DOI: https://doi.org/10.29070/y4jx8853

Nanocellulose Composites as Photocatalyst: Biodegradable, Ageless Polymers

Aditi Kandari [1] * , Prof. D.S.Negi [2]

1. Research Scholar, Department of Chemistry, Hemvati Nandan Bahuguna Garhwal (Central University), Uttarakhand, India
aditikandaris@gmail.com ,
2. Professor, Department of Chemistry, Hemvati Nandan Bahuguna Garhwal (Central University), Uttarakhand, India

Abstract: Environmental remediation and energy conversion are two potential uses for photocatalytic phytogenic green nanocellulose composites (PPGNCs), a new category of sustainable materials. The biocompatible matrix of these composites is made of nanocellulose obtained from plants, which is then combined with photocatalytic nanoparticles like zinc oxide (ZnO) or titanium dioxide (TiO_2). Because it improves photocatalyst stability and dispersion while reducing the use of harmful chemicals, the phytogenic method guarantees a green synthesis. PPGNCs have several potential uses, including the breakdown of organic contaminants, water purification, and antibacterial agents, due to their exceptional photocatalytic effectiveness when exposed to visible or ultraviolet light. Advanced functional materials can benefit greatly from their biodegradability, mechanical strength, and large surface area. Recent research has shown that they might be useful in solar energy collecting and for surfaces that clean themselves. The need for more study on scalability, long-term stability, and recyclability cannot be overstated. Encouraging sustainable nanotechnology development, PPGNCs provide an eco-friendly and economical answer to worldwide environmental problems.

Keywords: Photocatalytic, Phytogenic, Green Nanocellulose, Composites, polymers, biodegradable

-----------------------------X-----------------------------

INTRODUCTION

In an ecosystem, living things have interdependent relationships with inert elements like water, soil, and air. Living and nonliving objects interact in many ways in the environment. Rapid industrialisation, unplanned urbanisation, deforestation, and overexploitation of natural resources are only a few of the many actions taken by modern civilisation in response to the challenges posed by a growing human population. The continuous release of a great deal of energy and other contaminants into the environment is a byproduct of these processes; this, in turn, raises the concentration of harmful substances in the environment, which has a domino effect on pollution. Among the many forms of environmental contamination—including that of the air, soil, noise, heat, and light—water pollution stands out as the most serious threat. Along with health, nutrition, energy, and the economy, water affects every facet of human existence (Sajab MS, Chin SX. (2015).

Unfortunately, most water sources are now contaminated, despite the fact that water is essential for all forms of life. Concerns about pollution have grown in recent decades due to the release of industrial effluents into water sources. Foreign and potentially harmful species have multiplied in the polluted waterways. In addition to being bad for people and the planet, these things alter natural aquatic ecosystems and the creatures that inhabit there, which in turn impacts water quality and biodiversity. Even at low concentrations (l mg L−1), organic pollutants including pesticides, dyes, and medicines can cause harm to the environment (Abdelhamid HN. 2024). Skin rashes, headaches, diarrhoea, soreness in the muscles and joints, trouble breathing, and irregular pulse are just some of the symptoms that people may experience as a result of drinking dirty water. Severe illness, including cancer, skin irritation, and allergic responses, can result from breathing in or ingesting organic pollutants, which fall under the category of acute toxicity (Jalil AA, Abdulrasheed AA. 2019).

One growing ecological concern is the use of dyes, which are among the most visible organic contaminants. The widespread use of synthetic dyes in many different sectors has led to the undesired and damaging phenomena of their unregulated discharge into water reservoirs as industrial effluent, which is a major problem for the environment. Aniline blue, alcian blue, basic fuchsin, methylene blue, crystal violet, toluidine blue, and congo red are only a few synthesised dyes (Chand P, Singh V, Kumar D. 2020). Common sectors that utilise these dyes as colouring agents include food, paper, leather, textile, pharmaceutical, and paint. Around 7×10^1 tonnes of 1000 distinct kinds of pigments and dyes are produced every year, as per a recorded worldwide estimate. When discharged into water, these cancer-causing azo dyes cause detrimental structural alterations in the ecosystem. These poisonous, non-biodegradable chemicals not only pollute the food chain but also hinder aquatic plants' photosynthetic function by blocking light from reaching the water. These colours produce hypertrophication, which in turn lowers marine life's oxygenation capacity and causes significant harm to aquatic flora and wildlife. Indirectly affecting people, these harmful pigments bioaccumulate and biomagnify in aquatic environments due to human consumption of aquatic food (Sreekala MS, Thomas S. 2018).

Overview of nanocellulose

The most prevalent biopolymer on Earth, cellulose, is the source of a new sustainable nanomaterial called nanocellulose. Its high biodegradability, renewability, and customisable surface qualities have made it a highly sought-after material. Bacterial nanocellulose (BNC), cellulose nanofibers (CNFs), and cellulose nanocrystals (CNCs) are the three main types of nanocellulose. The various extraction or synthesis methods used to create each of these forms give them unique physicochemical properties. Research into nanocellulose and its possible uses in biomedicine, environmental remediation, energy storage, and photocatalysis has been driven by the growing need for eco-friendly and high-performance materials (Sharma A, Khamidun MH. 2022)

Types of Nanocellulose

i. Cellulose Nanocrystals (CNCs):

CNCs are rod-shaped nanostructures made from acid hydrolysed cellulose. Another name for them is nanocrystalline cellulose. Cellulose fibres that are very crystalline and nanoscale in size are produced by this procedure by carefully removing amorphous areas. CNCs are known for their exceptional optical characteristics, thermal stability, and mechanical strength, all of which are aided by their high crystallinity levels (60–90%). Composite materials, biomedical applications, and drug delivery systems have all heavily investigated CNCs because of their large surface area and adjustable surface chemistry.

ii. Cellulose Nanofibers (CNFs):

Mechanical, chemical, or enzymatic treatments are used to break down plant fibres into nanoscale fibrils, resulting in CNFs, also known as nanofibrillated cellulose. Because they keep some of their crystalline and amorphous areas, CNFs are less brittle and more flexible than CNCs. They are well-suited for usage as biodegradable packaging, reinforcing materials, or filtering membranes due to their outstanding mechanical characteristics, high aspect ratios, and barrier qualities. Coatings, films, and composites made from CNFs are a greener option than those made from synthetic polymers (Berglund L, Oksman K. 2020).

iii. Bacterial Nanocellulose (BNC):

In aqueous culture medium, some bacteria, such Komagataeibacter xylinus, biosynthesise BNC. In contrast to CNCs and CNFs, which originate from plants, BNC is produced by bacteria as pure nanofibrils by direct synthesis. Wound dressings, scaffolds for tissue engineering, and drug delivery systems are just a few examples of the biomedical uses that benefit greatly from its high water retention capacity, porosity, and biocompatibility. Chemical modification of BNC can also improve its functionality for a range of industrial uses.

IMPORTANCE OF GREEN SYNTHESIS AND PHYTOGENIC APPROACHES

In recent years, "green synthesis" has gained popularity as a less harmful substitute for traditional physical and chemical processes in the production of nanomaterials. To create nanoparticles and nanocomposites without using harmful chemicals, high temperatures, or energy-intensive procedures, green synthesis depends on living things including plants, fungus, algae, and bacteria. Because of its ease of use, low cost, and capacity to generate stable nanoparticles with improved functionality, phytogenic (plant-based) synthesis stands out among these methods. The phytogenic method makes use of organic reducing, stabilising, and capping agents found in plant extracts that are abundant in bioactive chemicals such terpenoids, alkaloids, flavonoids, and polyphenols. In addition to improving the synthesised nanomaterials' biocompatibility and stability, this approach gets rid of the necessity for harmful reducing chemicals like hydrazine or sodium borohydride (Kala LD, Subbarao PM. 2018).

Advantages of Green Synthesis over Conventional Methods

Conventional approaches to nanomaterial synthesis typically necessitate the employment of strong chemicals, substantial amounts of energy, and the production of harmful waste products. There has to be a development of more environmentally friendly alternatives to these procedures because they are quite dangerous to people and the planet. When compared to more traditional techniques, green synthesis, and phytogenic procedures in particular, have several benefits:

Eco-Friendly and Non-Toxic: Green synthesis reduces environmental pollution and toxicity hazards by eliminating the use of hazardous chemicals. The synthesis method is made safe and sustainable by using plant extracts.

Energy Efficiency: The energy consumption of green synthesis is frequently much lower than that of conventional techniques since it does not require high temperatures, pressure, or mechanical processes.

Biodegradability and Biocompatibility: The natural capping agents produced from plant metabolites provide nanomaterials synthesised by phytogenic processes their exceptional biocompatibility and biodegradability. Because of this, they are excellent choices for use in environmental, pharmacological, and biological fields.

Cost-Effectiveness and Scalability: Nanoparticle production becomes more affordable when commonly accessible plant resources are utilised. Green synthesis techniques are also easier to scale up for use in industry because of their simplicity.

Enhanced Functional Properties: The synthesised nanomaterials gain new capabilities, such antibacterial, antioxidant, and anti-inflammatory activities, when bioactive chemicals found in plant extracts are added (Abou-Zeid RE, Fouda A. 2020).

Phytogenic Approaches in Nanocellulose-Based Composites

The combination of nanocellulose's biodegradability, mechanical strength, and large surface area makes it a promising backbone for photocatalytic nanocomposites. Composites based on nanocellulose perform exceptionally well in energy and environmental applications when combined with photocatalytic nanoparticles like graphitic carbon nitride (g-C_3N_4), zinc oxide (ZnO), or titanium dioxide (TiO_2). In order to fabricate these composites in a way that guarantees the non-toxic and sustainable deposition of nanoparticles on nanocellulose surfaces, green synthesis employing phytogenic techniques is essential. During the creation of metal or metal oxide nanoparticles, plant extracts serve as agents that reduce and stabilise. The extracts' bioactive chemicals make it easy to reduce metal ions to nanoparticles without letting them aggregate, which guarantees that the nanocellulose matrix will have a consistent distribution of the materials. Light absorption, charge separation, and ROS formation are all improved, leading to an increase in the composites' photocatalytic efficiency. Furthermore, the nanoparticles' surface chemistry may be modulated by natural capping agents obtained from plant extracts, which in turn enhances their photocatalytic and antibacterial characteristics.

ROLE OF PLANT-DERIVED (PHYTOGENIC) REDUCING AND STABILIZING AGENTS

Materials science, health, energy, and environmental remediation are just a few of the many scientific domains that have benefited greatly from nanotechnology's progress. Unfortunately, conventional approaches to nanomaterial synthesis frequently need the use of harmful chemicals, a great deal of energy, and the production of harmful byproducts, all of which pose significant threats to both human and environmental health. One environmentally friendly option that has arisen to deal with these issues is green synthesis, which makes use of living things like plants, algae, and microbes to create nanoparticles. Because of its ease of use, low cost, and little impact on the environment, phytogenic or plant-based synthesis has become one of the most popular methods among these alternatives. Instead of using synthetic compounds like sodium borohydride ($NaBH_4$), hydrazine (N_2H_4), and citrate, plant extracts can be used as natural reducing and stabilising agents in the creation of nanoparticles and nanocomposites. To stabilise metal ions and reduce them into nanoparticles, plant extracts contain bioactive chemicals such as polyphenols, flavonoids, terpenoids, alkaloids, tannins, and proteins. Producing nanomaterials with exceptional stability and utility for use in catalysis, medicine, energy, and environmental sustainability is made possible by their dual functionality (Zerefa E, Abdisa E. 2020).

Mechanism of Plant-Mediated Reduction and Stabilization

There are typically three main processes involved in the synthesis of nanoparticles utilising plant extracts:

Metal Salt Precursor Selection – Silver nitrate ($AgNO_3$), zinc acetate ($Zn(CH_3COO)_2$), or titanium dioxide (TiO_2) are many examples of metal precursors that can be dissolved in water.

Reduction Process – The solution is then treated with the plant extract, which is abundant in bioactive chemicals, and the metal ions are reduced into their respective nanoparticles. In order to convert metal ions (such as Ag^+ to Ag^0), the biomolecules in the extract provide electrons.

Stabilization and Capping – To further prevent the nanoparticles from clumping together, the bioactive chemicals encase them. Because of this stabilisation, the produced nanoparticles have an improved bioavailability, dispersibility, and shelf life.

Many variables, including plant species, extraction technique, pH, temperature, and reaction time, influence how well plant extracts reduce and stabilise nanoparticles (Zhang L, Wang P. 2015).

Types of Phytogenic Reducing and Stabilizing Agents

Phytochemicals are a wide class of compounds found in plants that have reducing and stabilising properties. Some examples of the most common types of these biomolecules are:

Polyphenols

- Flavonoids, phenolic acids, and tannins are polyphenols that are very potent reducing agents due to their strong antioxidant characteristics.
- By giving electrons, these chemicals make it easier to reduce metal ions, which in turn forms stable nanoparticles.
- The catechins in green tea (Camellia sinensis), the tannins in oak bark, and the gallic acid in grapes are just a few examples.

Flavonoids

- Flavonoids aid in the creation of nanoparticles due to their hydroxyl (-OH) and ketone (=O) functional groups, which are involved in redox processes.
- Additionally, they encase nanoparticles in a protective shell, making them behave as capping agents.
- Onions and citrus fruits are good sources of quercetin, rutin, and kaempferol.

Terpenoids

- The five-carbon isoprene unit is the starting point for terpenoids, which are also called isoprenoids. Their strong reactivity makes them an essential component in metal ion reduction.

- The functionality and stability of nanomaterials are improved by these chemicals.
- Peppermint menthol, turmeric curcumin, and citrus peel limonene are a few examples (Kim IS, Bechelany M. 2019).

Alkaloids

- Secondary metabolites known as alkaloids have potent antioxidant and antibacterial effects, and they include nitrogen.
- They enhance the biological activity of the synthesised nanoparticles and help reduce metal ions.
- Some examples of natural analgesics are berberine, morphine, and quinine, which are all found in the bark of various plants.

Proteins and Enzymes

- By attaching to metal ions and enabling their reduction, certain plant proteins and enzymes serve as bio-templates in the creation of nanoparticles.
- Additionally, they improve nanoparticles' biocompatibility and functional characteristics.
- Casein, a protein derived from milk, peroxidase, and peptides derived from soy are a few examples.

PHOTOCATALYTIC MATERIALS IN NANOCELLULOSE COMPOSITES

There has been a lot of interest in photocatalysis for its potential energy and environmental benefits since it speeds up chemical reactions when light is present. By using semiconducting materials that can absorb light and produce electron-hole pairs, which in turn interact with environmental molecules to drive redox processes, photocatalysis becomes a reality. A state-of-the-art innovation, photocatalytic composites based on nanocellulose combine the distinctive characteristics of nanocellulose with those of photocatalytic materials. Biodegradability, mechanical strength, structural flexibility, and enhanced photocatalytic activity are some of the additional benefits that result from this integration.

Nanocellulose composites primarily employ photocatalytic compounds that are oxides of metals, such as graphitic carbon nitride (g-C_3N_4), zinc oxide (ZnO), and titanium dioxide (TiO_2). These materials are preferred due to their great efficiency in photocatalyzing a variety of processes, including the reduction of CO_2, the creation of hydrogen, and the breakdown of organic contaminants, all under visible or ultraviolet light. These photocatalytic compounds are stabilised and dispersed more effectively when incorporated in nanocellulose matrices, thanks to nanocellulose's large surface area, porosity, and mechanical strength. Essential for optimal photocatalysis, this synergy for more efficient light absorption, charge separation, and ROS production (Farooqi ZH, Din MI. 2020).

Titanium Dioxide (TiO_2) Nanoparticles in Nanocellulose Composites

Since it is non-toxic, stable, and has significant photocatalytic characteristics, titanium dioxide has been the subject of much research into photocatalysis. To enhance the photocatalytic destruction of organic pollutants, colours, and pathogens, TiO_2 nanoparticles are frequently used in nanocellulose-based composites. Nevertheless, applications that need visible light are out of the question for TiO_2 because of its broad band gap, which limits its photocatalytic activity to UV light. Combining TiO_2 with nanocellulose increases its surface area and dispersibility, which in turn enhances its activity, allowing it to overcome this constraint. Furthermore, TiO_2 may be enhanced in terms of photocatalytic effectiveness and its ability to absorb the visible light spectrum by surface modification using chemicals or biomolecules obtained from plants.

Zinc Oxide (ZnO) Nanoparticles in Nanocellulose Composites

Another well-known photocatalytic component of nanocellulose composites is zinc oxide, which finds widespread usage in antimicrobial and pollution degrading applications. ZnO is better at absorbing visible light than TiO_2 because its band gap is narrower. Nanocellulose composites enhanced by ZnO nanoparticles degrade organic colours and pharmaceutical impurities more efficiently than nanocellulose alone. Nanocellulose composites containing zinc oxide (ZnO) have several potential uses, including antimicrobial coatings for medical equipment and packaging, air and water purification, and other similar endeavours. By preventing particle aggregation and maintaining a large surface area for continuous photocatalytic activity, nanocellulose can greatly enhance the stability and reusability of ZnO.

Graphitic Carbon Nitride ($g\text{-}C_3N_4$) in Nanocellulose Composites

Graphitic carbon nitride, or $g\text{-}C_3N_4$, is a great option for renewable energy uses including hydrogen generation and carbon monoxide reduction because of its visible-light photocatalytic activity. In comparison to TiO_2 and ZnO, the metal-free photocatalyst $g\text{-}C_3N_4$ is more efficient for solar-driven reactions due to its distinctive layered structure and absorption spectra that extend into the visible light area. By improving charge carrier separation and easing electron transfer processes, $g\text{-}C_3N_4$, when added to nanocellulose composites, boosts the photocatalytic activity. In addition, the stability and durability of $g\text{-}C_3N_4$ are well-known, and the composite is made more durable for long-term usage with the inclusion of nanocellulose, which offers mechanical reinforcement. Solar hydrogen generation, CO_2 reduction, and visible light degradation of environmental pollutants are all areas where these composites have potential (Zahraa O, Bouchy M. 2001).

Synergistic Effects of Nanocellulose and Photocatalytic Materials

Nanocellulose has several uses and can enhance the performance and adaptability of photocatalytic materials, making it an ideal ingredient for photocatalytic composites. Photocatalytic compounds may be dispersed and stabilised using nanocellulose as a matrix due to its renewable nature, large surface area, and outstanding mechanical qualities. Improved interaction between the matrix and photocatalytic nanoparticles is achieved by functionalising the photocatalysts at places on the nanocellulose surface that contain natural hydroxyl groups. Nanocellulose also improves light absorption and photocatalytic reaction efficiency by increasing the accessible surface area for adsorption of reactants, which boosts photocatalytic performance. The photocatalysts are kept well-dispersed due to the structural features of nanocellulose, which also inhibit nanoparticle aggregation. This improves their stability and lifetime.

Films, membranes, and coatings are just a few of the many uses for nanocellulose composites due to their adaptability. While designing photocatalytic materials for use in bendable electronics, sensors, and surfaces that clean themselves, this flexibility will be invaluable. Since there is an urgent demand for environmentally benign and sustainable materials, these composites are very attractive in environmental applications due to the biodegradability and non-toxicity of nanocellulose.

Applications of Nanocellulose-Based Photocatalytic Composites

Environmental Remediation: Degradation of organic contaminants, dyes, and medicines in wastewater is facilitated by photocatalytic composites based on nanocellulose. By converting light into reactive oxygen species (ROS), photocatalysts can degrade hazardous pollutants into less dangerous byproducts, such as hydroxyl radicals (•OH) and superoxide ions ($O_2\bullet^+$). Since these composites can be powered by visible light, they are both environmentally friendly and energy efficient, making them ideal for use in solar-driven wastewater treatment systems.

Energy Conversion and Storage: For energy-related uses, such as photocatalytic hydrogen generation from water splitting and CO_2 reduction to create compounds with added value, photocatalytic composites based on nanocellulose are also being investigated. The composites are highly suitable for photocatalytic water splitting, an exciting technique for sustainable hydrogen generation, due to their high light absorption and electron-hole pair generation capabilities. Furthermore, dye-sensitized or perovskite solar cells can have their light-harvesting capabilities and recombination losses reduced by including these composites within the cell (Li J, Tan S, Xu Z. 2020).

Antimicrobial and Self-Cleaning Coatings: For example, photocatalytic nanocellulose composites have antimicrobial characteristics that make them a great choice for food packaging, medical device antimicrobial coatings, and self-cleaning surfaces. To achieve sterilisation without the use of chemicals or harsh detergents, nanocellulose matrices coated with photocatalytic nanoparticles (e.g., silver or zinc oxide) can destroy microorganisms when exposed to light. Healthcare and food safety are two areas that stand to benefit greatly from this use.

CONCLUSION

As a greener, more environmentally friendly option for environmental cleanup and other industrial uses, photocatalytic phytogenic nanocellulose composites are an encouraging step towards more sustainable materials. By combining nanocellulose's inherent characteristics with photocatalytic agents, these composites improve their antibacterial activity, self-cleaning capabilities, and ability to degrade contaminants. Wastewater treatment, biomedical applications, and packaging are just a few of the many areas that might benefit from the phytogenic synthesis method's biocompatibility, reduced toxicity, and alignment with green chemistry principles. Their mechanical strength, stability when exposed to light, and large surface area all contribute to their excellent functional qualities. Optimisation of synthesis techniques, improvement of long-term stability, and scaling up production for commercial viability remain hurdles, nevertheless. Investigations into novel phytogenic sources, integration of multifunctional features, and optimisation of photocatalytic performance should characterise future studies. In sum, these composites provide a long-term, efficient solution to technical and environmental problems, opening the door to novel nanotechnology uses.

References

1. Sajab MS, Chin SX. (2015) Cellulose nanofibrils: a rapid adsorbent for the removal of methylene blue. RSC Advances. 5(24):18204-18212.
2. Abdelhamid HN. (2024) Nanocellulose-based materials for water pollutant removal: A review. International Journal of Molecular Sciences. 25(15):8529.
3. Jalil AA, Abdulrasheed AA. (2019) A review on recent progression of photocatalytic desulphurization study over decorated photocatalysts. Journal of Industrial and Engineering Chemistry. 74:172-86.
4. Chand P, Singh V, Kumar D. (2020) Rapid visible light-driven photocatalytic degradation using Ce-doped ZnO nanocatalysts. Vacuum. 178:109364.
5. Sreekala MS, Thomas S. (2018) Polymeric biomaterials: State-of-the-art and new challenges. InFundamental biomaterials: polymers. Woodhead Publishing, pp. 1-20.
6. Sharma A, Khamidun MH. (2022) Photocatalytic degradation of disperse azo dyes in textile wastewater using green zinc oxide nanoparticles synthesized in plant extract: A critical review. Journal of Water Process Engineering. 47:102705.
7. Berglund L, Oksman K. (2020) Water purification ultrafiltration membranes using nanofibers from unbleached and bleached rice straw. Scientific Reports. 10(1):11278.
8. Kala LD, Subbarao PM. (2018) Estimation of pine needle availability in the Central Himalayan state of Uttarakhand, India for use as energy feedstock. Renewable Energy. 128:9-19.
9. Awad MA, Abou-Zeid RE, Fouda A. (2020) Multifunctional cellulose nanocrystal/metal oxide hybrid, photo-degradation, antibacterial and larvicidal activities. Carbohydrate polymers. 230:115711.
10. HC AM, Zerefa E, Abdisa E. (2020) Porous PVA/Zn–Fe–Mn oxide nanocomposites: methylene blue dye adsorption studies. Materials Research Express. 7(6):065002.
11. Li R, Zhang L, Wang P. (2015) Rational design of nanomaterials for water treatment. Nanoscale. 7(41):17167-17194.
12. Kim IS, Bechelany M. (2019) Nanofibers as new-generation materials: From spinning and nano-spinning fabrication techniques to emerging applications. Applied Materials Today. 17:1-35.
13. Farooqi ZH, Din MI. (2020) Environmentally benign extraction of cellulose from dunchi fiber for nanocellulose fabrication. International journal of biological macromolecules. 153:72-8.
14. Zahraa O, Bouchy M. (2001) Decolourization of textile industry wastewater by the photocatalytic degradation process. Dyes and pigments. 49(2):117-25.
15. Li J, Tan S, Xu Z. (2020) Anisotropic nanocellulose aerogel loaded with modified uio-66 as efficient adsorbent for heavy metal ions removal. Nanomaterials. 10(6):1114.