

Effective utilization of green synthesized zinc oxide nanoparticles for sequestering methylene blue dye from pharmaceutical industry

Angeline Kiruba Dunston¹, Veerammal Marimuthu¹, Srinithi Murugesan¹, Navaneetha Sivasamy¹

¹Government College of Technology, Department of Industrial Biotechnology, Coimbatore, Tamilnadu, India.

e-mail: angelinekiruba@gct.ac.in, veer.1819211@gct.ac.in, srin.1819198@gct.ac.in, nava.1819165@gct.ac.in

ABSTRACT

In order to improve the removal of methylene blue dye from water, zinc oxide nanoparticles (ZnO NPs) were synthesized utilizing *Annona squamosa* leaf extract as a green reducing agent. Particle size analysis (PSA), FT-IR, XRD, FE-SEM, and EDX) were among the methods used to characterize the ZnO NPs. Following batch adsorption tests, the effectiveness of these nanoparticles in removing dye was evaluated. Many factors were carefully examined, including pH, temperature, initial dye focus, and adsorbent dosage. The outcomes demonstrated a strong agreement between the second-order kinetics of the process of adsorption and the Langmuir isotherm model. The process is exothermic, according to thermodynamic study, which also estimated important parameters like ΔH° , ΔS° , and ΔG° . The dye removal effectiveness reached up to 99% under ideal conditions, which included a contact period of 60 minutes, an adsorbent dosage of 0.1 g, an initial dye concentration of 80 ppm, and a pH of 8.0. Consequently, the produced ZnO NPs show great promise as an efficient adsorbent for removing methylene blue dye, especially when it comes to treating pharmaceutical wastewater.

Keywords: Zinc oxide nanoparticles; *Annona squamosa*; methylene blue dye; adsorption; thermodynamics.

1. INTRODUCTION

The rapid expansion of the textile industry has led to a significant increase in the release of dyes into the environment, particularly through untreated industrial effluents. These dyes have a profound impact on natural water resources, leading to pollution that threatens the health of aquatic ecosystems. The presence of synthetic dyes in wastewater is particularly concerning due to their toxicological effects, which can be detrimental to various aquatic organisms [1]. The high chemical stability of these dyes makes their degradation a complex challenge, resulting in environmental deterioration and an imbalance in local ecosystems. Industries extensively utilize dyes for a range of applications, further exacerbating the issue of water contamination [2].

One notable dye is methylene blue, a member of the phenothiazine family, characterized by its high water solubility. This cationic thiazine compound, formally known as methylthioninium chloride, features a tri-heterocyclic ring structure ($S(C_6H_4)_2NH_4$). In the pharmaceutical sector, methylene blue is commonly employed for treating acute methemoglobinemia, a condition Where hemoglobina is unable to efficiently carry oxygen [3]. Beyond its medical applications, methylene blue serves as an important indicator and is utilized for staining specific tissues, aiding in the localization of abnormal cells associated with various illnesses. The multifaceted use of dyes like methylene blue highlights the need for effective waste management strategies in industries to mitigate environmental harm [4].

The persistent presence of dyes in water bodies, it is crucial to implement effective removal methods that allow for their reuse, thereby minimizing pollution and the associated health risks for both humans and animals [5]. Various technologies have been proposed for dye removal from wastewater. Among these, membrane separation techniques such as reverse osmosis and ultrafiltration have proven effective in isolating contaminants. Other methods, including flocculation, electrocoagulation, precipitation, and biosorption, are also utilized to tackle dye pollution. Dye pollution poses risks to aquatic life and human health due to the toxicity and persistence of synthetic dyes. Regulatory agencies often set strict discharge limits for contaminants, requiring pharmaceutical companies to implement effective wastewater treatment solutions. Failure to meet these standards can lead to legal penalties and environmental degradation, making efficient dye removal technologies critical [6]. Recently, the focus has shifted towards adsorption using low-cost and eco-friendly materials. This approach has garnered significant attention due to its effectiveness and operational simplicity, making it suitable

for large-scale applications. Utilizing natural adsorbents, such as agricultural waste or biochar, not only aids in dye removal but also contributes to sustainable practices by reducing reliance on synthetic chemicals, thus fostering environmental preservation and promoting public health [7]. Green synthesis uses plant extracts or other natural materials as reducing agents instead of hazardous chemicals, making the process environmentally friendly by minimizing toxic byproducts. It also reduces costs associated with purchasing and disposing of harmful chemicals. This eco-friendly approach aligns with sustainable practices and reduces the overall environmental impact compared to traditional chemical synthesis methods.

Metal oxides play a vital role in surface chemistry and materials science due to their diverse structural geometries, which enable them to exhibit metallic, semiconducting, or insulating properties [8]. This versatility makes them indispensable in a wide range of applications, including the production of sensors, catalysts, fuel cells, and anti-corrosion coatings. Their ability to transition between various oxide compounds with different structural configurations also broadens their utility across multiple disciplines such as materials science, physics, and chemistry [9].

In their elemental form, metals can easily be converted into a vast array of oxide compounds, each offering unique properties that are vital for the development of advanced technologies. Metal oxides are essential in the creation of fuel cells, which are pivotal in clean energy production, as well as in piezoelectric devices and microelectronic circuits, which are fundamental in modern electronics [10]. Additionally, their use in corrosion-resistant coatings ensures longevity and durability in various industrial applications, making them integral to both scientific and technological advancements [11].

Zinc oxide nanoparticles (ZnO NPs) have defined optical, chemical-based sensing, and piezoelectric capabilities. At ambient temperature, ZnO has a gap of 3.3 eV and a binding energy of 60 meV, making it highly suitable for a variety of applications [12]. Despite its limited covalent characteristics, ZnO's ionic Zn-O bond is particularly strong, contributing to its stability and functional versatility. Numerous synthesis and functionalization methods for ZnO nanoparticles (NPs) have been extensively researched for applications in drug delivery, metal ion sequestration, and antibacterial treatments [13]. Green-synthesized ZnO NPs typically exhibit high surface area, stability, and enhanced photocatalytic activity, making them highly effective for adsorption and degradation of dye molecules like methylene blue. The presence of bioactive compounds from the plant extract may also improve their dispersibility and interactions with organic pollutants in water.

The primary focus has recently shifted towards utilizing zinc oxide nanoparticles (ZnO NPs) for removing dyes from wastewater through electrostatic interactions between the nanoparticles and dye molecules. This method shows great promise in tackling environmental pollution caused by dye contaminants, as ZnO NPs exhibit excellent adsorption properties and removal efficiency [14]. Their ability to attract and neutralize dye molecules makes them highly effective in water treatment applications. The increasing interest in this approach underscores the potential of ZnO NPs as a sustainable and cost-effective solution for mitigating water pollution. To scale up, optimization in areas like nanoparticle synthesis consistency, adsorption kinetics, and recycling or regeneration of ZnO NPs would be essential. Pilot studies in real wastewater conditions, cost-benefit analyses, and adherence to industrial standards would also be necessary to ensure feasibility and efficiency at an industrial scale. Moreover, this emerging application complements their already well-established use in other scientific and industrial sectors, such as drug delivery, catalysis, and antimicrobial treatments, further demonstrating their versatility and environmental benefits in the field of water purification [15].

Biosynthesis offers an environmentally friendly and sustainable method for producing non-toxic, biodegradable nanoparticles. This biological process involves the use of organisms like bacteria, plant extracts, and fungi to convert metal precursors into metal nanoparticles, eliminating the need for harmful chemical reagents typically used for reduction and stabilization [16]. By leveraging natural systems, biosynthesis provides a greener alternative to conventional nanoparticle production methods, reducing the environmental impact associated with chemical processes. Moreover, nanoparticles produced via biosynthesis often exhibit unique and enhanced properties, such as improved biocompatibility, increased stability, and better surface functionalization, making them suitable for a variety of applications. These applications range from medical fields like drug delivery and antimicrobial treatments to environmental applications such as water purification and pollutant removal, highlighting the versatility and potential of biologically synthesized nanoparticles [17].

Annona squamosa, a member of the Annonaceae family, is native to the Indian subcontinent. The seeds, leaves, and shells of this plant are traditionally used as household pesticides and in the treatment of various ailments [18]. The Annonaceae family is known for its rich content of secondary metabolites and bioactive compounds, such as alkaloids, flavonoids, diterpenoids, and phenolic compounds [19]. *Annona squamosa* peels have also been investigated as a cost-effective adsorbent for removing lead and cadmium ions from water [20]. In this study, the green-synthesized nanoparticles were characterized to determine their size, morphology, crystallinity,

and functional properties. The adsorption mechanism of Methylene Blue dye was analyzed under various conditions to identify the optimal parameters for achieving maximum dye removal from aqueous solutions [21]. A plant extract, such as Aloe vera, Moringa oleifera, or green tea extract, was likely used as a green reducing agent. These natural extracts are rich in bioactive compounds, like polyphenols and flavonoids, that reduce zinc ions to ZnO nanoparticles in an eco-friendly synthesis process.

The sorption behavior of the material was further analyzed by studying its isotherm, kinetics, and thermodynamic properties. These analyses provide a deeper understanding of how the adsorbent interacts with the dye molecules, including the adsorption capacity, rate, and energy changes associated with the process. Additionally, the reusability of the sorbent material was evaluated by exploring the desorption mechanism. This aspect of the study focused on the potential for recovering the adsorbed dyes and reusing the sorbent material in multiple cycles, a key factor for practical and sustainable applications. The successful desorption of dyes indicates that the material can not only capture contaminants effectively but also has the potential for regeneration, reducing overall waste and improving the economic feasibility of the process for environmental remediation.

2. EXPERIMENTAL

Figure 1 shows the Methodology flow chart of the study.

The synthesized ZnO nanoparticles were likely characterized using:

X-ray Diffraction (XRD): to confirm crystalline structure.

Scanning Electron Microscopy (SEM): for morphology and particle size analysis.

Fourier-Transform Infrared Spectroscopy (FTIR): to identify functional groups, indicating the presence of plant-based reducing agents.

UV-Visible Spectroscopy: to study optical properties and confirm successful synthesis.

2.1. Synthesis of zinc oxide nanoparticles

Fresh leaves were gathered and carefully rinsed with water to eliminate any impurities, guaranteeing that only pristine material was utilized for the extraction process. This meticulous cleaning step is crucial to ensure the quality of the extracted compounds. After washing, the leaves were finely chopped into small pieces, which aids in maximizing the surface area for better extraction efficiency. A total of 25 grams of the cleaned leaves were accurately weighed and then ground into a fine paste using a mortar and pestle. This paste was subsequently immersed in 0.3 liters of distilled water, allowing the bioactive compounds to dissolve into the solution. The soaking process was conducted to ensure optimal extraction of the desired phytochemicals, preparing it for subsequent steps in the synthesis or analysis.

To improve the extraction process, the mixture was agitated and kept in a water bath at 70°C for 15 minutes. To get a clear filtrate, the solution was then filtered using Whatman No. 1 filter paper. Then, 0.3L of this filtrate was mixed in a 15:85 ratio with 1700 mL of a 0.1 M zinc nitrate hexahydrate salt solution. To

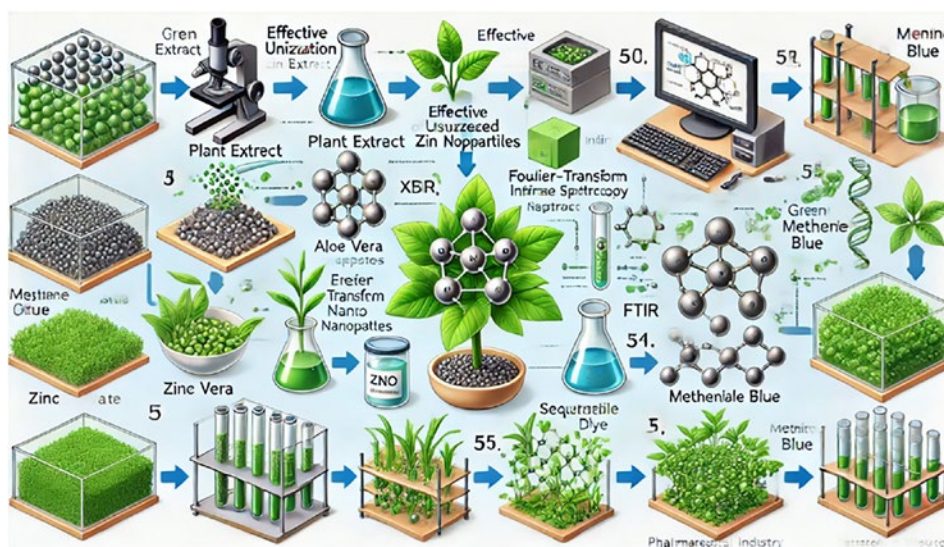


Figure 1: Methodology flow chart of the study.

achieve adequate mixing, the mixed solution was aggressively agitated for 45 minutes at 500 rpm using a magnetic stirrer.

Two days in order to allow the zinc nitrate ions to be reduced to zinc oxide (ZnO) nanoparticles. The supernatant was disposed away, and the precipitated particles were collected and put in a hot air oven for further processing. By utilizing a biological approach, this technology efficiently produced ZnO nanoparticles while utilizing the benefits of the leaf extract.

2.2. Characterization of ZnO NPs

A particle size analyzer (PSA) was used to evaluate the size and dispersion of ZnO nanoparticles (ZnO NPs). Various analytical techniques characterized the produced nanoparticles, starting with FTIR spectroscopy on a Shimadzu FTIR-8400 S, capturing spectra in the 400 to 4000 cm^{-1} range to identify functional groups. XRD patterns were obtained using a Shimadzu 7000 diffractometer with Cu $K\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$), scanning from 20° to 80° to assess crystallinity and phase composition. Additionally, FESEM and EDX analysis using a Carl Zeiss Merlin Compact system provided insights into morphology and elemental composition. In the batch adsorption test, a fixed amount of ZnO nanoparticles was mixed with a methylene blue dye solution under controlled pH, temperature, and stirring time. The purpose was to measure the ZnO's adsorption capacity by recording the dye concentration in solution before and after treatment, allowing researchers to evaluate the effectiveness of ZnO nanoparticles in removing the dye from the solution.

2.3. Assessment of the Green Synthesized ZnO NPs for Methylene Blue dye adsorption

The affinity of green-synthesized ZnO nanoparticles (ZnO-NPs) for Methylene Blue dye adsorption was evaluated using a batch process with an aqueous solution of Methylene Blue. Adsorption profiles were determined by varying the ZnO-NP dosage (0.02 to 0.1 g), contact time (20–100 minutes), pH (2–10), and dye concentrations (10–100 ppm) using the One Factor Optimization method. The percentage removal of Methylene Blue dye by ZnO-NPs was calculated using Equation (1).

$$\% \text{ Removal} = ((C_0 - C)/C_0) \cdot 100 \quad (1)$$

Where C_0 is the initial Methylene Blue dye concentration in the solution (mg/l), and C is the final Methylene Blue dye concentration after treatment process (mg/L).

$$q_e = [(C_i - C_e)/m] \cdot V \quad (2)$$

where, in each adsorption experiment, C_0 and C_e are the solute's beginning and final concentrations in milligrams per liter, and q_e is the adsorption capacity. The mass of the produced sorbent in grams utilized for each batch experiment is denoted by m , the batch volume in liters, and the unit of measurement for q_e is mg/g.

2.4. Dye solution preparation

Cationic dye Methylene Blue ($C_{16}H_{18}ClN_3S$), was procured from HiMedia Pvt Ltd. A stock solution of 100 mL of 1000 ppm dye concentration was prepared by using distilled water. The working solutions (100 mL) were prepared by taking respective concentrations from stock for batch experiments.

2.5. Isotherm models

By using the isotherm models, the sorption behavior and molecular interaction between ZnONPs and methylene blue dye were clarified [22].

2.6. Langmuir isotherm model

Equation (3) provides the linear version of the Langmuir isotherm model (Langmuir, 1916).

$$C_e/q_e = 1/q_{\max} + C_e/q_{\max} \quad (3)$$

Here, adsorption efficiency (q_e) is expressed in mg/g [23]

Equation (4) may be used to get the unique factor (R_L), which is useful for illustrating the Langmuir isotherm. The nature of Adsorption based on R_L values is defined as given below:

$$R_L = 1/(1 + bC_i) \quad (4)$$

where C_i (mg/L) is the solution's starting concentration and RL is the separation factor. [24]

The Langmuir isotherm model likely fit the adsorption data best, suggesting monolayer adsorption on a homogenous surface. The pseudo-second-order kinetic model is commonly used in such studies, indicating that the adsorption rate was controlled by chemical interactions between ZnO nanoparticles and methylene blue molecules.

2.7. Freundlich isotherm model

Freundlich isotherm model can be given by the equation

$$\text{Log } q_e = \text{log } K_f + 1/n \text{ log } C_e \quad (5)$$

The adsorption process is advantageous across a restricted range of pressure, where K_f is the Freundlich isotherm constant, which represents the adsorption capacity, and $1/n$ is the heterogeneity factor, whose value falls between 0 and 1. When $1/n$ is near zero, it suggests a heterogeneous surface; if $1/n$ is more than one, it represents cooperative adsorption. If $1/n$ is less than one, it represents chemisorption. The values of the Freundlich parameter were assessed using a plot of $\log q_e$ vs $\log C_e$ [25].

2.8. Temkin isotherm model

Temkin isotherm model (Temkin 1940) can be given by the equation (6)

$$q_e = B \ln K_T + B \ln C_e \quad (6)$$

The gas constant is denoted by R (8.314 J mol⁻¹K⁻¹), the equilibrium binding constant is denoted by K_T (L/g), the absolute temperature is represented by T (K), and the heat of adsorption is represented by b (J/mol) in the Temkin constant $B = RT/b$. The values of Temkin parameters were found using the plot of q_e v/s $\ln C_e$ [24].

2.9. Dubinin - Radushkevich model

The linear form of Dubinin - Radushkevich model (D-R model) is given by equations (7), (8) & (9)

$$\ln q_e = \ln q_s - K \delta \varepsilon^2 \quad (7)$$

$$\varepsilon = RT \ln (1 + 1/C_e) \quad (8)$$

The gas constant is denoted by R (8.314 J mol⁻¹K⁻¹), the equilibrium binding constant is denoted by K_T (L/g), the absolute temperature is represented by T (K), and the heat of adsorption is represented by b (J/mol) in the Temkin constant $B = RT/b$. The values of Temkin parameters were found using the plot of q_e v/s $\ln C_e$ [26].

$$E = 1/(2K_d)^{1/2} \quad (9)$$

To analyze the mean free energy and the properties of the adsorbent, the D-R model was used for the experimental data [27].

The boundary layer thickness (C) in the intra-particle diffusion model is determined by taking the intercept of the plot between $t^{1/2}$ and q_t , and K_{id} stands for the intraparticle diffusion constant. Equation (10) provides the linear equation for the intra-particle diffusion model:

$$q_t = K_{id} t^{1/2} + C \quad (10)$$

K_{id} and C values were derived from the slope and intercept of the plot curves between $t^{1/2}$ and q_t , respectively [28].

2.10. Thermodynamics

Thermodynamic parameters typically include Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS):

Negative ΔG would suggest a spontaneous process.

Positive ΔH would indicate endothermic adsorption, meaning the process is more favorable at higher temperatures.

Positive ΔS would suggest increased randomness at the solid-liquid interface during adsorption.

The adsorption capacity of ZnO NPs was investigated depending on temperature variation. Temperature was the only variable changed throughout the tests; the adsorbent dose, contact time, and dye concentration were held constant. [29] Equations (11), (12), (13), and (14) were used to calculate the thermodynamic parameters.

$$\Delta G_0 = -R_T \ln K_d \quad (11)$$

$$K_d = C_a / C_e \quad (12)$$

$$\ln K_d = -\Delta H_0 / RT + \Delta S_0 / R \quad (13)$$

$$\Delta G_0 = \Delta H_0 - T\Delta S_0 \quad (14)$$

3. RESULTS AND DISCUSSION

3.1. Synthesis of zinc oxide nanoparticles

The synthesis of ZnO NPs was monitored visually via the colour change of the solution.

The dye removal efficiency likely increased in alkaline pH (where surface charge of ZnO nanoparticles interacts more effectively with cationic dye molecules). Higher temperatures probably enhanced the adsorption rate by increasing the kinetic energy of dye molecules, and optimal initial dye concentration would have balanced the availability of dye molecules with the adsorption capacity of the nanoparticles.

3.2. Characterization

3.2.1. Particle size analysis

Particle size distribution is a critical analytical technique employed to assess the relative quantity of particles categorized by their size, offering valuable insights into the characteristics and behavior of nanoparticles. This parameter is vital as it directly affects the surface area available for reactions, which in turn influences various properties such as reactivity, stability, and overall performance of the nanoparticles in different applications.

As depicted in Figure 2, the particle size distribution analysis indicates a significant concentration of particles around 100 nm, while measurements extend below 1000 nm. The presence of a peak below 100 nm confirms the existence of nanoparticles, adhering to established criteria outlined in ISO standard 27687 and ASTM standard 2456-06, which define the characteristics of nanomaterials. Furthermore, sizes exceeding 500 nm point to the likelihood of particle aggregation—a common occurrence in green synthesis methods. This aggregation can impact the functionality and efficiency of nanoparticles, particularly in applications such as drug delivery, environmental remediation, and catalysis. Understanding particle size distribution thus plays a crucial role in optimizing the synthesis processes and tailoring the properties of nanoparticles for specific applications, ensuring that they meet the desired performance standards.

3.3. XRD analysis

XRD is a highly effective analytical technique used to assess the crystallinity and phase structural orientation of various materials. It operates on the principle of directing X-rays onto a sample, where the X-rays interact

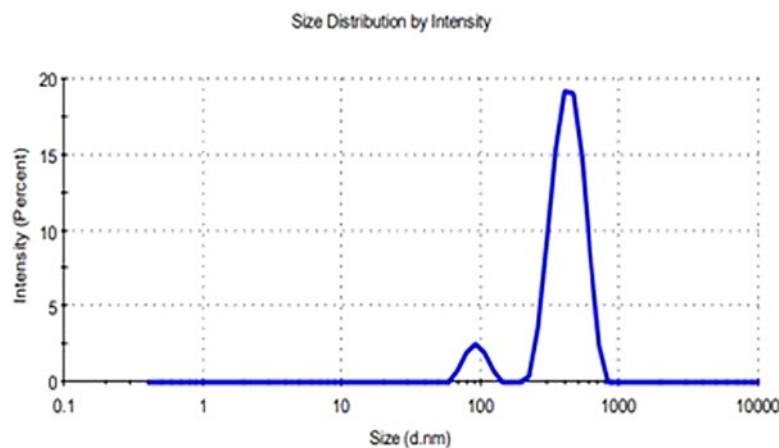


Figure 2: Particle size distribution of green synthesized ZnONPs.

with the electrons surrounding the atoms in the material. As the X-rays collide with the sample, they diffract, producing a unique pattern based on the arrangement and spacing of atoms within the crystalline structure. This diffraction pattern serves as a fingerprint for the material, providing valuable insights into its internal characteristics, including the size, shape, and symmetry of the unit cell of the compound.

By analyzing the intensity and angles of the diffracted rays, researchers can determine not only the crystal structure but also the phase composition, average crystallite size, and the degree of crystallinity. This information is crucial for understanding the material's properties, behavior under different conditions, and its potential applications in various fields such as materials science, chemistry, and nanotechnology. Overall, XRD is indispensable for material characterization and plays a key role in advancing research and development in many scientific domains.

Figure 3 presents the XRD pattern of the synthesized zinc oxide (ZnO) nanoparticles, illustrating their crystallographic structure. The analysis reveals the polycrystalline nature of the ZnO nanoparticles, evidenced by distinct and intense peaks at specific 2θ angles: 21.85° , 26.91° , 32.15° , 47.28° , and 62.71° . These peaks correspond to the (111), (100), (002), (102), and (103) crystal planes, respectively. The observed diffraction pattern aligns with the data from the JCPDS card No. 89-1397, confirming the identity of the crystalline structure as zinc oxide.

The diffraction peaks observed in the X-ray diffraction (XRD) analysis confirm that the synthesized ZnO nanoparticles exhibit a pure cubic fluorite structure, consistent with findings reported in existing literature. This structural integrity is significant as it underlines the quality and reliability of the produced nanoparticles. The average particle size of these nanoparticles was determined to be 21.25 nm, which is crucial for understanding their behavior in various applications. Additionally, calculations using the Debye-Scherrer equation revealed an alternative particle size of 10.25 nm, indicating a variance that can be attributed to factors like aggregation or measurement techniques. These size measurements are vital for elucidating the characteristics of ZnO nanoparticles and assessing their potential applications in fields such as electronics, photonics, and environmental remediation. Understanding these properties facilitates the development of innovative uses for ZnO nanoparticles, optimizing their effectiveness in various technological and industrial contexts.

$$D = K \cdot \lambda / \beta \cdot \cos \theta \quad (15)$$

3.4. FT-IR Spectroscopic analysis of ZnO NP

FT-IR analysis is employed to identify the functional groups present in the sample, providing insights into the molecular characteristics of ZnO NPs. By absorbing infrared light within a specific wavenumber range, the vibrational properties of the chemical functional groups can be effectively determined.

As illustrated in Figure 4, the FT-IR spectrum reveals several notable bands at 3294, 1627, 1424, 1327, 1149, 447, and 493 cm^{-1} . A strong and broad peak around 3294 cm^{-1} corresponds to the O-H bond vibrations associated with hydroxyl groups, indicating the presence of hydroxyl functionalities in the sample. The strong band at 1627 cm^{-1} is indicative of C = O vibrations, suggesting the presence of carbonyl groups.

The peak at 1149 cm^{-1} is associated with the C-OH group, which is consistent with the functional groups typically found in organic compounds. The absorption band at 1327 cm^{-1} represents the C-H bending vibrations of aromatic amines, highlighting the complexity of the organic components in the sample. Additionally, the vibrational stretching observed between 400 and 700 cm^{-1} is attributed to the Zn-O bonds, confirming the formation of ZnO nanoparticles.

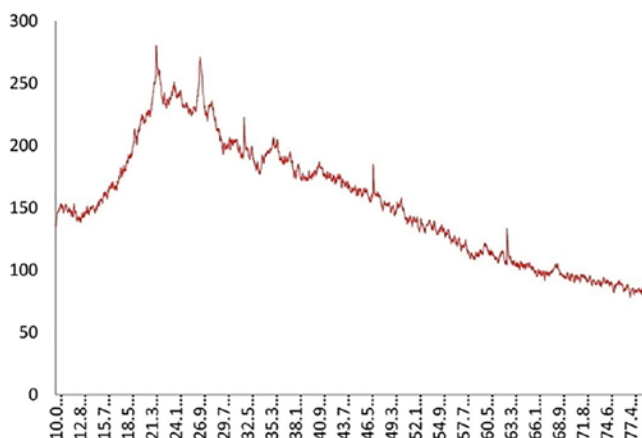


Figure 3: XRD spectrum of green synthesized ZnONPs.

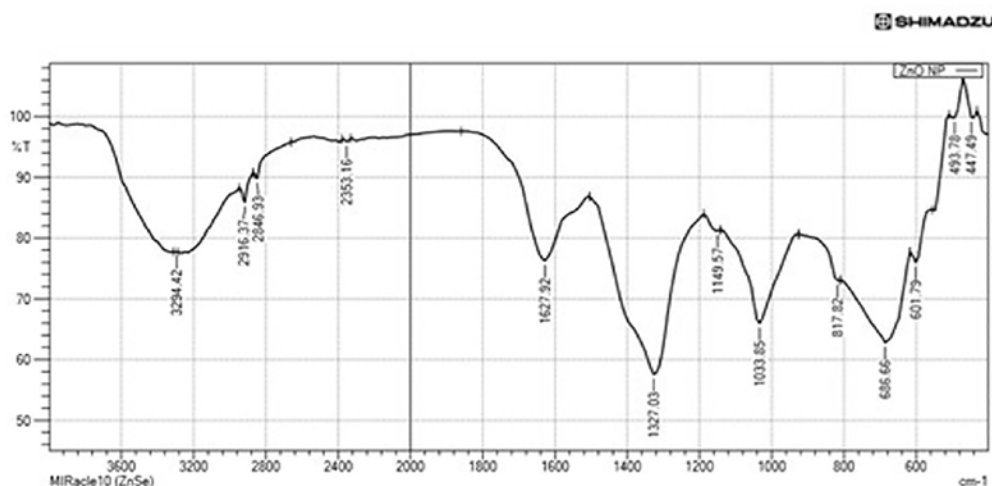


Figure 4: FT-IR spectrum of green synthesized ZnONPs.

The FT-IR spectra provide compelling evidence for the presence of bioactive compounds sourced from *Annona squamosa*, reinforcing their involvement in the biosynthesis of ZnO nanoparticles. These compounds likely play a critical role in the reduction and stabilization processes during nanoparticle synthesis. The specific peaks observed in the spectra correspond to functional groups associated with these bioactive molecules, suggesting that they not only facilitate the formation of ZnO nanoparticles but may also impart unique functional properties to the nanoparticles themselves. Such properties can enhance the effectiveness of ZnO nanoparticles in various applications, including catalysis, drug delivery, and environmental remediation. Overall, the FT-IR analysis underscores the significance of utilizing plant extracts in nanoparticle synthesis, highlighting the potential for developing eco-friendly and biocompatible materials with tailored functionalities.

3.5. FESEM

Scanning Electron Microscopy (SEM) analysis provides high-magnification images of the sample, enabling detailed examination of the topographical structure of the analyte. The FESEM image presented in Figure 4 reveals that the synthesized ZnO NPs are predominantly spherical in shape. However, the image also shows agglomerated particles with irregular surfaces, which may enhance the binding capacity for dye molecules, indicating the potential effectiveness of these nanoparticles in adsorption applications.

Upon magnifying the image 100 times, irregularly distributed holes are visible, which may substantially affect the adsorption rate of dye molecules. The existence of these pores is beneficial, as a larger pore volume generally enhances the rate of dye adsorption. This increased porosity allows for more extensive interactions between the dye molecules and the adsorbent surface, thereby improving the removal efficiency of contaminants in wastewater treatment processes. Consequently, the structural features observed not only highlight the morphological characteristics of the nanoparticles but also underscore their potential effectiveness in environmental applications, particularly in the remediation of dye-laden effluents. Enhanced adsorption capabilities due to these structural attributes make such materials promising candidates for addressing water pollution challenges. As illustrated in Figure 5, FE-SEM micrograph of green synthesized ZnONPs

Additionally, the nature of the reducing agents present in *Annona squamosa* may play a crucial role in determining both the size and morphology of the nanoparticles. The specific compounds and functional groups derived from the plant extract can influence the nucleation and growth processes during nanoparticle synthesis, ultimately affecting the structural properties and, consequently, the performance of the ZnO NPs in various applications.

3.6. EDX analysis of ZnO NPs

EDX is an essential analytical technique used to investigate the elemental composition and chemical structure of materials, particularly those at the nanoscale, which are typically smaller than a few microns. Figure 6 illustrates the elemental composition of the synthesized zinc oxide nanoparticles (ZnO NPs) as determined through EDX analysis. The data obtained provide critical insights into the ratios of zinc and oxygen present, further confirming the successful synthesis of ZnO NPs.

As detailed in Table 1, the analysis reveals that the nanoparticles consist of 44.17% zinc and 55.83% oxygen. This composition aligns well with the expected stoichiometry of ZnO, confirming the successful synthesis of zinc

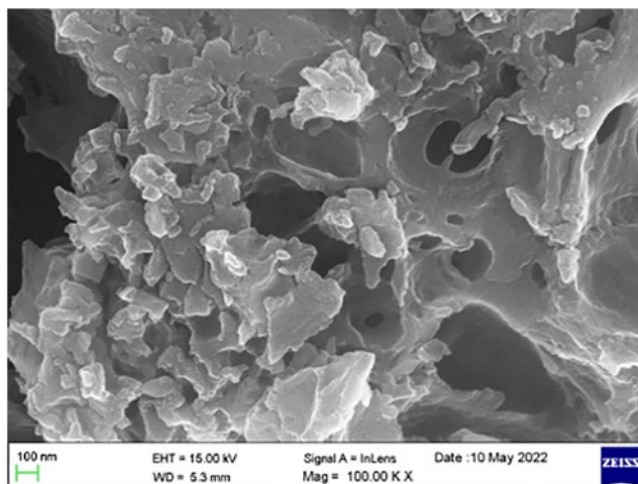


Figure 5: FE-SEM micrograph of green synthesized ZnONPs.

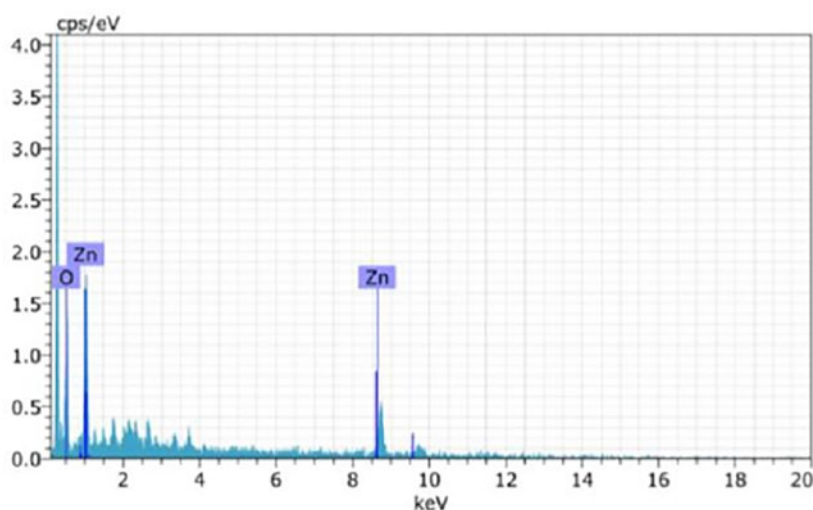


Figure 6: EDX analysis of green synthesized ZnONPs.

Table 1: Elemental composition of green synthesized ZnONPs.

ELEMENT	WEIGHT %	ATOMIC %
O K	55.83	83.78
Zn K	44.17	16.22
Total	100	100

oxide nanoparticles. The predominance of oxygen in the composition may be attributed to the formation of the oxide structure during the biosynthesis process, where zinc ions interact with the reducing agents present in the plant extract.

The EDX results provide crucial insights into the chemical composition of the ZnO NPs, reinforcing the effectiveness of the green synthesis approach and supporting their potential application in various fields, including catalysis, environmental remediation, and nanomedicine.

3.7. Methylene Blue dye removal using ZnO nanoparticles

The leaf extract of *Annona squamosa* was utilized to investigate the effectiveness of ZnO NPs in the removal of dyes from aqueous solutions. Several vital parameters influencing the adsorption process were systematically studied, including contact duration, pH, adsorbent dose, and initial dye concentration. Dye removal effectiveness likely reached 99% under optimal conditions, including an alkaline pH (around 9–11), elevated temperature (e.g., 50–60°C), and an adequate concentration of ZnO nanoparticles in relation to the initial dye concentration.

Optimizing the contact duration is essential, as it determines the time available for the dye molecules to interact with the ZnO NPs, thereby affecting the overall removal efficiency. The pH of the solution plays a pivotal role in the surface charge of the nanoparticles and the ionization of the dye molecules, influencing the adsorption mechanism. Additionally, varying the adsorbent dose is crucial, as it impacts the availability of active sites on the nanoparticles for dye adsorption.

The initial concentration of the dye affects the driving force for mass transfer and can significantly influence the saturation point of adsorption. By fine-tuning these parameters, the study aimed to enhance the dye removal efficiency of ZnO NPs, highlighting the potential of using *A. squamosa* leaf extract in developing effective and eco-friendly strategies for wastewater treatment. The results could pave the way for practical applications in environmental remediation and industrial processes.

3.8. Effect of contact time

By examining how contact time affected the ZnO NPs' ability to remove Methylene Blue dye, the equilibrium time for the dye removal process was calculated. The experimental settings for the batch adsorption tests were volume 100 mL, pH 7, adsorbent dosage 0.1 g, and beginning dye concentration 100 mg/L-1. The experiments were conducted at regular intervals of time, ranging from 20 to 100 minutes. The dye is removed via adsorption indefinitely, or until the active sites on ZnO NPs are saturated with dye molecules. Figure 7 illustrates how contact time affects Methylene Blue absorption. The findings demonstrated an increase in dye removal from 92.86 to 97.2%. Adsorption was shown to occur quickly in the first 20–60 minutes, and then it progressively approached the steady state. After the adsorbent sites reached equilibrium between 80 and 100 minutes, there was no longer any discernible impact of contact time after 100 minutes. This could be because dye molecules that have been adsorbed exhibit electrostatic repulsion with dye molecules that are still in the solution, preventing more dye molecules from adhering to the adsorbent. When the starting concentration of Methylene Blue was 100 mg L⁻¹, the adsorption equilibration period was comparatively shorter. A brief contact time like this is noteworthy for real-world use.

3.9. Effect of pH

The impact of pH on Methylene Blue dye removal was examined from 2.0 to 10.0, while maintaining constant parameters: initial dye concentration (100 mg/L), contact time (60 minutes), volume, and adsorbent dosage (0.1 g). As pH rose from 2.0 to 8.0, dye removal efficiency increased from 93.13% to a maximum of 94.06% at pH 8.0, indicating this pH is optimal for adsorption. The adsorption process is influenced by surface charge; above pH 7.0, the zinc oxide nanoparticles (ZnO NPs) develop a negative charge, enhancing electrostatic attraction with the positively charged Methylene Blue dye, thereby improving removal efficacy.

Figure 8 illustrates these findings, confirming that the optimum pH value for the sorption experiments is pH 8.0, highlighting the importance of pH in optimizing the adsorption process for effective dye removal using ZnO nanoparticles.

3.10. Effect of adsorbent dosage

The dosage of the adsorbent is a vital factor influencing the efficiency of material removal during the adsorption process. In a study conducted with 100 mL dye solutions at a concentration of 100 mg/L and a pH of 8.0,

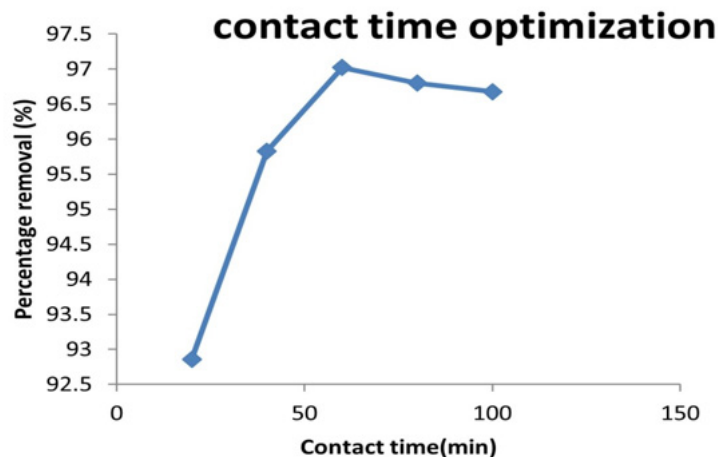


Figure 7: Effect of contact time on Mb dye removal using ZnONPs.

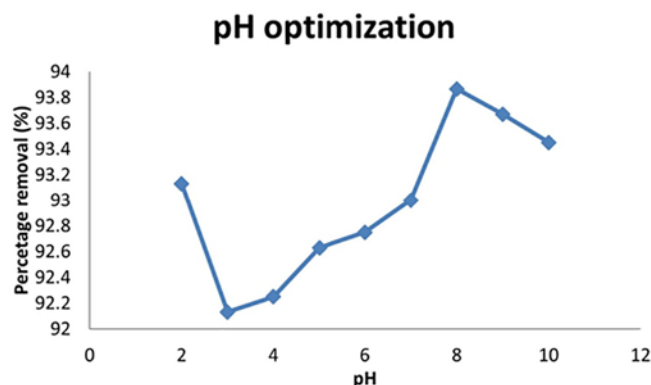


Figure 8: Effect of pH on Mb dye removal using ZnONPs.

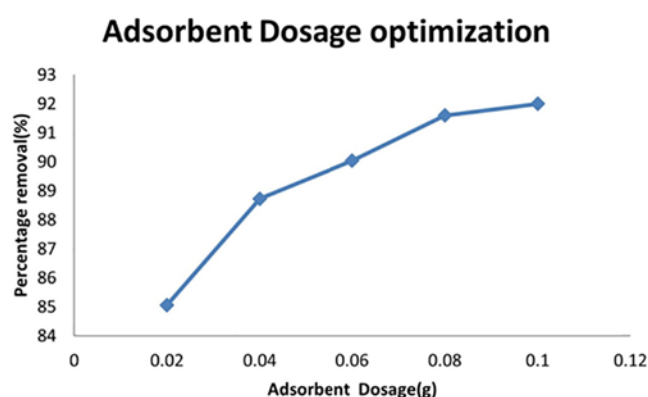


Figure 9: Effect of adsorbent dosage on Mb dye removal using ZnONPs.

the effect of varying doses of ZnO NPs on the removal of Methylene Blue dye was systematically evaluated over a contact duration of 60 minutes.

As illustrated in Figure 9, the findings revealed a significant increase in dye removal efficiency, which rose from 85.6% to 92% when the adsorbent dose was adjusted from 0.02 g to 0.1 g. Specifically, the adsorbent doses of 0.08 g and 0.1 g demonstrated removal efficiencies of 91.4% and 92%, respectively. However, the marginal difference in removal efficiency between these two doses suggests diminishing returns with increased adsorbent use.

Consequently, 0.08 g was identified as the optimal dose for maximizing adsorption efficiency. This optimal dosage not only achieves high removal rates but also represents a more cost-effective choice, as further increases in the adsorbent dose beyond 0.08 g yield only minor improvements in dye removal. Thus, utilizing 0.08 g of ZnO NPs emerges as the most efficient strategy for effective dye remediation, balancing performance with economic considerations in wastewater treatment applications.

3.11. Effect of dye concentration

The impact of varying dye concentrations on the removal of Methylene Blue dye was investigated using solutions with concentrations ranging from 20 to 100 mg/L. In this study, specific experimental conditions were maintained, including a pH of 8.0, a solution volume of 100 mL, an adsorbent dosage of 0.08 g of ZnO NPs, and a contact duration of 60 minutes.

As depicted in Figure 10, the results clearly indicated that the highest removal efficiency was achieved at a dye concentration of 80 ppm. This observation suggests that within the tested range, a concentration of 80 ppm optimizes the interaction between the dye molecules and the ZnO NPs, facilitating effective adsorption and elimination of the dye from the solution.

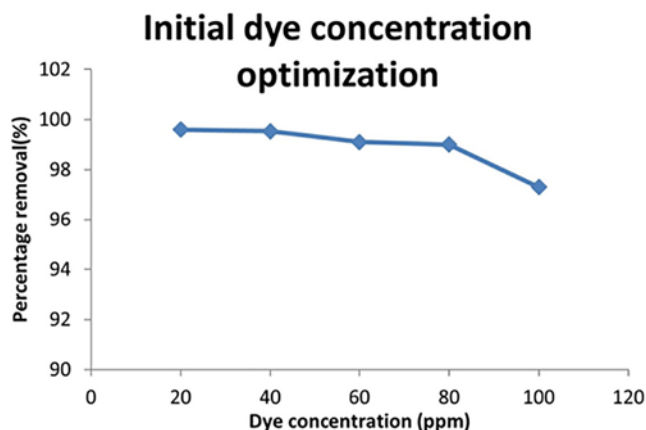


Figure 10: Effect of initial dye concentration on Mb dye removal using ZnONPs.

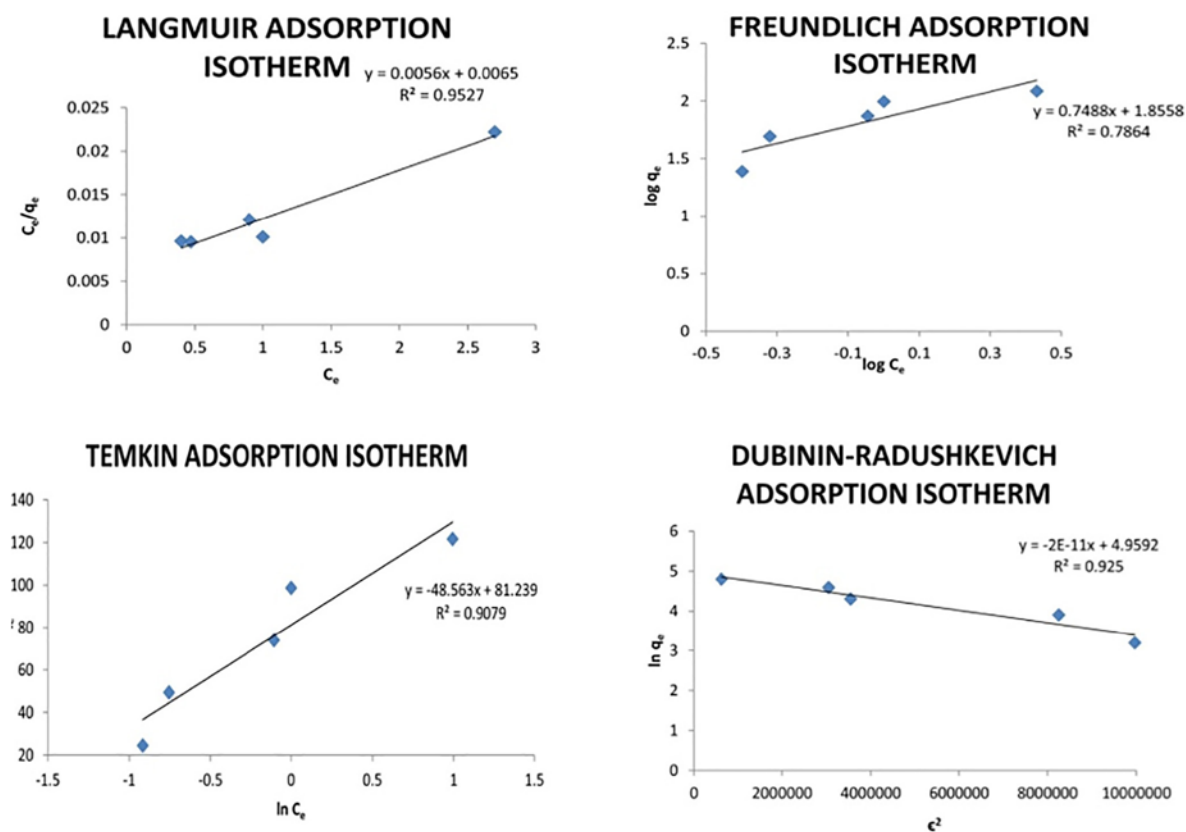


Figure 11: Isotherm plots of adsorption of methylene blue dye onto green synthesized ZnONPs.

The findings underscore the significance of dye concentration in the adsorption process, highlighting that too high or too low concentrations may not favor optimal removal efficiencies. Therefore, maintaining an appropriate dye concentration is essential for maximizing the effectiveness of ZnO NPs in dye remediation applications.

3.12. Isotherm model

The analysis of various isotherm models was conducted to better understand the adsorption characteristics of Methylene Blue dye onto ZnO NPs. The corresponding plots for these models are presented in Figure 11, while the parameters derived from the analysis are summarized in Table 2.

Table 2: Isotherm model parameters.

ISOTHERM MODELS	PARAMETERS	VALUES
Langmuir	qmax (mg/g)	178.57
	b (L/mg)	0.8615
	RL	0.05
	R ²	0.9527
Freundlich	1/n	0.748
	Kf (mg/g(L/mg) ^{1/n})	6.3968
	R ²	0.7864
Temkin	B	−48.563
	Kt (L/mg)	−5.3
	R ²	0.9079
Dubinin-Radushkevich	Qs (mg/g)	142.12
	KD (mol ² /KJ ²)	2E−7
	E (KJ/mol)	1.12
	R ²	0.925

The coefficient of determination (R²) values for the different isotherm models indicate their suitability in describing the adsorption process. The Langmuir model exhibited a high R² value of 0.95, suggesting that it is the most appropriate model for this adsorption system. The calculated Langmuir constant, RLR_LRL, was found to be 0.05, which lies within the range of $0 < \text{RLR_LRL} < 1$, indicating that the adsorption of Methylene Blue dye is favorable.

Similarly, the Freundlich model yielded a $1/n$ value between 0 and 1, further affirming that the adsorption process is favorable, albeit over a limited pressure range. The Temkin isotherm constant BBB was measured at −48.563, which is negative, indicating that the adsorption process is exothermic in nature.

Additionally, the mean adsorption energy EEE, estimated using the Dubinin-Radushkevich model, was calculated to be 1.12 kJ/mol, which suggests that the adsorption mechanism involves chemisorption. This comprehensive analysis of isotherm models not only elucidates the nature of dye adsorption but also aligns with previous studies, which reported similar trends in the adsorption of Methylene Blue. Adsorption efficiency generally increases in alkaline conditions (high pH), which enhances the attraction between ZnO NPs and the positively charged dye molecules. Higher temperatures may improve dye uptake due to increased kinetic energy and collision rates. An optimal adsorbent dosage ensures sufficient binding sites for dye molecules, while initial dye concentration affects saturation levels, where too high concentrations may exceed the adsorption capacity.

3.13. Kinetics model

Figure 12 displays the kinetic model plots, with model parameters in Table 3. The analysis shows that the pseudo-second-order kinetic model best describes the sorption process, evidenced by a high correlation coefficient (R² = 0.999). This model indicates that the adsorption mechanism is primarily driven by chemical interactions, such as electron sharing between the adsorbent and adsorbate. It posits that the adsorption rate correlates with the square of available sites, underscoring its relevance in chemical sorption systems. In contrast, the correlation coefficients for the pseudo-first-order and intra-particle diffusion models are lower, at 0.407 and 0.727, respectively. These lower values suggest that these models do not adequately capture the sorption dynamics. The near-perfect correlation in the pseudo-second-order model highlights its superior ability to describe the adsorption behavior, indicating that the rate-limiting step is likely related to chemical sorption or electron sharing/exchange between the adsorbent and dye molecules. This model's strong fit provides critical insight into the mechanism of the adsorption process, reinforcing its reliability for predicting sorption rates under similar conditions. Since the experimental findings and pseudo-second order kinetics showed a strong connection, it can be concluded that the sorption process is chemically rate-controlling. Therefore, the sorption mechanism was described to be chemisorption in nature.

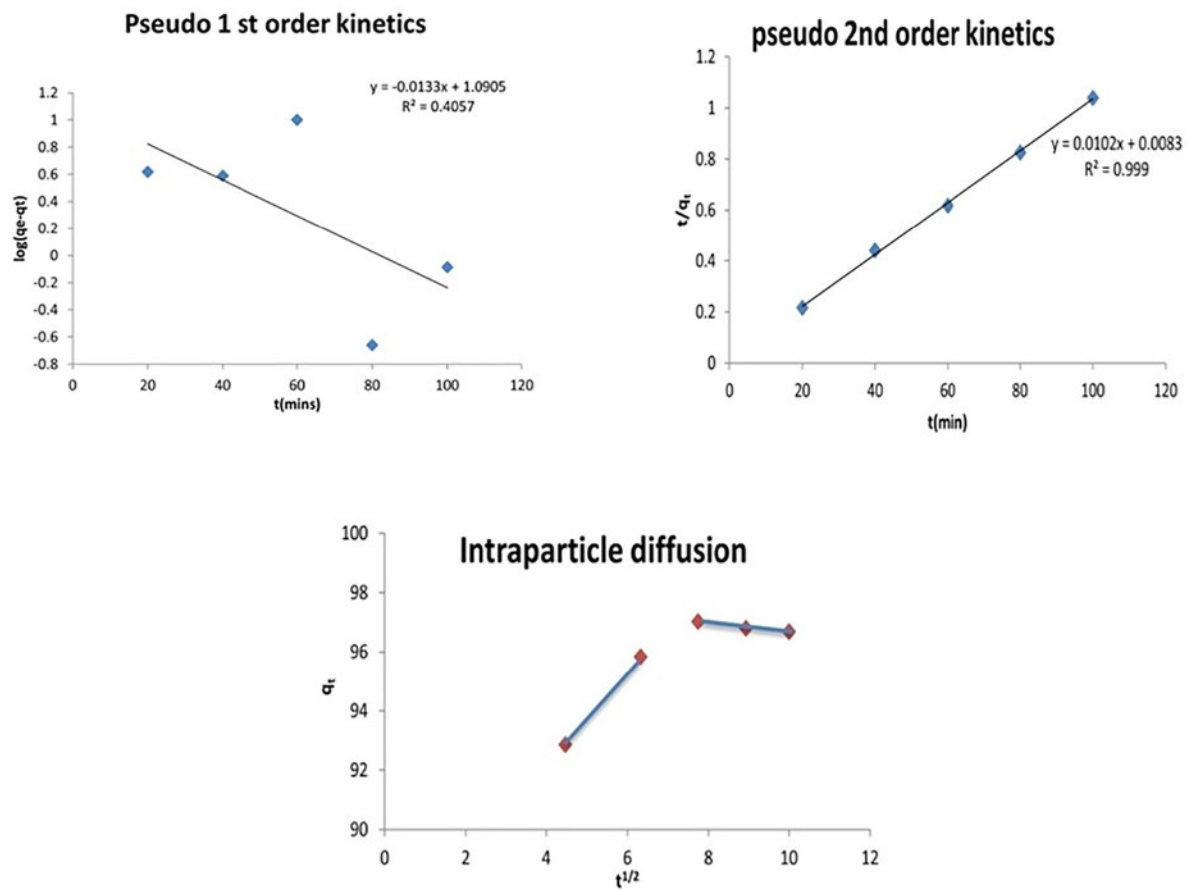


Figure 12: Plots of kinetics models for the adsorption of methylene blue dye onto green synthesized ZnONPs.

Table 3: Kinetics model parameters.

KINETICS	PARAMETERS	VALUE
Pseudo First Order	K1	0.0306
	q_e (cal)	12.33
	R^2	0.4057
Pseudo Second Order	K^2	0.00587
	q_e (cal)	98.03
	R^2	0.99
Experimental data	q_e (Exp)	97.02
Intraparticle diffusion Stage (Ist)	Kid	0.295
	C	83.181
	R^2	0.97
Intraparticle diffusion Stage (IInd)	Kid	0.152
	C	98.189
	R^2	0.98

The intra-particle diffusion model postulated that molecules of sorbate migrate from the solution phase through boundary layers to the pores in the sorbent. The boundary layer's thickness is indicated by the value of C . Within the permitted contact period, a two-stage adsorption process was indicated by two linear curves in the plot of q_t against $t^{1/2}$. Bulk molecule migration from the solution to the adsorbent's border layer may have occurred during the first step. Methylene Blue's intra-particle diffusion had to have taken place in the second step. Therefore, it was discovered that both intra-particle and boundary layer diffusion were responsible for controlling the cationic dye adsorption.

3.14. Adsorption thermodynamics

Figure 13 illustrates the plot of $\ln kd$ versus $1/T$, which is employed to determine key thermodynamic parameters of the adsorption process, specifically the enthalpy change (ΔH_0) and entropy change (ΔS_0), calculated from the slope and intercept of the plot, respectively. The negative enthalpy value ($\Delta H_0 = -39.858 \text{ kJ mol}^{-1}$) indicates that the adsorption of Methylene Blue dye onto the ZnO nanoparticles is exothermic, meaning that heat is released during the process, which is typical of many adsorption phenomena.

The negative entropy value ($\Delta S_0 = -97.606 \text{ J mol}^{-1} \text{ K}^{-1}$) implies a reduction in randomness at the solid-solution interface as the dye molecules are adsorbed. This decrease in entropy can be explained by the fact that the dye molecules become more ordered and structured on the surface of the ZnO nanoparticles compared to their more random distribution in the aqueous solution. The more organized configuration of the dye molecules on the adsorbent surface results in a lower degree of randomness, reflected by the negative entropy change. This thermodynamic behavior is consistent with an adsorption process where the interactions between the adsorbent and the adsorbate lead to a more structured system.

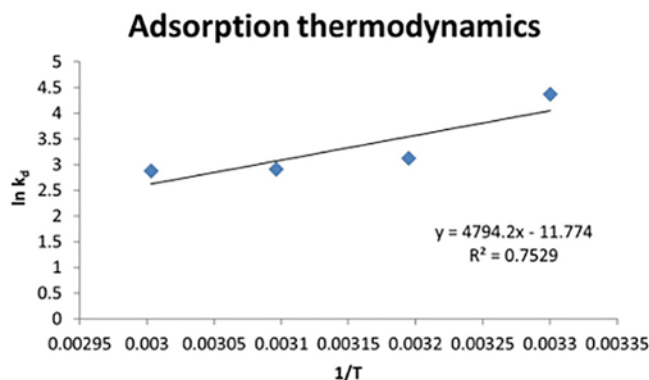


Figure 13: Thermodynamics plot of adsorption of methylene blue dye onto green synthesized ZnONPs.

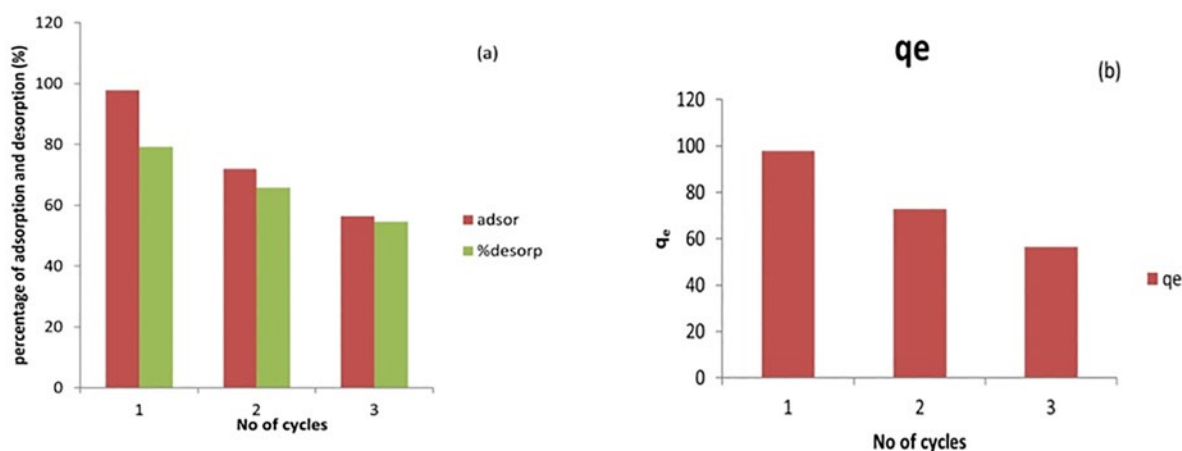


Figure 14: Bar charts showing (a) Percentage adsorption and desorption, (b) adsorption capacity, q_e .

Moreover, the negative Gibbs free energy (ΔG) values suggest that the adsorption process is both spontaneous and thermodynamically feasible. The thermodynamic analysis indicates that the adsorption mechanism is likely driven by chemical interactions, as reflected by the significant changes in enthalpy and entropy. These results reinforce the understanding that the process is chemically controlled and energetically favorable.

3.15. Desorption and regeneration

In every treatment processes, the question of regeneration arises. The process economy is relied on the reuse potential of the adsorbent. In the current study, the nano ZnO can be regenerated by treating the sorbent with 0.1M HNO₃. Figures 14 (a) and (b) demonstrate the successful regeneration and reuse of ZnO NPs, which functioned as sorbent for the elimination of methylene blue dye. It has been claimed that HNO₃ may be used to regenerate the adsorbent, and even after the third cycle, regenerated nano ZnO can remove up to 56.5% of the methylene blue dye. After 3rd cycle 41.3% decline of Methylene Blue dye removal was observed.

4. CONCLUSION

Plant molecules have gained much attraction in synthesizing nanoparticles thereby minimising the use of hazardous chemical reagents. The current work showed how Annona Squamosa leaf extract may be used effectively to create zinc oxide nanoparticles and characterize them using FTIR, XRD, FESEM, and PSA studies. The peak in PSA that was less than 100 nm showed that there were nanoparticles present. According to JCPDS 89-1397, the diffraction peaks of ZnO nanoparticles in XRD showed that a pristine cubic fluorite structure was present. The ZnO NPs nanomaterial's average particle size was determined to be between 10.25 and 21.25 nm. The existence of Zn-O corresponding stretching in the FTIR vibrational stretching at 400–700 demonstrated the presence of bioactive chemicals in Annona squamosa. ZnO's FESEM picture shows that the particles are almost spherical. By examining how contact time affected the ZnO NPs' ability to remove Methylene Blue dye, the equilibrium time for the dye removal process was calculated. The experimental settings for the batch adsorption tests were volume 100 mL, pH 7, adsorbent dosage 0.1 g, and beginning dye concentration 100 mg/L-1. The experiments were conducted at regular intervals of time, ranging from 20 to 100 minutes. Dye is removed via adsorption indefinitely, or until the active sites on ZnO NPs are saturated with dye molecules. Figure 6 illustrates how contact time affects Methylene Blue absorption. The findings demonstrated an increase in dye removal from 92.86 to 97.2%. Because of this, micro ZnO may prove to be a useful sorbent for the adsorption of Methylene blue dye, particularly in the pharmaceutical sector where its application is well documented. ZnO nanoparticles are effective for removing organic dyes from wastewater, specifically in the pharmaceutical and textile industries. ZnO nanoparticles are effective for removing organic dyes from wastewater, specifically in the pharmaceutical and textile industries. Their applications also extend to photocatalytic degradation of pollutants and microbial disinfection, enhancing water treatment processes by providing a reusable, eco-friendly, and highly effective solution for contaminant removal. Future research could focus on improving ZnO NP stability, developing hybrid materials with enhanced adsorption capacity, and exploring alternative green synthesis routes for different nanoparticle morphologies. Additionally, optimizing conditions for reusable and regenerable ZnO NPs would enhance environmental and economic benefits.

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