GREEN SYNTHESIS OF ZINC OXIDE NANOPARTICLES USING ALOE VERA: A STUDY ON OPTICAL PROPERTIES AND PHOTOCATALYTIC ACTIVITY

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Abstract:

The emergence of green synthesis provides an environmentally conscious alternative to conventional methods in the pursuit of sustainable nanotechnology. Exploring this environmentally friendly territory, our research reveals the fascinating realm of zinc oxide nanoparticles (ZnO NPs), which are made using the botanical expertise of Aloe barbadensis miller, also referred to as aloe vera. This work sets out to investigate the optical properties and photocatalytic capabilities of these biosynthesized nanoparticles with an emphasis on their potential use in the methylene blue (MB) degradation process. Green synthesis, a meticulous blend of botanical expertise and analytical precision, initiates with the careful synthesis of NPs using Aloe barbadensis miller leaves as a reducing agent. The resultant Aloe Vera-assisted ZnO nanoparticles (AL-ZnO) exhibit significant optical properties, as unveiled by UV-vis spectroscopy, indicating a semiconductor behaviour with an absorption peak at 310 nm. Tauc's equation reveals a bandgap energy of 4.37 eV, indicating direct electronic transitions within the AL-ZnO NPs. The particle size of 5.86nm was determined through a hyperbolic model. AL-ZnO showcases remarkable catalytic prowess in photocatalysis, achieving complete methylene blue degradation under soft sunlight within 105 minutes. This positions Aloe Vera-assisted ZnO NPs as potent catalysts for eco-friendly water treatment, marking a significant stride in green synthesis. The study also delves into the optical attributes of Al-doped ZnO nanoparticles, uncovering robust light-refracting capabilities and high optical conductivity. This positions them as ideal candidates for applications in solar cells and light-emitting devices, contributing to advancements in
renewable energy technologies. In essence, the research establishes Aloe Vera-assisted ZnO NPs as multifaceted, powerful catalysts with significant implications for both environmentally conscious water treatment and the broader domain of green synthesis.

**Keywords:** Zinc Oxide nanoparticle, Methylene Blue degradation, bandgap energy, photocatalytic activity, Green Synthesis, Aloe vera.

1. **Introduction:** Zinc oxide is an interesting metal oxide material that has gained attention in materials science recently because of its unique properties, which include broad radiation absorption, catalytic activity, high mechanical and chemical stability, electrochemical coupling, and non-toxic behaviour (Mohan & Renjanadevi, 2016). Its nano size is especially intriguing. Particles that range in size from one to one hundred nanometres are referred to as nanosized particles (Khan et al., 2019). Among the many types of nanoparticles, semiconductor nanoparticles have drawn major attention due to their unique properties and wide range of potential uses. Semiconductor nanoparticles are useful in electronics, medicine, and environmental remediation because they differ from their bulk counterparts in their electronic and optical properties. In this instance, semiconductor nanoparticles of particular interest are zinc oxide nanoparticles (Subhan et al., 2022). ZnO nanoparticles have gained prominence due to their exceptional photocatalytic activity, wide bandgap, and biocompatibility. These nanoparticles are noteworthy as semiconductor materials, playing a pivotal role in a diverse array of applications. Their multifunctionality and versatility make ZnO nanoparticles indispensable in various fields (Hossain et al., 2023).

The process of synthesis of nanoparticles is a significant factor that influences their properties and applications. While several methods exist for nanoparticle synthesis, green synthesis is gaining increasing popularity owing to its lower environmental impact (Patel, 2022). This eco-friendly approach involves the use of plant extracts, microorganisms, or other sustainable sources as reducing or stabilizing agents in the synthesis process. Green synthesis not only aligns with the principles of sustainability but also offers advantages such as reduced energy consumption, milder reaction
conditions, and the potential for scale-up cost-effectively (Patel, 2022). The use of natural sources, such as Aloe Vera in the synthesis of ZnO nanoparticles, exemplifies the commitment to environmentally conscious practices and underscores the significance of exploring green methodologies in nanotechnology (Bahrulolum et al., 2021). Biochemical pathways that are intrinsic to plants facilitate the reduction and stabilization of metal ions, which in turn facilitates the formation of nanoparticles. This green synthesis technique reduces the harmful effects that conventional synthesis techniques have on the environment while also opening up opportunities for the production of affordable and scalable nanoparticles. For instance, Aloe barbadensis miller has shown promise in the biogenic synthesis of zinc oxide nanoparticles (Boroumand Moghaddam et al., 2015). ZnO nanoparticle's photocatalytic activity gives their applications even more significance. The process of using light to trigger reactions on a photocatalyst's surface that breaks down pollutants and organic compounds. Methylene blue is a common and persistent dye that is present in industrial effluents and is used as a model pollutant in photocatalytic degradation research. Thanks to their increased capacity for photocatalysis, ZnO NPs present a viable way to effectively eliminate contaminants such as methylene blue from water-based settings (Bhapkar et al., 2023a), (Rasli et al., 2020). Because Methylene Blue is used widely in many industries and has detrimental effects on ecosystems, its degradation is essential to maintaining the sustainability of the environment. The photocatalytic degradation of MB by ZnO NPs becomes significant in this context, indicating the potential applications of these nanoparticles in wastewater treatment and environmental remediation(Bhuyan et al., 2015a), (Venkatesan et al., 2022).

The main objective of this project is to create ZnO NPs using the extract of Aloe barbadensis miller. These nanoparticles will subsequently go through a comprehensive optical characterization including optical conductivity, refractive index, a wide bandgap, semiconductor behaviour, and strong absorption in the ultraviolet region. Subsequently, the study aims to investigate the photocatalytic activity of ZnO nanoparticles.
nanoparticles in the degradation of methylene blue, offering valuable information about their potential as durable and efficient catalysts for water filtration and environmental preservation. Furthermore, the synthesised NPs are characterized by their efficient light absorption and re-emission, making them valuable for applications in photocatalysis, optoelectronics, and solar cells.

2. Experimental:

2.1 Materials

2.1.1 Plant material: Aloe barbadensis miller leaves that were healthy and fresh were gathered from the Siddhachalam Laboratory Garden. The leaves were washed in distilled water and then again in double distilled water to get rid of the dust and other impurities.

2.1.2 Chemical Materials: In the experiments, 99% pure zinc sulphate heptahydrate (ZnSO$_4$.7H$_2$O), ethylene glycol, urea, and sodium hydroxide (NaOH) were used. All the chemicals were analytical reagent-grade chemicals and were obtained from E. Merck Mumbai, India. The water used to make the solutions was deionized.

2.2 Procedure

2.2.1 Leaf extract preparation: Aloe barbadensis miller leaf peels were collected carefully and the gel portion was thrown away. To make an aqueous extract solution, small pieces of peel were cut with a knife and ground in distilled water using a pestle and mortar. The aqueous extract was then filtered to eliminate debris using Whatman filter paper no. 1 (Chaudhary et al., 2018).

2.2.2 Synthesis of ZnO Nanoparticles: Al-ZnO beaker was filled with distilled water and ZnSO$_4$.7H$_2$O was dissolved to create a 0.5 M solution that was used to make ZnO NP. The solution was vigorously stirred with a magnetic stirrer while a 0.5 M NaOH solution was added drop by drop to adjust the
pH of the mixture. Concurrent additions of urea, ethylene glycol, and pre-processed Aloe barbadensis miller leaf extract were made to the mixture. Zn (SO4) (OH)$_6$.0.5H$_2$O was generated by stirring the mixture for four to five hours at 70 °C. After filtering, the resulting white precipitate was collected and rinsed four times with distilled water and absolute ethanol. Subsequently, the precipitate was separated and allowed to evaporate overnight at 70°C in a hot air oven. This process turned the wet precipitate into dry powder. Finally, the product was air-calcined in a muffle furnace for one hour at 825°C (Shamhari et al., 2018), (Chaudhary et al., 2018).

2.3 Characterization of ZnO nanoparticles: To verify that ZnO was formed, the samples of synthesized nanoparticles were examined, employing distilled water as the blank reference and a UV-visible spectrophotometer (Shimadzu's UV-1900 UV-Visible Spectrometer, Japan) that operates in the 200–800 nm wavelength range. The band gap energy was computed using Tauc's equation, and the absorbance Spectrum was studied to ascertain their optical properties. The obtained values of the absorption peak and optical band gap were used to calculate additional significant parameters (Bhuyan et al., 2015b) (Sowri Babu et al., 2013).

2.4 Photocatalytic Activity Assessment: The photocatalytic activity of synthesized AL-ZnO NPs in the presence of direct sunlight was measured using MB degradation. Two distinct 100-millilitre reaction mixtures of MB were prepared; the first sample consisted of 100 millilitres of MB alone, which was stored in the sun; the second sample included 100 millilitres of MB combined with 5 milligrams of green AL-ZnO nanoparticle, which was also stored in the sun. For roughly 105 minutes, sunlight was added to the reaction mixture. The resultant reaction mixture was kept at 700 rpm with continuous stirring under solar radiation. A UV-visible spectrometer that operated at regular intervals of 15 minutes between 200 and 900 nm was used to analyze the supernatant, which was obtained by removing 5 mL of
the reaction mixture and centrifuging at 9000 rpm for 10 min. This allowed for the
determination of the MB solution from both samples. The entire process took place
outside between 11:30 am and 1:15 pm and took 105 minutes to
complete (Thambidurai et al., 2020).

3. Result and discussion:

3.1 UV-Vis Absorption Spectrum: The synthesized ZnO NPs' absorption spectrum is
shown in Figure 1, where an excitonic absorption peak is seen at about 310 nm.
Additionally, the noticeable sharp absorbance of AL-ZnO NPs indicates that the
nanoparticle distribution is monodispersed (Jiménez Reinosa et al., 2016). Before
the UV-Vis measurement, the ZnO nanoparticles were dissolved in ultrapure water.
The typical UV-Vis absorption spectrum of ZnO, where the absorption edge is
known to occur in the UV region, is consistent with the observed absorption peak
at 310 nm, which corresponds to electronic transitions within the ZnO
nanoparticles. The direct bandgap transition of ZnO, which indicates the excitation
of electrons from the valence band to the conduction band, is responsible for the
absorption in the ultraviolet region (Fadillah et al., 2021). Because the absorption
peak indicates that there are electronic transitions present in the material, it provides
crucial information about the optical properties of the ZnO nanoparticles. The
observed absorption peak at 310 nm confirms the successful synthesis of the target
material. The absorption peak's narrow and distinct shape indicates that the ZnO
nanoparticles have a uniform size distribution and a distinct morphology (Singh et
al., 2012). Furthermore, the observed UV-Vis absorption peak at 310 nm of the
synthesized ZnO nanoparticles suggested that they are semiconductors, which has
implications for potential applications in several fields.
3.2 Bandgap: Bandgap energy, which is the energy difference between the valence and conduction bands of a semiconductor material, can be correlated with the material's absorption peak energy using the formula $E_g = \frac{\lambda}{1240}$ (Jayachandran et al., 2021). Which can be applied to determine the bandgap's energy. Where $\lambda$ is the wavelength in nanometres (nm) and $E_g$ is the bandgap energy in electron volts (eV) (Chaudhary et al., 2018). In our work, 4.37 eV is the determined bandgap energy using this formula. Another method for determining the band gap energy of nanoparticles is to use the Tauc plot method, which involves drawing a graph between $(\alpha h\nu)^n$ vs. $h\nu$ (Liu et al., 2007) when expressed by equation $(\alpha h\nu) = B (h\nu - E_g)^n$. Where the $h\nu$ is photon energy and the $\alpha$ is absorption coefficient, $n$ is the exponent value that describes the nature of the electronic transition between the valence band and conduction band and $B$ is a constant factor, $h\nu$ stands for photon.
energy. The value of $n$ can be $1/2$, $2$, $1/3$, or $3$ in $(\alpha h \nu)^2$, the value of $y=1/n$ represents the permitted direct, permitted indirect, forbidden direct, and forbidden indirect transitions, respectively. In this study, $n=1/2$ (figure 2) was used to obtain the value of bandgap energy and we find that bandgap energy value 4.37 eV estimated through the plot between $(\alpha h \nu)^2$ vs. $h \nu$, where $n=1/2$ was taken, which indicates allowed transition of electrons (Perumal et al., 2016).

Figure 2: bandgap of AL-ZnO Nanoparticles

This value of bandgap energy is further used to determine other data in this study. Figure 2 shows the estimated band gap for ZnO nanoparticles from the Tauc plot of $(\alpha h \nu)^2$ vs. $h \nu$. By extending the straight section to the energy axis at $= 0$, the $E_g$ can be found. With the help of this Tauc plot, it is possible to determine that the mode of transition in AL-ZnO is direct ($n=1/2$) (Bindu & Thomas, 2017). The semiconductor behaviour of ZnO NPs with a wide band gap is represented by the band gap energies, which show that an electron must be promoted from the valence band to the conduction band and allowed to conduct electricity, requiring about 4.37
eV of energy. This value is somewhat higher than the bulk band gap of ZnO (3.37 eV), which is a consequence of quantum confinement effects and could be brought on by strain during the formation of ZnO nanoparticles. Additionally, greater transparency and UV absorption potential are indicated by a wider band gap (Bindu & Thomas, 2017).

3.3 Size of nanoparticle: The size of the nanoparticles is important when it comes to changing the overall characteristics of a material. Thus, to explore the properties of the material, it becomes essential to study the size evolution of semiconducting nanoparticles. One technique that is frequently used to analyze the optical properties of particles with nanoscale size is UV-visible absorption spectroscopy. The average particle size in a nano colloid can also be determined using the absorption onset from UV-vis absorption in addition to optical characteristics (Pesika et al., 2003). A lot of empirical or theoretical formulas are suggested by different researchers to estimate the size of nanoparticles with the help of calculated bandgap energy. In the present work, the following hyperbolic band model has been used to estimate the average particle size by taking into account the strong absorption edge in the sample's absorption spectra:

\[ R = \sqrt[2]{\frac{2\pi^2h^2E_{g\text{bulk}}}{m^*(E_{g\text{nano}}^2-E_{g\text{bulk}}^2)}} \]

where \( h \) is Planck's constant (6.626*10^{-34} J s), \( E_{g\text{b}} \) is the bulk band gap, \( R \) is the radius, \( m^* \) is the effective mass of the specimen (\( m^* = 29.15*10^{-31} \) kg for ZnO), and \( E_{g\text{n}} \) is the bandgap at strong absorption edge in our case it is 4.32nm. In our case, the absorbance value of 310 nm corresponds to a computed radius (\( R \)) of 2.84nm. To find the diameter of the AL-ZnO nanoparticle, the computed radius is then multiplied by two (2R). As a result, the estimated particle size for 2R is 5.68nm (Nemade & Waghuley, 2013), (Debanath & Karmakar, 2013).

3.4 Refractive Index (n): Nanoparticles, particularly semiconducting or metallic ones, have a refractive index that determines their interaction with light, impacting
light scattering, absorption, and emission. This refractive index is crucial in designing optical devices, influencing transparency and response to external stimuli. The refractive index \( n \) is calculated using the following formula (Abdelghani et al., 2022) resulting in a calculated value of 2.49:

\[
N = \sqrt{\frac{12.417}{\sqrt{E_g - 0.365}}}
\]

This value reflects a strong light-refracting ability, crucial for optical applications. The refractive index of 2.49 implies high transparency across the visible and UV spectrum, making it an ideal candidate for photodetectors and solar cells. The calculated value signifies the material's efficiency in bending light, a property desirable for optical devices where light manipulation is essential.

### 3.5 Optical Conductivity (\( \sigma_{\text{opt}} \))
Nanoparticles exhibit high optical conductivity, enabling them to conduct electric current in response to photon absorption and emission. Quantum confinement effects and increased surface area significantly impact this conductivity, making it ideal for optoelectronic applications like solar cells. The optical conductivity (\( \sigma_{\text{opt}} \)) is determined by the given formula (Abdullah et al., 2015):

\[
\sigma_{\text{opt}} = \alpha n c / 4\pi
\]

The calculated value of optical conductivity was \( 1.4 \times 10^{10} \text{ s}^{-1} \) which is quite high and indicates the efficient absorption and re-emission of photons, making it well-suited for applications in solar cells and light-emitting devices. The material's ability to absorb and release photons at this rate signifies its potential for effective utilization in devices requiring optimal optical responses, such as those used in renewable energy technologies and advanced lighting systems (Abdelghani et al., 2022).

### 3.6 Photocatalytic Activity
The photocatalytic performance of ZnO NPs synthesized in this study was evaluated using the photocatalytic degradation of MB in the
presence of sunlight. The strongest absorption band was found at 658 nm in the UV-vis spectrum of MB, which also displays a broad band at 381 nm. Monitoring variations in the intensity of MB's absorption maxima at 658 nm allowed researchers to examine the ZnO photodegradability of MB. Under solar radiation, a 100 ml solution of methylene blue, both with and without ZnO NP, is kept in a glass jar for the investigation. UV-vis spectroscopy is used to monitor changes in the main absorption band. Figures 3 and 4 depict the photocatalytic disintegration of MB, which was monitored for 105 minutes at 15-minute intervals.

![UV-visible spectrum of methylene blue adsorption under sunlight in the absence of AL-ZnO.](https://doi.org/10.26434/chemrxiv-2024-83hjj)

Figure 3. The UV-visible spectrum of methylene blue adsorption under sunlight in the absence of AL-ZnO.

The results demonstrate that, in the absence of a catalyst, MB does not deteriorate after 105 minutes of sunlight exposure; however, a gradual degradation of the methylene blue solution was noted and is depicted in Fig 3 Conversely, when AL-ZnO NP was present as a catalyst, the MB's colour intensity gradually diminished.
and, as a result of the ZnO NP's presence under solar radiation, the MB's colour completely discoloured in 105 minutes (figure 4). The visible UV-vis band, which exhibits a continuous sharp edge widening from the initial to the final peak and the complete disappearance of both absorbance peaks within 90 to 105 minutes, can be used to monitor the degradation of the methylene blue compound. The figure shows that when exposed to sunlight in the presence of synthesised AL-ZnO nanoparticles, the reaction took nearly 105 minutes to completely degrade the methylene blue solution. This suggests that synthesised AL-ZnO NP has the potential to act as a catalyst for the degradation reaction in MB under solar light (Ankamwar et al., 2017a).

![Figure 4. The UV-visible spectrum of methylene blue adsorption under sunlight in the presence of AL-ZnO.](image)

**3.7 Comparison with Existing Literature:** The results of our investigation into the photocatalysis of AL-ZnO NPs for the removal of MB are strikingly similar to those reported in several earlier studies (Narath et al., 2021) (Abdel Messih et al.,...
The photocatalytic process yielded consistent and repeatable results, as evidenced by the close alignment of the absorption values recorded with those reported in the literature. Notably, the trend of methylene blue decolourization over specific time intervals, ranging from 15 minutes to 105 minutes, is consistent with findings from previous studies. The reliability and robustness of the AL-ZnO NP-based photocatalytic process are demonstrated by the congruence of our results with the corpus of current literature. ZnO-NP's potential as a dependable catalyst for the efficient removal of methylene blue is highlighted by the high degree of agreement between the results of different studies, thereby validating their use in wastewater treatment applications. This consistent performance is crucial to demonstrating AL-ZnO NP's value in environmental remediation and emphasizes its potential as a long-term remedy for the degradation of organic pollutants in water. Further research could concentrate on optimizing reaction parameters and exploring potential partnerships with other photocatalytic materials to increase AL-ZnO NPs' efficacy in methylene blue removal processes.

4. **Conclusion:** The ZnO nanoparticles synthesised by Aloe Vera are environmentally conscious change agents, playing a part in the symphony of green synthesis and catalytic proficiency. Their semiconductor behaviour is demonstrated by the absorption peak at 310 nm, which is consistent with the goal of sustainable nanomaterials. Their optical characteristics are richly patterned by the calculated bandgap energy and particle size, which holds great potential for use in various fields. Taking a stab at photocatalysis, these nanoparticles show remarkable effectiveness in breaking down methylene blue in the presence of sunlight, suggesting their potential for use in water treatment applications. Our results agreement with previous research highlight the durability and dependability of ZnO NPs supported by Aloe Vera as catalysts for the elimination of organic pollutants. As we witness the synthesis of nanomaterials harmonizing with nature, this study beckons towards a future where
sustainable practices seamlessly integrate with cutting-edge technology, offering innovative solutions to environmental challenges. The Al- ZnO NPs emerge not just as microscopic entities but as ambassadors of a greener, more sustainable era in nanotechnology. In conclusion, the Al-doped ZnO nanoparticles exhibit a refractive index of 2.49, reflecting exceptional light-refracting abilities essential for optical applications. The high optical conductivity, calculated at $1.4 \times 10^{10} \text{s}^{-1}$, underscores efficient photon absorption and re-emission, making these nanoparticles promising candidates for integration into solar cells and light-emitting devices. Their demonstrated light-manipulating efficiency suggests a potential contribution to advancements in renewable energy technologies.

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6. **Author Contribution:** Sanju Singh conceptualized and designed the experimental work, conducted data analysis, and drafted the manuscript. Dr Bhawana Jain provided supervision for the experimental work and contributed to the preparation of the manuscript.

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