Current development, potentials, and challenges of biological synthesis of nanoparticle (as a photocatalyst): A review

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Abstract. Nanoparticles can be applied potentially in various areas of industrial processes because of their unique mechanical and optical properties, antimicrobial abilities, and catalytic capabilities. This paper aims to analyze the current status of research and development of producing high-value nanoparticles as a photocatalyst using the principle of green chemistry and to identify the potentials and challenges of the new green synthesis in its further developments. The biological method is considered effective and environmentally friendly in producing nanoparticles as a photocatalyst. These efforts can be realized by utilizing natural reducing agents. The bioreductor compounds are available in plants and their waste is in large quantities. It is also reported that some kinds of microorganisms may be used in the biological synthesis of nanoparticles effectively. Some potentials and challenges for it, further research and development were identified, presented, and discussed. Biologically, the synthesis of nanoparticles is considered to be more energy efficient because the process is simpler by utilizing microorganisms, plants and horticultural food waste extracts as a medium for the synthesis of nanoparticles.

1. Introduction
Nanoparticles (NPs) are solid particles that range in size from 1-100 nm. They have different physicochemical properties from other materials and are highly dependent on the size, charge, composition, and coating process that allows them to adhere to these nanoparticles [1]. Over time, the use of nanoparticles has increased so that they can be applied in various fields of science, related to their unique optical properties [2], antimicrobial abilities [3], mechanical properties [4], and catalytic capabilities [5,6]. Nanoparticle synthesis can be carried out either by physical, chemical, or biological methods as well as other hybrid methods.

The physical and chemical methods are very useful for the production of monodispersed nanoparticles. The use of toxic and dangerous chemicals makes this method quite dangerous and can have a considerable impact on the environment. In addition, the use of hazardous chemicals allows the adsorption of the nanoparticles so that they have a dangerous effect when applied to medical purposes. Therefore, it is necessary to develop an environmentally friendly and sustainable method for the synthesis of nanoparticles [7]. Green chemistry demands an approach for the bio-production of nanoparticles through a highly stable and eco-friendly process with no toxic chemical and large scale production. There are various chemical and physical procedures for the synthesis of nanoparticles, either through the wet or dry method approaches. Physical and Chemical processes include vapor deposition, plasma, ultrasonic
irradiation, precipitation, microemulsion, reduction methods, sol-gel, and hydrothermal techniques. The increase in production costs will occur because the application of these techniques requires a high amount of energy [8].

Therefore, it is necessary to develop a nanoparticle synthesis that is safe, environmentally friendly, and energy-efficient. To fulfill this, biological synthesis is a promising alternative [9]. The production of nanoparticles based on biological materials such as algae, fungi, viruses, bacteria or plants has been carried out in recent years [10]. This is done because it is known that the metal ion reduction rate is quite high at ambient temperature and pressure conditions, and is capable of releasing some enzymes that will hydrolyze metal ions [7].

2. Biological synthesis

Figure 1 shows the mechanism of nanoparticle formation. The process is initiated by changing the metal ions in solution from a mono- or divalent oxidation state to a zero-valence state [11]. Nucleation will occur due to the reduction of metal ions by biomolecules in the extract of food waste. In the next phase, thermodynamically stable nanoparticles will be formed due to the accumulation of particles on low-energy surfaces. In the next stage, the biomolecules produced by the food waste will also function as natural surfactants for the capping process which will make the nanoparticles more stable and affect the formation of nanoparticles at a later stage.

![Figure 1. Biological synthesis of metallic nanoparticles using food waste extract [11].](image)

The principle of green chemistry in biological synthesis is basically a process that in its application uses renewable raw materials, optimizes the utilization of waste to produce chemical products, namely nanoparticles. It aims to reduce threats to the safety of the environment and humans. Green chemistry is also known as benign environmental chemistry, clean chemistry, atomic economics, or benign design chemistry. The application of green chemistry is based on twelve principles that can be seen in figure 2.

The cell membrane which is composed of lipids and membranes is the main biological entity [13] of most of the synthetic biochemical conversions that follow the oxidation-reduction mechanism. The dynamic and flexible composition of this membrane means that the effect of the composition is not always constant, thus facilitating the reduction-oxidation reaction. Thus, it is hoped that the synthesis of nanoparticles can use extracellular and intracellular microorganisms in optimal environmental conditions.
| Principle | Description |
|-----------|-------------|
| Prevention | Prevention takes precedence over remediating waste. |
| Minimize harmful chemicals | Synthesis of chemicals is sought to use and produce substances with the least harmful to human health and the environment. |
| Minimize the use of derivatives | Use of reduced additives to reduce the amount of waste generated. |
| Design the degradation | To simplify the breakdown of chemical products at the end of their functions. |
| Energy saving | Minimizing energy use in the process. |
| Monitoring and prevention | Monitoring and prevention of substance formation must be carried out directly dangerous at every stage of the synthesis process. |
| Minimize the potential | Minimize the potential for accidents, such as the emergence of emissions of hazardous substances, explosions, and fires. |

**Figure 2.** The application of green chemistry is based on twelve principles [12].
Figure 3. The mechanism of using microorganisms in the synthesis of nanoparticle [13].

Other studies suggest that most of the extracellular synthesis of nanoparticles occurs due to electrostatic attraction between microorganism membranes containing negatively charged phospholipids and a combination of salts which are positively charged metal ions [14]. In the synthesis of nanoparticles, as shown in figure 3, salt is an important ingredient to add. Variations in metal salts and culture parameters need to be investigated further to obtain specific nanoparticles. The color change in the media is an early indicator of the formation of nanoparticles qualitatively.

3. Synthesis of nanoparticle (ZnO and TiO)

3.1. Synthesis of ZnO

Potential applications of zinc oxide nanoparticles include high catalytic efficiency, strong adsorption capability, high isoelectric point (9.5), biocompatibility, and fast electron transfer kinetics for biosensing purposes [15]. Biological synthesis is carried out using milk sap from Calotropis procera which will be used as a reducing agent and as a surface stabilizer. The results obtained are that the size of the ZnO nanoparticles is an average of 5-40 nm with a spherical shape [15], and reports for the photoluminescence of the ZnO sample suggest five emitting bands, namely three blue bands at 417 nm, 440, and 462 nm, possibly a green band at 520 nm, and one red band at about 675 nm.

Aloe barbadensis Miller leaf extract has been investigated for the synthesis of green ZnO nanoparticles [16]. Experiments were carried out using aloe vera extract which was cooked and not cooked. The synthesis of nanoparticles with different concentrations (50%, 25%, 15%, 10%, 5%) was prepared with distilled water and the volume was made up to 250 ml. Then zinc nitrate was dissolved and stirred at 150°C for 5-6 hours, allowed to cool at room temperature then the supernatant was removed. The resulting product was pale white, it was then centrifuged, and dried at 80°C for 7-8 hours. The results of the characterization of zinc oxide nanoparticles showed different dispersions of poly and particle sizes of 25-45 nm with an average size of 35 nm. The nanoparticles formed are stable, this is due to the interaction of amino groups and carboxylate groups with the zinc surface [16].
The synthesis of ZnO-NPs from *Physalis alkekengi* extract has been investigated [17]. There were two stages, first was to prepare the plant and then synthesize ZnO-NPs. Plant preparation included extraction from *P. alkekengi* using methanol; followed by extracting the Zn produced using sulfuric acid to form zinc sulfate; then reacted with chlorophyllin to form zinc chlorophyllin, and the final step was the synthesis of ZnO-NPs by direct deposition of zinc chlorophyllin in dilute ammonia. The resulting residue was filtered 3 times with filter paper, then the pH was adjusted by adding sodium hydroxide solution (10%) until the pH became 11. The next step was concentrating with an evaporator to 25% of the original volume and extracted 3 times with petroleum ether and a funnel separator. The pH value was again adjusted to 3 by adding uric acid. The product of the reaction was C\textsubscript{12}H\textsubscript{18}O\textsubscript{4}N\textsubscript{2} (CO\textsubscript{2}H)\textsubscript{2} [19], which was further dried and reacted again with 150 mL H\textsubscript{2}SO\textsubscript{4} (1.00 mol L\textsuperscript{-1}) at 85°C for 360 minutes. Furthermore, filtering and evaporation of up to 20% were carried out. The solution was re-reacted with C\textsubscript{12}H\textsubscript{18}O\textsubscript{4}N\textsubscript{2} (CO\textsubscript{2}H)\textsubscript{2} at 60°C for 80 minutes to form C\textsubscript{32}H\textsubscript{30}O\textsubscript{4}Zn (CO\textsubscript{2}H)\textsubscript{2} then heated and added with NH\textsubscript{3}H\textsubscript{2}O (1.25 mol L\textsuperscript{-1}) until pH 6. The resulting precipitate was centrifuged, washed with ethanol, and dried. The ZnO nanoparticles produced were porous, rod-shaped which had an average size of 55 nm [17].

Another investigation of synthesis ZnO-NPs from another plant; *Sedum alfredii* also has been conducted [20]. Same with green synthesized of ZnO-NPs from *Physalis alkekengi* extract, there were two phases of the synthesis. The only difference lies in the plants used, namely *Sedum alfredii*. The resulting ZnO-NPs characteristic was pseudo-spherical, with an average particle size of 53.7 nm.

Vimala [21] has conducted other related research to the green synthesis that has been carried out with the use of *Borassus flabellifer* fruit extract for ZnO-NPs. The process stages were generally carried out in the same stages as the previous process. Experiments were carried out at different concentrations, namely 5%, 10%, 15%, 25%, and 50%. The structure of the ZnO-NPs formed was rod-like and porous with an average size of 55 nm.

El-Waseif [22] apart from investigating the synthesis of titanium nanoparticles, also carried out a study on ZnO-NPs using *L. johnsonii*. The results of the analysis show that the absorbance for ZnO-NPs was 492 nm with a spherical shape that had an average size between 4-9 nm.

### Table 1. Bio-synthesised of ZnO using plant or microorganism sources.

| Nanoparticle | Size & shape                  | Plant/ microorganism            | Year | References |
|--------------|-------------------------------|--------------------------------|------|------------|
| ZnO          | Spherical and granular natur, in the range of 5-40 nm. | The latex from *Calotropis procera* | 2011 | [15]       |
| ZnO          | Spherical and stable, 25-45 nm | *Aloe barbadensis Miller* leaf extract | 2011 | [16]       |
| ZnO          | Crystalline poly-dispersed, a mean particle size of 72.5 nm | *Physalis alkekengi* extract | 2011 | [17]       |
| ZnO          | Pseudo-spherical, a mean particle size of 53.7 nm. | *Sedum alfredii* | 2011 | [20]       |
| ZnO          | Porous in nature and rod like structure with an average size of 55 nm. | *Borassus flabellifer* fruit extract | 2014 | [21]       |
| ZnO          | Spherical in shape and polydispersed with maximum particles in size range within 4-9 nm | *Lactobacillus johnsonii* | 2018 | [22]       |
| ZnS          | Spherical, 2-5 nm              | *Desulfo bacteriaceae*       | 2000 | [23]       |

### 3.2. Synthesis of TiO
Titanium oxide is a popular material that is often used as a catalyst for water purification and degradation of organic compounds, such as humic acid in peat swamp water and dyes such as indigo carmine and methylene blue. The use of this material as an ultrafiltration membrane coating used for drinking water treatment as an alternative technology for the conventional separation of organic substances has been investigated [24]. The presence of TiO$_2$ will increase the ability of the membrane to photocatalytic processes. This is due to the fact that TiO$_2$ has beneficial properties such as being a semiconductor, chemically and physically stable, has high activity, is resistant to abrasion (scratches) [25], and is relatively inexpensive [26].

It is known that the structure of the titanium oxide crystals greatly affects its catalytic activity (rutile, anatase, or brookite). Likewise, the surface area, size, or porosity of the nanoparticles to be produced. Pure TiO$_2$ with a metastable crystal anatase structure having a wide band gap (3.2 eV) has been made as a UV-activated photocatalyst that is predominantly used because of its stability and high oxidation potential and its chemically beneficial properties [27]. Table 2 shows the investigation of the biosynthesized of TiO$_2$ by some plants and microorganisms.

| Nanoparticle | Size & shape | Plant/ microorganism | Year | References |
|--------------|--------------|----------------------|------|------------|
| TiO$_2$      | Spherical 23 ± 2 nm in ranges | Annona squamosa peel | 2012 | [28]       |
| TiO$_2$      | Spherical, 100 to 150 nm | Nyctanthes arbor-tristis leaf extracts | 2011 | [29]       |
| TiO$_2$      | Spherical and quite polydisperse, 36 to 68 nm with calculated average size of 49.5 nm | Eclipta prostrata leaf extracts | 2012 | [30]       |
| TiO$_2$      | Irregular, 25 up to 110 nm | Catharanthus roseus leaf extract | 2011 | [31]       |
| TiO$_2$      | Spherical shape and clusters with an average size of 32.58 nm | Psidium guajava | 2014 | [32]       |
| TiO$_2$      | Irregular shape in size range within 4–9 nm | Lactobacillus johnsonii | 2018 | [33]       |
| TiO$_2$      | 150 nm | Lactobacillus | 2011 | [34]       |
| Ti$^+$       | Spherical, 40-60 nm | Lactobacillus sp. | 2007 | [35]       |

Research on *Annona squamosa* L. (Annonaceae) to synthesize TiO$_2$-NPs has been carried out [28]. The main ingredient, namely the fresh skin of *A. squamosa*, was processed to become a powder, then 4 g was dissolved in distilled water (40 mL) at room temperature (25°C). The extract obtained was then filtered in stages using nylon mesh (Spectrum) and Millipore hydrophilic filter (0.22 μm). TiO(OH)$_2$ solution was prepared in the Erlenmeyer flask by adding 5 mM TiO(OH)$_2$, 100 mL of distilled water and dissolved for 2 hours. The TiO$_2$ solution was formulated by adding 20 mL of *A. squamosa* extract and 80 mL of 5 mM TiO$_2$ (at room temperature under stirring for 6 hours). The solution was then observed using scanning electron micrographs. Based on the observations, the morphology of TiO$_2$ nanoparticles was spherical, in the form of aggregates with a size of 40-60 nm. This phytochemical result showed that *A. squamosa* extract was able to reduce titanium ions to metal nanoparticles.

Biological synthesis of TiO$_2$ NPs nanoparticles using *E. prostrata* leaves by a simple water reduction method has been conducted [30]. An aqueous extract of *E. prostrata* was prepared by boiling 10 g of the ingredients using 100 mL of double distilled water at 60°C for 10 minutes. The solution was then filtered gradually using nylon mesh (Spectrum) and followed by a Millipore hydrophilic filter (0.22 μm) for use in further experiments. Synthesis of TiO$_2$ nanoparticles was previously carried out by preparing an
Erlenmeyer flask containing 100 mL of TiO(OH)_2 (5mM), stirred for 2 hours, then 85 mL 5 mM TiO_2 were taken and mixed with 15 mL of dilute *E. prostrata* extract at room temperature under stirring conditions for 24 hours. The formation of nanoparticles was characterized by a light green color change. The results of characterization using XRD in the rutile [30] phase showed a polydispersion pattern and ranged in size from 36 to 68 nm with an average size of 49.5 nm.

Evaluation of TiO_2 nanoparticles synthesized using *L. johnsonii* in MRS broth at an absorbance of 409 nm was carried out using UV, FTIR, and TEM [22]. Based on the reading of FTIR results, it was found that TiO_2 nanoparticles had a stronger protein ability to bind to metals so that they could prevent particle agglomeration. TEM images of the TiO_2 NPs record an irregular shape with an average size of 4-9 nm.

The synthesis of Titanium nanoparticles was carried out using *Lactobacillus sp* [34] which was started by preparing the filtrate which was diluted 5 times at a pH of 2-4 solution, then added with 10% sugar solution and incubated for 24 hours. After 24 hours, about 20 ml 0.025 (M) of titanium dioxide solution was added and stirred with the help of a magnetic stirrer for 0.5 hours and incubated for 3–4 days (a precipitate would form at the bottom of the Erlenmeyer and a change in pH). Then the filtering process was carried out using Whatman paper and dried under a blow of hot air [34]. The filtered and dried nanoparticles were used for characterization using X-rays and TEM. The synthesized nanoparticles were spherical with a size of 40-60 nm.

4. Potential application and the challenges of metal oxide as nanoparticle

Nanotechnology has a wide potential for application in various fields, including as a catalyst, biomedicine, electronic components, optical science, engineering, and others. The use of titanium dioxide (TiO_2) as a photocatalyst is considered effective to degrade and inhibit the growth of scattered pollutant parameters either on the surface of the water (waste) or those that spread in the air [36]; therefore TiO_2 is implemented for various purposes, including as a photocatalyst, gas sensor, solar devices and biomaterials [35].

One of the applications of nanoparticles in wastewater treatment was carried out [37] On secondary effluent palm oil mill (POMSE) using a photocatalytic process using ZnO-polyethylene glycol (ZnO-PEG) nanoparticles [37]. The photoreactor for the POMSE treatment process is shown in Figure 4. The photoreactor was equipped with a light source (365 nm UV lamp) with a power of 15 W. The reaction temperature took place at room temperature (25°C) by immersing it in a water bath. For the analysis process of reaction results, 5 ml of sample water was taken at 5-minute intervals and the mixed solution (POMSE and ZnO) was subsequently separated using a Gy Frozen 1736R centrifuge model for 20 minutes.

![Figure 4. The experimental setup of photocatalysis process [37].](image-url)
The results obtained were that the optimum processing conditions occurred at pH 6.5 with the addition of a ZnO-PEG photocatalyst of 0.5 g / L in the 50% proportion of POMSE dilution. The color change that occurred was not too large, but the use of PEG polymers in ZnO-PEG photocatalysts was useful in reducing nanoparticle agglomeration. This is due to the adsorption process on the surface of the nanoparticles.

The application of TiO2 photocatalysts has also been carried out by Chen [38] using NTO photocatalysis as pre-treatment followed by the use of constructed wetlands. The initial stages of the experiment were to first treat household and agricultural wastewater (figure 5, COD was 36.2 ± 7.4) with TiO2 photocatalysis (coated on α-alumina) before transferring it to a bench-scale wetland system. The hydraulic retention time was 2 days, and it was found that there was a reduction in the levels of halomethane and haloacetic acid so that the value was below the maximum contamination threshold allowed for drinking water.

![Figure 5. Wetland treatment technologies [38].](image)

According to Hermann [39], factors that influence photocatalysis performances include photoreactor design, light wavelength, light intensity, photocatalyst, initial concentration of reactants, temperature, pH, oxygen content, and the presence of certain ions. Therefore, in order to obtain a better photocatalytic degradation performance, it is recommended to provide a larger surface area for the reaction. A potential photocatalyst with unique properties is TiO2. It has the ability to mineralize a wide spectrum of pollutants with relatively lower operating costs, and a simple experimental design [40].

TiO2 NPs can be synthesized biologically using *Lactobacillus sp*. As described above and this topic will become the main focus of the research to be carried out. This research will optimize the photoreactor performance so that it can be applied for the processing of POMSE. The research results will be compared with the results of other studies, such as the results of the study with the use of ZnO NPs by Zainuri [37].

5. Conclusion

Biological synthesis of nanoparticles is considered to be more capable of providing several advantages compared to the physical and chemical synthesis, including being more environmentally friendly with more efficient energy use due to its simpler process. Several studies have been reported and discussed in
the description above which describe that microorganisms, plants, and waste extracts from horticultural food can be used as a medium for the synthesis of nanoparticles.

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