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A Comprehensive Review on Green Synthesis of ZnO Nano Particles and its Applications in Photocatalysis

Dr. Santosh Kumar Nathsharma¹

¹Lecturer in Chemistry, Stewart Science College, Cuttack, Odisha

Abstract

One of the biggest issues facing humanity globally is water pollution. The discharge of untreated wastewater from urbanisation and population growth poses a serious danger to natural water supplies. Metal oxide is one of the most often used photosensitive catalysts in the photocatalysis process, which breaks down pollutants. Instead of using metal oxide in its bulk form, nanosized metal oxide is being employed to boost the photocatalytic activity. This review highlights the significant potential of green-synthesized ZnO nanoparticles (ZnO NPs) in photocatalytic applications. Various plant-based methods, including the use of brinjal calyxes and rosin from Pinus latteri, have demonstrated eco-friendly, low-cost, and efficient routes for ZnO NP synthesis. Overall, green synthesis offers a sustainable alternative to conventional chemical methods, producing highly active and environmentally benign nano catalysts. This makes green-synthesized ZnO NPs as promising candidates for wastewater treatment and broader environmental remediation efforts.

Keywords; Metal oxide, Water pollution, Photocatalytic process, Green synthesis, Advanced oxidation processes (AOPs), Zinc oxide nanoparticle (ZnO NPs), etc.

INTRODUCTION

Urbanisation and population growth pose a serious danger to natural resources. According to statistics, approximately 1.2 billion individuals lack access to pure potable water, and millions of individuals have died as a result of maladies caused by contaminated water [1]. The wastewater from a variety of businesses is a major cause of pollution in natural waterways. The World Bank estimates that almost 20% of water contamination is caused by textile dyeing and treatment wastewater [2], [3]. Numerous hazardous chemicals found in the discharged industrial effluent have the potential to damage aquatic life as well as humans. Chemical coagulation is used after a biological process in a traditional wastewater treatment procedure [4]. The techniques used by this treatment unit are efficient in treating a variety of contaminants, but they are expensive since they need specialised equipment and a lot of energy. Additionally, the production of a lot of by-products causes issues with proper disposal [5], [6]. As a result of these issues, the primary focus of textile effluent remediation has shifted to advanced oxidation processes (AOPs). "The hydroxyl radical" is created and used as a potent oxidant in this process to break down the compounds until all of the ingredients have broken down or mineralised into carbon dioxide and water [7]. Photocatalysis is the most often studied AOPs process. Due to its environmentally benign and detoxifying properties, photocatalysis, which adopt "semiconductor materials like titanium dioxide (TiO₂), zinc oxide (ZnO), and iron oxide", is becoming more popular for treating wastewater [8], [9].

Many contaminants are now emitted into the environment as a result of industrial growth. The textile industry is one of the sources of organic pollution, which is harmful to both humans and the environment. Numerous methods, such as membrane filtration, adsorption, enhanced oxidation, coagulation combined with sedimentation, biological processes, catalysis, and photocatalysis, have been suggested to remove organic contaminants from water [10].



The complete removal of organic pollutants has been the subject of much investigation due to the advantages of using semiconductors as photocatalysts. Semiconductors may speed the complete degradation of organic materials when they are activated by light that has an energy value higher than their bandgap [11]. TiO2 and ZnO are two common semiconductors used as photocatalysts. Because ZnO absorbs more light in the ultraviolet spectrum, it has a better quantum efficiency than TiO₂. ZnO is also an inexpensive photocatalyst that exhibits strong photocatalytic activity, stability, light sensitivity, and nontoxicity [12]. Organic compounds may undergo photodegradation with the use of ZnO catalysts when exposed to light. Since light with an energy greater than the ZnO bandgap drives electrons from the valence band (VB) to the conduction band (CB), "photogenerated holes form in the VB and photogenerated electrons form in the CB" [13]. Organic materials are oxidised by the O2. and OH radicals that are produced when these photogenerated electrons and holes move to the surface of ZnO and react with H2O and O2. Furthermore, ZnO nanoparticles (NPs) are harmless to human cells, have a high biocompatibility, and have strong antibacterial action against bacteria. Numerous investigations have shown ZnO's antibacterial properties, as well as the fact that nanoscale ZnO exhibits stronger antibacterial activity than big ZnO [14].

Numerous methods for creating materials at the nanoscale have been studied. Out of these methods, chemical and physical pathways have their own drawbacks, including negative environmental impacts brought on by the use of substances that are not ecologically friendly or by the discharge of heat into the atmosphere [15]. Thus, the creation of environmentally friendly methods is required. As an alternative method of producing nanomaterials, the biosynthetic process, which employs plant extracts, is a feasible option due to its rapid turnaround time, low cost, and environmental safety. Green techniques have been used in several investigations to synthesise ZnO nanoparticles from seaweeds, fruits, plants, and plant extracts [16].

Numerous firms throughout the world are very interested in nanotechnology. It is described as an area of study that focusses on creating materials that are very small—within the nanometre range. Since their characteristics vary from those of their bulk counterparts, nanomaterials are special [17]. They have a higher relative surface area because of their tiny size, which improves their qualities. The two primary methods for obtaining nanomaterials are the "top-down" and "bottom-up" techniques. Large materials are

broken down into nanoparticles in the "top-down" method [18]. This approach, however, produces particles with a broad range of sizes and morphologies. Growing nanoparticles from a single atom is known as the "bottom-up" strategy, and it is much more prevalent in the synthesis of nanomaterials [19]. Better size and form nanoparticles were produced as a consequence of this method, which is advantageous for certain applications. Green synthesis has received increased attention in the synthesis process in recent years. Generally speaking, green synthesis uses safe, non-toxic, and ecologically friendly chemicals. In this synthesis process, the total cost decreased since no more chemicals were required [20].

Photocatalytic process

Since almost entire pollutants have been successfully degraded in the past, "advanced oxidation processes (AOPs)" are one of the newer methods for treating wastewater. AOPs may degrade pollutants by producing reactive oxygen species, including hydroxyl (·OH) and superoxide (O₂-) radicals. The creation of these radical species may occur in a number of ways [2]. The Fenton process, photocatalysis, ozonation, and photolysis are the four most prevalent and well-known routes. Ozonation and photolysis are processes that produce radical species by combining hydrogen peroxide with UV and ozone, respectively [21]. The Fenton method, which uses hydrogen peroxide and ferrous ions as a catalyst, is now used in wastewater treatment. The last process is photocatalysis, which uses materials that absorb light, like semiconductors, to create radical species. Due to the fact that photocatalysis uses sustainable solar energy and doesn't need the use of chemicals, it has been gaining traction among these four techniques. As a result, photocatalysis is regarded as a sustainable and green process [22].

Using a photocatalyst to speed up a photoreaction is known as photocatalysis in chemistry. Reaction intermediates are frequently formed by the interaction between the excited phase of the photocatalyst and the reaction partners, and the excited state regenerates itself after every cycle of such interactions [23]. Electron-hole pairs are frequently generated by solid catalysts when they are subjected to "visible or ultraviolet light", which results in Free radicals. The three main types of photocatalysts are "heterogeneous, homogeneous, and plasmonic antenna-reactor catalysts". The needed catalytic reaction and the desired application determine which catalyst is used [24].





Green synthesis metal oxide nanoparticles

Nanoparticle synthesis has been the subject of recent research that has concentrated on the green chemistry pathway. For the production of nanoparticles, this pathway employs biological entities, including plants, microorganisms, and carbohydrates. Previous studies synthesised demonstrated that nanomaterials from renewable materials exhibited superior morphology and size [25]. Additionally, the green synthesis process offers numerous benefits, including its simplicity, ease, economy, and mildness. The focus of this section will be on greenly synthesised metal oxide nanoparticles, such as "iron oxide nanoparticles (IONPs), zinc oxide nanoparticles (ZnO NPs), and titanium dioxide nanoparticles (TiO2 NPs)", for the purpose of photocatalytic pollution degradation [26]. The use of the green synthesised metal oxide nanoparticles with corresponding green agent for photocatalytic degradation is shown in **Table 1** [2].

ZnO NPs, or zinc oxide nanoparticles, are an interesting choice for the photocatalytic degradation of colours. Despite being typically synthesised, zinc oxide (ZnO) may be discovered in nature as "the mineral zincite" in the earth's crust [27]. An n-type semiconductor, ZnO exhibits a high percentage of UV absorption, a wide direct band gap width (3.37 eV), and "a substantial excitation binding energy (60 meV)". The wurtzite structure has the thermodynamic coefficient among its three crystal structures, which are rocksalt, wurtzite, and cubic (zinc mix). In 200 minutes, the synthesised sample was able to destroy Rhodamine B dye by up to 98%. Pullulan, a biopolymer, was used in our earlier work to produce "ZnO NPs". Within 60 minutes, the dyes rhodamine B and methyl orange were effectively degraded under UV light [28].

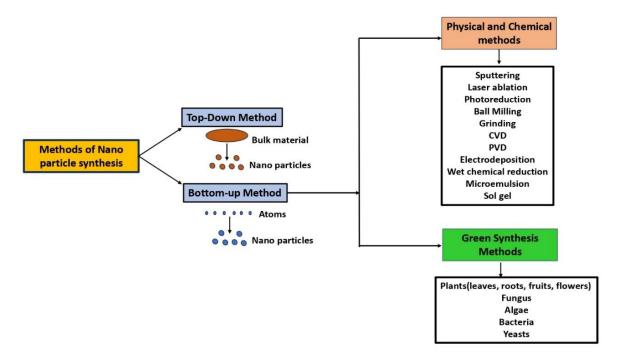
Table 1 Greenly produced metal oxide nanoparticles and their use in photocatalysis [2]

Biomaterial	Size and morphology	Pollutants	Photodegradation	Light irradiation
Abelmoschus esculentus mucilage	Spheres and rod like 29 – 70 nm	Methylene Blue Rhodamine B	95 % (60 min) 100 % (50 min)	UV
Eucalyptus Leaf extract	Agglomerated particles	Malachite green	90 % (60 min)	UV
Averrhoe carrambola fruit extract	Flake like 20 nm	Congo red	93 % (180 min	UV
Cynara scolymus leave extract	Spherical 66 nm	Methyl violet Malachite green	94 % (120 min) 90 % (120 min)	UV
Punica granatum leaves extract	Spherical 10 – 30 nm	Coomassie brilliant blue R-250	~89 % (180 min	Visible
Cyanometra ramiflora leaves extract	Nanoflowers	Rhodamine B	98 % (200 min)	Visible

Different approaches for synthesis of NPs

NP synthesis may be done in two main ways: "top-down" and "bottom-up" ("Figure 1). Size reduction, which dissolves bulk material into tiny particles top-down, is how NPs are made. This approach may be carried out by a variety of physical and chemical procedures, including lithography, mechanical "(such as milling and grinding), sputtering, chemical etching, thermal evaporation, pulsed laser ablation, and photoreduction" [29]. One major problem with the top-down approach, however, is that the surface structure is not complete. The bottom-up approach uses a variety of methodologies, including "sol-gel chemistry, chemical

vapour deposition (CVD), coprecipitation, microemulsion, pyrolysis, hydrothermal, solvothermal, radiation-induced, and electrodeposition techniques, in addition to wet chemical procedures (such as chemical reduction/oxidation of metal ions)" [30]. "Atoms, molecules, and smaller particles" are assembled into NPs through bottom-up synthesis, which is also known as the self-assembly approach. Nevertheless, they are unfavourable due to the "high investment costs, environmental toxicity, high energy demands, lengthy response times", and non-ecofriendly residues resulting from the use of potentially dangerous and noxious ingredients [31].



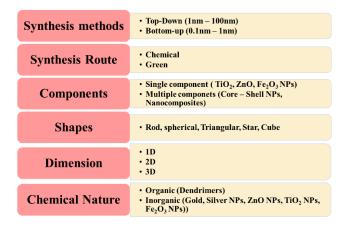
"Figure 1 Different methods of NP synthesis"

Green synthesis philosophy developed naturally as many terms and ideas came together and separated to form a web of green chemistry. The interconnectedness of the several sub disciplines of green synthesis is shown in "Figure 2. There isn't enough room in the "nano" cosmos to fit into one mode. Consequently, "the size, shape, content, homogeneity, and aggregation" of NPs are among the characteristics that determine their categorisation. The various modes of classification of NPs using several conventional techniques is shown in "Figure 3.

A diameter of less than 100 nm is a characteristic of zinc oxide (ZnO) nanoparticles. In comparison to their size, they have a large surface area and strong catalytic activity. The exact chemical and physical properties of zinc oxide nanoparticles are influenced by the many techniques employed to produce them [32]. Potential methods for the production of ZnO nano-particles include "laser ablation, hydrothermal methods, electrochemical depositions, sol-gel method, chemical vapour deposition, thermal combustion decomposition, methods, ultrasound, microwave-assisted combustion method, two-step mechanochemical-thermal synthesis, anodisation, coprecipitation, electrophoretic deposition, and precipitation processes that utilise solution concentration, pH, and washing medium". At ambient temperature, ZnO has an energy gap of 3.37 eV, making it a wide-bandgap semiconductor [33].



"Figure 2 The web of green chemistry displays alternative nomenclature for eco-friendly methods."



"Figure 3 Various modes of classifications of NPs."



LITERATURE REVIEW

(Ounis Dkhil et al., 2025) [34] "Zinc oxide nanoparticles (ZnO NPs)" were produced utilising a straightforward and environmentally friendly precipitation process using a chia seed (Salvia hispanica)-based capping agent. Under UV-LED irradiation, the synthesised ZnO NPs' capacity to para-nitrophenol (4-nitrophenol, PNP) destroy diclofenac sodium (DCF) was used to assess their photocatalytic efficiency; they achieved elimination rates of over 98%. By thoroughly characterising the reaction intermediates, the degradation process is made clear. These results demonstrate the possibility for efficient environmental cleanup of organic and pharmaceutical contaminants using ZnO NPs made from chia seed extract.

(Redjili et al., 2025) [35] Uses "leaf extract as a natural reducing agent" to create ecologically friendly zinc oxide nanoparticles (ZnO NPs) and evaluates their antibacterial and photocatalytic properties. A reduction in band gap energy and an increase in Urbach energy were observed in UV-Vis spectroscopy as "the extract concentration and annealing temperature were increased". antibacterial effectiveness was shown by the ZnO NPs' antimicrobial activity when tested against Candida albicans and "both Gram-positive and Gram-negative bacteria". Studies on the photocatalytic degradation of methylene blue dye showed that the annealed samples had a higher efficiency of up to 74%, especially at 500 °C. According to this study, "green-synthesized ZnO NPs" have a lot of potential uses, such as environmental catalysis, water purification, and antibacterial agents. By providing viable answers for both technical and ecological problems, it advances sustainable nanotechnology.

(Zango et al., 2025) [36] This study thoroughly investigates the green production pathways, modifications, and catalytic uses of ZnO nanoparticles in order to address important environmental issues. Furthermore, the paper includes a thorough analysis of the use of "ZnO-based photocatalysts" for the breakdown of various organic pollutants, such as "dyes, medications, phenolic compounds, herbicides, pesticides, PAHs, and PFAS". Clarifying the mechanics behind these degradation processes provides insights into the variables affecting photocatalyst effectiveness. The review ends by highlighting ZnO nanoparticles' promising potential as environmentally friendly photocatalysts and the need for further study to improve their functionality and address real-world application issues.

(Avinash et al., 2024) [37] Aloe vera latex extract (Avle) was used as the fuel in a bio-combustion process to create

the nanocrystalline zinc oxide (ZnO). It was discovered that "the acid red-88 (AR-88) dye" was active at 500 nm when used to assess "ZnO's photo-degradation capabilities". When exposed to UV light for 120 minutes, the photodegradation rate of the AR-88 dye decreased its colour by as much as 75.8%. The cyclic voltammetry data indicates that ZnO NPs have outstanding electrochemical properties. The proton diffusion coefficient of ZnO electrode material was determined to be $9.30 \times 10-5 \mathrm{cm}2\mathrm{s}-1$. Based on its electrochemical behaviour, ZnO is a good electrode catalyst for detecting substances like glucose and paracetamol.

(Mousa et al., 2024) [38] Through a chemical process, zinc oxide nanoparticles (ZnO NPs) were successfully synthesised from "pomegranate (P.M.), beetroot (B.S.), spinach, and a diverse array of plant extracts" in this study. Beetroots were employed to produce the most efficient ZnO NPs, which exhibited "a degradation efficiency of $87 \pm 0.5\%$ and a kinetic rate constant of $0.007 \, \text{min}{-}1$ ". "The ratio of the two intensity (0 0 2) and (1 0 0) crystalline planes" was also examined in order to pinpoint a certain orientation in (0 0 2) that is linked to the formation of oxygen vacancies in ZnO, which enhances their photocatalytic activity. Effective charge transfer and enhanced absorption of light by "the inter-band gap states" are also responsible for the rise in photocatalytic efficacy.

(Shubha et al., 2024) [39] Explain how ZnO nanoparticles (ZnO-CB NPs) are made using the solution combustion method and "an aqueous extract of brinjal calyxes as fuel". For ecological applications like wastewater treatment, the synthesised ZnO-CB NP shows great promise as a photocatalyst, with removal efficiencies of "99.3%, 99.6%, and 99.5% of the MG, BB1, and AO36 dyes, respectively". In addition, "the methyl ester of Millettia pinnata oil (MPME)" was blended with commercial diesel (MPME20) to incorporate the synthesised ZnO-CB NP as a component. In order to investigate the impact of the synthesised ZnO-CB NP on the purity of emissions of various greenhouse gases, such as "hydrocarbons, COx, and NOx, it was introduced to the MPME20" in varying concentrations.

(S. Singh & Jain, 2024) [40] UV-vis spectroscopy reveals that the resulting "Aloe Vera-assisted ZnO nanoparticles (AL-ZnO)" have important optical characteristics, including "a semiconductor behaviour with an absorption peak at 310 nm". In photocatalysis, AL-ZnO has exceptional catalytic ability, degrading methylene blue completely in 105 minutes under mild sunshine. Aloe vera-assisted ZnO NPs are now potent catalysts for ecologically friendly water treatment, marking a significant breakthrough in green synthesis.





Strong light-refracting characteristics and high optical conductivity are also shown by the optical properties of Aldoped ZnO nanoparticles. This makes them perfect candidates for use in light-emitting devices and solar cells, advancing the technologies of renewable energy. The study essentially identifies "ZnO NPs aided by aloe vera as versatile", potent catalysts with important ramifications for green synthesis in general and ecologically aware water treatment in particular.

(Nemma & Sadeq, 2023) [41] The study's simple, economical, and environmentally friendly synthetic method "Ag NPs, ZnO NPs, produced and nanocomposites" with success. In order to investigate the photo-degradation activity of Ag/ZnO nanocomposites on Methylene Blue (MB) dye, two distinct plant extracts were used in their synthesis. (FE-SEM) findings showed clustering of NPs with variable shapes and spherical nanorods. The distinct photodegradation properties of the resultant metal/semiconductor oxide nanocomposites were not present in the individual Ag NPs and ZnO NPs.

(Nhu et al., 2022) [14] "Zinc oxide nanoparticles (ZnO NPs)" were successfully synthesised in a green manner using rosin and zinc chloride as salt precursors. Methylene blue (MB) and methyl orange (MO) were photodegraded by ZnO NPs acting as catalysts in visible and ultraviolet light. With a ZnO NP dose of 2 g/L and 210 minutes under UV light, the results demonstrate that the generated ZnO material efficiently removed "MB and MO (cinitial = 10 mg/L) with efficiencies of 100% and 82.78%, respectively". Under the same circumstances, the synthesised material's photocatalyst activity was also examined; however, it produced lower efficiencies. In experiments on the antibacterial activity of ZnO NPs, the generated ZnO samples demonstrated the highest (i.e., 100%) antibacterial efficiency against E. coli.

(Kahsay et al., 2019) [42] Using "Dolichos Lablab L. aqueous leaf extract as the capping and decreasing agent", we present a straightforward one-pot green production process for zinc oxide (ZnO) nanostructures. Using the synthesised ZnO nanostructures as "a catalyst, methylene blue (MB), rhodamine B (RhB), and orange II (OII)" underwent photodegradation under visible and near-UV light. The findings demonstrated that, during a 210-minute period, the "photodegradation of ZnO nanostructures was most efficient for MB (80%), RhB (95%), and OII (66%), at pH values of 11, 9 and 5 respectively". Furthermore, the antibacterial nanostructures' efficacy against **Sphingomonas** paucimobilis and Bacillus pumilus employing the agar well diffusion technique revealed the maximum zones of inhibition, "measuring 18 mm and 20 mm, respectively". As a result, ZnO nanostructures may find use as bactericidal and photocatalyst components.

CONCLUSION

As a result, this study emphasises the considerable potential of green-synthesised "ZnO nanoparticles (ZnO NPs) for photocatalytic uses". Various plant-based methods, including the use of brinjal calyxes and rosin from Pinus latteri, have demonstrated eco-friendly, low-cost, and efficient routes for ZnO NP synthesis. These greensynthesized ZnO NPs have shown excellent photocatalytic degradation capabilities against several hazardous dyes such as malachite green (MG), brilliant blue (BB1), acid orange 36 (AO36), methylene blue (MB), methyl orange, and acid red 88 (AR-88). Among the different nanostructures, Ag/ZnO nanocomposites (NCs) synthesized using plant extracts exhibited superior photocatalytic activity compared to pure Ag or ZnO NPs. Notably, ZnO NPs prepared through green methods also demonstrated shorter half-lives and higher degradation efficiencies under UV light compared to visible light. Overall, green synthesis offers a sustainable alternative to conventional chemical methods, producing highly active and environmentally benign ZnO NPs which acts as a promising candidate for wastewater treatment and broader environmental remediation efforts.

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