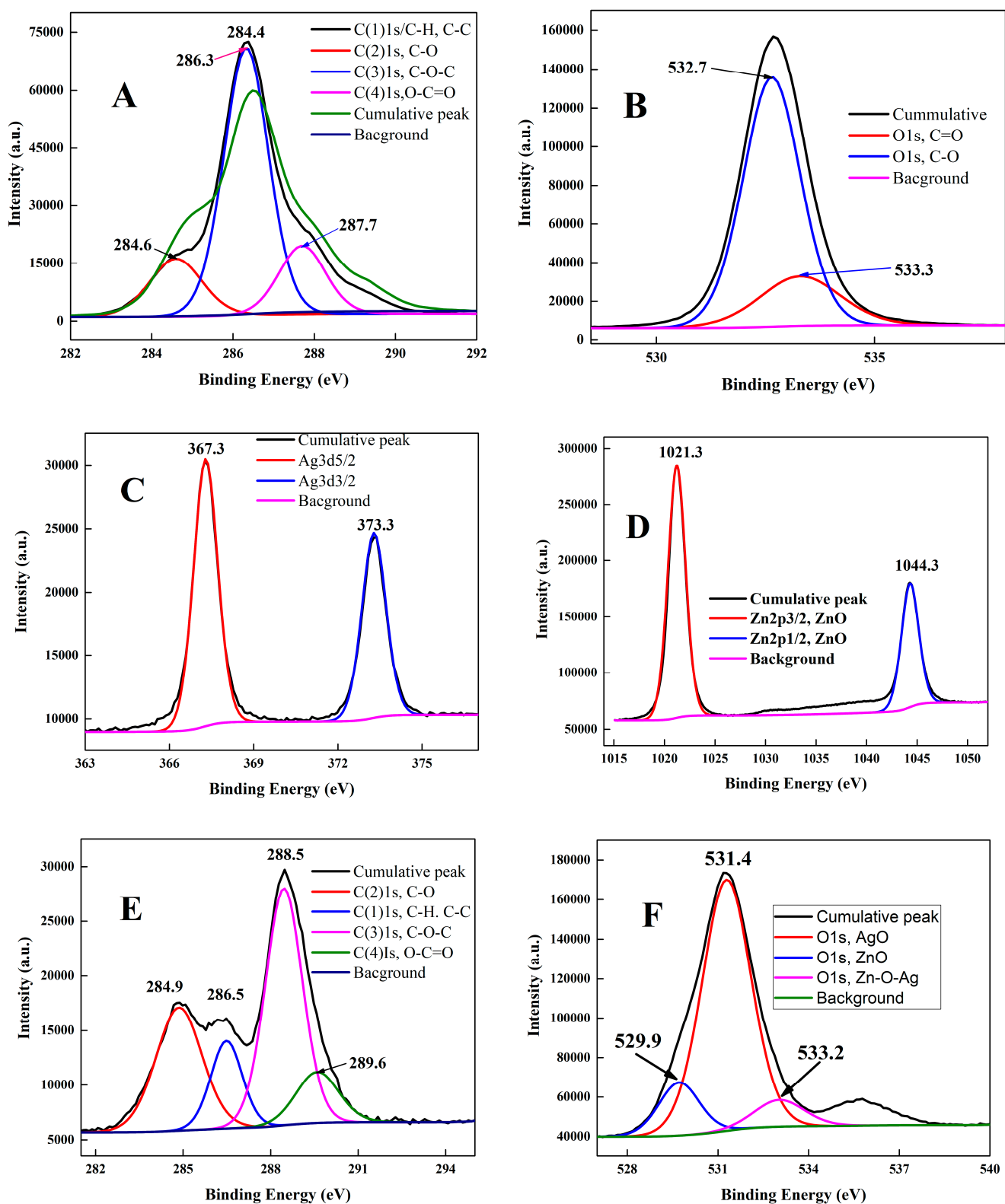


Figure 3. X-ray photoelectron core-loss spectra of (A) C1s for CNC, (B) O1s for CNC, (C) Ag 3d in Ag-ZnO, (D) Zn 2p in ZnO, (E) C1s for the CNC/Ag-ZnO composite, and (F) O1s for the composite of CNC/Ag-ZnO.

The difference of 23.0 eV between the two Zn 2p binding energies (1044.3 and 1021.3 eV) indicates that the zinc in the nanoparticles is in a +2 oxidation state [45,46]. Additionally, Figure 3C presents the high-resolution Ag 3d spectrum, which shows two dis-

tinct peaks at 367.3 (Ag 3d_{5/2}) and 373.3 eV (Ag 3d_{3/2}). The 6.0 eV splitting between these two peaks confirms the metallic nature of silver within the Ag-ZnO nanoparticles [46,47].

In the C1s spectrum (Figure 3E), in contrast to pure CNC, the CNC/Ag-ZnO shows a slight shift in the C–C peak to 284.9 eV and an intensified C=O peak at 288.5 eV, along with the emergence of an O–C=O peak at 289.6 eV, indicating increased oxidation and surface functionalization [48]. The O1s spectrum (Figure 3F) further confirms these changes, with pure CNC showing peaks at 532.7 (C=O) and 533.3 eV (C–O), while CNC/Ag-ZnO introduces a new 529.9 eV peak (ZnO lattice oxygen, O^{2−}) and an intensified and shifted peak at 531.4 eV (C=O), signifying stronger oxidation effects. The presence of ZnO in nanocomposites has been consistently identified through XPS, confirming Zn-related oxygen peaks that indicate successful material incorporation [49].

3.1.3. Optical Properties of Prepared Nanocomposites

Figure 4 presents the UV-Vis absorption spectra for pure ZnO, Ag-ZnO, and CNC/Ag-ZnO nanocomposites. The pure ZnO nanostructure shows an absorption edge at roughly 390 nm, which correlates to a band gap energy of 3.18 eV. The observed band gap of our synthesized ZnO, 3.18 eV, is slightly lower than the bulk literature value, 3.37 eV. This is primarily due to structural defects, specifically oxygen vacancies and zinc interstitials, which introduce sub-bandgap energy levels (Urbach tails) near the conduction band. Additionally, lattice strain induced during low-temperature chemical synthesis can narrow the energy gap relative to the bulk crystalline ZnO. For the Ag-ZnO nanostructures, the absorption edge is observed around 393 nm, indicating a slightly smaller band gap of 3.15 eV. CNC/Ag-ZnO nanocomposites show similar absorption spectra to Ag-ZnO catalyst. The absorption edge is observed around 380 nm, indicating a smaller band gap of 3.02 eV. The bandgap reduction in Ag-doped ZnO is a combination of two key mechanisms: creation of defect states within the ZnO bandgap and plasmonic effects from metallic silver nanoparticles [40,50,51]. The defect states from substitutional Ag directly narrow the electronic bandgap. The substitution of Zn²⁺ ions with Ag atoms creates new energy levels, or defect states, within the original ZnO bandgap. These states form an intermediate band that serves as a stepping stone for electron excitation from the valence band, enabling the absorption of lower-energy photons. This directly narrows the electronic bandgap [50,51]. The LSPR effect from metallic Ag nanoparticles provides an additional pathway for UV-A light absorption, making the material effective for UV-A light-driven photocatalysis and optoelectronics [40,51]. The band gap values summarized in Table 2 were determined from Tauc plots. Notably, the absorbance spectrum of the Ag-ZnO nanostructures also exhibits a characteristic surface plasmon resonance (SPR) peak around 440 nm. This peak confirms the presence of Ag (0) nanoparticles on the surface of the ZnO. Prior research suggests that Ag nanoparticles in the size range of 10–50 nm, when incorporated into ZnO nanostructures, can significantly enhance photocatalytic activity under direct light due to intense photon scattering [37–39,52–54].

The SPR band in the Ag-ZnO nanostructures appears slightly broader and shifted towards longer wavelengths (red shift) compared to pure Ag. This shift could be attributed to strong electronic interactions at the interface between the neighboring ZnO and Ag nanoparticles [40,41,55,56]. The position of the SPR band of CNC/Ag-ZnO nanocomposite is almost unchanged from the spectrum of Ag-ZnO, which is at 440 nm. This indicates that the silver nanoparticles are successfully incorporated into the CNC/ZnO matrix and are the dominant contributor to the absorption in the UV-A range. The SPR band of the CNC/Ag-ZnO nanocomposite remained virtually unchanged compared to that of the Ag-ZnO precursor, appearing at 440 nm. This consistency indicates that the silver nanoparticles were successfully incorporated into the CNC/ZnO matrix and remain the primary contributors

to the absorption in the UV-A spectrum. Another band at <200 nm is observed in the CNC/Ag-ZnO composite, corresponding to the electronic absorption of CNCs. Overall, the spectra confirm the successful formation of a plasmonic composite material.

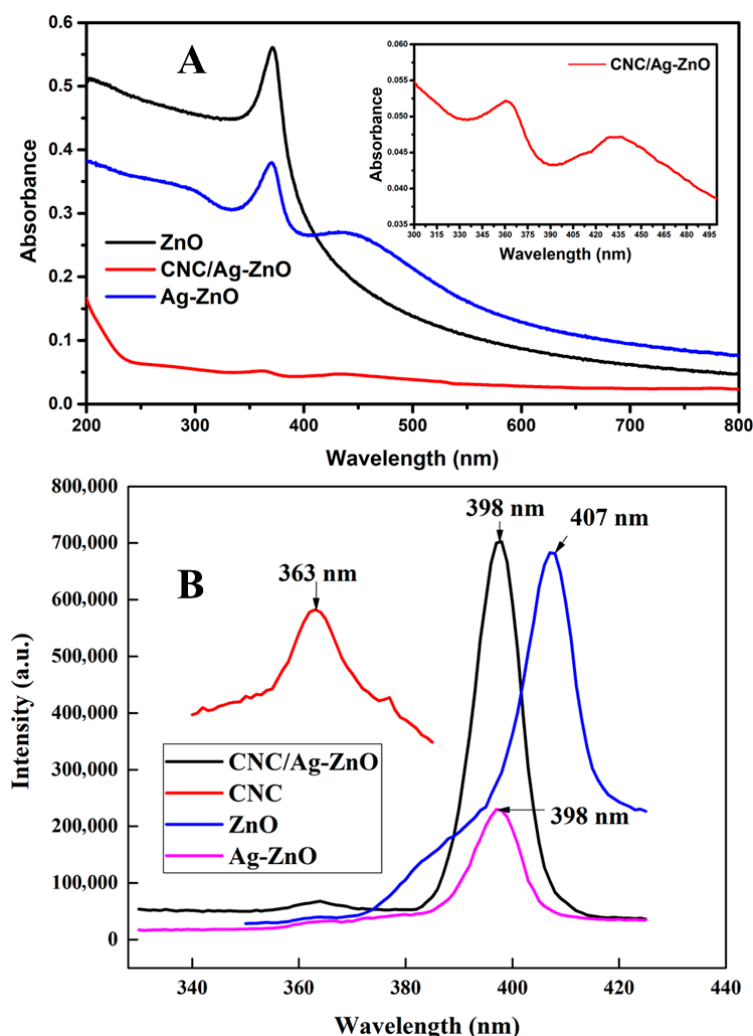


Figure 4. (A) UV-visible absorption spectra of ZnO, Ag-ZnO, and CNC/Ag-ZnO (inset figure shows magnified spectra of CNC/Ag-ZnO). (B) The photoluminescence (PL) spectra of CNC, ZnO, Ag-ZnO, and CNC/Ag-ZnO composites.

Table 2. Band gap values of the prepared photocatalysts.

Photocatalyst	$\lambda_{\max}$ of Photocatalyst (nm)	Band Gap (eV)
ZnO	370	3.18
Ag-ZnO	370, 442	3.15
CNC/Ag-ZnO	365, 435	3.02

3.1.4. Photoluminescence (PL) Analysis of CNC/Ag-ZnO Nanocomposite

Photocatalytic efficiency is fundamentally governed by the separation and recombination dynamics of photogenerated electron–hole (e^-/h^+) pairs [57,58]. High PL intensity signifies the rapid radiative recombination of photogenerated (e^-/h^+) pairs. This process reduces the steady-state concentration of available charge carriers, thereby limiting the generation of reactive oxygen species (ROS) and consequently suppressing the photocatalytic degradation efficiency [35,59]. Essentially, a stronger PL signal indicates that the energy is being dissipated as light rather than being utilized to drive the chemical

mineralization of organic pollutants [60]. As illustrated in Figure 4B, the PL spectrum of pure ZnO exhibits a characteristic emission peak at 407 nm, typically attributed to near-band-edge (NBE) transitions and shallow donor levels of oxygen vacancies. Upon the formation of the Ag–ZnO binary and CNC/Ag–ZnO ternary nanohybrids, this peak undergoes a distinct hypsochromic (blue) shift to 398 nm. This shift is driven by the Burstein–Moss effect, wherein Ag incorporation increases the free carrier concentration and shifts the Fermi level into the conduction band, alongside the strong electronic coupling between ZnO excitons and the SPR of the Ag nanoparticles [35,59]. The Ag–ZnO composite exhibits a significantly lower PL intensity than pure ZnO, following the Stern–Volmer quenching phenomenon. This confirms that Ag incorporation effectively quenches ZnO fluorescence, thereby extending the lifespan of photogenerated charge carriers by suppressing radiative recombination [61]. In this study, the CNC/Ag–ZnO nanocomposite shows enhanced performance compared to the binary Ag–ZnO composite. This is because the CNCs act as a stabilizing template, increasing the surface area of active sites and improving dye adsorption via electrostatic interactions. Furthermore, the CNCs facilitate superior charge separation, which, combined with the electron-trapping capacity of Ag, significantly increases the production of ROS (OH and O_2^-) for more efficient mineralization of the dye [35,59].

3.1.5. Thermogravimetric Analysis of the Nanocomposites

Figure 5A,B displays the thermograms of the prepared photocatalysts. Thermogravimetric analysis (TGA) revealed an initial weight loss for ZnO nanorods (NRs) up to 200 °C, attributed to the evaporation of adsorbed moisture, chemisorbed/weakly bound water, and the decomposition of any volatile organic impurities. Similarly, the TGA curve for the Ag–ZnO nanocomposite showed an initial weight loss in the same temperature range (up to 200 °C), attributed to the loss of surface-bound moisture. The thermogram of CNC shows a single change at 251 °C, which corresponds to the decomposition of the cellulose backbone. In the case of CNC/Ag–ZnO, the thermogram shows three prominent changes at 94, 222, and 683 °C. The first change is due to the release of the moisture from the nanocomposites. The second change corresponds to the decomposition of the cellulose backbone, and the last big change is attributed to the melting point of the Ag–ZnO nanoparticles. This region is also found in the thermogram of Ag–ZnO at a higher temperature, at around 739 °C. Incorporation of Ag–ZnO over CNC has reduced the thermal stability of the photocatalyst nanoparticles. The lower thermal stability of CNC/Ag–ZnO is due to the presence of CNC. The CNC component, an organic material (cellulose), is typically less thermally stable than the inorganic Ag–ZnO component, thereby reducing the composite's high-temperature stability. Figure 5B displays the derivative thermogravimetry (DTG) curves for the CNC, ZnO NR, Ag–ZnO, and CNC/Ag–ZnO composite photocatalysts. The CNC/Ag–ZnO composite exhibits endothermic peaks at 56, 134, 265, and 748 °C, indicating that the degradation follows an energetically favorable pattern.

3.1.6. X-Ray Diffraction (XRD) Analysis

Figure 5C displays the X-ray diffraction (XRD) patterns of the synthesized Ag–ZnO nanocomposite, revealing the presence of both cubic phase silver (Ag), as identified by ICDD card no. 00-004-0783, and hexagonal phase zinc oxide (ZnO). In contrast, Figure 5C also shows XRD patterns that can be indexed solely to the hexagonal phase of ZnO, matching ICDD card no. 00-036-1451. The absence of any other peaks related to crystalline phases containing silver or zinc confirms the successful formation of the Ag–ZnO nanocomposite using the solvothermal method. This formation likely occurred via the direct reduction of Ag^+ ions to metallic Ag, with ethanol serving as a mild reducing agent [42,62]. It is

important to note that any amorphous compounds containing silver or zinc would not be detectable in these XRD patterns (Figure 5C). There is indeed some overlap between the ZnO and Ag diffraction patterns; the characteristic Ag (111) peak at 38.2° is clearly distinguishable from the ZnO phases, confirming the presence of metallic silver. To further validate this, we utilized UV–Vis spectroscopy, which revealed a distinct surface plasmon resonance (SPR) band between 400 and 450 nm (Figure 4A). This optical signature is unique to Ag nanoparticles and is entirely absent in the pure ZnO spectrum, providing conclusive evidence of the composite's formation. The XRD pattern of CNC exhibits characteristic diffraction peaks of cellulose I β at 2θ values of 15.1° , 16.5° , 22.6° , and 34.6° , corresponding to the (1–10), (110), (200), and (004) crystallographic planes, respectively.

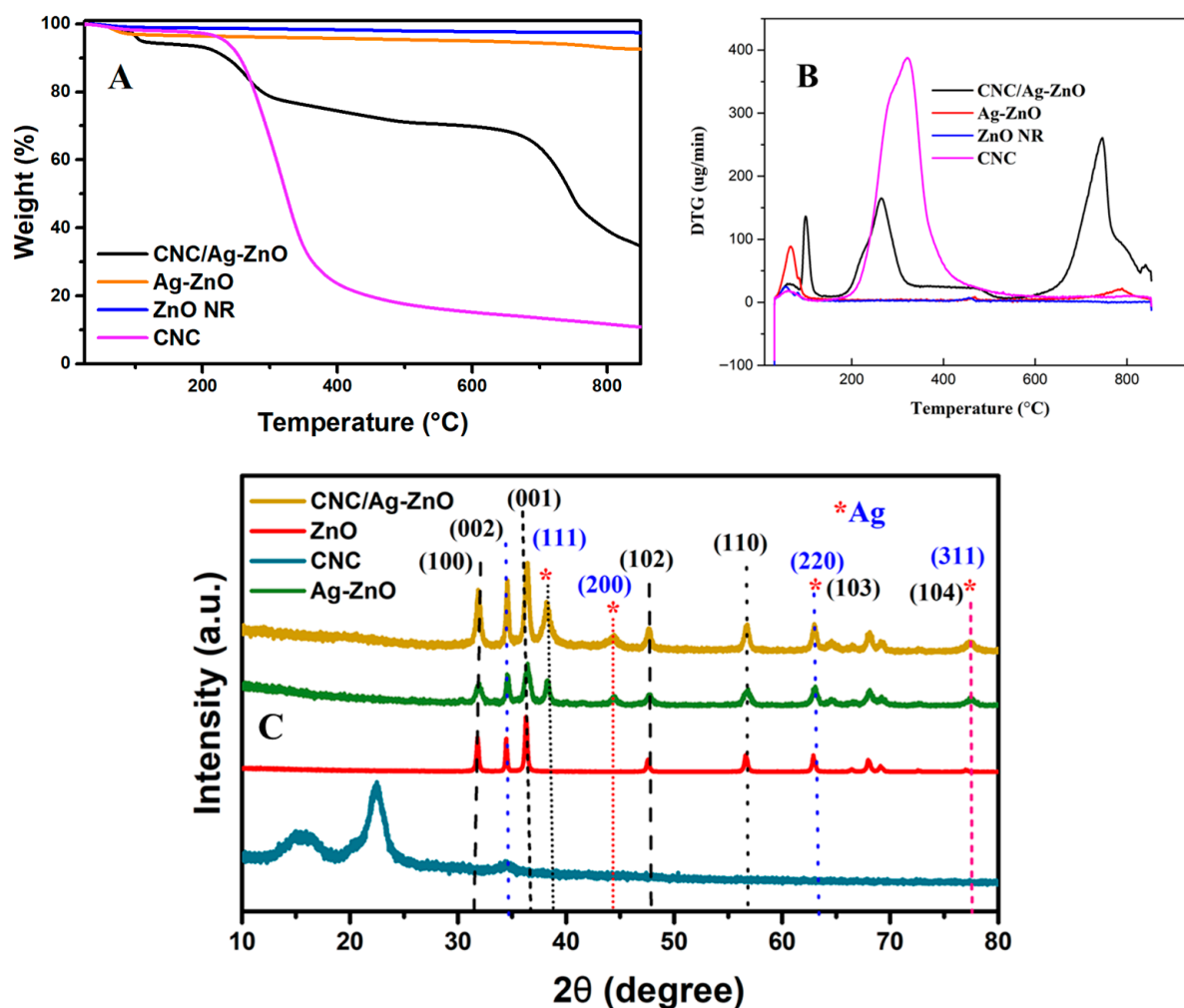


Figure 5. (A) TGA thermograms of ZnO, Ag-ZnO, CNC, and CNC/Ag-ZnO nanocomposites; (B) DTG thermograms of ZnO, Ag-ZnO, CNC, and CNC/Ag-ZnO nanocomposites; and (C) XRD patterns of ZnO, CNC, Ag-ZnO, and CNC/Ag-ZnO nanocomposites.

3.1.7. TEM Analysis

The transmission electron microscopy (TEM) image of nanocellulose (Figure 6A,B) presents a high-resolution view of its morphological features. The image displays an evenly distributed network of nanocellulose fibrils, characterized by their elongated rod-like structures. The contrast variations in the micrograph suggest a well-defined structure with a relatively uniform size distribution. The observed fibrillar network, with nanometer-scale diameters, is indicative of the CNCs' nanoscale dimensions. These findings align with previous studies, where rod-like CNCs with diameters ranging from 4 to 15 nm and lengths

between 0.2 and 1 μm were reported [63]. Additionally, dark regions in the image may correspond to agglomerated or overlapping CNC structures, potentially resulting from drying during sample preparation. The overall homogeneity of the dispersion suggests effective synthesis and processing [6]. The histogram derived from the TEM image of CNC (Figure 6C) illustrates the diameter distribution of CNC strands. The histogram reveals that the CNC strands exhibit a size distribution predominantly between 10 nm and 60 nm, with the highest frequency observed around 30–40 nm. This distribution closely aligns with previous studies where CNCs extracted via sulfuric acid hydrolysis demonstrated diameters typically in the range of 4–60 nm [64]. The presence of CNC strands with diameters extending up to ~ 100 nm suggests some degree of agglomeration or bundling, a phenomenon commonly reported in TEM analyses of CNC due to strong hydrogen bonding interactions among cellulose chains [65]. The TEM analysis of the CNC-Ag/ZnO composite (Figure 6B,D) reveals a distinct distribution of Ag/ZnO nanoparticles within the cellulose nanocrystal matrix. The image shows well-defined, spherical-to-slightly elongated Ag/ZnO nanoparticles dispersed throughout the CNC matrix. The darker regions, corresponding to Ag/ZnO nanoparticles, demonstrate varying levels of aggregation, which may be attributed to particle–particle interactions.

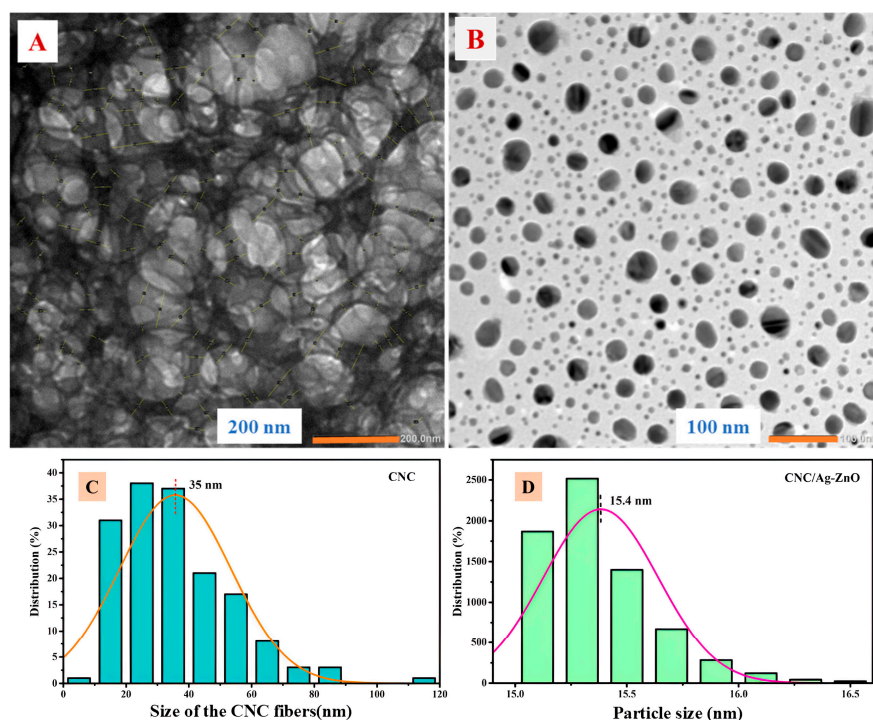


Figure 6. TEM image of (A) CNC and (B) CNC/Ag-ZnO; histogram of (C) CNC and (D) CNC/Ag-ZnO.

A similar morphology was observed in ZnO/CNC composites, where ZnO nanoparticles appeared well-distributed within the cellulose matrix, forming spherical and rod-like structures [38]. The relatively even dispersion of Ag/ZnO within the CNC matrix suggests a strong interfacial interaction between the nanoparticles and cellulose nanocrystals, which is crucial for enhancing the functional properties of the composite [66]. The TEM micrograph of the CNC-Ag/ZnO composite (Figure 6B) reveals a heterostructure containing two distinct populations of nanoparticles. The larger particles are attributed to the ZnO as rod-like structures, while the smaller, more electron-dense particles distributed across the CNC/ZnO surface are characteristic of Ag nanoparticles. The histogram derived from these images (Figure 6D) shows a primary particle size distribution of 15.0–16.5 nm, with a peak at approximately 15.35 nm. While the average size aligns with expected

dimensions for Ag/ZnO nanostructures [67], the visual evidence suggests a controlled distribution of Ag clusters integrated with the ZnO matrix. Although specific EDX mapping of individual particles was not conducted to definitively separate the two species, the Gaussian fit confirms a narrow overall distribution, suggesting a synergistic growth process during synthesis.

3.2. Photocatalytic Studies of the Nanocomposites

3.2.1. Effect of pH

Figure 7A depicts the effects of pH on the photodegradation of MB by CNC/Ag-ZnO. CNC/Ag-ZnO shows excellent photocatalytic activity in the pH ranges of 5 to 12. Below pH 5, the catalyst shows the worst photocatalytic performance compared to the higher pH conditions. This subpar performance is due to the blockage of active sites on the catalyst surface by H^+ ions.

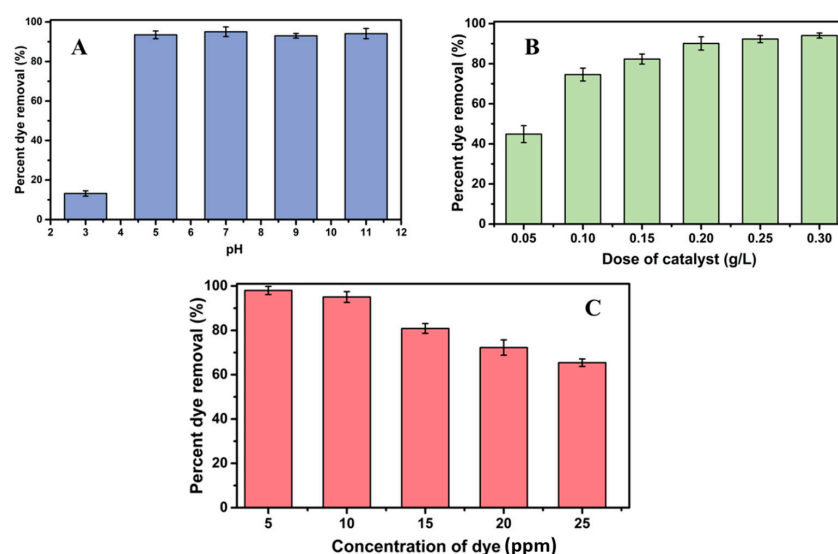


Figure 7. Photocatalytic degradation of MB by CNC/Ag-ZnO nanocomposite (A) Effect of pH (dose of catalyst: 0.3 g L^{-1} and concentration of MB: 10 ppm). (B) Effect of the dose of catalyst (pH of the solution: 7 and concentration of MB: 10 ppm). (C) Effect of concentration of MB (pH of the solution: 7 and dose of catalyst: 0.3 g L^{-1}).

Consequently, the MB molecules are repelled by electrostatic interactions with the catalyst surface. Moreover, the generation of $OH^\bullet$ is slow, leading to poor photocatalytic performance. The photocatalytic activity of the catalyst is positively influenced by the availability and rate of generation of $OH^\bullet$. Under alkaline pH conditions, the opposite phenomenon occurs, with more negative charges accumulating on the catalyst, leading to better adsorption of MB and higher generation of $OH^\bullet$ due to the greater availability of OH^- ions.

3.2.2. Effect of the Dose of the Catalyst

The catalyst dose significantly influences its photocatalytic performance. Figure 7B shows the effect of catalyst dose on the photocatalytic activity of CNC/Ag-ZnO. A higher catalyst dose significantly increases the photodegradation rate by providing more active surface sites. Increased photoactive sites on the catalyst surface lead to a higher population of $OH^\bullet$ under UV irradiation. In addition, more adsorption sites are also available for secondary removal of MB from the solution.

3.2.3. Effect of Initial Concentration of MB Dye

The photocatalytic performance of CNC/Ag-ZnO was evaluated by increasing the concentration of the MB solution. Figure 7C displays the effect of the concentration of MB on the photocatalytic activity of the CNC/Ag-ZnO nanocomposite. The MB concentration was varied from 5 ppm to 25 ppm, and the results showed excellent photocatalytic activity up to 15 ppm. Removal of MB at concentrations above 15 ppm was more difficult and time-consuming. Ineffective light irradiation over the catalyst surface is the reason behind its decreased performance. At higher concentrations, light is scattered by the dye solution, preventing it from reaching the catalyst surface and slowing the generation of $\text{OH}^\bullet$. However, CNC/Ag-ZnO still performs well at a high MB concentration due to CNC's superior adsorption capacity. A substantial amount of dye is adsorbed by the CNC component, enabling effective irradiation and resulting in good performance.

3.2.4. Pseudo-First-Order Kinetic Studies of the Prepared Catalysts

By monitoring the decrease in absorbance intensity over the course of the irradiation period, the progress of dye decolorization (photodegradation) was monitored. Organic dyes usually degrade photocatalytically according to pseudo-first-order kinetics, in which reaction time (t) and $\ln(C_t/C_0)$ have a linear relationship. The Langmuir–Hinshelwood kinetic model provides a good description of the reaction since it occurs on the photocatalyst's surface [68]. The associated normalized concentration (C_t/C_0) is directly proportional to the dye's absorbance normalized to its initial maximum absorbance (A_t/A_0) at any given irradiation duration. The initial concentration of the MB solution was denoted as C_0 , and the concentration at any given time was denoted as C_t , determined by measuring the absorbance of the MB solution using a UV-spectrophotometer. C_0 and C_t corresponded to the absorbance values A_0 and A_t , respectively. The photocatalytic degradation curves of the prepared photocatalysts of ZnO, Ag-ZnO, CNCs, and CNC/Ag-ZnO composites are depicted in Figure 8. The degradation activity of the prepared photocatalysts is presented in Table 3 and in Figure 8A. The degradation of MB by CNCs, ZnO, Ag-ZnO, CNC/Ag-ZnO (0.25 g L^{-1}), and CNC/Ag-ZnO (0.30 g L^{-1}) is 76, 64.4, 69, 95, and 96.2%, respectively, in 120 min. Zinc oxide (ZnO) is a well-known semiconductor photocatalyst because its electrons move readily, it has a wide band gap (3.37 eV), and it can strongly oxidize substances upon exposure to UV-C light. However, the effectiveness of ZnO as a photocatalyst is often hindered by the quick recombination of the electrons and holes generated by light, and its poor absorption of UV-A light [69]. Combining silver (Ag) with ZnO to form Ag-ZnO composites enhances photocatalytic activity compared to ZnO alone. When Ag nanoparticles are deposited on ZnO, a Schottky barrier forms at their interface. This barrier helps to separate the light-generated charges more effectively. Additionally, the surface plasmon resonance (SPR) effect of Ag allows the composite to absorb more light in the UV-A range, further enhancing its performance [70–74]. This results in significantly improved MB degradation rates. The ternary composite of CNC/Ag-ZnO showed the best photocatalytic activity. CNCs offer a high surface area, excellent dispersion medium, and abundant hydroxyl groups that enhance the anchoring of Ag-ZnO nanoparticles. This network structure minimizes particle agglomeration, improves light harvesting, and facilitates better dye adsorption, leading to higher photocatalytic degradation efficiencies under sunlight or UV-A light [27,46].

This feature was enabled by the presence of CNC, which substantially removed MB via superior adsorption. Consequently, Ag-ZnO in the nanocomposites was much more efficient at photocatalytically removing MB due to its lower concentration. Moreover, even lower doses of the nanocomposite removed MB more effectively over a longer period of photodegradation. Figure 8B represents the kinetic study of the photodegradation of MB

under UV irradiation. In this experiment, 10 ppm of MB dye solution and 0.3 g L^{-1} of CNC, ZnO, Ag-ZnO, and CNC/Ag-ZnO were used. Another investigation using 0.25 g L^{-1} of CNC/Ag-ZnO was conducted to understand the photocatalyst's activity. The experiment lasted 2 h. It can be observed that each catalyst degrades the MB's capability under UV irradiation. It was found that 95 and 96.2% of MB dye can be removed by 0.25 and 0.30 g L^{-1} of CNC/Ag-ZnO, respectively, in 2 h under UV-A light.

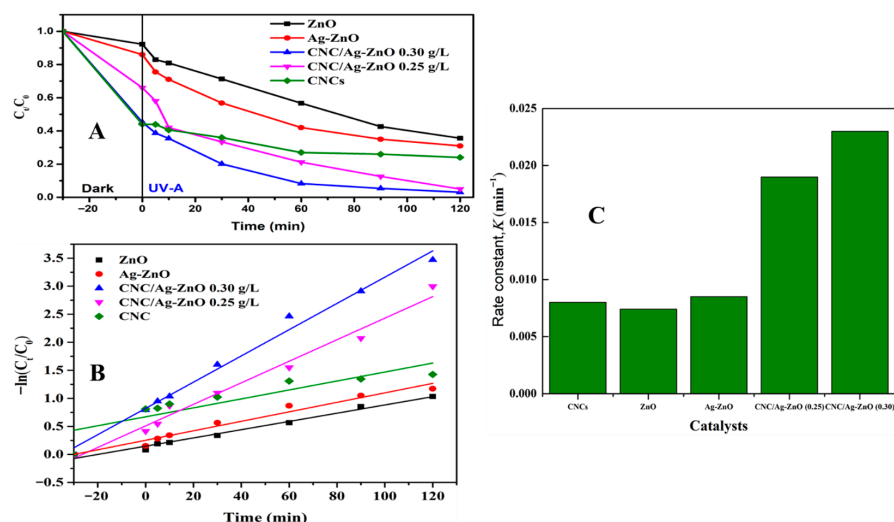


Figure 8. Photocatalytic degradation curves of photocatalysts using MB as the model dye: (A) concentration profile of MB with the irradiation time, (B) linear fittings of reaction kinetics data, and (C) the rate constant values of the prepared catalysts (pH of the solution: 7, dose of catalyst: 0.3 g L^{-1} , and initial concentration of MB: 10 ppm).

Table 3. Calculated photodegradation parameters of the prepared photocatalysts. (solution pH: 7; dye concentration: 10 ppm; reaction time: 120 min).

Photocatalysts	Degradation (%)	R ² Values	Rate Constant (min ⁻¹)
CNCs (0.3 g L^{-1})	76	0.74325	0.00798
ZnO (0.3 g L^{-1})	64.4	0.98434	0.00735
Ag-ZnO (0.3 g L^{-1})	69	0.9679	0.00846
CNC/Ag-ZnO (0.25 g L^{-1})	95	0.97956	0.01921
CNC/Ag-ZnO (0.30 g L^{-1})	96.2	0.98759	0.02341

A plot of $-\ln(C_t/C_0)$ versus irradiation time was linearly fitted (Figure 8B), and the slope corresponded to the rate constant (k) of the prepared photocatalysts. The calculated k values were 0.00798, 0.00735, 0.00846, 0.01921, and 0.02341 min^{-1} for CNC, ZnO, Ag-ZnO, CNC/Ag-ZnO (0.25 g L^{-1}), and CNC/Ag-ZnO (0.3 g L^{-1}), respectively (Figure 8C).

Understanding the correlation between the rate constant and photodegradation activity is essential. CNC/Ag-ZnO (0.3 g L^{-1}), which exhibited the highest k value of 0.02341 min^{-1} , achieved a maximum MB dye degradation of 96.2% (Figure 9A). In comparison to CNC, ZnO, and Ag-ZnO, the ternary composite CNC/Ag-ZnO (0.3 g L^{-1}) showed 20.2, 31.8, and 27.2% higher degradation efficiencies, indicating its superior performance. As shown in Figure 9B, the ternary CNC/Ag-ZnO composite exhibits 4% greater degradation activity compared to the physical mixture of CNC and the Ag-ZnO binary composite. The reduction of such photocatalytic efficiency of the mixture of CNC and Ag-ZnO might be due to the absence of any physical or chemical interaction that holds together CNC and Ag-ZnO. CNC might act as an effective dispersion medium for the Ag-ZnO catalyst in the physical mixture, thereby preventing aggregation. The surface charge, quantified by the zeta potential, of the CNC/Ag-ZnO composite plays a crucial role in the photodegradation of the cationic dye, MB, as shown in Figure 9D,E. The maximum MB degradation was

found at pH 7. This enhancement is due to the strong electrostatic attraction between the highly negatively charged catalyst surface and the positively charged MB molecules. This powerful attraction significantly enhances the adsorption of MB onto the composite surface, thereby increasing the local concentration of the dye, facilitating more efficient contact with the photogenerated reactive species ($\cdot\text{OH}$ and $\text{O}_2\cdot^-$) and maximizing overall photodegradation activity.

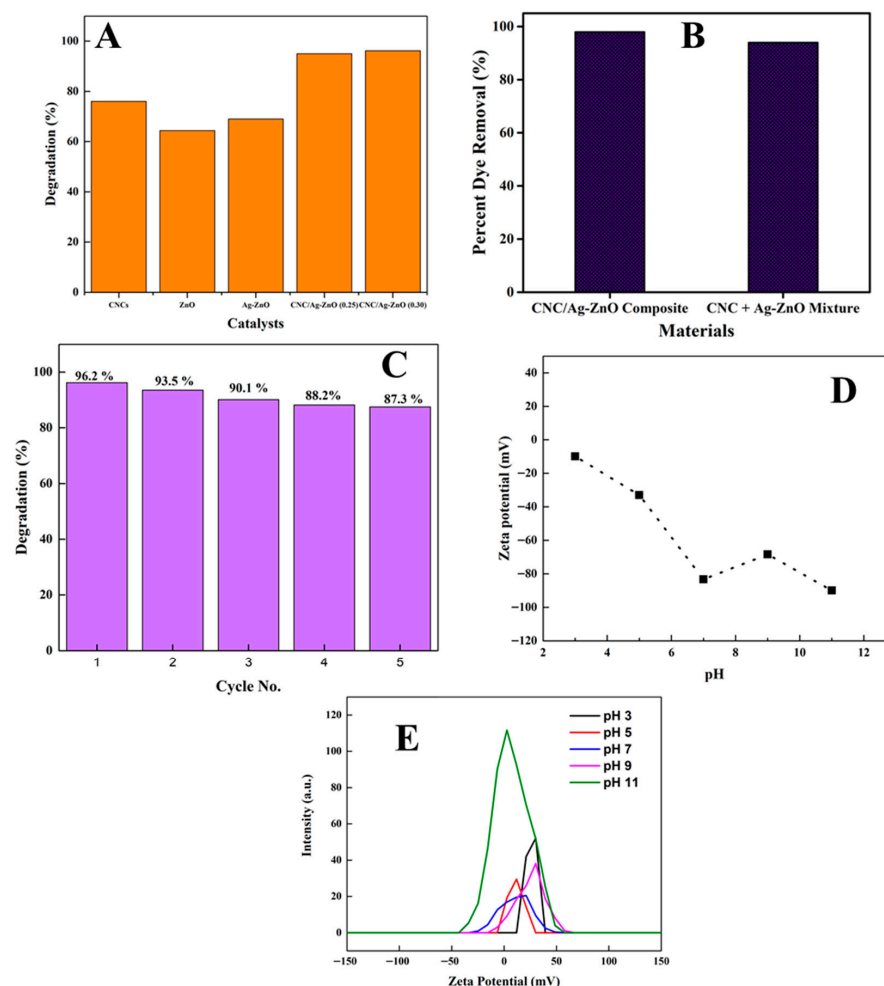


Figure 9. (A) Photodegradation (%) of MB under UV irradiation for 120 min using different catalysts. (B) Comparison of the degradation of MB between CNC/Ag-ZnO composite and their physical mixture of CNC and the binary composite Ag-ZnO. (C) Reusability of the prepared ternary CNC/Ag-ZnO (pH of the solution: 7, dose of catalyst: 0.3 g L⁻¹, and initial concentration of MB: 10 ppm). (D) The variation in zeta potential of the composite CNC/Ag-ZnO with pH. (E) The charge distribution of the CNC/Ag-ZnO composite at various pH values.

3.2.5. Reusability and Stability of the CNC/Ag-ZnO Composites

Reusability and stability are critical considerations in determining the practical application of a photocatalyst. To evaluate these qualities, the spent photocatalyst was collected after each photodegradation cycle, washed with water and methanol, and then dried under vacuum at 90 °C for 24 h. The regenerated photocatalyst was then used in new photodegradation tests with identical, ideal conditions. Figure 9C demonstrates that the photodegradation activity was 96.2% in the first cycle but only dropped to 87.3% after five successive cycles. This small drop-in activity strongly suggests that the photocatalyst is reusable.

3.2.6. GC-MS/MS Identification of Degradation Intermediates and Toxicity Evolution

MB dye photo-catalytically degraded through a complex sequence of oxidative and reductive processes that turn the tricyclic chromophore (m/z 319) into multiple different classes of intermediates. In order to create intermediates like Azure A, B, and C (Figure 10A), methyl groups are gradually removed from the auxochrome groups during stepwise N-demethylation, which usually starts the process [73,74]. The widespread fragmentation of the dye is confirmed by the chromatogram (Supplementary Materials), which has a crucial base peak at 12.968 min that indicates the rupture of the central N-S heterocyclic link, destroying the dye's chromophore.

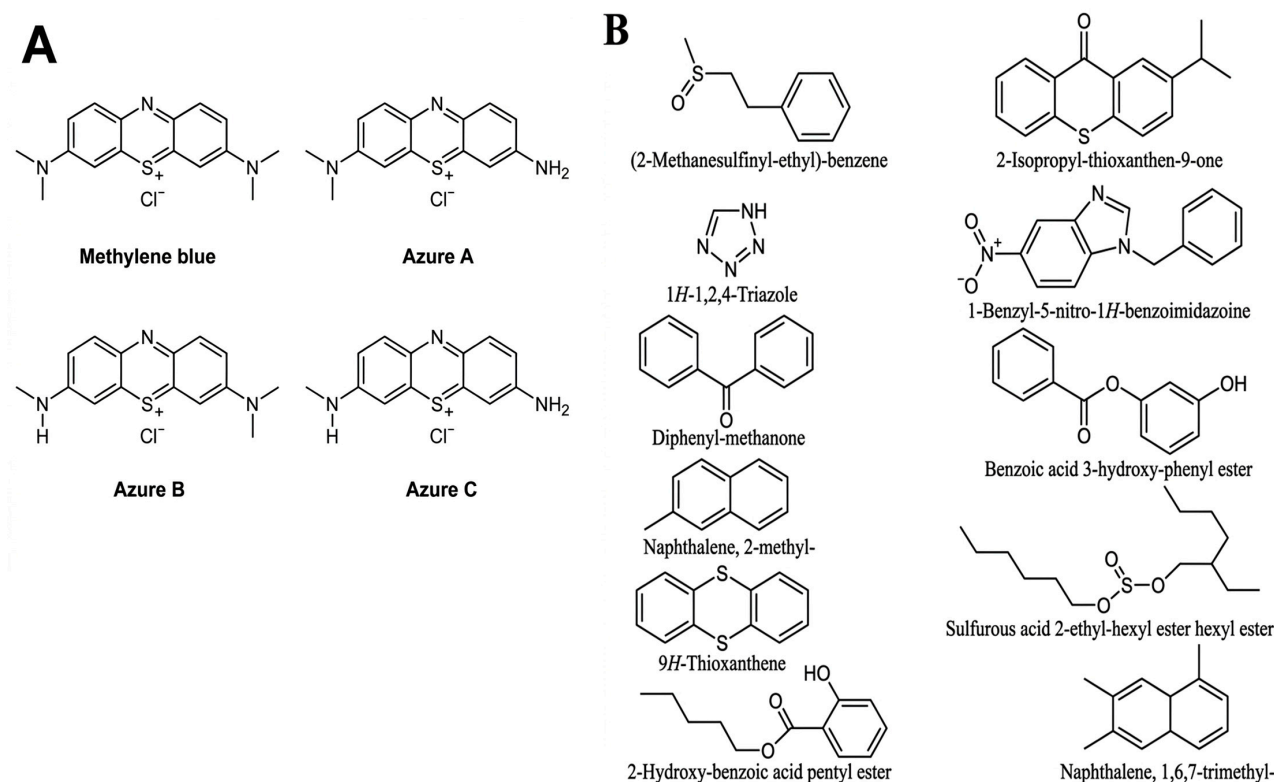


Figure 10. (A) Structure of MB dye and common degraded products from the literature. (B) Identification of new degradation intermediates of MB dye via GC–MS/MS.

The tentative identification (NIST library matching: 68.2–93.7%) of several new decomposition products (Figure 10B and Supplementary Materials) by GC-MS/MS, which reveal previously undiscovered steps in the mineralization pathway, is a significant novelty of this study. A distinct sulfur mineralization pathway is revealed by the detection of sulfoxide (RT 9.01 min) and sulfurous acid, 2-ethylhexyl hexyl ester (RT 13.80 min). These intermediates offer structural evidence of an asymmetric cleavage mechanism in which, prior to its ultimate transformation into inorganic sulfate (SO_4^{2-}), the sulfur atom is bound to aromatic or aliphatic fragments during oxidation [73]. The conversion of the phenothiazine core into thioxanthene (RT 11.55 min) and 9H-Thioxanthene-9-one, 2-isopropyl- (RT 16.34 min) further demonstrates selective denitrogenation and suggests a complex skeletal rearrangement that stabilizes the sulfur-carbon bridge before final mineralization. Additionally, 1H-1,2,4-Triazole (RT 7.14 min) and 1-Benzyl-5-nitro-1H-benzoimidazole (RT 3.19 min) have been identified as new molecular markers for nitrogen stabilization. Instead of immediately mineralizing into NO_3^- or NH_4^+ , these fused-ring and cyclic imide structures indicate that nitrogenous fragments go through oxidative cyclization and ring-contraction. The systematic collapse of the dye into simple organic acids is confirmed

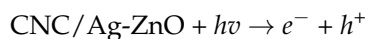
by the transition from stable C₁₃ diaryl structures, such as benzophenone (RT 9.08 min), naphthalene, 2-methyl- (RT 7.92 min), naphthalene, 1,6,7-trimethyl- (RT 8.18 min) and 1,3-benzenediol, monobenzoate (RT 9.88 min), to single-ring esters, such as benzoic acid, 2-hydroxy-, pentyl ester (RT 8.41 min) [75]. The last intermediate stages of full mineralization into CO₂, H₂O, and inorganic ions are represented by these low-molecular-weight fragments, which include succinic and oxalic acids [75,76].

The identification of these intermediates provides an important perspective on the environmental safety of the photocatalytic process. Benzophenone, which is categorized as a potential carcinogen (IARC Group 2B), shows a transient increase in the toxicity profile of the solution in the early stages of the reaction [77]. Similarly, the emergence of bemegride, a CNS stimulant, underscores the need for extended catalytic treatment beyond simple decolorization. By promoting the quick fragmentation of these stable C₁₃ skeletons, the CNC/Ag-ZnO nanocomposite acts as a catalyst to mitigate these risks. The effluent has been successfully detoxified, shifting from high-risk intermediates to benign aliphatic compounds such as succinic acid, benzoic acid, 2-hydroxy pentyl ester, and other simple organic acids. Unlike systems that lead to the accumulation of stable aromatic amines, the current catalytic pathway prioritizes a total mineralization route [75]. Prolonged catalytic treatment can effectively close this toxic window and ensure that the final treated water is safe for environmental discharge.

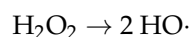
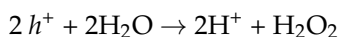
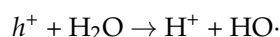
3.2.7. Degradation Mechanism of MB Dye and Recent CNC-Based Photocatalysis

Based on the results obtained in this study and a literature report [73], a possible degradation diagram of MB dye is shown in Figure 11. The degradation mechanism of MB dyes by CNC/Ag-ZnO nanocomposite can be broken down into the following four steps:

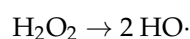
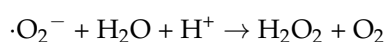
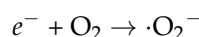
- (1) When the CNC/Ag-ZnO nanocomposite was exposed to incident light, it became activated. This activation generated electron-hole pairs, which were responsible for the subsequent oxidation and reduction processes.



- (2) The adsorbed water molecules on the nanocomposite's surface were oxidized, which led to the production of hydroxyl radicals.



- (3) Reduction reaction took place in the conduction band, using oxygen from the atmosphere.



- (4) The MB dye molecules were degraded by hydroxyl radicals, which are highly oxidative and non-selective.

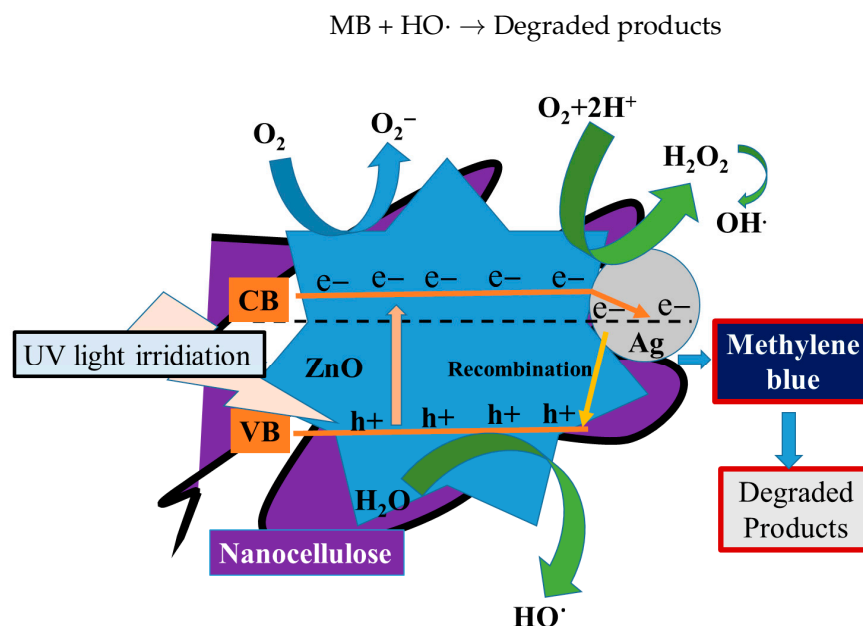


Figure 11. Schematic diagram representing the possible mechanisms that occur during the photocatalytic degradation of MB when using an Ag-ZnO/cellulose nanocomposite as a photocatalyst.

The photocatalytic activity of our prepared CNC-based ternary composite is comparable to that of other CNC-based catalysts from the literature (Table 4). The CNC/Ag-ZnO catalyst developed in this research achieves 96.2% MB degradation in 120 min with a low catalyst loading. Under the stated experimental conditions, the activity of CNC/Ag-ZnO nanocomposite is the highest. This is because it requires an extremely low catalyst dose of only 0.3 g L⁻¹, which is the lowest among all catalysts listed. This low dose requirement makes it highly cost-effective and efficient in its material use. The catalyst's band gap of 3.02 eV indicates its primary function under UV-vis light, a characteristic it shares with most of the catalysts in the table. From Table 4, CNC/TiO₂/MnO₂ can degrade the MB solution within a very short time (5 min); however, the catalyst dose is very high compared to our work. In their work, they used 200 mg of catalyst in 100 mL of MB solution, which was approximately 6.67 times higher than the catalyst amount we used in our work. We dispersed only 30 mg of catalyst in 100 mL of MB solution for the photocatalytic degradation.

Table 4. Degradation of MB by recent CNC-based photocatalysts, as reported in the literature.

Catalyst	Pollutants and Conditions	MB Concentration (ppm)	Dose of Catalyst (g L ⁻¹)	Degradation Activity (%)	Band Gap	Time (min)	Reference
CNC/ZnO/TiO ₂	MB under UV-vis light	5	0.5	98	3.2	180	Oyewo et al. (2021) [78]
CNC/TiO ₂ /MnO ₂	MB under visible light	800	2.0	97	1.75	5	Song et al. (2022) [79]
CNCs/Ag@ZnO	MB under visible light	20	0.3	96	3.08	180	Salem et al. (2022) [33]
CNC/ZnO	MB under UV-vis light	32	0.8	95	3.1–3.2	150	An et al. (2020) [80]
g-C ₃ N ₄ /CNC/PAM	MB under visible light	5	10.0	80	2.88	360	Li et al. (2023) [81]
CNC/Ag-ZnO	MB under UV-A light	10	0.3	96	3.02	120	This work

3.2.8. CNC/Ag-ZnO Composite Recycling and Measurement of Photostability Using ICP-MS

To evaluate the reusability of the CNC/Ag-ZnO composite, it was recycled and reused for four consecutive cycles. The same catalyst sample was reused for multiple cycles, and after each cycle, it was rinsed with DI water and dried in air. The structural integrity and resistance to photocorrosion of the CNC/Ag-ZnO nanocomposites were quantitatively evaluated by measuring the concentration of leached Zn²⁺ ions in the degraded MB solution

using ICP-MS. The results obtained from ICP-MS analysis have been tabulated in Table 5. Zinc oxide-based photocatalysts are often limited by their susceptibility to dissolution under UV irradiation. This phenomenon is primarily driven by photocorrosion, a process where the catalyst itself undergoes chemical degradation due to the behavior of photogenerated charge carriers [13,82].

Table 5. Determination of Zn^{2+} ion concentration (ppb) in degraded MB solutions after successive recycling and reuse of the CNC/Ag-ZnO composite using ICP-MS.

Sample ID	Description	Concentration of Zn^{2+} Ions $\times 10^3$ (ppb)
F&PRD-1	Degraded MB solution from cycle-1	0.96
F&PRD-2	Degraded MB solution from cycle-2	1.25
F&PRD-3	Degraded MB solution from cycle-3	3.72
F&PRD-4	Degraded MB solution from cycle-4	5.57

When ZnO is exposed to sunlight or UV irradiation, it absorbs photons with energy ≥ 3.37 eV, creating electron–hole pairs (e^-/h^+). While these carriers are meant to generate radicals for dye degradation, they often cause anodic photocorrosion. In this process, the photogenerated holes (h^+) oxidize lattice (O_2^-) ions rather than water molecules in solution. This destabilizes the crystal lattice, leading to its dissolution and the leaching of Zn^{2+} ions [83,84]. The incorporation of CNC and silver (Ag) nanoparticles significantly modulates this behavior due to the synergistic effect of the CNC/Ag-ZnO heterostructure [85–87]. The Ag nanoparticles act as electron sinks, while the CNC provides a protective scaffold, both of which prevent the accumulation of photo-generated electrons on the ZnO surface that would otherwise trigger the release of Zn^{2+} ions. As shown in the ICP-MS data from this study, the samples exhibited clear instability after recycling and reuse of CNC/Ag-ZnO composites. The leached Zn^{2+} ion concentrations were 960, 1250, 3720, and 5570 ppb for the first, second, third, and fourth consecutive recycling and reuse cycles of CNC/Ag-ZnO, indicating a gradual decrease in composite stability. Sample F&PRD 1 demonstrated the highest photostability with a minimal zinc release of 960 ppb. Sample F&PRD 4 exhibited the highest leaching rate of 5570 ppb, indicating greater photocorrosion under the same experimental conditions. The results confirm that the repeated reuse of the composite over multiple cycles leads to a loss of catalytic stability due to photocorrosion and Zn^{2+} leaching.

3.2.9. Interfacial Passivation Mechanism in Ethanol

The passivation of inorganic nanoparticle surfaces by nanocellulose in ethanol is governed by a heterogeneous surface-adsorption mechanism, which occurs despite the complete insolubility of the CNC macromolecules in ethanol [88]. This interaction is primarily driven by the high density of surface hydroxyl ($-\text{OH}$) groups—located at the C2, C3, and C6 positions of the anhydroglucose units—which remain chemically active and accessible even in non-aqueous solvents [89]. These groups facilitate strong interfacial hydrogen bonding and van der Waals forces with the inorganic nanoparticle of Ag-ZnO surface [90]. The binding is further stabilized by the low polarity of ethanol, which promotes a “solvent-driven” association where the insoluble CNC chains prefer to associate with the solid nanoparticle surface to minimize the system’s total interfacial free energy [91]. Once adsorbed, the CNC acts as a rigid physical barrier, providing steric stabilization that effectively prevents nanoparticle agglomeration during processing [92]. This mechanism is corroborated by multiple analytical techniques, such as FTIR peak shifts, which confirm the formation of interfacial hydrogen bonds, while XRD patterns prove that the inorganic crystalline structure remains intact under the protective CNC layer [93].

4. Conclusions

This study successfully developed an eco-friendly CNC/Ag–ZnO nanocomposite via a solvothermal method, integrating silver and zinc oxide into a natural cellulose nanocrystal matrix. Multi-technique characterization (XRD, FTIR, TEM, PL, and XPS) confirmed the successful anchoring of Ag nanoparticles and the preservation of CNC crystallinity, while TGA/DTG analysis verified the high thermal stability of the composite. The composite exhibited exceptional photocatalytic activity, achieving 96.2% degradation of MB within 120 min under UV-A light. This performance is attributed to the synergistic effect of Ag nanoparticles, which extended light absorption and inhibited ZnO photocorrosion, and the CNC matrix, which prevented nanoparticle agglomeration. Moreover, the optimization of the parameters was conducted and found to be pH 7, a catalyst dose of 0.3 g L^{-1} , and an initial MB concentration of 10 ppm, which shows the best photocatalytic degradation reaction. The practical viability of the catalyst was further validated by its high photostability. ICP-MS analysis showed negligible Zn^{2+} leaching, while GC-MS/MS confirmed the degradation intermediates. By combining sustainable CNC with a robust metallic system, this research provides a scalable, solar-driven solution for industrial wastewater treatment. Future work will focus on optimizing the synthesis for mass production and on evaluating the composite's efficacy against a broader spectrum of organic pollutants to facilitate its transition from laboratory success to large-scale industrial application.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/jcs10040216/s1>.

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