The potential of green seaweed (*Caulerpa* sp.) extract to synthesis ZnO nanoparticles with zinc nitrate as a precursor and pH variations

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Abstract. The potential of green seaweed *Caulerpa* sp. as a reducing agent, stabilizer, and capping agent and the benefits of zinc oxide (ZnO) nanoparticles in the food and non-food is exciting to be developed. The research was aimed to understand the potential of green seaweed (*Caulerpa* sp.) to become ZnO nanoparticles capping agent with ten mM zinc nitrate as a precursor and pH variations of 8-12. The analysis included function groups, particle size distribution, and % mass O and Zn composition. The result found that spectra at wave number 574 cm\(^{-1}\) were Zn–O stretching vibration from solution pH synthesis of 11. Size distribution was homogenous, but it still had not met the size of nano. The average particle size ranged from 992.37-1369.36 nm, and the smallest particle size was obtained at a ZnO synthesized at a pH of 8. The composition from ZnO synthesis at solution pH of 9 was 7.68% O and 92.32% Zn. *Caulerpa* sp. extract could produce a synthesis of ZnO with ten mM zinc nitrate as a precursor and solution pH variations. Although the biosynthesis had not produced a ZnO with nanoparticles size yet, the particle size distribution had been homogeneous. The biosynthesis at pH 9, %mass Zn and O for ZnO produced had been similar to the ZnO standard.

1. Introduction

Green methods for synthesizing nanoparticles are widely used because they provide several advantages, such as environmentally friendly, safe processes, and are relatively cost-effective. This method uses plants, bacteria, yeast, algae, and others. Plant extracts containing phytochemical compounds can reduce and stabilize agents during the synthesis process [1]. Nanoparticles have been applied in various fields, like electronics, cosmetics, coatings, packaging, and biotechnology medicine.

Research on the zinc oxide (ZnO) synthesis using green seaweeds of *Ulva lactuca* [2] and *Caulerpa peltata* using variations in the concentration of precursor solution, the concentration of filtrate/extract, reaction temperature, pH, and reaction time [3] had been carried out. ZnO from *Ulva lactuca* extract and antibiofilm and larvicidal activities has an absorbance band at 325 nm and average crystallite sizes of 10–50 nm nanoparticles. The ZnO biosynthesis with brown seaweed *Sargassum* sp and *Padina* sp extract used zinc nitrate as a precursor [3], resulting in ZnO particle size ranging from 1,396.53-3,090.50 and 655.91-3,253.06 nm.

In Indonesia, research on the biosynthesis of ZnO nanoparticles using green seaweed has not been extensively carried out. The abundance of green seaweed, both in type and quantity, and the extent of ZnO nanoparticles benefits in the food and non-food fields, this research was carried out to know the
potential of green seaweed Caulerpa sp. become ZnO nanoparticles with ten mM zinc nitrate as a precursor and solution pH variations, 8-12 to add information on the benefits of Caulerpa sp.

2. Material and methods

2.1. Materials
The materials used in this research were green seaweed Caulerpa sp. freshly harvested from Binuangeun Waters, Banten. The Caulerpa sp. was then brought to Research and Development Center for Marine and Fisheries Product Processing and Biotechnology’s laboratory in Jakarta. Caulerpa sp. was washed in the laboratory three times and oven-dried at 60 °C for a week. The Caulerpa sp. was milled until it became flour. Chemicals used for synthesis were ZnNO₃, NaOH, HCl, and deionized water. Chemical analysis such as ZnO Sigma Aldrich, KBr, and ethanol.

The equipment used was a cool box, hammer mill, hot plate, freeze dryer, pH meter, oven vacuum, and furnaces. Analysis tools include instrumentation such as Fourier Transform Infrared Spectroscopy (FT-IR) Perkin Elmer spectrophotometers, Particle Size Analyzer (PSA) Beckman Coulter, and Scanning Electron Microscopy/Energy Dispersive Spectroscopy (SEM/EDS) Jeol.

2.2. Methods
The production stages of ZnO from Caulerpa sp. extract [4]:
- Caulerpa sp. flour as much as 1 g was added into 100 mL ultrapure (Type 1) water and heated at 100 °C for 25 minutes. The extract was filtered using Whatman No. filter paper 1 and stored at 4 °C;
- 5 mL of seaweed extract was added to 95 mL of zinc nitrate solution (ZnNO₃) 10 mM, and then the solution was stirred and heated at 80 °C for 10 minutes. The pH of the solution was varied to 8-12 using 0.1 M HCl solution or 0.1 M NaOH solution and kept stirring for 1 hour;
- The precipitate was washed with deionized water three times. After that, the precipitate was dried in a vacuum oven at a temperature of 100 °C overnight. Furthermore, the process continued with the calcination process at 450 °C for 4 hours

The parameters measured were functional analysis groups using FT-IR instruments [5, 6], particle size distribution using PSA instruments [7], and the element composition using SEM/EDS instruments[8].

3. Results and discussion

3.1. The functional groups of ZnO – Caulerpa sp. extract with pH variation
The FTIR spectra in Figure 2 show a difference in intensity and peak width after the Caulerpa sp extract interacted with the zinc nitrate precursor solution. The loss of absorption band 2,922.3 cm⁻¹ on the FTIR spectrum of Caulerpa sp. extract indicated a suspected reaction during the bioreduction process. The spectra with bands at wavenumbers 3,465.9-3,466.2 cm⁻¹ showed the O-H stretching; 2,426.2-2,426.3 cm⁻¹ the triple bond region of C≡C medial alkyne (disubstituted); 1,634.0-1,646.8 cm⁻¹ stretching vibration of the group (NH)C=O; and 826.1- 839.7 the sulfate group polysaccharides. The presence of a wave number of 1,384.1-1,384.2 cm⁻¹ in ZnO nanoparticles from Caulerpa sp. showed many N-O functional groups thought to be derived from the zinc nitrate solution as precursor [9]. The analysis on functional groups of standard ZnO at a wavenumber of 495 cm⁻¹ is useful to treat ZnO biosynthesized from Caulerpa sp. extract at pH 11.

Band shift in the FTIR spectrum of nanoparticles ZnO of all samples indicated the involvement of polyols, terpenoids, and proteins had functional groups such as amines, alcohols, and carboxylic acids during the bioreduction process. According to [10,11,12], the band at wavelength 400-600 cm⁻¹ was the stretching vibration of Zn-O. Spectra from ZnO from Caulerpa sp. extract obtained from this research were the following [4,13,14,15].

2
Caulerpa sp extract in ZNO₃ solution was heated at 80 °C for 10 minutes

The solution pH was set between 8-12

The solution was stored at room temperature then filtered

The precipitate was dried in a vacuum oven at 100 °C overnight

The ZnO earned after calcination process at 450 °C for 4 hours

**Figure 1.** The production stages of ZnO from Caulerpa sp. extract.
The functional groups of ZnO from Caulerpa sp. extract with pH variation.

3.2. The particle size distribution of ZnO – Caulerpa sp. extract with pH variation
The particle size distribution of ZnO produced from the biosynthesis of Caulerpa sp. extract can be seen in Table 1. The smallest average particle size was ZnO from the biosynthesis of Caulerpa sp. extract at pH 8. The size distribution was homogeneous but did not meet the nanosize requirement (0-100 nm). Many chemical compounds in Caulerpa sp. contributed to the trapping of zinc nitrate precursors or templates. A ZnO synthesis had the smallest average particle size of 232.48 nm with a concentration of Zn(CH$_3$COO)$_2$.2H$_2$O precursor solution, which was 0.05 M and pH 7 [14]. The ZnO with an average particle size of 825.04-1,642.10 nm was synthesized with 0.1 M ZnCl$_2$ precursor and pH 10 [15].

The size particles of ZnO produced was highly dependent on the template size of nanoparticles surface around [16]. [4] stated that the aggregation of ZnO nanoparticles at low pH leads to the formation around the nucleation.

3.3. Mass percentage of Zn and O of ZnO – Caulerpa sp. extract
Table 2 showed that % mass Zn and O of ZnO standard and ZnO produced with pH biosynthesis variations. The ZnO produced with element composition similar to ZnO standard was ZnO produced from the biosynthesis of Caulerpa sp. extract at pH 9. [14] state the optimum ZnO nanoparticle
formation process based on composition element was using a concentration precursor of Zn(CH₃COO)₂·2H₂O 0.15 M and pH 8. However, this EDS data could not confirm that the sample content was a ZnO compound with wurtzite crystals.

### Table 1. Particle size distribution of ZnO – Caulerpa sp. extract with pH variations.

| No | Sample     | Size (nm) |
|----|------------|-----------|
| 1  | ZnO pH 8   | 992.37    |
| 2  | ZnO pH 9   | 1194.26   |
| 3  | ZnO pH 10  | 1124.03   |
| 4  | ZnO pH 11  | 1369.36   |
| 5  | ZnO pH 12  | 1053.57   |

### Table 2. Mass percentage of Zn and O of ZnO – Caulerpa sp. extract with pH variations.

| No | Sample     | Mass (%)         |
|----|------------|------------------|
| 1  | ZnO standard | Zn 91.09, O 8.91 |
| 2  | ZnO pH 8    | Zn 82.94, O 17.06|
| 3  | ZnO pH 9    | Zn 92.32, O 7.68 |
| 4  | ZnO pH 10   | Zn 63.68, O 36.32|
| 5  | ZnO pH 11   | Zn 59.42, O 40.58|
| 6  | ZnO pH 12   | Zn 74.42, O 25.58|

### 4. Conclusions

The production of ZnO from the biosynthesis of green seaweed Caulerpa sp. extract with pH variations has been carried out. The result showed that Caulerpa sp. extract could be synthesized into ZnO with ten mM zinc nitrate as a precursor and solution pH variations. Although the biosynthesis had not produced ZnO nanoparticles size yet, the particle size distribution was homogeneous. The biosynthesis at pH 9, the mass percentage of Zn and O for ZnO produced had been similar to the standard ZnO.

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