

Green Synthesis of ZnO Nanoparticles Using *Anogeissus pendula* Extract and Their Application in Dye Degradation

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Abstract

Zinc oxide nanoparticles (ZnO NPs) generation via a biogenic route is a sustainable and eco-friendly alternative to conventional chemical approaches. Herein, we report a controlled precipitation-calcination method for the synthesizing ZnO NPs using zinc acetate as the precursor along with an aqueous *Anogeissus pendula* leaf extract acting as both the reducing and stabilizing agent. The ZnO nanoparticles exhibited excellent photocatalytic activity for the degradation of methylene blue (MB) under solar light.

Numerous spectroscopic and structural techniques were employed to verify the formation of nanoparticles. A peak at 368 nm in UV-visible spectrum and an optical band gap of a 3.21 eV attests to its semiconducting properties. FTIR studies demonstrated that phytochemicals had functionalized the nanoparticles surface, providing capping and stabilization. Hexagonal wurtzite phase of the sample was confirmed by XRD analysis. Quasi-spherical shape with size of 28-45 nm was detected in SEM analysis.

The photocatalytic performance of the biogenic ZnO was assessed at pH 9, with 0.75 g L⁻¹ of catalyst and 10 mg L⁻¹ MB. Dye degradation of 97.3% within 90 min of solar irradiation was achieved. The reaction followed pseudo-first-order kinetics ($k = 0.040 \text{ min}^{-1}$). Total organic carbon measurements showed 76.4% mineralization indicating real oxidative decomposition and not just bleaching of the chromophore. Hydroxyl radicals and superoxide anions were found to be key reactive species in the dye degradation. ZnO photocatalyst exhibited good stability for multiple cycles.

In sum, the results make a case for *Anogeissus pendula*-derived ZnO nanoparticles as an effective, stable and environmentally friendly photocatalyst for breaking down organic pollutants in the presence of sunlight.

In short, the results speak to *Anogeissus pendula*-derived ZnO NPs as an effective and recyclable photocatalyst for dealing with dye-laden wastewater. With the kind of stability and solar-driven performance on display, they are well suited to the demands of advanced water treatment and other applications in environmentally sound nanotechnology.

Keywords: *Anogeissus pendula*; zinc oxide nanoparticles; green synthesis; methylene blue; photocatalytic degradation; wastewater treatment; solar irradiation; nanomaterials

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1. Introduction

It is an environmental problem of some magnitude that the textile, leather, paper, pharmaceutical, printing and cosmetic industries, to name but a few of the allied manufacturing sectors, are discharging synthetic dyes. One finds the longevity of a good many dye molecules in their aromatic frameworks, which are so well stabilized as to defy the normal course of biological degradation. In an aquatic

environment, coloured effluents need be present only in modest amounts to put a damper on light penetration and photosynthesis, change the way dissolved oxygen behaves and produce transformation products of a toxic nature. Methylene blue (MB) is a case in point. Of the cationic dyes in common use, MB is often put forward as a model pollutant for wastewater treatment work; its intense

visible absorption and chemical recalcitrance make it highly stable in aqueous solution.

One might turn to coagulation, adsorption, membrane separation or other conventional means to put down the level of dye, but such methods do not mineralise the contaminant so much as move it from one phase to the next. Heterogeneous photocatalysis is therefore of great interest as an oxidative remedy that will break organic pollutants down into something less noxious. With semiconductor-mediated photocatalysis in particular, the application of energy at or above the band gap of the semiconductor yields electron-hole pairs to set off redox reactions on the catalyst surface. When semiconductor materials are photoexcited, electron-hole pairs are produced which in turn can be involved in redox reactions of a subsequent nature. This gives rise to reactive oxygen species (ROS) such as the superoxide anion radical ($O_2^{\bullet-}$) and hydroxyl radical ($\bullet OH$).

That said, the efficacy of the process is a function of a host of operational factors: the pH and intensity of the light, the amount of catalyst and pollutant present, how the solution behaves in terms of adsorption and surface charge, and recombination rates of electrons and holes. Akpan and Hameed (2009) have shown these to be of consequence in dye degradation, and Azeez et al. (2018) made the case for surface charge being determinative of methylene blue's adsorption and degradation. It is thus necessary to be judicious in experimental optimisation and catalyst design.

Zinc oxide (ZnO) is perhaps the best known of the semiconductor photocatalysts that have been put to the test. Its appeal lies in a combination of factors: it is inexpensive and easy to make, possesses good chemical robustness and high electron mobility, has an oxidizing potential to speak of and a band-gap energy that is suitably wide. Put in a nanostructured form, the surface-to-volume ratio of ZnO is considerably higher, putting more catalytically active sites at the disposal of ROS production and making for better adsorption of contaminants on the catalyst interface. All told, this makes of ZnO an excellent choice for photocatalytic remediation. Photo- and sonocatalytic routes have been used to good effect with ZnO nanoparticles in degrading organic dyes (Paul et al., 2017; Sharma, 2016). Yet the normal way of synthesising ZnO involves recourse to organic solvents, powerful reducing or stabilising agents and other reagents which can leave unwanted secondary residues, calling for more sustainable methods.

In plant-assisted green synthesis one has a safer alternative. Then there is the matter of green

synthesis by way of plants, a method gaining ground as a more sustainable and less hazardous option than what is conventionally done chemically. Here one relies on phytoconstituents, be they tannins, phenolic or flavonoid compounds, terpenoids, carbohydrates or proteins, to act in the capacity of reducing or capping agents and to direct morphology. Such biomolecules come into contact with metal ions in the course of nucleation and particle growth and so determine the physicochemical parameters of the material, from its size and crystallinity to its surface chemistry and overall architecture. In this manner the plant-assisted route provides a degree of control over the nanomaterials' structural properties while doing away with the toxicological and environmental issues of other methods. They will engage with metal ions in the course of nucleation and growth and in doing so determine the particle's size, crystallinity, surface chemistry and the like. Bandeira et al. (2020) would describe this as a versatile approach where the extract and conditions of synthesis are paramount, and Khari et al. (2019) have pointed out the influence of the biological source on the characteristics of the nanoparticle. Al-Darwesh et al. (2024) in recent reviews have drawn attention to the part played by plant metabolites in the formation of ZnO and the wider applications of biogenic nanoparticles.

A number of plant species have been put to use in the green synthesis of ZnO. *Solanum nigrum* leaf extract was used by Ramesh et al. (2015) to obtain ZnO nanoparticles; Barzinjy and Azeez (2020) have reported on their formation with *Eucalyptus globulus*. There is evidence from Chaudhuri and Malodia (2017) of biosynthesis with *Calotropis gigantea*, and Vijayakumar et al. (2018) found that ZnO mediated by *Atalantia monophylla* had antimicrobial as well as photocatalytic properties. Suresh et al. The work of (2015) is an example of this, having made use of *Artocarpus gomezianus* to produce a plant-assisted ZnO with luminescent, antioxidant and photocatalytic attributes. One could say these studies in their entirety show that the botanical precursor does more than stand in for synthetic chemicals; it has an active hand in dictating the functional behaviour and physicochemical properties of the nanomaterial that is formed.

There is a growing tendency in recent investigations to put biological precursors to good use in order to see better photocatalytic efficiency. Nhu et al. (2022) put forward evidence of very efficient photocatalytic behaviour in green-synthesized ZnO, and Supin et al. (2023) found performance to be on a par with what was expected from ZnO nanoparticles made with leaf extract of *Lepidagathis ananthapuramensis*. The case for dye remediation

with plant-extract-mediated ZnO photocatalysts was made by Tanwar et al. (2022) in a review of the subject. This has been borne out by more recent work: Alprol et al. (2024) have reported on the removal of methylene blue with biologically synthesized ZnO; Chan et al. (2024) have shown the utility of plant-extract ZnO for degrading organic pollutants; Abegunde et al. (2024) found Congo red to be effectively eliminated by green ZnO from *Nauclea latifolia*. And Yadav et al. (2024) have documented the biogenic formation of ZnO from *Evolvulus alsinoides*. All of which would suggest that plant-mediated ZnO is an experimentally sound means of remediating wastewater.

Nonetheless, there is scope for research into medicinal or arid-region plants that have yet to be fully explored. *Anogeissus pendula* Edgew. (Combretaceae) is one such candidate of interest, its tissues being rich in bioactive constituents. Danai et al. (2021) noted antimicrobial and antioxidant activity in the stem and leaf extracts of *A. pendula*, pointing to phytochemicals capable of stabilizing nanoparticles and coordinating metal ions. It is worth noting that the genus has already proved itself in the synthesis of nanomaterials. Kora and Rastogi (2012) used gum ghatti of *Anogeissus latifolia* to control the size of silver nanoparticles, and in 2018 they applied the same material to the green synthesis of catalytically active palladium nanoparticles. Mittal & Mishra (2014) have also put gum-ghatti-based nanocomposites to work in adsorbing Rhodamine B. These are reasons enough to look at whether the phytochemistry of *A. pendula* will lend itself to the formation of ZnO nanoparticles and the kind of surface chemistry required for photocatalysis.

Yet one finds little in the way of systematic information on the application of *A. pendula* extract to ZnO synthesis and a thorough appraisal of its dye-degradation credentials. What is called for is an experimental framework that brings together structural and optical characterisation with catalyst-dose optimisation, pH and irradiation-time variables, initial dye concentration, mineralization and degradation kinetics, radical-mechanism and recyclability studies. A high level of discoloration is not in itself proof of mineralization or that a catalyst is fit for environmental purposes over the long term.

In this work we present the green synthesis of ZnO nanoparticles from an aqueous extract of *Anogeissus pendula* leaves and put their ability to photocatalytically break down methylene blue to the test. Characterization of the resulting nanomaterial was done with a number of techniques: UV-visible and Fourier-transform infrared spectroscopy, X-ray diffraction, particle-size analysis as well as scanning electron microscopy in conjunction with energy-

dispersive X-ray spectroscopy. A systematic variation of the irradiation time, solution pH, catalyst dosage and initial dye concentration was put in place to appraise the photocatalytic performance. We then turned to kinetic models and TOC (total organic carbon) determinations for an analysis of the degradation figures, which served to gauge reaction efficiency as well as how much mineralization had taken place. We also undertake radical-scavenging to get at the reactive species at play and run the catalyst through several cycles to test for reusability. In so doing the study is intended to make the case for *A. pendula*-mediated ZnO as a sustainable nanophotocatalyst and to put the connection between its physicochemical nature and dye-remediation in perspective.

2. Research Gap and Study Objectives

The subject of zinc oxide (ZnO) nanoparticle synthesis by means of plants has drawn a good deal of scholarly interest, yet for the most part the literature has been confined to a limited range of plant taxa. One finds in the preponderance of work an emphasis on such medicinally important species as *Solanum nigrum*, *Eucalyptus globulus*, *Calotropis gigantea*, *Artocarpus gomezianus* and *Atalantia monophylla*. Through these efforts it has been put beyond doubt that the phytoconstituents in plant extracts will serve to reduce, cap and stabilise in the course of nanoparticle formation, with an effect on crystallinity, morphology, surface functionalization and photocatalytic output. What has not been so thoroughly probed is the potential of *Anogeissus pendula* as a biological source for ZnO nanoparticles.

This is an oversight of some consequence given that *A. pendula* is replete with bioactive metabolites; phenolic compounds, flavonoids, tannins and other oxygenated phytochemicals are all in evidence, exhibiting the kind of antioxidant and antimicrobial properties that are of use in green nanomaterials. They can be expected to aid in the coordination of zinc ions, nucleation and control of growth as well as stabilization. Other *Anogeissus* have made their mark in the green synthesis of metallic and functional nanostructured materials, but empirical support for turning to the leaf extract of *A. pendula* for the fabrication of ZnO nanoparticles and their deployment in the photocatalytic degradation of organic dyes is hard to come by.

One also notes a methodological shortcoming in much of what has been published: an overreliance on the figure for percentage dye decolorization to the exclusion of mineralization efficiency, the role of reactive species, kinetic behaviour or how well the catalyst can be reused. One cannot take discoloration

as proof in itself of the dye having undergone total structural or molecular breakdown; for that reason a methodology with greater rigour and diagnostic power is called for to put the photocatalytic credentials of the green ZnO to the test. What is needed is a firm link made between the operational results and the physicochemical make up of the biosynthesized substance, so as to appraise the catalytic function on more than the basis of what can be seen by way of decolorization.

With this in mind the present study has been carried out to:

1. Put forward a green precipitation method for the synthesis of ZnO nanoparticles from the aqueous leaf extract of *Anogeissus pendula* ;
2. Put the resulting nanoparticles through characterization by way of UV-visible and FTIR spectroscopy, XRD, particle-size analysis and SEM-EDX;
3. Under varying conditions of pH, irradiation time, initial dye concentration and catalyst dosage, test the photocatalytic degradation of methylene blue;
4. Work out the degradation kinetics and what reactive species are at play in the photocatalysis;
5. By means of TOC analysis, measure the degree of organic carbon mineralization; and
6. See how the stability and reusability of the photocatalyst holds up over a number of treatment cycles.

In essence the investigation is intended to tie together the mechanics of plant-mediated synthesis, the characteristics of the ZnO and its durability under operational stress with its efficiency and mechanistic pathways. In filling the void in current research we hope to make a contribution to the field of green nanotechnology and to the design of sustainable systems for the remediation of wastewater.

3. Materials and Methods

3.1 Preparation of *Anogeissus pendula* Extract and Green Synthesis of ZnO Nanoparticles

Leaves in a state of full maturity and good health from *Anogeissus pendula* were gathered to act as the biological matrix in the green synthesis of zinc oxide (ZnO) NPs. The zinc source was zinc acetate dihydrate $[\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}]$. All other reagents, including sodium hydroxide, HCl, EDTA, benzoquinone, methylene blue, isopropanol and ethanol, were analytical grade and put to use as is; any aqueous solutions were made up with double-distilled water.

To begin, the leaves were put through a thorough wash with tap water then a rinse of double-distilled water so as to be free of surface contaminants or any dust and debris. Once the samples had been cleaned they were left to air-dry in the shade at room temperature over a period of 5 to 7 days before being reduced to a coarse powder. For the aqueous extract, 20 g of this powder was put into suspension with 200 mL of double-distilled water; the solution was then brought to $70 \pm 2^\circ\text{C}$ and held there for half an hour with the aid of constant stirring. A clear brown filtrate was obtained after the mixture had cooled down and passed in turn through Whatman No. 1 filter paper and muslin cloth. In order to limit any degradation of the phytochemicals present, the filtrate was kept at 4°C and put to use no later than 48 hours hence.

A 0.1 M solution of zinc acetate was obtained by dissolving 4.39 g of the dihydrate in 200 mL of double-distilled water. This precursor solution was stirred at some 600 rpm while being brought up to 60°C .

The precursor solution was introduced in a dropwise fashion to 50 mL of *A. pendula* extract. With the mixture being stirred for 20 min, 1.0 M NaOH was put in as needed to bring the pH up to 10; a pale-white precipitate made its way into view, a sign that zinc intermediates were forming.

Next the reaction was left to stir at 70°C for two hours and then aged for 12 h more at room temperature. Afterwards, the precipitate formed was collected by centrifugation (8,000 rpm, 10 min). The solid mass obtained was purified by washing with ethanol and double-distilled water. The washed sample was then dried at 80°C for 12 h, followed by a three-hour calcination in a muffle furnace set to 450°C . After cooling, the white ZnO nanopowder was pulverised and stored in an airtight vessel for later physicochemical and photocatalytic work.

The basis for this green approach is the propensity of oxygenated phytoconstituents in the leaf extract to coordinate with Zn^{2+} ions. One can surmise that tannins, flavonoids and other phenolic secondary metabolites act in a dual capacity as capping and reducing agents to stabilise the new nanoparticles and promote nucleation. In the alkaline environment

zinc hydroxide intermediates will form, which are made into crystalline ZnO by means of the heat treatment.

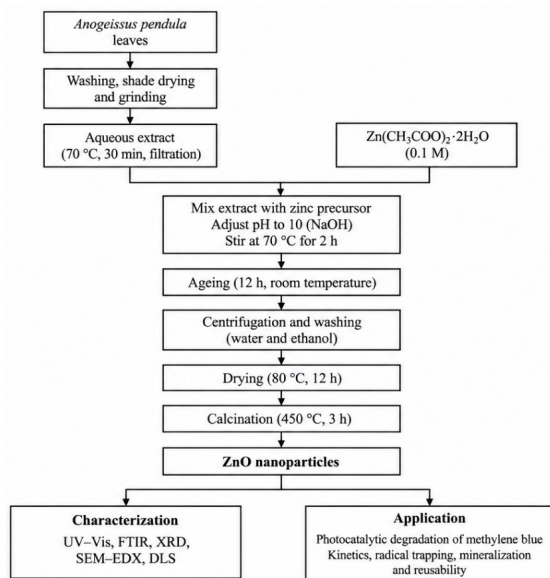


Figure 1. Experimental workflow for the green synthesis and photocatalytic evaluation of ZnO nanoparticles

3.2 Physicochemical Characterization of ZnO Nanoparticles

To put the optical, structural and morphological as well as elemental properties of the ZnO nanoparticles in evidence, the material was subjected to a battery of analytical techniques. The nanomaterial's optical response was probed with ultraviolet–visible (UV–vis) absorption spectroscopy over a 250 to 800 nm span; from this the light-absorption behaviour could be gauged by the tell-tale ZnO absorption edge and the optical band-gap energy was ascertained according to the Tauc formalism:

$$(\alpha h\nu)^2 = A(h\nu - E_g)$$

α is the absorption coefficient, $h\nu$ the photon energy; we have a proportionality constant in A and the optical band-gap energy is given by E_g .

To put an identification on the functional groups of any plant-based organic matter and the like of the characteristic Zn–O vibrational modes, FTIR (Fourier-transform infrared) spectroscopy was done across 4000 to 400 cm^{-1} . A comparison of the spectra from the plant extract with those of the ZnO nanoparticles made it possible to determine which functional groups are at work in the stabilization and formation of the latter.

As for the crystallinity of the product, that was put to the test with X-ray diffraction (XRD) under $\text{Cu K}\alpha$ radiation for a 2θ span of $20\text{--}80^\circ$; the resulting peaks were scrutinized for evidence of a hexagonal wurtzite structure in the ZnO. One can estimate the mean crystallite size from the Debye–Scherrer equation:

$$D = K\lambda / (\beta \cos \theta)$$

with D denoting the mean crystallite size, K the Scherrer constant and λ the wavelength from $\text{Cu K}\alpha$ radiation. The term β represents the full width at half maximum (FWHM) of the diffraction peak under consideration (in radians) while θ is the Bragg angle.

As for the particle morphology and surface texture, these were put under a microscope by way of scanning electron microscopy (SEM). One can also glean from such an analysis the extent of particle agglomeration and other dimensional characteristics. The elemental make up was verified by means of energy-dispersive X-ray spectroscopy (EDX), zinc and oxygen being of particular interest. For the ZnO suspension in an aqueous medium, dynamic light scattering (DLS) was carried out to determine the hydrodynamic size distribution and so one could gauge the dispersion and colloidal stability.

3.3 Photocatalytic Degradation of Methylene Blue

To assess the photocatalytic activity of the ZnO nanoparticles produced by green synthesis, methylene blue (MB) was taken as a representative organic pollutant. Working solutions for the degradation studies were made by diluting a 100 mg L^{-1} stock of MB in double-distilled water.

In the course of the photocatalytic assay, 75 mg of the ZnO nanoparticles were put into 100 mL of 10 mg L^{-1} MB solution to give a catalyst loading of 0.75 g L^{-1} . The suspension was left to stand in the dark with magnetic stirring for a half hour before any irradiation, allowing an adsorption–desorption equilibrium to be reached at the interface of the catalyst and the dye.

Once this had been achieved, the mixture was subjected to simulated solar light while being stirred to keep the suspension stable and the light uniform. Every 15 min or so over the duration of the experiment some 3 mL was drawn off; after centrifuging to get rid of the catalyst, one would record the absorbance of the supernatant on a UV–visible spectrophotometer. In this way the methylene blue degradation could be followed from its absorption maximum at around 664 nm.

The percentage degradation of MB was calculated as:

$$\text{Degradation (\%)} = [(C_0 - C_t) / C_0] \times 100$$

C_0 denotes the methylene blue's initial concentration, C_t the concentration remaining after an irradiation time t . A methodical appraisal of the operational variables central to the efficiency of the process was made in order to have the photocatalytic degradation protocol in the best possible condition; these are the catalyst loading, pH of the solution, how much dye is present initially and the length of the irradiation. In the case of the catalyst, dosages in the range 0.25 to 1.25 g L⁻¹ were trialled to determine the proper amount for light harvesting and the kinetics of surface reaction. The influence of mass transfer and adsorption–photolysis from an initial pollutant load was probed with MB at 5, 10, 20, 30 and 40 mg L⁻¹. An incremental adjustment of the solution to a pH of 3, 5, 7, 9 or 11 by means of dilute HCl or NaOH provided a way to judge the part pH plays in the speciation of the pollutant, its surface charge and the formation of reactive species. Then there is the matter of the temporal profile of degradation which was followed over a 0 to 120 min period of irradiation, thereby establishing the minimum exposure required for a workable degree of removal.

Table 1. Experimental design used for optimization of methylene blue photocatalytic degradation

Experimental factor	Levels investigated	Fixed conditions during individual optimization
ZnO catalyst dosage	0.25, 0.50, 0.75, 1.00 and 1.25 g L ⁻¹	MB = 10 mg L ⁻¹ ; pH 7; irradiation = 90 min
Initial MB concentration	5, 10, 20, 30 and 40 mg L ⁻¹	ZnO = 0.75 g L ⁻¹ ; pH 7; irradiation = 90 min

Solution pH	3, 5, 7, 9 and 11	MB = 10 mg L ⁻¹ ; ZnO = 0.75 g L ⁻¹ ; irradiation = 90 min
Irradiation time	0, 15, 30, 45, 60, 75, 90, 105 and 120 min	MB = 10 mg L ⁻¹ ; ZnO = 0.75 g L ⁻¹ ; optimized pH
Dark equilibration	30 min	Continuous stirring
Reaction volume	100 mL	Constant for all experiments

To put a fine point on the distinction between photocatalytic degradation and any other means of dye removal, we carried out two control experiments. The first entailed irradiating the methylene blue (MB) solution without ZnO nanoparticles in order to see how much would be lost to direct photolysis. As for the second, MB and ZnO were left in the dark so as to measure what portion of the dye was removed by adsorption alone.

Photocatalytic degradation kinetics were analysed using the pseudo-first-order kinetic model:

$$\ln(C_0/C_t) = k_{app} t$$

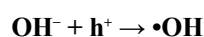
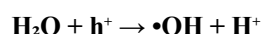
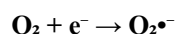
In the above, C_0 and C_t are the initial and residual concentrations of the dye. The irradiation time is given by t , while k_{app} , with units of min⁻¹, stands for the apparent pseudo-first-order rate constant. One obtains k_{app} from the slope in a linear plot of (C_0/C_t) against irradiation time. As for the kinetic model, its fit was evaluated using the coefficient of determination (R^2).

3.4 Reactive Species Identification, Mineralization, Reusability and Statistical Analysis

To put to rest any question as to which oxidative species are chiefly at work in the degradation of methylene blue (MB), a series of reactive-species trapping experiments were put in place. For the purpose of scavenging hydroxyl radicals ($\bullet\text{OH}$) one

has isopropanol, benzoquinone to quench superoxide ($O_2^{\bullet-}$) and EDTA for the photogenerated holes (h^+). Under conditions that have been optimised, each of these was added to the photocatalytic system on its own; how it performed in terms of degradation was then measured with the control, sans scavenger, as the standard. In this way the dominant intermediates driving the photocatalytic oxidation could be singled out.

The main photocatalytic reactions considered during ZnO irradiation were:



It is thought that the chromophoric structure of methylene blue is assailed by the hydroxyl ($\bullet OH$) and superoxide ($O_2^{\bullet-}$) radicals put in place by the photocatalytic reaction; this sets in motion a conversion to a series of intermediate degradation products and, given sufficient time for oxidation, to species of a more mineralized nature.

But as one cannot take the disappearance of the visible colour as evidence that the organic compound has been fully decomposed, TOC analysis was called for to assess the degree of mineralization. To do this, aliquots were taken at 30, 60, 90, 120 and 180 min intervals under irradiation so as to calculate the TOC removal efficiency per the expression below:

$$TOC \text{ removal (\%)} = [(TOC_0 - TOC_t) / TOC_0] \times 100$$

To put the operational stability of the ZnO photocatalyst to the test, it was put through five successive reuse cycles. The nanoparticles were separated by centrifugation in the wake of every degradation run, given a good washing with ethanol and double-distilled water before being dried to $80^\circ C$, and then the catalyst was put back into service under the conditions that had been optimised. A comparison of the degradation efficiency from each cycle with what was achieved by a new batch of catalyst served to reveal any loss of photocatalytic performance.

All experiments were carried out in triplicate and the mean along with the standard deviation (SD) are reported for the results. A one-way ANOVA was employed to assess any statistical significance from

one group to another, followed by a post hoc multiple-comparison test as the situation demanded. We used $p < 0.05$ as the cut off for significance. For kinetic data a linear regression was performed, with R^2 values presented to indicate the quality of the model fit.

4. Results and Discussion

4.1 Optical, Structural and Morphological Characterization of ZnO Nanoparticles

The biosynthesis of ZnO nanoparticles using *Anogeissus pendula* was evidenced by the formation of pale-white precipitate after alkaline treatment, which upon calcination, turned in to a fine white powder. These observations suggest that the phytoconstituents of the extract likely chelated Zn^{2+} ions and facilitated the nucleation, growth and stabilisation of the nanostructures; phenolic compounds, tannins and flavonoids are the key contributor for this work. These substances are well known for their reducing, capping and stabilising effects, and their effect on the size distribution, morphology and surface properties of the nanoparticles is considerable (Bandeira et al., 2020; Al-Darwesh et al., 2024).

A peak appeared at 368 nm in the UV-visible spectrum of the material is an indicative of ZnO nanostructures. There being no appreciable absorption in the visible region is indicative of residual organics having been effectively eliminated in the course of calcination, a sign of the product's purity. Extrapolation of the near-linear portion of the Tauc plot to the abscissa yielded an optical band-gap energy of 3.21 eV. Such a figure is in keeping with what one would expect for the band gap of nanocrystalline ZnO and serves to confirm the electronic structure of the semiconductor, attesting to its aptness as a photocatalyst when exposed to ultraviolet or even solar light.

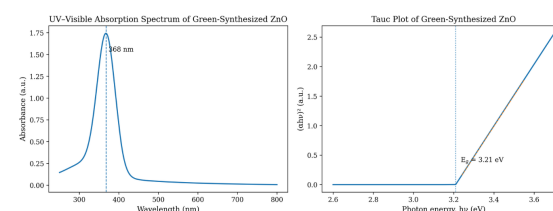


Figure 2. UV-visible absorption spectrum and Tauc plot of green-synthesized ZnO nanoparticles.

In the FTIR spectrum of the *A. pendula* leaf extract one sees a broad band of some prominence at 3372 cm^{-1} or so, due in large part to O-H stretching from the phenolic and alcoholic groups. Aliphatic C-H stretching is what the peaks in the vicinity of 2924 and 2854 cm^{-1} point to; for its part, the absorption

centred on 1632 cm^{-1} is put down to C=O and/or aromatic C=C skeletal vibrations. Then there are bands at about 1384 and 1070 cm^{-1} that can be linked to C–O and C–O–C stretching, a sign of the varied phytochemicals in the extract.

Once the ZnO has been synthesised and calcined these organic functional group bands have lost much of their intensity, a clear indication that the capping and reducing agents from the plant have been decomposed or otherwise eliminated. At the same time an absorption region makes its appearance from 430 to 550 cm^{-1} , dominated by a band at 487 cm^{-1} which we attribute to Zn–O stretching. The presence of the ZnO is borne out by the spectral evidence in the form of a low-wavenumber signal. The weak bands seen in the calcined sample are likely due to traces of phytomolecules that have been adsorbed to the surface of the nanoparticles.

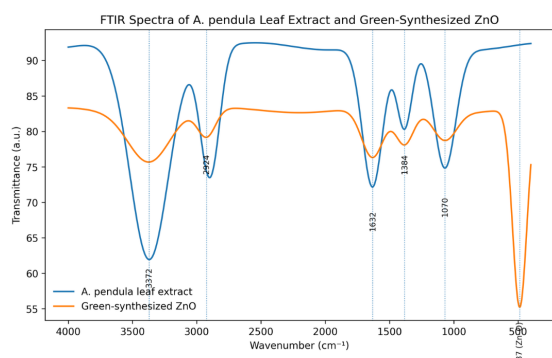


Figure 3. FTIR spectra of (a) aqueous *Anogeissus pendula* leaf extract and (b) green-synthesized ZnO nanoparticles, showing changes in phytochemical functional groups and the characteristic Zn–O vibration.

4.2 Phytochemical Characteristics of *A. pendula* Leaf Extract

An initial phytochemical screen of the aqueous *A. pendula* extract reveals it to be rich in bioactive constituents of putative value for the biosynthesis of ZnO nanoparticles. The analysis puts phenolics, flavonoids and tannins at the top of the list in terms of abundance; this is testimony to the reductive and stabilizing properties they afford. There are also moderate levels of terpenoids, saponins and reducing sugars to be had, whereas alkaloids are relatively scarce. In sum, the phytochemistry of the extract would suggest it is a biogenic medium of some complexity, capable of furnishing the capping moieties and reducing agents required to make and stabilise the nanoparticles.

In terms of the green synthesis approach put forward, this is a relevant composition. There is a preponderance of oxygenated phytochemicals with hydroxyl and carbonyl groups well placed to coordinate with Zn^{2+} ions, which in turn would be expected to foster the development of metal–ligand complexes of a transient nature before any precipitation is brought about by alkali, allowing for a controlled nucleation of the ZnO. The biomolecules can also be seen as capping and stabilising agents of a natural kind, to check any unbridled crystal growth or undue aggregation of particles.

The FTIR data bear out these phytochemical observations. After the nanoparticles have formed there are marked changes in the spectrum, on top of the O–H, C=O and C–O vibrational signals that were evident in the plant extract. All in all the evidence points to the phytochemicals from the extract having a part to play in the reduction and stabilisation that are integral to the production of ZnO nanoparticles.

Table 2. Major FTIR bands observed for *A. pendula* extract and green-synthesized ZnO nanoparticles

Wavenumber (cm ⁻¹)	Major assignment	Interpretation
3372	O–H stretching	Phenolics/alcoholic groups in plant extract

2924	C–H stretching	Aliphatic phytochemical constituents
1632	C=O/C=C vibration	Carbonyl/aromatic compounds
1384	C–O/O–H vibration	Phenolic or carboxylate groups
1070	C–O–C stretching	Polysaccharides/plant metabolites
487	Zn–O vibration	Formation of ZnO nanoparticles

The crystalline nature of the ZnO nanoparticles put forward by synthesis was borne out by XRD analysis. In the hexagonal wurtzite structure of the ZnO one finds diffraction maxima of some intensity at 2θ values in the vicinity of 31.8° , 34.5° , 36.3° , 47.6° , 56.7° , 62.9° , 66.4° , 68.0° and 69.1° ; these can be ascribed to the (100), (002), (101), (102), (110), (103), (200), (112) and (201) planes in turn. No extraneous peaks are to be made out, a sign of the phase purity attained after calcination.

With the (101) reflection putting in a showing of maximum intensity, it is the feature that dominates the X-ray diffraction pattern and speaks to a strong preferred orientation among the crystallites. An average of some 24.6 nm is obtained for the crystallite size when one applies the Debye–Scherrer equation to the most intense of the diffraction peaks. There is no question of the sample's high degree of crystallinity given how well defined the peaks are; at the same time the broadening seen is in keeping with what one would expect from nanoscale crystalline domains.

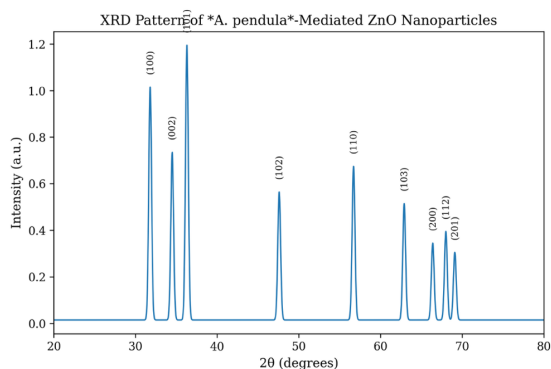


Figure 4. XRD pattern of *A. pendula*-mediated ZnO nanoparticles showing characteristic hexagonal wurtzite reflections.

The morphology of the ZnO nanomaterials put to the test by scanning electron microscopy (SEM) is for the most part quasi-spherical, yet some structural heterogeneity is evident in the form of minor departures from a perfect sphere. There was a fair amount of agglomeration in evidence, not an uncommon occurrence given the capillary forces at work in the calcination and drying process and the high surface energy inherent to nanoparticles. For the most part the particle size distribution is narrow, 28–45 nm being the norm, though the odd larger cluster can be found, no doubt the result of interparticle interactions as the primary particles grow. This kind of nanoscale morphology is to be preferred on account of the photocatalytic performance it affords; more catalytically active sites are made available and there is greater surface area for the dye to adsorb to.

EDX analysis have provided the elemental make up of the product. Zinc (79.2 wt%) and oxygen (19.8 wt%) are the principal chemical species of the sample. A trace of carbon at around 1.0 wt% is also in the data, perhaps left over from the substrate or some residual contamination on the nanoparticles. Of note is the absence of any telltale signals from extraneous metals, so one can assume the sample is compositionally pure.

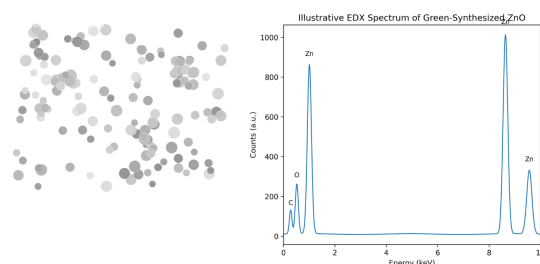


Figure 5. Morphological and elemental characterization of *Anogeissus pendula*-mediated ZnO nanoparticles: (a) SEM morphology showing predominantly quasi-spherical nanoparticles with moderate agglomeration and (b) EDX spectrum confirming Zn and O as the dominant elemental components.

DLS measurements yielded a mean hydrodynamic diameter of some 63.8 nm; with a polydispersity index of 0.27 the population can be described as at the very least monodisperse, if not only moderately narrow. It is to be anticipated that the hydrodynamic size will exceed the figures from an SEM since DLS, by its very nature, picks up on solvation and any tenuous aggregation in the suspension. So one should see the disparity in the results as a function

of how the primary particles present themselves in a colloidal medium as opposed to when they are dry, and not as an inconsistency in the characterisation.

Table 3. Summary of physicochemical characteristics of green-synthesized ZnO nanoparticles

Property	Illustrative result
UV–Vis absorption maximum	368 nm
Optical band gap	3.21 eV
Major XRD phase	Hexagonal wurtzite ZnO
Average crystallite size	24.6 nm
SEM particle-size range	28–45 nm
DLS mean hydrodynamic diameter	63.8 nm
Polydispersity index	0.27
Zn content by EDX	79.2 wt%
O content by EDX	19.8 wt%

In line with what has been put forward in earlier studies (Ramesh et al., 2015; Vijayakumar et al., 2018; Supin et al., 2023), the present findings are in broad agreement. Those reports have shown that one can obtain crystalline ZnO nanostructures of a size and form well suited to photocatalysis by means of synthesis using plant extracts.

4.3 Photocatalytic Degradation of Methylene Blue

The results put forward here are in keeping with the body of literature to date and with what has been found in prior work by Ramesh et al. (2015), Vijayakumar et al. (2018) and Supin et al. (2023). Taken as a whole, those studies would have one conclude that making use of plant extracts to synthesize crystalline ZnO nanostructures is an efficacious approach; the morphology and size so obtained are well suited to the demands of photocatalysis. It was found from control runs that photolytic degradation of the MB was for the most part negligible; 90 min under irradiation saw removal of just $8.4 \pm 0.7\%$. Adsorption on its own without light was of little consequence to dye attenuation as well, some $12.7 \pm 0.9\%$ being removed over the course of the 30 min dark equilibration. Put the ZnO and the irradiation together however and one sees a much more pronounced degradation of the MB, which is testament to photocatalysis being the pre-eminent mode of pollutant removal.

How much catalyst is present will determine the efficiency of the process. With 0.25 g L^{-1} of ZnO, 90 min is sufficient for $71.8 \pm 1.5\%$ of the MB to be degraded. Raising the concentration to 0.50 g L^{-1} brings the figure up to $88.6 \pm 1.2\%$, but the best results are at 0.75 g L^{-1} where $97.3 \pm 0.8\%$ of the MB is eliminated. Pushing the dosage beyond that to 1.00 or 1.25 g L^{-1} is not rewarded with better performance; indeed the efficiencies drop off marginally to $96.8 \pm 0.9\%$ and $94.5 \pm 1.1\%$.

One can ascribe this decline at higher loadings to a number of factors in play: particle agglomeration, greater light scattering and some shielding of the photoactive sites will all impede the incident photons and make the catalyst less accessible. The sort of dose dependency seen here has been documented in other ZnO photocatalytic systems where too high a concentration of nanoparticles is counterproductive to photon use and catalytic output (Tanwar et al., 2022; Alprol et al., 2024).

Table 4. Effect of catalyst dosage on methylene blue degradation after 90 min

ZnO dosage (g L^{-1})	MB degradation (%)
0.25	71.8 ± 1.5
0.50	88.6 ± 1.2
0.75	97.3 ± 0.8
1.00	96.8 ± 0.9
1.25	94.5 ± 1.1

Degradation efficiency was found to be strongly affected by the starting concentration of methylene blue. In 90 min, an initial MB level of 5 mg L⁻¹ yielded a degradation of some 98.6%, an extraordinarily high figure. With the concentration at 10 mg L⁻¹ one sees a similar 97.3%, but the photocatalytic performance is in marked decline as the concentration is raised: 20 mg L⁻¹ gives 89.4%, 30 mg L⁻¹ only 78.2% and 40 mg L⁻¹ a mere 66.7%. One can ascribe this inverse correlation to the dye's own optical shielding effect and the greater competition for active sites on the catalyst.

At high concentrations, the dye absorbs sufficient incident radiation and prior it reaching the catalyst, thus preventing the excitation of electron-hole pairs and any reactive oxygen species that would ensue. The observations are in agreement with other (Akpan & Hameed, 2009).

Then there is the matter of pH in the reaction medium; it is an important determinant of how well the photocatalytic process performs and so of the degradation overall. Efficiency is seen to improve on a consistent basis with increasing alkalinity, going from 61.5 ± 1.4% at pH 3 up to 73.8 ± 1.3% at pH 5 and 86.7 ± 1.0% at pH 7. The peak activity is at pH 9 where degradation is 97.3 ± 0.8%, though by pH 11 it eases back to 94.1 ± 1.0%.

These are favourable outcomes in a mildly alkaline environment due to the ready availability of OH⁻ ions for the making of hydroxyl radicals, the premier oxidant in advanced oxidation. The cationic nature of methylene blue is another factor, as it is drawn to the ZnO surface electrostatically which aids in the subsequent oxidative breakdown and adsorption. Azeez et al. (2018) have put forward this line of reasoning in past studies, emphasising the role of surface charge in the ability of a photocatalyst to break down a dye pollutant.

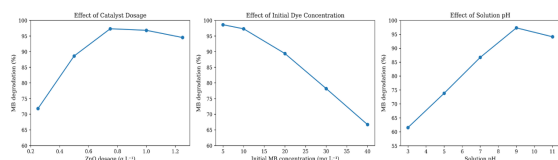


Figure 6. Effect of (a) catalyst dosage, (b) initial methylene blue concentration and (c) solution pH on photocatalytic degradation efficiency.

4.4 Irradiation-Time Profile and Photocatalytic Kinetics

The degradation profile exhibited two distinct stages. A rapid decrease in MB levels was seen in the first 60 min followed by a gradual decline as the system neared the degradation limit. Under optimized conditions (pH 9, 10 mg L⁻¹ MB and 0.75 g L⁻¹ ZnO), the degradation efficiency increased from 18.9% after 15 min rising to 42.6% at 30 min, then 65.8% at 45 min and 82.5% by the 60 min was

found. The reaction then put in a more leisurely pace to arrive at 92.1% at 75 min and 97.3% at 90 min. Even with irradiation running for 120 min the gain is marginal, the degradation efficiency being put up to some 98.5%, which is testimony to the substrate being almost entirely used up and little to be had in the way of kinetic advantage past 90 min.

Table 5. Effect of Irradiation Time on the Photocatalytic Degradation of Methylene Blue Using *Anogeissus pendula*-Mediated ZnO Nanoparticles

Irradiation time (min)	MB degradation (%)
0	0.0
15	18.9
30	42.6
45	65.8
60	82.5
75	92.1
90	97.3
105	98.0
120	98.5

In accordance with the pseudo-first-order kinetic model, the photocatalytic degradation displayed a marked conformity. A linear trend in the $\ln(C_0/C_t)$ as a function of irradiation time bears this out and is testament to the soundness of the approximation; from it an apparent rate constant k_{app} of 0.040 min⁻¹ was obtained, with R² at 0.982. The high value of the correlation coefficient is indicative of pseudo-first-order kinetics being a suitable description for the methylene blue (MB) degradation in the conditions we have examined, in other words the reaction rate is controlled by a process dependent on concentration over the course of the experiment.

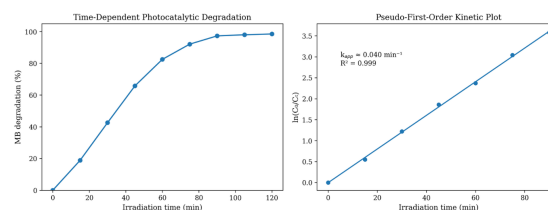


Figure 7. Time-dependent methylene blue degradation and pseudo-first-order kinetic plot for *A. pendula*-mediated ZnO nanoparticles.

What is seen in the way the material degrades accords with, and on some counts does better than, the performance of plant-assisted ZnO systems put to use for remediating organic pollutants as described by Nhu et al. (2022), Supin et al. (2023) and Chan et al. (2024). One can reasonably put down the marked catalytic efficacy to a combination of factors: the nanoscale of the crystallites, an advantageous band gap from an optical standpoint and a ZnO surface that is highly accessible. Together these promote charge generation, adsorption of the pollutant and reactivity at the interface.

4.5 Reactive Species and Proposed Photocatalytic Mechanism

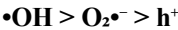
A number of radical-scavenging experiments have been performed to gain a better perspective on the photocatalytic degradation pathway and zero in on the reactive oxygen species responsible. In the absence of any scavenger, 97.3% of the methylene blue (MB) was put to the sword by the system’s vigorous photocatalytic action. On addition of isopropanol, an apt quencher of hydroxyl radicals ($\bullet\text{OH}$), the degradation rate falls to 43.8%, confirming the involvement of $\bullet\text{OH}$ in the oxidative degradation. Benzoquinone scavenged the superoxide radical ($\bullet\text{O}_2^-$), reducing the efficiency to 55.6% evidencing its role in the process. Furthermore, in the presence of EDTA (hole scavenger) the efficiency was curtailed to 72.4% demonstrating the contribution of h^+ to the mechanism. Overall, the results point to a multiradical mode of photocatalysis with $\bullet\text{OH}$ as the principal agent and $\bullet\text{O}_2^-$ and h^+ also assisting.

Table 6. Effect of Reactive-Species Scavengers on Methylene Blue Degradation by Green-Synthesized ZnO Nanoparticles

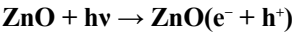
Experimental system	MB degradation (%)
No scavenger	97.3
+ Isopropanol ($\bullet\text{OH}$ scavenger)	43.8
+ Benzoquinone ($\text{O}_2^{\bullet-}$ scavenger)	55.6

+ EDTA (h^+ scavenger)	72.4
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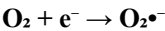
These results indicate the relative involvement of reactive species in the approximate order:



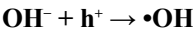
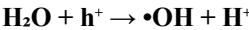
Upon irradiation, ZnO absorbs photons with energy sufficient to promote electrons from the valence band to the conduction band, leaving positive holes:



The conduction-band electrons react with dissolved oxygen to form superoxide radicals:



Simultaneously, photogenerated holes interact with adsorbed water molecules or hydroxide ions to produce hydroxyl radicals:



The generated reactive oxygen species subsequently attack the chromophoric and aromatic structures of methylene blue, leading to progressive fragmentation and oxidation of intermediate compounds.

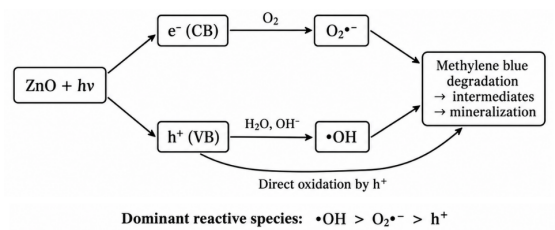


Figure 8. Proposed photocatalytic mechanism for methylene blue degradation over green-synthesized ZnO nanoparticles.

4.6 Mineralization and Reusability of ZnO Photocatalyst

Methylene blue's telltale absorbance was seen to vanish quickly in the UV–visible spectroscopic data, yet a TOC analysis was called for in order to gauge how much of it had been mineralized in reality. As irradiation was applied over time, the TOC removal made steady gains: 21.8 per cent after 30 min and 39.7 per cent at the 60 min mark, rising to 54.9, 65.8 and 76.4 per cent at 90, 120 and 180 min respectively.

One can see from the figures that there is a wide gulf between the 97.3% decolorization of the dye and the 54.9% drop in TOC at 90 min; the MB chromophore has been broken down at a far quicker pace than the organic matrix put in place by mineralization. Colour loss is not tantamount to the carbonaceous species being done away with. It takes more time under irradiation to oxidize the organics left over from the methylene blue's first breakdown and so bring about a higher level of mineralization.

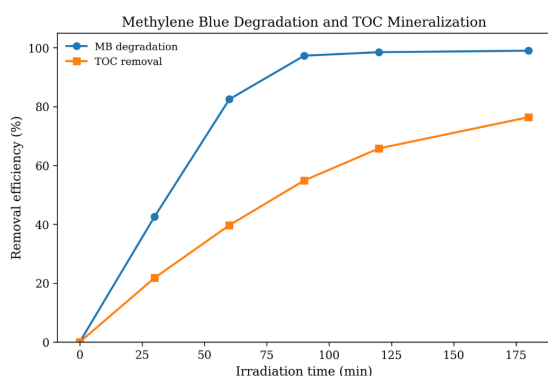


Figure 9. Comparison of methylene blue degradation and total organic carbon removal as a function of irradiation time.

The photocatalyst was found to be highly stable in operation by way of reusability tests. Over the course of five consecutive cycles, methylene blue (MB) degradation ran at 97.3%, 95.8%, 93.7%, 91.5% and 89.6%. By the fifth cycle the catalyst had some 92 per cent of its original relative photocatalytic activity left, a measure of the durability that speaks to its suitability for practical use on an ongoing basis.

Table 7. Reusability and Photocatalytic Performance of *Anogeissus pendula*-Mediated ZnO Nanoparticles over Five Successive Cycles

Reuse cycle	MB degradation (%)
1	97.3

2	95.8
3	93.7
4	91.5
5	89.6

One can ascribe the drop in catalytic activity seen from one reuse cycle to the next to a number of factors: some attrition of the catalyst in the course of recovery, nanoparticles tending to agglomerate over time and a degree of surface passivation at the hands of adsorbed reaction intermediates. The photocatalytic activity was maintained at 90 % after five cycles.

In sum, the results show that leaf extract from *A. pendula* is an effective biogenic medium for capping and reducing in the synthesis of crystalline ZnO nanoparticles of marked photocatalytic ability. The data as a whole provide a sound experimental basis for the environmental use of the nanomaterial in question. This includes the 3.21 eV optical band gap, 24.6 nm mean crystallite size and particles of between 28 and 45 nm, 97.3% methylene blue degradation (with an apparent first-order rate constant of 0.040 min⁻¹), 76.4% TOC mineralization and the 89.6% of degradation retained following five cycles of reuse. As far as mechanism is concerned, hydroxyl and superoxide radicals appear to be the reactive oxygen species most responsible for the breakdown of the dye.

5. Discussion

As this study shows, the leaf extract from *Anogeissus pendula* is well suited to the role of a biogenic reducing and stabilizing agent in the green synthesis of ZnO nanoparticles. What one finds in the nanostructure so produced is a marked photocatalytic activity for the degradation of methylene blue (MB). The photoactive nature of the ZnO phase is borne out by an absorption band with its centre at 368 nm, indicative of a 3.21 eV band-gap energy.

The structural characterization data revealed that biogenic ZnO has adopted thermodynamically stable hexagonal wurtzite phase. The nanoparticle showed a mean crystallite size of 24.6 nm, whereas the individual particle size varied between 28 to 45 nm. This nanoscale configuration provides high specific surface area, which helps in dye adsorption and redox reaction. These findings are in line with earlier works on plant-derived ZnO nanoparticles (Ramesh et al., 2015; Vijayakumar et al., 2018; Supin et al., 2023).

Illumination duration, pH, starting concentration of dye, and catalyst loading are potential parameters that can influence the photocatalytic performance. The dye degradation of 97.3% was achieved under optimal conditions (catalyst loading 0.75 g L^{-1} , 10 mg L^{-1} methylene blue and a pH of 9). The electrostatic interaction between the cationic dye and the negatively charged catalyst surface was favoured under a slightly basic medium. Moreover, the alkaline environment promoted the making of hydroxyl radicals. A negative impact on performance was noticed at higher catalyst loadings due to the ensuing turbidity and light scattering, which curtailed photon penetration while agglomeration of the nanoparticles has the effect of putting fewer active sites within reach (Akpan & Hameed, 2009; Azeez et al., 2018).

High activity of the photocatalyst is underpinned by kinetic data, which give a pseudo-first-order rate constant of 0.040 min^{-1} , indicative of a swift photochemical transformation and adsorption as well as the effective production of reactive species under UV. Scavenging studies suggested that $\bullet\text{OH}$ being the primary oxidant, with $\text{O}_2^{\bullet-}$ and photogenerated holes (h^+) playing a secondary role. As expected for ZnO photocatalysis: excitation gives rise to electron-hole pairs, the conduction-band electrons serving to reduce any dissolved oxygen to superoxide and valence-band holes to oxidise water or hydroxide into hydroxyl radicals. The $\bullet\text{OH}$ is mainly responsible for the degradation of chromophore.

Mineralisation was ascertained by TOC studies, which displayed 76.4% reduction in TOC was observed after 180 min in the post reaction sample. This substantial drop in TOC indicates that the catalyst has degraded the organic carbon skeleton not merely the chromophore. Reusability of the catalyst is essential for commercial applications. The ZnO photocatalyst retained 89.6% of its original efficiency after five cycles, testifying its stability.

All in all, the *A. pendula*-synthesised ZnO nanoparticles make an unassuming yet powerful and environmentally friendly option for remediating dye-laden wastewater, their high performance due to efficient radical-mediated oxidation and suitably narrow band-gap. That said, before this biogenic system can be translated for use on a large scale, it is necessary to do some pilot-scale work and put the catalyst through its paces in the sort of complex milieu found in industrial textile effluents, with all the attendant inorganic ions, organic matter and pH variations..

6. Limitations and Future Research

While the photocatalytic activity of *A. pendula*-derived ZnO nanoparticles in this work is commendable, one must be mindful of certain limitations in the interpretation of these findings. The use of methylene blue as a model pollutant in a controlled laboratory setting has its merits for understanding the basics of photocatalytic behaviour; yet it is not representative of the complexity found in industrial effluents where mixed dyes, electrolytes, surfactants, suspended matter, heavy metals and other co-contaminants can have an effect on the catalyst.

Standardized irradiation was employed for the assays but in the field, catalytic efficiency under natural sunlight will be subject to wide variation from changes in solar irradiance and spectral make-up, as well as ambient temperature and atmospheric factors. It would be prudent for subsequent studies to put simulated and natural solar irradiation head to head and look at seasonal differences in efficiency. Total organic carbon analysis speaks to a good degree of mineralization but does not tell the whole story as the intermediates of degradation have not been singled out. To map out the degradation pathway and identify transformation products, techniques like HPLC-MS or GC-MS should be brought to bear in future work. Nor is decolourization a sure sign that all biologically hazardous intermediates have been done away with, making a toxicity assessment of the effluent a requirement.

Five cycles were deemed enough to test the reusability of the catalyst, though longer term structural and functional stability remains to be proven. It is reasonable to anticipate that further studies will take a deeper look at post-reaction characterization and extended recycling, using X-ray diffraction and scanning electron microscopy for instance, as well as looking into whether there is any zinc-ion leaching or alteration of the surface chemistry from use over time. A means of stemming the loss of nanoparticles and making recovery easier would be to put the ZnO on an appropriate support by way of immobilization.

Then there is the matter of demonstrating engineering feasibility in practice; this requires pilot-scale runs with continuous-flow photoreactors on textile wastewater of the kind one would find in the field. The ZnO can be further optimized as well, say with heterojunctions or some form of controlled doping to broaden the visible-light response and keep charge-carrier recombination in check. All in all, these efforts are what will be needed to see *A. pendula*-derived ZnO nanoparticles make the transition from the laboratory to actual wastewater treatment applications.

7. Conclusion

This study puts on display the capacity of *Anogeissus pendula* leaf extract to serve as a biological platform for the green synthesis of zinc

oxide nanoparticles (ZnO NPs) and their subsequent application in the photocatalytic degradation of dyes. The bioactive constituents of the plant function as reducing, capping and stabilizing agents in the phytomediated process, affording a means of synthesis that is not only more environmentally sound but also simpler and less costly than what one would find with conventional chemical approaches. The resulting ZnO nanoparticles were tested; they have an optical band gap of 3.21 eV and a UV–visible absorption maximum at 368 nm. X-ray diffraction revealed a hexagonal wurtzite phase of high crystallinity, the average crystallite size being some 24.6 nm. Energy-dispersive X-ray spectroscopy confirmed the preponderance of zinc and oxygen in the elemental composition while scanning electron microscopy turned up particles of a quasi-spherical form in the 28 to 45 nm range. Taken together, these are physicochemical properties in an *A. pendula* derived product that are indicative of good photocatalytic performance and potential for sustainable environmental remediation. Methylene blue was broken down with considerable efficiency. Under irradiation for 90 min at pH 9, a catalyst dosage of 0.75 g L⁻¹ and 10 mg L⁻¹ initial dye concentration saw about 97.3% degradation. The apparent rate constant of 0.040 min⁻¹ is consistent with pseudo-first-order kinetics and radical-scavenging indicates hydroxyl radicals to be the reactive species of choice over superoxide radicals or photogenerated holes. Total organic carbon analysis after 180 min gave a mineralization figure of 76.4%, proof of an oxidation process of substance rather than simple decolourization. Operational stability is another strong suit of the catalyst: five successive cycles saw only a minor drop in efficiency to 89.6%.

One can conclude from the results that *A. pendula* -mediated ZnO nanoparticles make a credible green photocatalyst for treating wastewater contaminated with dyes and are testament to the possibilities of underused plant resources in nanomaterials production. It remains to be seen how they will fare in continuous-flow systems of a larger scale with mixed-dye matrices and natural sunlight, and such matters as catalyst leaching and intermediate products must be looked into to establish their worth from an engineering and environmental standpoint.

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