Synthesis and characterization of CMC-wrapped Nano-ZnO for photocatalytic degradation of dye under sunlight
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ABSTRACT
This research work focused on studying the fabrication of biopolymer carboxymethyl cellulose (CMC) wrapped ZnO nano-composite materials (ZnO-CMC NCs) and its applications in the photocatalytic degradation of methylene blue (MB) using under sunlight Irradiation. ZnO-CMC NCs were synthesized by using zinc acetate dihydrate as a precursor under alkaline conditions followed by the addition of capping agent CMC followed by calcination at various temperatures. The materials were characterized by FTIR, UV-Vis and powder XRD studies. The presence of CMC as a capping agent not only facilitated the nucleation and growth of (nanoparticles) NPs but also it provided stability and functionalization to the NPs. The varying calcination temperature played a significant role in influencing the size of NCs during the synthesis process. The crystallite size of ZnO-CMC NCs were found to be 19.5959 nm, 21.2518 nm, 23.5000 nm, 27.5930 nm, 34.9789 nm at 250°C, 350°C, 450°C, 550°C, and 650°C calcinations temperature respectively. It was observed that size increases slightly by increasing the calcination temperature from 250°C to 450°C. However, further increase in calcination temperature increases crystallite size significantly. The degradation of MB dye has been studied under UV-Vis spectrophotometer and it was observed that synthesized ZnO-CMC NCs were very efficient in the photocatalytic degradation of MB under natural sunlight. We believe that, these synthesized CMC-wrapped ZnO NCs will find wide range of photocatalytic applications for the treatment of organic pollutants in various dyes used in the chemical industries.

Keywords: ZnO-CMC NCs; FTIR; XRD analysis; calcination; photocatalyst; methylene blue

1. Introduction
In today’s scenarios smart materials occupied most of the applied fields due to its unique properties than other conventional materials. The Nanoparticles materials frequently have improved or unique physical, chemical, and biological capabilities. Nanoparticles have diverse uses, including electronics, energy, medicine, environmental cleanup, and materials research. They are used in a variety of fields, including medicine (e.g., drug delivery, imaging, diagnostics)¹¹,¹²; electronics and optoelectronics¹¹³,¹⁴ (e.g., transistors, LEDs, solar cells), environmental sensing and remediation¹¹⁵,¹⁶ energy storage and conversion (e.g., batteries, fuel cells), and...
advanced materials (e.g., coatings, composition)\textsuperscript{(7)} Because of their unique features, nanoparticles are suitable for targeted medication administration and imaging\textsuperscript{(6-7)}. Therapeutic medicines can be delivered with enhanced efficacy and less negative effects by using nanoparticles that are precisely engineered to target sick cells or tissues. Since nanoparticles have a large surface area and reactivity, they are used for environmental cleanup. They can be used to degrade and remove contaminants from soil, water, and the air. Certain nanoparticles can increase photocatalytic degradation of contaminants or adsorb heavy metals, while others have catalytic characteristics that can aid in the breakdown of organic pollutants\textsuperscript{(8,9)}. Materials such as polymers, metals, and ceramics can be reinforced with nanoparticles to increase their hardness, wear resistance, and mechanical strength\textsuperscript{(10)}. Advanced functional materials can be developed as a result of their ability to modify materials' optical, thermal, and electrical characteristics. Batteries and supercapacitors, for example, employ nanoparticles to increase the density of energy and charge-discharge rates\textsuperscript{(11)}. Moreover, light absorption and catalytic processes in fuel cells and solar cells, respectively, are improved by the use of nanoparticles, which helps to provide sustainable and effective energy. Sensory and diagnostic applications can benefit from the unique optical, magnetic, and electrical characteristics of nanoparticles. To enable early illness diagnosis, they can function as biosensors that identify certain biomarkers or analytes\textsuperscript{(12)}.

Metallic, metal oxide, composite type metal oxides, and other types of nanoparticles were created. Since they have so many uses and special qualities, metallic nanoparticles are frequently regarded as important material. They are better than their bulk equivalents in terms of electrical, optical, and catalytic characteristics. The high surface area-to-volume ratio and quantum effects resulting from their tiny size are the cause of these features. The distinctive electrical structure and large surface area of metallic nanoparticles make them effective catalysts\textsuperscript{(13)}. Due to this, they are useful in fuel cells, other catalytic processes, and chemical reactions. The present study aims to synthesize metallic ZnO nanoparticles (NPs) using capping agent carboxymethylcellulose (CMC) and investigate their photocatalytic activity.

Zinc oxide nanoparticles have superior antimicrobial and antifungal characteristics, which renders them appropriate for a range of medicinal applications. They can be utilised to enhance wound healing and prevent infections in ointments, coatings, and dressings\textsuperscript{(14)}. Because of its capacity to both absorb and disperse ultraviolet (UV) light, zinc oxide (ZnO) nanoparticles are frequently included in sunscreens and cosmetic products\textsuperscript{(15)}. By creating a physical barrier that shields the skin from UV radiation and either reflecting or absorbing it, they offer efficient UV protection. Gases such as hydrogen sulphide, nitrogen dioxide, and carbon monoxide can all cause reactions in ZnO nanoparticles. Gas sensors for industrial hazard protection and environmental safety surveillance can employ them\textsuperscript{(16)}. Catalytic activity of ZnO nanoparticles is encouraging in a range of chemical processes. For the synthesis of organic molecules, such as the synthesis of methanol, they can act as catalysts\textsuperscript{(17)}. ZnO nanoparticles are distinguished by their distinct optical and electrical characteristics. Light-emitting diodes (LEDs), solar cells, and sensors are developed using them\textsuperscript{(18)}. Because of its large surface area and electrochemical characteristics, ZnO nanoparticles are utilised in supercapacitors and batteries\textsuperscript{(19)}. According to some research, ZnO nanoparticles may have anticancer effects by preventing
the proliferation of cancer cells while mostly sparing healthy cells. They show potential for photodynamic therapy and tailored medication delivery in the treatment of cancer[20]. There has been research on ZnO nanoparticles as possible substitutes for conventional antibiotics. They might be utilised to treat infections since they have shown antibacterial action against a variety of drug-resistant bacteria[21].

Carboxymethyl cellulose (CMC) is a soluble in water polymer that is made from cellulose, a polysaccharide that is naturally present in plant cell walls. Cellulose may be chemically modified to produce CMC. This alteration yields a highly functional, water-soluble polymer with a variety of advantageous characteristics. CMC is a linear polymer made up of glucose molecules that repeat and are joined by β-(1→4) glycosidic bonds. By adding negative charges and boosting the polymer's water solubility, the carboxymethyl groups are joined to the hydroxyl groups (-OH) on the cellulose backbone. The average quantity of carboxymethyl groups per unit of glucose is known as the degree of substitution (DS), and it can vary, resulting in various applications and attributes of CMC [22].

Figure 1. Structure of Carboxymethyl Cellulose(CMC).

The high water solubility of CMC makes it easier to dissolve and disperse in aqueous solutions, making it one of its primary characteristics. The polymer becomes hydrophilic when carboxymethyl groups are present, which enables it to form stable colloidal solutions[23]. Shear-thinning, or pseudoplastic, behaviour is shown by CMC, which means that under shear stress, its viscosity reduces. Because of this feature, CMC may be used as an emulsifier[26], thickening agent[24], and stabilizer[25] in a variety of sectors, including food, medicine, and personal care. CMC has the ability to make flexible and mechanically strong films. These films have a variety of uses, including coatings and protective layers[27]. Because CMC is thought to be non-toxic and biocompatible, it can be used in biomedical and pharmaceutical applications. It has been thoroughly studied for tissue engineering and medication delivery systems [28, 29]. As a stabilising agent, CMC keeps suspensions, colloids, and nanoparticles from aggregating and precipitating. In a variety of aqueous conditions, it can stabilise nanoparticles and improve their dispersibility[30]. pH has the ability to affect the solubility and characteristics of CMC. Because of the deprotonation of carboxyl groups, which results in more negative charges and better solubility, CMC shows enhanced solubility at higher pH levels[31]. CMC gives solutions viscosity and a gel-like consistency by acting as a thickening and gelling agent. Applications like food additives
The photocatalytic degradation of methylene blue (MB) under solar radiation was investigated in this study utilising biopolymer-wrapped ZnO nanoparticles coated in carboxymethyl cellulose (CMC). The existence of all life on Earth depends on water, a vital resource whose accessibility and qualities are crucial. Being one of the main sources of very harmful organic and inorganic contaminants, industrial waste water may seriously poison living things. The industrial revolution and excessive discharge into several natural water sources are to blame for the pollution's climax in the past century. The growth of the dye industry over the past few decades has had detrimental effects on living things and species. Hence there is a need to develop an environmentally friendly efficient process for removal of MB from wastewater. One of the most common substances that contaminate water is industrial dyes. Methylene blue, an organic dye, poses a serious risk to both human health and the environment due to its toxicity, carcinogenicity, and lack of biodegrade ability\[^33\]. Therefore, the development of an effective and ecologically friendly method for removing MB from wastewater is necessary.

Because of their diverse range of uses and unique physicochemical properties, ZnO nanoparticles have garnered a lot of attention. Excellent electrical, optical, and catalytic properties of ZnO nanoparticles make them useful for a variety of applications, including sensors, solar cells, optoelectronic devices, photo catalysts, and many more. Therefore, creating ZnO nanoparticles is an essential step in putting them into practise. ZnO nanoparticle production has been carried out using a variety of techniques. ZnO nanoparticles are created via the Sol-gel process by hydrolysing and condensing metal precursors. In order to start the reaction, a basic or acid is often added after a zinc salt has been dissolved in an appropriate solvent. ZnO nanoparticles are then produced by drying and calcining the resultant gel\[^34\]. This approach produces ZnO nanoparticles by precipitating a solution comprising a zinc salt and a precipitating agent. Precipitation reactions result in the creation of ZnO nanoparticles, which may be collected by centrifugation or filtering before being cleaned and dried\[^35\]. A zinc precursor reacts in an aqueous solution at high pressures and temperatures in the hydrothermal synthesis process.

Typically, a base or acid is added to a zinc salt solution after it has been dissolved in a solvent to maintain the pH. After that, the mixture is heated and enclosed inside a high-pressure vessel to promote the formation of ZnO nanoparticles. Particles are gathered, cleaned, and dried when the process is finished\[^36\]. ZnO nanoparticle production is made easier by the microwave assisted approach, which involves microwave irradiation. After combining a zinc precursor with an appropriate solvent or surfactant, the combination is microwave-irradiated. The generation of nanoparticles is encouraged and reaction kinetics are accelerated by the microwave energy\[^37\]. The solvothermal synthesis approach involves reacting a zinc precursor in a solvent environment that is both hot and pressurised. The reaction takes place in a confined vessel at high pressure and temperature, which promotes the formation of ZnO nanoparticles. After being recovered, cleaned, and dried, the necessary nanoparticles are created\[^38\]. To maintain a steady pH, an acid or basic is often added after a zinc salt solution has been dissolved in a solvent. The mixture is subsequently heated and confined within a high-
pressure vessel to promote the formation of ZnO nanoparticles. When the procedure is complete, the particles are collected, cleaned, and dried. The utilisation of microwave irradiation in the microwave aided technique facilitates the creation of ZnO nanoparticles. A zinc precursor is combined with a suitable solvent or surfactant, and then the mixture is microwave-irradiated. The microwave radiation promotes the formation of nanoparticles and speeds up reaction kinetics. In the solvothermal synthesis method, the zinc precursor interacts in a solvent environment at high temperatures and pressures. ZnO nanoparticles are produced by the electrochemical approach, which makes use of an electrochemical cell configuration. An appropriate cathode material is selected, and a zinc electrode serves as the anode. ZnO nanoparticles are deposited and gradually develop on the cathode surface as a result of the electrochemical interaction between the electrolyte and the zinc electrode.

2. Experimental section

2.1. Materials

Zinc Acetate dihydrate (Zn(CH₃COO)₂·2H₂O), Sodium hydroxide (NaOH), Methylene Blue (C₁₆H₁₈CIN₃S), carboxymethyl cellulose, ethanol. All the chemicals were purchased from Himedia chemicals, India and are of analytical grade.

2.2. Synthesis of biopolymer CMC wrapped ZnO nanoparticle

It is synthesized by a precipitation method. Firstly, zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O) weighed and solution was prepared in double distilled water and the NaOH solution was added dropwise to the firstly prepared zinc acetate solution with constant stirring until the white zinc hydroxide Zn(OH)₂ suspension is observed. Then, CMC solution was added dropwise to the solution mixture by continued stirring of mixture for 2 hours. Then after the capping process, it was washed with distilled water two times and ethanol to remove the impurities and dried in oven at 60°C after that CMC capped ZnO nanoparticle was subjected to process of calcination at 250°C for 3 hours and then similar procedure was followed to prepare another sample by varying the calcination temperature at 350°C, 450°C, 550°C and 650°C respectively.

2.3. Reaction involved in ZnONPS formation

The overall reaction for the formation of ZnO nanoparticles from zinc acetate dihydrate and sodium hydroxide can be summarized as follows:

\[ \text{Zn} (\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O} + 2\text{NaOH} \to \text{ZnO} + 2\text{CH}_3\text{COONa} + 3\text{H}_2\text{O}. \]

Different characterization techniques were used to characterise the synthesized nanoparticle using Fourier Transform Infrared spectroscopy (FTIR). The crystalline structure size were determined through XRD.
2.4. Method of photo degradation

The 5 ppm methylene blue dye solution was prepared by adding 0.25 mg of methylene blue dissolved in 50 mL of distilled water. The specific amount i.e. 0.02g of the synthesized CMC capped ZnO nanoparticles was added in 5ml Methylene blue solution and mixed thoroughly to ensure uniform dispersion. Then the dye solution containing synthesized CMC capped ZnO nanoparticle was exposed to sunlight for a particular duration. During the exposure the sample was collected at regular time intervals to monitor the degradation progress.

3. Characterization

3.1. FTIR

FTIR is a technique used to analyse molecular vibrations and functional groups in a sample. The FTIR instrument emits infrared light onto the sample, which interacts with the molecules. The molecules absorb specific frequencies of infrared light, causing them to vibrate. The resulting spectrum is a plot of absorbance (intensity of absorbed light) against wavenumber (inverse of wavelength). Wavenumber is measured in reciprocal centimeters and corresponds to the energy of the molecular vibrations. Peaks on the FTIR spectrum correspond to specific vibrational modes of functional groups present in the sample. By comparing these peaks
to reference spectra, we can identify the types of chemical bonds and functional groups present. The FTIR spectra of all the samples have been recorded using Bruker Alpha II. We have observed peaks related to both ZnO and CMC components.

3.2. X-ray Diffraction (XRD)

X-ray diffraction (XRD) is a potent method for examining a material’s crystallographic characteristics and revealing details about its atomic structure. Usually, a sample container is used to store the finely powdered ZnO CMC nanoparticles. The sample is subjected to X-ray radiation using a Bruker D8 Advance (Eco). Diffraction occurs when X-rays contact with the nanoparticles’ crystal lattice, producing a diffraction pattern. This pattern is made up of a number of peaks that represent distinct angles at which constructive interference takes place. Bragg’s Law, which connects the diffraction angle, X-ray wavelength, and crystal lattice spacing, establishes the locations of the peaks in the diffraction pattern. By analysing the positions and intensities of the diffraction peaks, we can determine the crystal structure of the nanoparticles. The width of the diffraction peaks provides information about the average crystallite size of the nanoparticles. Broader peaks indicate smaller crystallites. The size of the nanoparticles are calculated through Debye Scherrer equation.

4. Result and discussion

4.1. FTIR

The FTIR spectra of synthesized ZnO-CMC nanoparticles, calcined at varying temperatures 250, 350, 450, 550, 650°C have been shown by Figure 4. The ZnO peak appeared between 560 cm\(^{-1}\) and 670 cm\(^{-1}\) in all spectra but it become sharp at higher calcination temperature which shows the transformation of Zn (OH)\(_2\) to ZnO \[^{40}\]. The small peaks have been seen between 3500 cm\(^{-1}\) to 3700 cm\(^{-1}\) is assigned to O-H stretching that signifies the hygroscopic nature of ZnO that disappears on higher calcination temperatures \[^{41-44}\]. The peaks about 2800 cm\(^{-1}\) shows the C-H stretching \[^{45}\] and the peaks around 1600 to 1700 cm\(^{-1}\) shows C=O stretching vibrations \[^{43}\].

Figure 4. FTIR spectra of ZnO NPs@CMC at different calcination temperature.
4.2. XRD

Figure 5. XRD of ZnO-CMC calcinated at 250°C.

Figure 6. XRD of ZnO-CMC calcinated at 350°C.

Figure 7. XRD of ZnO-CMC calcinated at 450°C.
The XRD data were utilised to calculate the average crystallite size of CMC-ZnO NPs. Debye-Scherrer method was used to estimate the size of crystallites. The Debye Scherrer equation is given as

$$D = \frac{K\lambda}{\beta \cos \theta}$$

Where,

- $D =$ Crystallite size in nm
- $K =$ Scherrer constant (0.9)
- $\beta =$ fullwidth half maximum (FWHM) of diffraction (in radians)
Increasing calcination temperature can have a significant effect on the size of CMC (carboxymethyl cellulose) wrapped ZnO nanoparticles. Generally, higher calcination temperatures can lead to particle growth and agglomeration. The process involves crystallization and sintering of the nanoparticles, which can cause them to fuse together and form larger particles. The crystallite size of ZnO-CMC calcinated at 250°C, 350°C, 450°C, 550°C, 650°C is found to be 19.59 nm, 21.25 nm, 23.50 nm, 27.59 nm, 34.97 nm respectively. It was observed that crystallite size increases slightly by increasing the calcination temperature from 250°C to 450°C further increase in calcination temperature increases crystallite size significantly. This result is in agreement with previous research work[46].

Figure 10. UV absorbance plot of Photocatalytic degradation of MB dye by ZnO-CMCNP calcinated at 450°C.

Figure 11. UV-V absorbance plot of Photocatalytic degradation of MB dye by ZnO-CMC NP calcinated at 550°C.
Figure 12. UV absorbance plot of Photocatalytic degradation of MB dye by ZnO-CMC NP calcinated at 650°C.

The UV absorbance plot of ZnO-CMCNPs' photocatalytic degradation of MB dye at different calcination temperatures (450°C, 550°C, and 650°C) shows the dye degradation across a number of time intervals (from one to three hours). In the MB dye's UV absorption spectra, an MB monomer is linked to the strongest absorption peak, which is located at around 664 nm. An MB dimer is responsible for the shoulder peak, which is located at roughly 612 nm. In the ultraviolet area, two more bands with maxima at 292 and 245 nm (linked to substituted benzene rings) emerged. The absorbance peak's strength steadily drops over time as the photocatalytic degradation occurs. The decrease in absorbance signifies that the number of Methylene Blue dye molecules in the solution is diminishing due to its degradation. A change in the absorbance peak's location was also seen, along with a drop in absorbance intensity. This shift is either towards blue shift (shorter wavelengths) or redshift (longer wavelengths). As the MB dye molecules decompose, their chemical structures alter, causing the shift. It is possible that the smaller fragments created during the degradation process or intermediate degradation products correlate to these new peaks identified. This observation is found to be consistent with earlier study on MB that was conducted[33].

4.3. Mechanism of photocatalytic degradation

By electrostatic interactions, the positively charged MB dye molecules are drawn to the negatively charged CMC layer on the ZnO nanoparticles. In order to prepare the nanoparticles for the photocatalytic degradation process, the dye molecules are adsorbed onto their surface. Electrons in the ZnO nanoparticles' valence band are promoted to move to the conduction band when they are exposed to UV light by absorption of the light's energy by the CMC around the nanoparticles. Pairs of electrons are produced. ZnO's conduction band's excited electrons react with nearby oxygen molecules (O₂) to produce reactive oxygen species (ROS), including hydroxyl radicals (OH-) and superoxide radicals (O₂⁻), strongly reactive, these ROS have the ability...
to cause organic substances, such as the MB dye, to degrade. The produced reactive oxygen species (ROS) interact with the adsorbed MB dye molecules on the ZnO nanoparticles wrapped in CMC. Dyes eventually deteriorate due to the ROS’s oxidation of the dye molecules and subsequent disintegration into simpler, less complicated molecules. The MB dye’s broken down products are released into the surrounding solution from the surface of the CMC-wrapped ZnO nanoparticles as the photocatalytic degradation process proceeds. The stepwise representation of the possible mechanismis given below.

**Step 1:** Absorption of photons

ZnO nanoparticles (ZnO-NPs) absorb photons from a light source, typically UV light, leading to the generation of electron-hole pairs (e⁻/h⁺)

\[
\text{ZnO-NPs + hv} \rightarrow \text{ZnO-NPs (e⁻/h⁺)}
\]

**Step 2:** Generation of reactive oxygen species (ROS)

The excited electrons (e⁻) in ZnO-NPs transfer to molecular oxygen (O₂), generating superoxide radicals (O₂⁻).

\[
\text{ZnO-NPs (e⁻)} + \text{O₂} \rightarrow \text{ZnO-NPs + O₂⁻}
\]

**Step 3:** Reaction with water

Superoxide radicals (O₂⁻) react with water (H₂O) to form hydroperoxyl radicals (HO₂⁻).

\[
\text{O₂⁻ + H₂O} \rightarrow \text{HO₂⁻ + OH⁻}
\]

**Step 4:** Degradation of methylene blue dye the hydroperoxyl radicals (HO₂⁻) generated in the previous step attack the methylene blue dye (MB) molecules, leading to their degradation.

\[
\text{HO₂⁻ + MB} \rightarrow \text{Degradation products}
\]

**Overall equation:**

\[
\text{ZnO-NPs + hv + O₂ + H₂O + MB} \rightarrow \text{ZnO-NPs + O₂⁻ + HO₂⁻ + OH⁻ + Degradation products}
\]

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*Figure 13. Mechanism of Photocatalytic degradation of MB dye by ZnO-CMC NPs Under UV irradiation.*
5. Conclusion

The formation of CMC-capped ZnO nanoparticles has been successfully prepared using the reaction of zinc acetate dihydrate and sodium hydroxide, followed by calcination at various temperatures. The FTIR characterization findings showed that well-dispersed ZnO nanoparticles were formed. The addition of carboxymethyl cellulose (CMC) as a capping agent not only aided nanoparticle nucleation and development, but also enhanced nanoparticle stability and functionalization. During the synthesis process, the variable calcination temperature had a substantial impact on the size of nanoparticles. ZnO CMC crystallite sizes are reported to be 19.59 nm, 21.25 nm, 23.50 nm, 27.59 nm, and 34.97 nm when calcined at 250°C, 350°C, 450°C, 550°C, and 650°C, respectively. It was observed that crystallite size increases slightly by increasing the calcination temperature from 250°C to 450°C further increase in calcination temperature up to 650°C crystallite size increases significantly. The UV absorbance plot clearly showed that the synthesised ZnO-CMC NPs effectively degraded the MB dye at various calcination temperatures. As a result, these CMC-wrapped ZnO nanoparticles may be used as photocatalysts for dye degradation and the remediation of organic contaminants in different dyes.

Acknowledgment

We thankfully acknowledge to Department of Chemistry, Institute of Science, Banaras Hindu University, India for XRD analysis of nanoparticle samples.

Competing interests

The author declare no competing interests.

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14


