ISSN: 1410-8917
e-ISSN: 2597-9914

Jurnal Kimia Sains dan Aplikasi 26 (12) (2023): 457-465

Jurnal Kimia Sains dan Aplikasi
Journal of Scientific and Applied Chemistry

Journal homepage: http://ejournal.undip.ac.id/index.php/ksa

Biosynthesis of ZnO Nanoparticles Mediated by *Crescentia cujete* L Leaves Extract and The Photocatalytic Activities Towards Methylene Blue

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https://doi.org/10.14710/jksa.26.12.457-465

Article Info

Article history:

Received: 22nd August 2023
Revised: 15th December 2023
Accepted: 22nd December 2023
Online: 30th December 2023

Keywords:
Nanoparticle; ZnO; Green synthesis; *Crescentia cujete* L; Photocatalytic

Abstract

ZnO nanoparticles were synthesized using the precipitation method and using water extract of *Crescentia cujete* L leaves as a capping agent. ZnO nanoparticles with a hexagonal wurtzite structure were successfully synthesized with low production cost and environmentally friendly. According to XRD characterization, there is no impurity peak, indicating the ZnO nanoparticles have high purity and crystallinity. SEM images show the morphology of ZnO nanoparticles with semi-spherical shapes and an average size of 32.49 nm. The photocatalytic activity of ZnO nanoparticles was evaluated using a UV A lamp as a source of photonic energy toward methylene blue dye. Various irradiation times were carried out from 0, 10, 20, 30, 40, to 50 minutes, and a UV spectrophotometer was used to detect the concentration of methylene blue remains in collected samples. Increasing the irradiation times leads to increasing the photocatalytic activity of ZnO nanoparticles. At 50 minutes of exposure to a UV A lamp, the degradation percentage of methylene blue dye is 36.37%.

1. Introduction

Methylene blue (3,7-bis (dimethylamino) phenothiazine chloride tetra methylthionine chloride) is one of the cationic dyes made from thiazine dye and possesses a benzene structure. The characteristics of methylene blue are that it is environmentally toxic, carcinogenic, mutagenic, and difficult to decompose. Methylene blue has become one of the other dyes commonly applied in clothing, paper, leather, and textile industries due to its low cost and ease of obtaining. One of the side effects of using methylene blue in industries is the waste, which can contaminate the aquatic environment [1]. Pollution of the aquatic environment will have an impact on human life and living organisms. Some harmful effects on human beings are nausea, diarrhea, vomiting, dizziness, headache, fever, anemia, irritation of the skin with redness and itching, and irritation of the mouth [2].

Based on literature studies, researchers have studied various methods for dealing with textile dye waste contamination, some of which are adsorption [3], bioremediation [4], membrane filtration [5], and photodegradation [6]. Photodegradation is an attractive method among researchers because the method is easy to apply, has a low cost, and causes no secondary pollution. Photodegradation uses UV light to degrade the methylene blue dye to form simple molecules such as CO_2, H_2O, sulfate, chloride, and nitrate ions. These simple molecules are harmless and do not contaminate the aquatic environment like methylene blue dye [1]. The principle of the photodegradation method is using a photocatalyst from semiconductor materials such as TiO_2 [7], Fe_2TiO_5 [8], and ZnO and CuO nanoparticles [9].

ZnO is an inorganic semiconductor material n-type with a band gap value of about 3.29 eV at room temperature [10]. ZnO nanoparticles are also non-toxic, have good thermal stability, and are easy to handle and synthesize. Due to their excellent characteristics, ZnO nanoparticles have been widely applied in photocatalysts [11], gas sensors [12], antibacterial [13], adsorbent for

metal ions [14], and supercapacitor electrode materials [15]. Various methods have evolved to synthesize ZnO nanoparticles, such as sol-gel [16], precipitation [17], sonochemical [18], hydrothermal [19], and solvothermal [20]. But most are costly, unavailable, ineffective, and sometimes require high temperatures. The precipitation method has recently garnered significance owing to its cost-effectiveness, utilization of low temperatures, facilitation of particle size distribution control at the nanoscale, and relatively brief synthesis duration. [21].

Two common principles are applied in synthesizing ZnO nanoparticles: conventional and green chemistry. Conventional principles generally require high cost, high-temperature synthesis, long-term synthesis, use of some toxic reagents, and generating waste to the environment. Whereas the green chemistry principle prioritizes environmentally friendly synthesis, the process is eco-friendly, minimizes hazardous chemicals, low temperature, and pressure synthesis, leads to energy saving process, and can be used at large scale [22, 23].

In the green chemistry approach, some of the reagents can be replaced by natural materials. The water extract from leaves, fruits, roots, flowers, and even rods from plants can be used as a capping agent, stability agent, and reduction agent in synthesizing metal and metal oxide nanoparticles. The capping agent is a chelating agent that can control the particle size to obtain an even size distribution and reduce the agglomerate between the particles [22]. This phenomenon happened due to the secondary metabolites in plant extracts: alkaloids, flavonoids, tannins, polyphenols, terpenoids, amides, and saponins. The previous research reported that ZnO nanoparticles had been successfully synthesized using water extracts of *Cayratia pedata* leaves [23], *Lavandula angustifolia* leaves [24], *Myristica pragrans* fruits [25], coconut husk [26], and orange peel fruit [27].

Many researchers have successfully synthesized ZnO nanoparticles using leaf extract and used them as photocatalysts in the degradation reaction of methylene blue. Basit *et al.* [9] reported that ZnO nanoparticles have been successfully synthesized through an eco-friendly method using *Coriandum sativum* as a capping agent. The average crystallite size of the synthesized ZnO nanoparticles was 54.7 nm and showed an irregular shape from SEM characterization. The synthesized ZnO nanoparticle was successfully applied as a photocatalyst in the photodegradation of methylene blue dye. Saridewi *et al.* [11] successfully synthesized ZnO nanoparticles using *Sansevieria trifasciata* extract through the sol-gel method. ZnO nanoparticles demonstrated effective photodegradation of methylene blue dye in 120 minutes.

In this study, the water extracts of *Crescentia cujete* L were used as a capping agent. In previous research, *Crescentia cujete* L leaves extract was utilized to synthesize silver nanoparticles. The silver nanoparticles synthesized have good stability and are applied as antibacterial agents. *Crescentia cujete* L leaves extract contains essential phytochemicals such as flavonoids, saponins, and tannins [28]. We assumed that the phytochemicals could act as a capping and stabilizing agent in the synthesis of ZnO nanoparticles. The formation and crystallite sizes of ZnO nanoparticles were confirmed using XRD analysis, and the morphology and particle size were determined using SEM analysis. The synthesized ZnO nanoparticles were then evaluated for their photocatalytic activities in the photodegradation reaction of methylene blue.

2. Experimental

2.1. Materials

All the chemicals used in this study were analytical grade, and all the solutions were prepared in demineralized water. The chemicals were zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$) with high purity (≥98%, Merck), sodium hydroxide (NaOH), demineralized water, and methylene blue dyes. All the chemicals were used as received without further purification. The plant used in this synthesis was *Crescentia cujete* L leaves.

2.2. Preparation of *Crescentia cujete* L Leaves Extract

Crescentia cujete L leaves were freshly collected from Lampung, Indonesia. Extracts were prepared by washing *Crescentia cujete* L under running water to remove any impurities. Then, the leaves were dried under the sunlight to remove residual water. The leaves were then chopped into small pieces using a blender machine and measured to a weight of 10 grams. The leaves were then mashed and mixed using 200 mL of demineralized water to obtain 5% w/v. The mixtures were then stirred at 80°C and filtered by filter paper to obtain the pale green extract. The extract was then stored in the refrigerator for further application as a capping agent in the synthesis of ZnO nanoparticles and for FTIR characterization.

Figure 1(a) shows *Crescentia cujete* L leaves used in this study; the leaves were relatively young, and the color is deep green. Figure 1(b) depicts the copped *Crescentia cujete* L leaves. The chopping process was employed to optimize the extraction of phytochemical compounds. The leaves were thoroughly dried to prevent leaf decay. Extraction was carried out at a temperature below 80°C to prevent any potential structural damage to the phytochemical compounds. Extraction of *Crescentia cujete* L produces the brownish-green solutions, as shown in Figure 1(c).

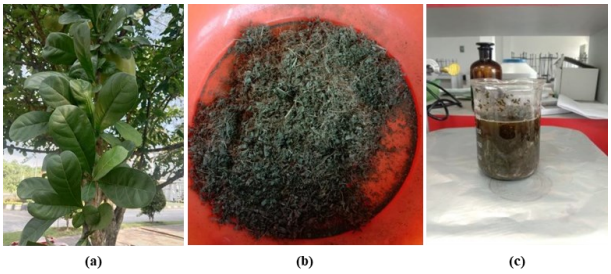

Figure 1. (a) *Crescentia cujete* L leaves, (b) the crushed leaves, and (c) the extraction process of the leaves

2.3. Phytochemical Screening of *Crescentia cujete* L Leaves Extract

Phytochemical screening of *Crescentia cujete* L leaf extracts was conducted to confirm the secondary metabolites contained in the leaf extract. The preliminary phytochemical screening of the leaf extract was performed using the standard protocol described by previous research [29]. This method aimed to identify the presence of flavonoids, alkaloids, phenolics, tannins, and saponins.

2.3.1. Flavonoids Test

Approximately 3 mL of leaf extract was added into 1 mL of 10% NaOH solution. The formation of the yellow solution was indicative of the presence of flavonoids. The plant extract (3 mL) underwent the addition of a few drops of concentrated hydrochloric acid and a small amount of magnesium powder. The observation of a color change to orange signified the presence of flavonoid compounds in the extract.

2.3.2. Alkaloids Test

A few drops of concentrated hydrochloric acid were added to 3 mL of leaf extract, and then a few drops of Dragendorff's reagent were added. The formation of an orange precipitate indicates the presence of flavonoid content in the extract.

2.3.3. Phenolics/Tannins Test

Several 1% ferric chloride drops were added to the tube containing 3 mL of leaf extract. The formation of a greenish-black or dark blue color on the tube indicates the presence of phenolic and tannin content in the extract.

2.3.4. Saponins Test

Approximately 3 mL of leaf extract and 3 mL of distilled water were added and thoroughly mixed through shaking. The formation of a stable foam was taken as a positive test for saponins.

2.4. Synthesis of ZnO Nanoparticles

A solution comprising 50 mL of 0.1 M $Zn(CH_3COO)_2$ was combined with 25 mL of *Crescentia cujete* L leaves extract. Gradual addition of 0.1 M NaOH was performed to the mixture until a pH of 12 was attained [24]. The mixture was stirred for 3 hours at room temperature using a magnetic stirrer at 600 rpm. After stirring, a precipitate was formed in the mixture, subsequently filtered through a Whatman paper filter. It was then washed using demineralized water to eliminate organic residues from the extract. The white precipitate was dried at 120°C for 5 hours to remove the solvents. Finally, ZnO powders were calcined at 150°C for 3 hours.

2.5. Characterization

FTIR analysis was conducted on the leaf extract of *Crescentia cujete* L using SHIMADZU IRSpirit. This analysis aimed to provide information and predictions regarding the functional groups of its secondary metabolites. The formation of ZnO nanoparticles was identified through an X-ray diffractometer employing Cu-Kα radiation (SHIMADZU XRD-7000), with a recorded range of 2θ from 20 to 80°. The morphology of ZnO nanoparticles was observed using a Scanning Electron Microscope (Zeiss) at magnifications of 10,000 and 20,000 times. Estimation of the crystallite size of ZnO nanoparticles is calculated using the Debye-Scherrer equation (Equation (1)).

$$d = \frac{0.9\,\lambda}{\beta_{hkl}\cos\theta_{hkl}} \quad (1)$$

Where, d is the crystallite size of synthesized ZnO nanoparticles for (hkl) phase, λ is the X-ray wavelength of Cu Kα radiation (0.15406), β is full width at half maximum (FWHM) at (hkl) peak in radian, and θ diffraction angle for (hkl) phase in degrees [30].

2.6. Photocatalytic Activity

A simple reactor was assembled in the shape of a box, enclosed with aluminum foil. A UV A lamp was affixed to the reactor's top interior, while a hotplate magnetic stirrer was positioned at the base for agitation. The photocatalytic activity was evaluated by dispersing 50 mg of ZnO nanoparticles in 20 mL of 10 ppm methylene blue solution. Furthermore, the suspension was irradiated under a UV A lamp inside the reactor while the magnetic stirrer was on. Varied durations of exposure to UV light, ranging from 0 to 50 minutes in intervals of 10 minutes, were implemented. Following individual exposure of collected samples to a UV lamp, concentrations of methylene blue were measured at a wavelength of 664.5 nm using a UV-visible spectrophotometer. The photocatalytic efficiency of ZnO nanoparticles against methylene blue is calculated using Equation (2) [18].

$$DE(\%) = \frac{(C_t - C_0)}{C_0} x\ 100\% \quad (2)$$

Where, DE (%) is the percentage photocatalytic degradation efficiency of photocatalyst, C0 is the initial concentration of methylene blue (mg/L), and Ct is the methylene blue concentration at a certain reaction time (mg/L).

3. Results and Discussion

3.1. Phytochemical and FTIR Analysis of the *Crescentia cujete* L Leaves Extract

The preliminary phytochemical screening was performed to confirm the presence of secondary metabolites in *Crescentia cujete* L leaf extract. The results of phytochemical screening indicated that the extract contains flavonoids, alkaloids, phenolics, tannins, and saponins. Table 1 shows the qualitative phytochemical screening of *Crescentia cujete* L leaves extract based on the color change of the extract compared to the control in Figure 2.

Table 1. Phytochemical screening result

Secondary metabolites test	Reagent	Result
Flavonoids	NaOH	Yellowish-orange solution (+)
	HCl + Mg	Orange solution (+)
Alkaloids	HCl + Dragendorff	Orange precipitate
Phenolics	$FeCl_3$	Greenish-black solution (+)
Tannins	$FeCl_3$	Greenish-black solution (+)
Saponins	Distilled water	Foam (+)

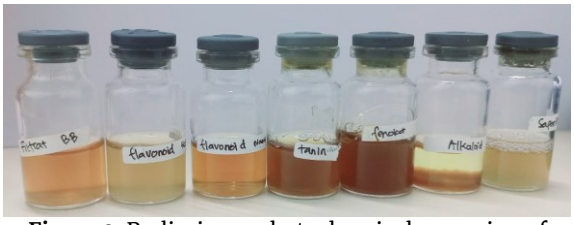

Figure 2. Preliminary phytochemical screening of *Crescentia cujete* L leaves extract

The phytochemical screening is supported by FTIR analysis of the *Crescentia cujete* L leaves extract. From Figure 3, the appearance of a peak at 1083.72 cm^{-1} is due to the C–O stretching of ether or alcohol functional groups, which are estimated from flavonoids and saponins. The band observed at 1332.04–1550.22 cm^{-1} signifies the C–N (amine or amide) characteristic, which is anticipated in alkaloids. Additionally, the aromatic C=C vibration detected in this range indicates the presence of flavonoids, phenolics, and tannins. The presence of a C=O bond in 1697.83 cm^{-1} is estimated from flavonoids and tannins.

The presence of peaks at 2899.49 and 2972.30 cm^{-1} indicates the C–H aliphatic or alicyclic groups, which are anticipated in compounds such as saponins, alkaloids, flavonoids, phenolics, and tannins. Additionally, the wavenumber at 3278.43 cm^{-1} corresponds to the vibration of O–H hydroxyl functional groups, suggesting the potential presence of flavonoids, phenolics, tannins, and saponins. The identified peaks at 3374.61–3502.36 cm^{-1} are due to the presence of N–H amine or amide, which is estimated from alkaloids [31, 32]. The results of FTIR analysis confirmed the presence of flavonoids, alkaloids, phenolics, tannins, and saponins in *Crescentia cujete* L leaves extract.

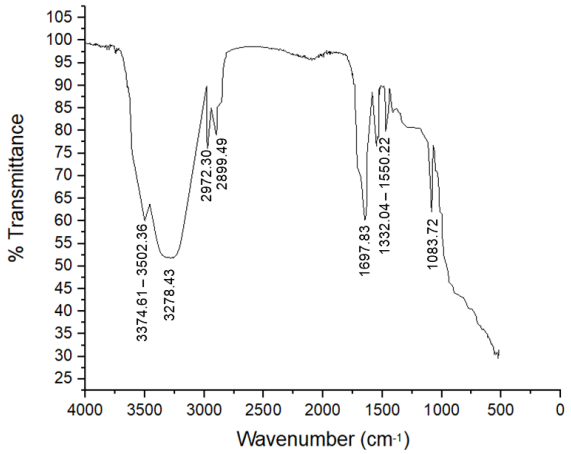

Figure 3. FTIR analysis of *Crescentia cujete* L leaves extract

3.2. Synthesis of ZnO Nanoparticles

The Lampung Province in Indonesia is recognized for its diverse floristic resources; therefore, it becomes important to study the potential of various plants in that region to serve as capping and stabilizing agents in the synthesis process of ZnO nanoparticles. *Crescentia cujete* L is an economical and medicinal plant of wide indigenous uses, including hypertension, diarrhea, respiratory ailments, stomach troubles, infertility problems, cancer, and snakebite. Water extract of *Crescentia cujete* L leaves contains various secondary metabolites, specifically flavonoids, saponins, and tannins [33]. The phytochemical compounds can control the growth of particles and the particle's morphology and also protect the surface from aggregation during the synthesis process. The water extract of *Crescentia cujete* L contains hydroxyl functional on the flavonoids and saponins. The hydroxyl functional groups and Zn^{2+} from the precursor, attracted by electrostatic interaction, form the Zn-flavonoids complex [34].

The addition of NaOH into $Zn(NO_3)_2.6H_2O$ acts as a precipitant to form $Zn(OH)_2$ precipitate. Synthesis by precipitation method was carried out at a pH of 12 to maximize the formation of $Zn(OH)_2$ precipitate. The stirring process used a magnetic stirrer to maximize the reaction between the precursors. It was carried out at room temperature to avoid structural damage to the phytochemical compounds of the extract. The synthesis process was followed by heating at 120°C for 5 hours to remove water and organic residues. The role of the *Crescentia cujete* L leaf extract is limited to the synthesis process in solution form, and it undergoes decomposition during the heating stage. Calcination at 150°C for 3 hours is intended to complete the crystallization process to obtain the crystalline phase of ZnO nanoparticles. The powder of ZnO nanoparticles is depicted in Figure 4. The overall reaction for forming ZnO nanoparticles is expressed through Equations (3) and (4).

Figure 4. Synthesized ZnO nanoparticle

$$Zn(NO_3)_{2(aq)} + 2NaOH_{(aq)} \rightarrow Zn(OH)_{2(s)} + 2NaNO_{3(aq)} \quad (3)$$

$$Zn(OH)_{2(s)} \rightarrow ZnO_{(s)} + H_2O_{(g)} \quad (4)$$

3.3. X-ray Diffraction Analysis

The crystallinity and phase purity of the synthesized ZnO nanoparticles can be determined through analysis using a powder X-ray diffractometer. In Figure 5, the XRD diffractogram illustrates the relationship between the intensity of diffracted rays and diffraction angles for the synthesized ZnO nanoparticles. The observed diffraction peaks of the synthesized ZnO nanoparticles closely aligned with the standard (JCPDS Card no. 36-1451), confirming the hexagonal wurtzite structure in the crystallographic system [35]. The diffraction peaks were observed at 2θ = 31.92, 34.58, 36.42, 47.73, 56.77, 62.92, 68.01, 69.10, and 72.70. All the diffraction peaks correspond to the lattice planes (110), (002), (101), (102), (110), (103), (112), (201), and (004), respectively. The lattice plane (101) is the primary diffraction peak, indicating the maximum growth of ZnO nanoparticles occurred in the (101) plane direction [36].

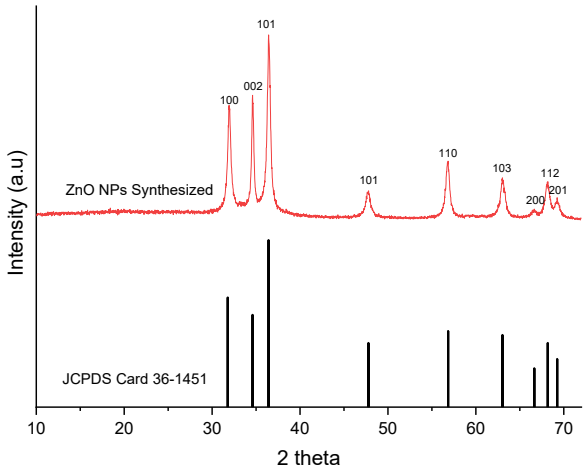

Figure 5. Diffractogram of synthesized ZnO nanoparticles

Table 2 shows the crystallite size of synthesized ZnO nanoparticles. The average crystallite size of synthesized nanoparticles was estimated at 19.55 nm. There is no second phase detected by XRD analysis, indicating that the ZnO nanoparticles have high-purity crystalline with no impurities.

3.4. SEM Analysis

A scanning electron microscope was used to study the surface morphology of synthesized ZnO nanoparticles. SEM images were taken in different magnifications to study the shape and size of synthesized ZnO nanoparticles. Figure 6(a) shows the SEM images of synthesized ZnO nanoparticles in magnifications of 10,000 and (b) 20,000. In the present investigation, the synthesized nanoparticles are agglomerated with semi-spherical shapes. The agglomeration of the nanoparticles due to its crystal growth and the presence of organic residues from *Crescentia cujete* L leaves extract.

The size of ZnO nanoparticles was estimated using ImageJ by taking as many as 100 points from the SEM image. According to ImageJ analysis on SEM images, the average size of ZnO particles is 32.49 nm with a uniform distribution. These findings align with prior research where ZnO nanoparticles were synthesized utilizing *Memordica charantia* leaf extract. The nanoparticles exhibited an average size below 100 nm, and their morphology appeared spherical, with particle boundaries that were not distinctly visible [37].

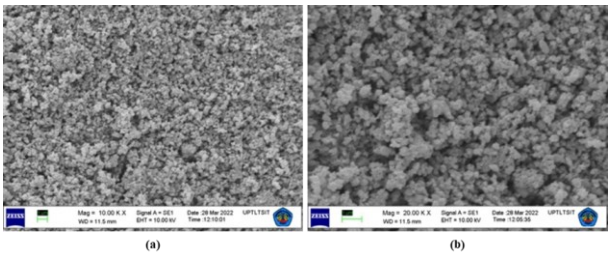

Figure 6. SEM images of synthesized ZnO nanoparticles in magnifications of (a) 10,000 times and (b) 20,000 times

Table 2. Crystallite size of synthesized ZnO nanoparticles

No.	2θ	FWHM	hkl	Crystallite size (d)
1	31.92	0.00708	110	20.35
2	34.58	0.00467	002	31.04
3	36.42	0.00691	101	21.11
4	47.73	0.01012	102	14.97
5	56.77	0.00804	110	19.58
6	62.92	0.01014	103	16.02
7	68.01	0.00872	112	19.16
8	69.10	0.01047	201	16.07
9	72.70	0.00977	400	17.61

3.5. Photocatalytic Activity

The photocatalytic activity of semiconductor materials is influenced by several factors, including irradiation time, pH, photocatalyst dosage, dye concentration, and the specific type of UV lamp employed [2]. In this study, irradiation times varied, starting from 10, 20, 30, 40, and 50 minutes. Irradiation time on photocatalytic activity describes the contact or interaction time between the photocatalyst and UV light. During the test, stirring was carried out to avoid the precipitation of the ZnO. As shown in Figure 7, the absorbance of methylene blue gradually decreases in time, indicating that the concentration of methylene blue also decreases.

The concentration of methylene blue before and after exposure to a UV lamp was compared to measure the photocatalytic efficiency of synthesized ZnO nanoparticles. The irradiation time is directly correlated with the percentage of methylene blue degradation, where the percentage increases over time. The measured photocatalytic efficiency was 0%, 2.48%, 26.44%, 29.41%, 36.3%, and 36.7%, corresponding to irradiation times of 0, 10, 20, 30, 40, and 50 minutes, respectively. During the 50th minute, no significant increase was observed compared to the 40th minute. In a prior study conducted by Wagh *et al.* [37], it was reported that non-annealed ZnO nanoparticles (synthesized at low temperatures) could decompose methylene blue up to 40% within an irradiation time of 40 minutes. Based on the evaluation of photocatalytic activity and a comparison with prior research, it has been discovered that the synthesized ZnO nanoparticles exhibit an intermediate level of photocatalytic efficiency against methylene blue.

ZnO is semiconductor inorganic materials n-type which have negative charges. Figure 8 is the proposed mechanism of light-induced electron transport and photocatalytic decomposition reaction of methylene blue. During UV irradiation, the electron from the valence band (VB) is excited to the conduction band (CB) due to the photonic energy (hv) having greater energy than the band gap of ZnO (Equation (5)). The excited electrons will form electron holes (positive charges, h^+) in the valence band. The formed electron holes/positive holes (h^+) in the valence band will oxidize the absorbed water and hydroxide ions to generate powerful hydroxyl radicals ·OH (Equation (6)). The excited electrons to conduction bands will oxidize dissolved oxygen species to generate superoxide radicals anions $\cdot O_2^-$ (Equation (7)).

The formed ·OH radicals react with methylene blue dye absorbed on the surface of ZnO and then converted to simple compounds such as H_2O, CO_2, and other mineral acids (Equation (8-10)) [38]. Spectrophotometer UV Vis could confirm the decomposition of methylene blue by the changes of the absorbance; at the same time, the color of methylene blue gradually changes from dark blue to colorless, indicating that methylene blue was gradually decomposed.

$$ZnO + Uv\ light\ (photon) \rightarrow ZnO\ (h^+_{VB}) + ZnO\ (e^-_{CB}) \quad (5)$$

$$ZnO\ (h^+_{VB}) + H_2O \rightarrow \cdot OH + \cdot H \quad (6)$$

$$ZnO\ (e^-_{CB}) + O_2 \rightarrow \cdot O_2^- \quad (7)$$

$$\cdot O_2^- + H+ \rightarrow \cdot HO_2 + \cdot HO_2 \rightarrow H_2O_2 + O_2 \quad (8)$$

$$ZnO\ (e^-_{CB}) + H_2O_2 \rightarrow \cdot OH + OH^- \quad (9)$$

$$\cdot OH + Methylene\ Blue \rightarrow H_2O + CO_2 + mineral\ acids \quad (10)$$

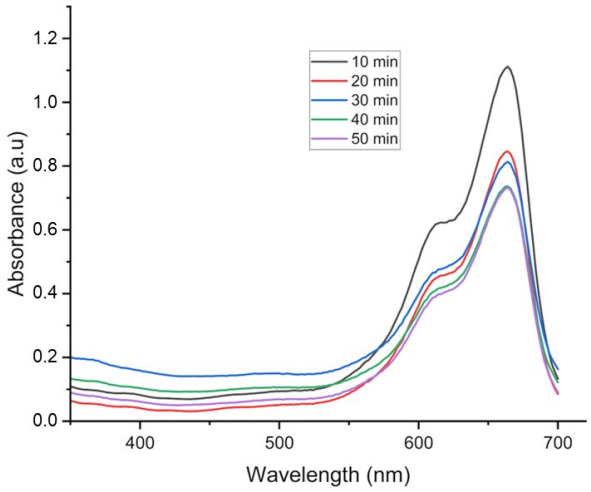

Figure 7. The UV-Vis absorption spectra of methylene blue changes with photocatalytic

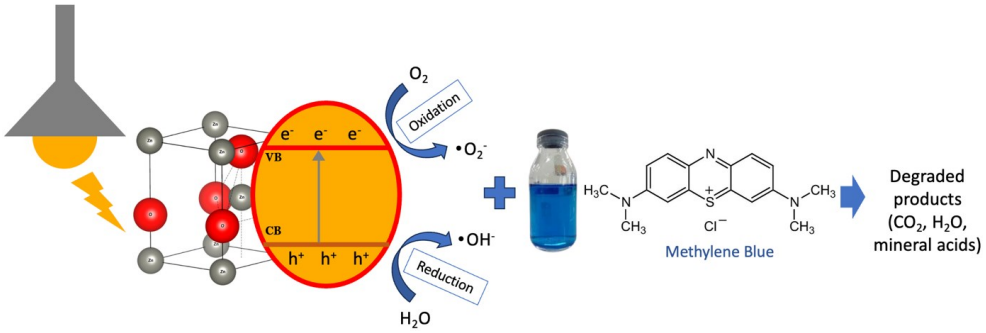

Figure 8. Photocatalytic mechanism of ZnO nanoparticles towards methylene blue dye

4. Conclusion

Crescentia cujete L leaf extract plays an active role in synthesizing ZnO nanoparticles to produce materials with a uniform and nanoscale size distribution. The synthesized ZnO nanoparticles have an average particle size of 32.49 nm. The secondary metabolites contained in the *Crescentia cujete* L leaves extract can limit the interactions between Zn^{2+} ions in the solution and control their growth, forming nanoparticles with nanoscale size. Based on the results of the XRD characterization, no impurity phase was detected, indicating that the material has high-purity crystalline. The SEM and XRD characterization results support the photocatalytic activity evaluations, demonstrating an intermediate percentage of methylene blue degradation of up to 36.37% with an irradiation time of 50 minutes.

References

[1] Peter Olusakin Oladoye, Timothy Oladiran Ajiboye, Elizabeth Oyinkansola Omotola, Olusola Joel Oyewola, Methylene blue dye: Toxicity and potential elimination technology from wastewater, *Results in Engineering*, 16, (2022), 100678 https://doi.org/10.1016/j.rineng.2022.100678

[2] Idrees Khan, Khalid Saeed, Ivar Zekker, Baoliang Zhang, Abdulmajeed H. Hendi, Ashfaq Ahmad, Shujaat Ahmad, Noor Zada, Hanif Ahmad, Luqman A. Shah, Tariq Shah, Ibrahim Khan, Review on Methylene Blue: Its Properties, Uses, Toxicity and Photodegradation, *Water*, 14, 2, (2022), 242 https://doi.org/10.3390/w14020242

[3] A. V. Ramesh, Dharmasoth Rama Devi, Satish Mohan Botsa, K. Basavaiah, Facile green synthesis of Fe_3O_4 nanoparticles using aqueous leaf extract of *Zanthoxylum armatum* DC. for efficient adsorption of methylene blue, *Journal of Asian Ceramic Societies*, 6, 2, (2018), 145-155 https://doi.org/10.1080/21870764.2018.1459335

[4] Lucas R. Pinheiro, Diana G. Gradíssimo, Luciana P. Xavier, Agenor V. Santos, Degradation of Azo Dyes: Bacterial Potential for Bioremediation, *Sustainability*, 14, 3, (2022), 1510 https://doi.org/10.3390/su14031510

[5] Y. Chaouqi, R. Ouchn, M. El Bouchti, O. Cherkaoui, M. Hlaibi, Oriented Membrane Processes for Extraction of Methylene Blue and Blue P3R Dyes Across Polymer Inclusion Membranes Containing Chitin as New Extractive Agent, *IOP Conference Series: Materials Science and Engineering*, 948, (2020), 012022 https://doi.org/10.1088/1757-899X/948/1/012022

[6] Haithem Bel Hadjltaief, Sameh Ben Ameur, Patrick Da Costa, Mourad Ben Zina, Maria Elena Galvez, Photocatalytic decolorization of cationic and anionic dyes over ZnO nanoparticle immobilized on natural Tunisian clay, *Applied Clay Science*, 152, (2018), 148-157 https://doi.org/10.1016/j.clay.2017.11.008

[7] Chentao Hou, Bo Hu, Jiaming Zhu, Photocatalytic Degradation of Methylene Blue over TiO_2 Pretreated with Varying Concentrations of NaOH, *Catalysts*, 8, 12, (2018), 575 https://doi.org/10.3390/catal8120575

[8] Z. Z. Vasiljevic, M. P. Dojcinovic, J. D. Vujancevic, I. Jankovic-Castvan, M. Ognjanovic, N. B. Tadic, S. Stojadinovic, G. O. Brankovic, M. V. Nikolic, Photocatalytic degradation of methylene blue under natural sunlight using iron titanate nanoparticles prepared by a modified sol–gel method, *Royal Society Open Science*, 7, 9, (2020), 200708 https://doi.org/10.1098/rsos.200708

[9] Raja Abdul Basit, Zeeshan Abbasi, Muhammad Hafeez, Pervaiz Ahmad, Jahanzeb Khan, Mayeen Uddin Khandaker, Kholoud Saad Al-Mugren, Awais Khalid, Successive Photocatalytic Degradation of Methylene Blue by ZnO, CuO and ZnO/CuO Synthesized from *Coriandrum sativum* Plant Extract via Green Synthesis Technique, *Crystals*, 13, 2, (2023), 281 https://doi.org/10.3390/cryst13020281

[10] Klinton Davis, Ryan Yarbrough, Michael Froeschle, Jamel White, Hemali Rathnayake, Band gap engineered zinc oxide nanostructures *via* a sol–gel synthesis of solvent driven shape-controlled crystal growth, *RSC Advances*, 9, 26, (2019), 14638-14648 https://doi.org/10.1039/C9RA02091H

[11] Nanda Saridewi, Selviana Rustanti, Agustino Zulys, Siti Nurbayti, Isalmi Aziz, Adawiah Adawiah, Synthesis of ZnO Nanoparticle using Lidah Mertua (*Sansevieria trifasciata*) Extract through Sol-Gel Method and Its Application for Methylene Blue Photodegradation, *Bulletin of Chemical Reaction Engineering & Catalysis*, 18, 3, (2023), 375-385 https://doi.org/10.9767/bcrec.19647

[12] S. G. Onkar, S. B. Nagdeote, A. S. Wadatkar, Prashant B. Kharat, Gas sensing behavior of ZnO thick film sensor towards H_2S, NH_3, LPG and CO_2, *Journal of Physics: Conference Series*, 1644, (2020), 012060 https://doi.org/10.1088/1742-6596/1644/1/012060

[13] Carolina Rosai Mendes, Guilherme Dilarri, Carolina Froes Forsan, Vinícius de Moraes Ruy Sapata, Paulo Renato Matos Lopes, Peterson Bueno de Moraes, Renato Nallin Montagnolli, Henrique Ferreira, Ederio Dino Bidoia, Antibacterial action and target mechanisms of zinc oxide nanoparticles against bacterial pathogens, *Scientific Reports*, 12, (2022), 2658 https://doi.org/10.1038/s41598-022-06657-y

[14] Julia de O. Primo, Carla Bittencourt, Selene Acosta, Ayrton Sierra-Castillo, Jean-François Colomer, Silvia Jaerger, Verônica C. Teixeira, Fauze J. Anaissi, Synthesis of Zinc Oxide Nanoparticles by Ecofriendly Routes: Adsorbent for Copper Removal From Wastewater, *Frontiers in Chemistry*, 8, (2020), 571790 https://doi.org/10.3389/fchem.2020.571790

[15] Irum Shaheen, Khuram Shahzad Ahmad, Camila Zequine, Ram K. Gupta, Andrew G. Thomas, Mohammad Azad Malik, Facile ZnO-based nanomaterial and its fabrication as a supercapacitor electrode: synthesis, characterization and electrochemical studies, *RSC Advances*, 11, (2021), 23374-23384 https://doi.org/10.1039/D1RA04341B

[16] Kalpesh Anil Isai, Vinod Shankar Shrivastava, Photocatalytic degradation of methylene blue using ZnO and 2%Fe–ZnO semiconductor nanomaterials synthesized by sol–gel method: a comparative study, *SN Applied Sciences*, 1, 10, (2019), 1247 https://doi.org/10.1007/s42452-019-1279-5

[17] Kovo G. Akpomie, Soumya Ghosh, Marieka Gryzenhout, Jeanet Conradie, One-pot synthesis of zinc oxide nanoparticles via chemical precipitation for bromophenol blue adsorption and the antifungal activity against filamentous fungi, *Scientific Reports*, 11, (2021), 8305 https://doi.org/10.1038/s41598-021-87819-2

[18] Nanda Saridewi, Sri Komala, Agustino Zulys, Siti Nurbayti, Latifah Tulhusna, Adawiah Adawiah, Synthesis of ZnO-Fe_3O_4 Magnetic Nanocomposites through Sonochemical Methods for Methylene Blue Degradation, *Bulletin of Chemical Reaction Engineering & Catalysis*, 17, 3, (2022), 650-660 https://doi.org/10.9767/bcrec.17.3.15492.650-660

[19] Bekele Bulcha, Jule Leta Tesfaye, Degefa Anatol, R. Shanmugam, L. Priyanka Dwarampudi, N. Nagaprasad, V. L. Nirmal Bhargavi, Ramaswamy Krishnaraj, Synthesis of Zinc Oxide Nanoparticles by Hydrothermal Methods and Spectroscopic Investigation of Ultraviolet Radiation Protective Properties, *Journal of Nanomaterials*, 2021, (2021), 8617290 https://doi.org/10.1155/2021/8617290

[20] Ying Wang, Chuanxi Yang, Yonglin Liu, Yuqi Fan, Feng Dang, Yang Qiu, Huimin Zhou, Weiliang Wang, Yuzhen Liu, Solvothermal Synthesis of ZnO Nanoparticles for Photocatalytic Degradation of Methyl Orange and *p*-Nitrophenol, *Water*, 13, 22, (2021), 3224 https://doi.org/10.3390/w13223224

[21] Jagpreet Singh, Tanushree Dutta, Ki-Hyun Kim, Mohit Rawat, Pallabi Samddar, Pawan Kumar, 'Green' synthesis of metals and their oxide nanoparticles: applications for environmental remediation, *Journal of Nanobiotechnology*, 16, (2018), 84 https://doi.org/10.1186/s12951-018-0408-4

[22] Shuaixuan Ying, Zhenru Guan, Polycarp C. Ofoegbu, Preston Clubb, Cyren Rico, Feng He, Jie Hong, Green synthesis of nanoparticles: Current developments and limitations, *Environmental Technology & Innovation*, 26, (2022), 102336 https://doi.org/10.1016/j.eti.2022.102336

[23] Ashwini Jayachandran, Aswathy T. R., Achuthsankar S. Nair, Green synthesis and characterization of zinc oxide nanoparticles using *Cayratia pedata* leaf extract, *Biochemistry and Biophysics Reports*, 26, (2021), 100995 https://doi.org/10.1016/j.bbrep.2021.100995

[24] Gulzar Ahmed Rather, Anima Nanda, Ezekiel Raj, Narayanasamy Mathivanan, B. K. Nayak, Green synthesis of ZnO nanoparticles using the leaf extract of *Lavandula angustifolia* and evaluation of their antibacterial activity against human pathogens, *International Journal of Health Sciences*, 6, S2, (2022), 13478-13485 https://doi.org/10.53730/ijhs.v6nS2.8539

[25] Shah Faisal, Hasnain Jan, Sajjad Ali Shah, Sumaira Shah, Adnan Khan, Muhammad Taj Akbar, Muhammad Rizwan, Faheem Jan, Wajidullah, Noreen Akhtar, Aishma Khattak, Suliman Syed, Green Synthesis of Zinc Oxide (ZnO) Nanoparticles Using Aqueous Fruit Extracts of *Myristica fragrans*: Their Characterizations and Biological and Environmental Applications, *ACS Omega*, 6, 14, (2021), 9709-9722 https://doi.org/10.1021/acsomega.1c00310

[26] S. Shwetha Priyadharshini, Jayachamarajapura Pranesh Shubha, Jaydev Shivalingappa, Syed Farooq Adil, Mufsir Kuniyil, Mohammad Rafe Hatshan, Baji Shaik, Kiran Kavalli, Photocatalytic Degradation of Methylene Blue and Metanil Yellow Dyes Using Green Synthesized Zinc Oxide (ZnO) Nanocrystals, *Crystals*, 12, 1, (2022), 22 https://doi.org/10.3390/cryst12010022

[27] Tu Uyen Doan Thi, Trung Thoai Nguyen, Y. Dang Thi, Kieu Hanh Ta Thi, Bach Thang Phan, Kim Ngoc Pham, Green synthesis of ZnO nanoparticles using orange fruit peel extract for antibacterial activities, *RSC Advances*, 10, 40, (2020), 23899-23907 https://doi.org/10.1039/D0RA04926C

[28] M. A. Sáncheza, J. A. Fiscal Ladino, Antimicrobial evaluation of silver nanoparticles using extracts of *Crescentia cujete* L., *Brazilian Journal of Biology*, 84, (2023), e270215 https://doi.org/10.1590/1519-6984.270215

[29] Laila Khamsatul Muharrami, Fatimatul Munawaroh, Taslim Ersam, Mardi Santoso, Phytochemical Screening of Ethanolic Extract: a Preliminary Test on Five Medicinal Plants on Bangkalan, *Jurnal Pena Sains*, 7, 2, (2020), 96-102 https://doi.org/10.21107/jps.v7i2.8722

[30] Mebrahtu Hagos Kahsay, Synthesis and characterization of ZnO nanoparticles using aqueous extract of *Becium grandiflorum* for antimicrobial activity and adsorption of methylene blue, *Applied Water Science*, 11, (2021), 45 https://doi.org/10.1007/s13201-021-01373-w

[31] Made Pharmawati, Luh Putu Wrasiati, Phytochemical screening and FTIR spectroscopy on crude extract from *Enhalus acoroides* leaves, *Malaysian Journal of Analytical Sciences*, 24, 1, (2020), 70-77

[32] Prince Kumar Singh, Jagreeti Singh, Tapas Medhi, Aditya Kumar, Phytochemical Screening, Quantification, FT-IR Analysis, and *In Silico* Characterization of Potential Bio-active Compounds Identified in HR-LC/MS Analysis of the Polyherbal Formulation from Northeast India, *ACS Omega*, 7, 37, (2022), 33067-33078 https://doi.org/10.1021/acsomega.2c03117

[33] Musbau B. Olaniyi, Ibraheem O. Lawal, Aishat A. Olaniyi, Proximate, phytochemical screening and mineral analysis of *Crescentia cujete* L. leaves, *Journal of Medicinal Plants for Economic Development*, 2, 1, (2018), https://doi.org/10.4102/jomped.v2i1.28

[34] Fatai Oladunni Balogun, Saheed Sabiu, Retracted: A Review of the Phytochemistry, Ethnobotany, Toxicology, and Pharmacological Potentials of *Crescentia cujete* L. (Bignoniaceae), *Evidence-Based Complementary and Alternative Medicine*, 2023, (2023), 9827389 https://doi.org/10.1155/2023/9827389

[35] Jun Xu, Yubo Huang, Shihui Zhu, Nedra Abbes, Xiaoning Jing, Liang Zhang, A review of the green synthesis of ZnO nanoparticles using plant extracts and their prospects for application in antibacterial textiles, *Journal of Engineered Fibers and Fabrics*, 16, (2021), 15589250211046242 https://doi.org/10.1177/15589250211046242

[36] Lorna Lorna, Inayatul Mutmainna, Dahlang Tahir, Paulus L. Gareso, The Effect of Additional Iron Sand on The Crystal Size and Strain of ZnO, *Indonesian Physical Review*, 5, 3, (2022), 168-176 https://doi.org/10.29303/ipr.v5i3.178

[37] Snehal S. Wagh, Chaitali V. Jagtap, Vishal S. Kadam, Shoyebmohamad F. Shaikh, Mohd Ubaidullah, Bidhan Pandit, Dipak B. Salunkhe, Rajendra S. Patil, Silver doped ZnO Nanoparticles Synthesized for Photocatalysis Application, *ES Energy &*

Environment, 17, (2022), 94-105
http://dx.doi.org/10.30919/esee8e720

[38] Mohamed Awad Fagier, Plant-Mediated Biosynthesis and Photocatalysis Activities of Zinc Oxide Nanoparticles: A Prospect towards Dyes Mineralization, *Journal of Nanotechnology*, 2021, (2021), 6629180
https://doi.org/10.1155/2021/6629180