Green synthesis of zinc oxide nanoparticles using *Moringa oleifera* L. water extract and its photocatalytic evaluation

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**Abstract.** Green synthesis of Zinc Oxide Nanoparticles (ZnO-NPs) using *Moringa oleifera* L extract is successfully carried out. ZnO-NPs is precipitated out with the help of *Moringa oleifera* L water extract and thermally treated at 300, 350, 400, 450, and 500°C prior characterization. The prepared ZnO-NPs were characterized using Fourier Transform Infrared (FTIR), X-ray diffraction (XRD), and The Ultraviolet-visible (UV-Vis). The photocatalytic activity was determined based on its ability to decompose methylene blue in solution. FTIR analysis result shows the absorption band at 422–497 cm⁻¹ which associated with stretching of Zn-O, and the intensity of O-H bond (3417 cm⁻¹) decreases with increasing calcination temperature. The XRD spectrum shows a significant increase in electron properties and bond formation as the temperature increase. Calcination at 500°C results in the achievement of methylene blue degradation as a pollutant model of 80% after 60 minutes of exposure. This study shows that *Moringa oleifera* L. water extract can be used as a green alternative in ZnO-NPs synthesis and calcination temperature affects the photocatalytic activity of the prepared nanoparticles.

1. Introduction

Nanotechnology is a developing field of science that has great potential in medical, biotechnology, agriculture, and microbiology as well as in green chemistry [1-4]. The nanoparticle has been reported to exhibit unique characteristics and applications such as photocatalytic activity, optical and electronic properties, and antimicrobial agents [4,5]. There are many methods in preparation of nanoparticle by high technology including chemical reduction [6], lithography [7], beam epitaxy [8] but the material used by these processes expensive, and non-environmental friendly. To overcome this problem, in recent years, the green synthesis of nanoparticles has attracted a lot of scientists due to the abundance of natural resources and because of the method considered more environmental-friendly. Biological methods in nanoparticle synthesis are reported to have advanced as chemical and physical methods. In this method, the raw materials of fruit, plant leaves, vegetables, roots, and other parts of the plant are used to prepare nanoparticle [9].

*Moringa oleifera* L is one of the abundant plant materials with a relatively fast growth rate. *Moringa oleifera* L is a common vegetable and a good source of protein, beta-carotene, vitamin A, B, C and E, riboflavin, nicotinic acid, folic acid, pyridoxine, amino acid, mineral and various phenolic compound, good fatty acid, omega 3 and omega 6. The phenolic compound in *M. oleifera* L is a good
source of antioxidant and antimicrobial that can be used for both pharmaceutical and food industry purposes [10].

In this research, ZnO nanoparticles were synthesized by adopting the biological method. *M. oleifera* L was used as reducing and stabilizing reagent for textile industry application as a catalyst in colorant waste degradation process by modelling it with methylene blue.

2. **Experiment**

2.1 **Materials**

*Moringa oleifera* L. leaves, Zinc Acetate Dihydrate (Zn(CH$_3$COO)$_2$.2H$_2$O) (Merck) and distilled water.

2.2 **Extract of Moringa Oleifera L**

Samples are synthesized with a modified method developed by Elumalai (2015). *M. oleifera* L leaves are washed twice using tap water and then washed again using distilled water. The leaves then dried under direct sunlight for three days. Dried leaves are powdered using a mechanical blender and sieved. *M. oleifera* L leaves water extract is prepared by dispersing 10 gram of leaves in 200 ml distilled water and heated to 60°C for 30 minutes, filtering it with filter paper (Whatman No. 1) [11].

2.3 **Synthesis of ZnO NPs using extract Moringa Oleifera L**

10 ml of water extract is heated to 80°C for 5 minutes in Beaker glass under continuous stirring. To the mixture, 1 gram of *M. oleifera* L leaves to powder, and 3 grams of Zinc Acetate are added and stirred for 5 minutes at 600 rpm. Paste-like mass is recovered and heat-treated for 5 hours at 80°C. The dried mass then calcined at 300, 350, 400, 450 and 500°C for 2 hours [11].

2.4 **Material Characterization**

Crystallite size determined from the quantitative analysis of X-ray diffraction (XRD) spectroscopy (Shimadzu 7000) with CuKα is a source of radiation (λ=1,5405 Å) over the diffraction angle range 15° ≤ 2θ ≤ 80°, operation at 30 kV and 10 mA. Fourier transform infrared (FTIR) spectroscopy (IRPrestige-21) (Shimadzu Corp.) equipped with a bright ceramic light source, a KBr beam splitter, and a deuterated triglycine sulfate doped with L-alanine (DLATGS) detector. The Ultraviolet-visible (UV-Vis) absorption spectra were recorded by Shimadzu UV-Vis Spectrophotometer UV-1800.

2.5 **Photocatalytic Mechanism**

Photocatalytic degradation of methylene blue by ZnO nanoparticles synthesized using *M. oleifera* L is studied using self-assembled lamp apparatus. Halogen lamp (300 W, OSRAM 645, Germany) is used as the light source 0.06 grams of sample is suspended in 50 ml methylene blue with a total dye concentration of 1 x 10$^{-5}$ M. Initial absorbance of the sample is measured using Shimadzu UV-Vis UV-1800 Spectrophotometer. The mixture then exposed to the light source, and the absorbances are measured at 30 minutes interval until the mixture is decolorized. Degradation percentage of the methylene blue after the photocatalytic degradation process is calculated based on the given formula:

\[
D \% = \frac{C_0 - C_t}{C_0} \times 100\%
\]

where D (%) is the degradation percentage, $C_0$ is the initial absorbance, and $C_t$ is the absorbance after t time.

3. **Result and Discussion**

Figure 1 shows the FTIR spectrum of ZnO NPs synthesized using *M. oleifera* L at various calcination temperature.
Figure 1. FTIR Spectrum of ZnO-NPs with calcination temperature 300°C -500°C

Wideband at 3417 cm\(^{-1}\) correlated with -OH vibration in a water molecule (H\(_2\)O). The shrinkage of the -OH peaks indicates the better removal of water molecules from the nanostructure at the higher annealing temperature. Wideband at 1419 cm\(^{-1}\) correspond to C-H bonding in the alkene compound. IR band at 1118 cm\(^{-1}\) corresponds to C-O bonding that may indicate the existence of alcohol or carboxylic acid molecules [11]. Such vibration may also come from heterocyclic molecules, for example, from alkaloid or flavonoid molecules and amide (I) bonding from protein and enzyme come from the extract or powdered leaves [12]. The absorption peak at 400-600 cm\(^{-1}\) correspond to metal-oxide bonding, and strong peak at 420 cm\(^{-1}\) indicate the existence of Zn-O bonding, thus imply the formation of ZnO-NPs [13].

The XRD analysis results of ZnO-NPs synthesized using M. oleifera L at varying annealing temperatures are shown in Figure 2. Diffraction patterns identified as (100), (002), (101), (110), (103), and (112) from the wurtzite structure of ZnO-NPs. The diffraction peak at (101) is the major peak with increasing intensity as the annealing temperature is raised. Sharper peaks from the samples also indicate better crystallinity and the purity of the nanoparticles [14,15]. The average of crystalline size was determined using Debye-Scherrer formula as follow:

\[
D = \frac{\frac{k\lambda}{B\cos\theta}}
\]

where, \(k\) is a constant (0.9), \(\lambda\) is an X-ray wavelength (0.154 nm), \(B\) is the full width at half the maximum (FWHM), and \(\theta\) is the diffraction angle [16].

The average crystalline size (Table 1) tend to become smaller as the annealing temperature increase. This phenomenon may be caused by as the material is thermally treated, more electrons are released from the medium, which led to more formation of the ZnO-NPs. Another possible explanation is that more organic molecules from the M. oleifera L. extract are removed at higher calcination temperatures.
Figure 2. XRD spectrum of ZnO-NPs for various calcination temperature (300°C to 500°C)

Table 1. Average crystal size, band gap, Rate constant (k) and correlation coefficient (R²) for ZnO NPs

| Sample          | Temperature°C | Average Crystallite Size (nm) | Band Gap (eV) | Rate constant k min⁻¹ | Correlation coefficient values (R²) |
|-----------------|---------------|------------------------------|---------------|-----------------------|-------------------------------------|
| Moringa Oleifera L- ZnO NPs | 300 | 40.05 | 2.60 | 0.011 | 0.995 |
|                 | 350 | 23.70 | 3.02 | 0.013 | 0.940 |
|                 | 400 | 34.21 | 2.79 | 0.010 | 0.998 |
|                 | 450 | 18.89 | 2.58 | 0.016 | 0.990 |
|                 | 500 | 19.20 | 2.43 | 0.027 | 1.000 |

Figure 3 shows the bandgap calculation of ZnO-NPs synthesized with M. oleifera L with calcination temperature at 350°C. The results of the bandgap calculation for all samples are shown in Table 1. Bandgap calculation is performed using this following equation:

\[ \alpha = \frac{A (h \nu - E_g)^{1/2}}{h \nu} \]  \hspace{1cm} (3)

where \( A \) is the proportional coefficient, \( h \) is the Planck constant, \( \nu \) is the light frequency, and \( E_g \) is the band gap [17-21]. The bandgap value of ZnO-NPs annealed at 300°C is 2.60 eV and then increased to 3.02 eV at 350°C annealing temperature. The bandgap then constantly decreased as the calcination temperature increased to 400, 450, and 500°C, which are 2.79, 2.58, and 2.43 eV consecutively. The decrease in bandgap energy can be explained by the alteration of the sp-d electron, which comes from p-d and s-d interaction [15, 18-30].
Figure 3. The band gap of ZnO-NPs for the calcination temperature 350°C

Figure 4. (a) UV-Vis spectra for different time of measure (0-120 min) and different calcination temperature (300°C -500°C). (b) The correlation between calcination temperature with degradation determined from UV-Vis (a).

The results of the photocatalytic degradation study of methylene blue solution are shown in Figure 4. The maximum absorption band of methylene blue (Figure 4.a) is shown to be around 600-700 nm, and the absorbance is decreased as after a certain amount of exposure time. At the end of reaction time, the methylene blue solution is discolored, which indicate the successful degradation of the dye with the help of ZnO-NPs with degradation percentage >75% for all samples. Samples calcined at 300, 350, and 400°C degrades 70, 80, and 81% of the methylene blue initial concentration consecutively in
120 minutes interval. Samples calcined at 450°C can remove 76% of the dye after 90 minutes and samples calcined at 500°C give the best results with 80% degradation percentage after 60 minutes of exposure time. This result shows that sample calcined at higher temperature produces the smallest average particle size can accelerate the degradation process as reported by Shuang et al. (2018). Larger particle size exhibits a smaller surface area and shows inferior photocatalytic activity [20-30]. Kinetic reactions can be observed by plotting linear curves with the various calcination temperature by the equation:

$$\ln\left(\frac{C_0}{C_t}\right) = kt$$

where, $C_0$ is the initial concentration, and $C_t$ is the concentration at time $t$, and $k$ is the first-order rate constant [19]. The photocatalytic performance in this study shows an increase which was affected by the increasing calcination temperature.

![Figure 5](image)

**Figure 5.** (a) The photocatalytic performance of ZnO NPs using *Moringa Oleifera* L. (b) Kinetic of photocatalytic degradations.

Figure 5. shows the value of the degradation rate constant ($k$) and the correlation coefficient ($R^2$) of calcined samples from 300 to 500°C are clearly shown in Table 1. The best correlation is for samples calcined at 500°C. From these results shows the effect the particle size and the bandgap strongly influence the level of the electron-hole pair combination as reported by Nguyen et al. which were increasing accelerate in the photocatalyst performance [22, 23, 30].

4. Conclusion

In this research, the synthesis of ZnO-NPs using *Moringa Oleifera* L was successfully carried out with a calcination temperature of 300-500°C. The crystallite size and the bandgap energy was decreased from 40.05 to 19.20 nm and from 2.60 eV to 2.43 eV respectively. The O-H bond in the FTIR spectrum shows decrease intensity of the peaks with increasing the calcination temperature which may due to the treatment the sample caused electrons to be released from the medium material. UV-Vis the
photocatalysis process that the most degraded samples for 60 minutes were samples calcined at 500°C with 80% degradation probably due to the small particle size, which could accelerate the catalyst process. These results indicate that ZnO synthesis using Moringa Oleifera L. is very promising for photocatalysis applications as well as being environmentally friendly.

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