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Research paper

Biosynthesis of Zinc Oxide Nanoparticles for Corrosion Protection Application

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Abstract

The present study reports the successful synthesis of biosynthesized zinc oxide nanoparticles (ZnONPs). The *Pandanus Amaryllifolius* leaves extract was used as reducing agent with zinc nitrate hexahydrate as precursor. The effects of synthesis temperature on biosynthesis of ZnONP's are discussed. The biosynthesized ZnONPs were characterized by X-ray diffraction (XRD) ; and they were found to exhibit the hexagonal wurtzite structure. The diffractograms revealed well-defined, strong and sharp peaks at 2θ positions that correspond to its crystallinity with average size of 16.25 nm. Micrograph images from Field Emission Scanning Electron Microscope (FESEM) have shown polydispersed spherical shape of the biosynthesized ZnONPs. Smaller grain sizes were produced at low synthesis temperature of 60ºC. The elemental composition analysis confirmed the presence of zinc and oxygen by Energy Dispersive X-ray (EDX). The corrosion inhibition efficiency of mild steel in 1.0 M hydrochloric acid (HCl) solution was determined by weight loss method. Of significance, good corrosion inhibition efficiency of 79.43% was obtained by incorporating the biosynthesized ZnONP's at synthesis temperature of 60ºC.

Keywords: *Zinc oxide nanoparticles, corrosion protection, mild steel, biosynthesis, Pandanus Amaryllifolius.*

1. Introduction

Metal oxide nanoparticles is one of the multifunctional materials that can be manipulated into wide nanotechnology applications across all sciencetific fields, such as chemistry, biology, physics, materials science, and engineering. In case of nanoparticles, they are effectively a bridge between bulk materials and atomic or molecular structures which draws the attention of scientific researchers to focus on their synthesis. Among all metal oxide nanoparticles, zinc oxide nanoparticles (ZnONPs) are in the forefront of research due to their unique properties and wide applications [1]. ZnONPs exhibit high catalytic efficiency, high absorption of light, strong adsorption ability and fast electron transfer kinetics which make it a promising material in paint products, bio-sensing properties, [2], [3] and hybrid solar cells [4]. Due to such a wide range of applications, numerous methods concerning the fabrication of ZnONPs have been developed. Chemical and physical processes such as sol-gel technique, solvothermal synthesis, chemical reduction, laser ablation and inert gas condensation have been used in obtaining ZnONP's [5-7]. Even though chemical method of synthesis has advantageous as it takes short period of time to synthesize large quantities of ZnONP's, however the process and yield could be toxic and lead to it having non-environmentally friendly by-products which may cause harm to human body in the long term. In addition, some chemical reactions require critical conditions of temperature and pressure as reported by [8]. Increasing awareness towards green synthesis (biosynthesis) of metal oxide nanoparticles has led to the development of an eco-friendly approach for the synthesis of ZnONP's. The techniques for obtaining nanoparticles using naturally occurring reagents such as vitamins, sugars, plant extracts, biodegradable polymers, and microorganisms as reductants and capping agents have been proven as preferred alternative green synthesis [9-12]. Among the reagents mentioned above, plant based materials can be considered as the best candidates. Nanoparticles produced by plants are more varied in size and shape and more stable compared to those that are produced by microorganisms [13] On top of that, they are suitable for large-scale biosynthesis of nanoparticles [14].

Although biosynthesis of ZnONP's by plants such as *Aloe barbadensis miller* [15], *Azadirachta indica* [16], *Allium sativum* [17] have been reported, the potential of plants as biological materials for the synthesis of nanoparticles is yet to be fully explored. From this point of view, this study aims at the biosynthesis of ZnONPs from prepared *Pandanus amaryllifolius* leaves extract. Hence, the effect of both ZnONPs and *Pandanus amaryllifolius as* environmentally friendly corrosion inhibitor of mild steel in 1.0 M hydrochloric acid (HCl) solution by weight loss method have been investigated. It is strongly believed that flavonoids natural products contained in *Pandanus amaryllifolius* are responsible to exhibit good corrosion inhibition efficiency. The effects of different synthesizing temperature on biosynthesis of ZnONPs is also discussed. This novel synthesis of ZnONPs using aqueous extract of *Pandanus amaryllifolius* leaves can be utilized as a promising environmentally friendly corrosion inhibitor and simple alternative to alleviate the corrosion rate, protect metal surfaces against corrosion and preserve industrial facilities.

2. Methodology

2.1 Preparation of *Pandanus Amaryllifolius* Leaves Extract

Fresh leaves *Pandanus amaryllifolius* were collected. The leaves were washed several times with water to remove dust particles and then sun dried to remove residual moisture. The extract used for the reduction of zinc ions to ZnONPs was prepared by placing 300 g of washed dried fine cut leaves in 1000 ml glass beaker along with 900 ml of sterile distilled water. The mixture then was boiled at temperature of 80ºC for 60 minutes. The extract was cooled to room temperature and was filtered using filter paper before being stored in a refrigerator for further use.

2.2 Biosynthesis of ZnONPs

225 ml of zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$) precursor solution with concentration of 5 mM was poured into three different beakers and heated at temperatures of 60ºC, 70ºC and 80ºC. 25 mL of *Pandanus.Amaryllifolius* was added in each solution at temperatures 60ºC, 70ºC and 80ºC. 1M sodium hydroxide (NaOH) was added dropwise until reaching pH level 12 in each solution while stirring. The pH level was constant throughout the synthesis process for all solutions. The solutions were heated until there was a colour change from light yellow to deep yellow. The solutions were left for 24 hours and were filtered using filter paper to obtain the precipitate formed and left to dry for another 24 hours. The filtered paste was collected in a ceramic crucible and dried in an oven at 40ºC for 5 hours.

2.3 Characterization

Field emission scanning electron microscopy (FESEM) provides both morphological and topographical information especially for nanomaterials at magnifications of 10x to 300,000x, with particularly boundless depth of field. Energy Dispersive X- ray (EDX) is a chemical microanalysis technique used in conjunction with FESEM to characterize the elemental composition of the sample. XRD is a quick analytical technique fundamentally used for phase identification of a crystalline material and can give information on unit cell dimensions. Crystallite size can be calculated using Debye – Scherer's formula given by the equation:

$$D = K\lambda / (\beta \cos \Theta) \quad (1)$$

where;

D = the crystallite size,
λ= the wavelength of the X- ray radiation (λ= 0.15406 nm)
K = usually taken as 0.89
β = the line width at half maximum height

The *Pandanus amryllifolius* leaves extract were tested by Harbone method to determine the presence of flavonoids. This method was performed by using three different types of chemicals, 0.1 M of lead (II) aceate, 1.0 M of sodium hydroxide and 0.1 M of ferric chloride. The test was conducted by addition of 1 ml of *Pandanus amryllifolius* leaves extract to a few drops of the chemicals (0.1 M of lead II acetate solution, 1.0 M of sodium hydroxide solution and 0.1 M of ferric chloride solution). The solutions were then stirred for a minute and the changes were observed and recorded. The sample preparation was performed with five mild steel coupons with cross section of 2 x 2 cm. Each mild steel was polished with sand paper to remove impurities and dust. Then, the mild steel was rinsed with ethanol and left to dry before being weighed. Table 1 describes the test solution preparation.
The examined coupons were immersed with test solution for seven days at room temperature. The coupons were taken out from the solution, cleaned, dried and reweighed. The weight was recorded as weight loss in milligram (mg). The weight loss is converted to a corrosion rate. Corrosion rate and inhibition efficiency are calculated by using formulas as described by [18].

Table 1: Metal coupon description

Metal coupon	Solution
A	1M HCl
B	1M HCl + 2 mL *Pandanus amaryllifolius* extract
C	1M HCl + 0.01 M zinc oxide nanoparticles (60ºC)
D	1M HCl + 0.01 M zinc oxide nanoparticles (70ºC)
E	1M HCl + 0.01 M zinc oxide nanoparticles (80ºC)

3. Results and discussion

3.1 Biosynthesis of ZnONPs

ZnONPs were successfully synthesized using *Pandanus amaryllifolius* leaf extract as reducing agent and zinc nitrate solution as precursor. The precipitates of Zn $(OH)_2$ were reduced to Zn^{2+} and $2OH^-$ in the presence of water and thermal energy [19]. Fig. 1 shows the boiling process of *Pandanus amaryllifolius* leaves and the extract obtained. The plant extract contains novel secondary metabolites such as phenolic acid, flavonoids, alkaloids and terpenoids. These compounds are primarily responsible for the reduction of ionic into bulk metallic nanoparticles.

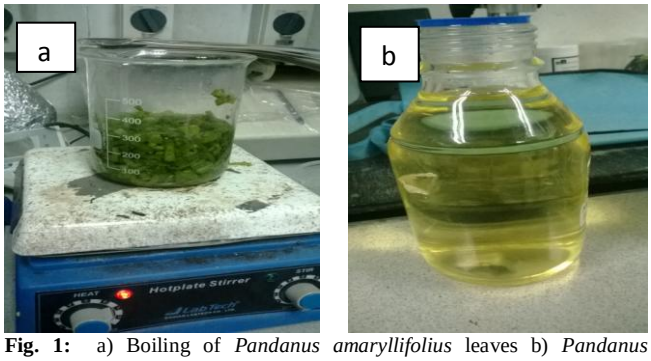

Fig. 1: a) Boiling of *Pandanus amaryllifolius* leaves b) *Pandanus amaryllifolius* leaves extract

3.2 FESEM-EDX analysis

Formation of ZnONPs synthesized at temperatures of 60ºC, 70ºC and 80ºC were evidently successfully as observed from FESEM-EDX results. Highly stable and spherical ZnONPs are produced by using zinc nitrate and *Pandanus amaryllifolius* leaf extract. The results showed an increase in the average particle size and particle agglomeration for higher synthesis temperatures. The average size of ZnONPs at temperatures 60ºC, 70ºC and 80ºC were 24.15 nm, 27.19 nm and 35.69 nm as seen in Fig. 2 a), b) and c) respectively. Compared to [20], the particle sizes of ZnONPs were estimated to be 98 ± 43, 135 ± 77, and 458 ± 243 nm, for synthesis temperatures of 65ºC, 70ºC and 75ºC respectively. This clearly shows that ZnONPs with different particles sizes can be obtained by varying the synthesis temperature. At higher synthesis temperature, it was found that the grain size was bigger and has extremely serious agglomeration. This agglomeration was due to polarity and electrostatic interaction of ZnONPs. The increased particle size decreased the surface area and the agglomeration weakened the binding to the surface. ZnONPs of smaller sizes can easily penetrate through the surface due to their large interfacial area, thus enhancing corrosion inhibition efficiency. So it is best to say that the properties of ZnONPs in corrosion inhibition may be disrupted as the particle sizes increase. For this study, synthesizing zinc

oxide at 60ºC would be the optimum temperature for the biosynthesis as the corrosion efficiency is subsequently enhanced.

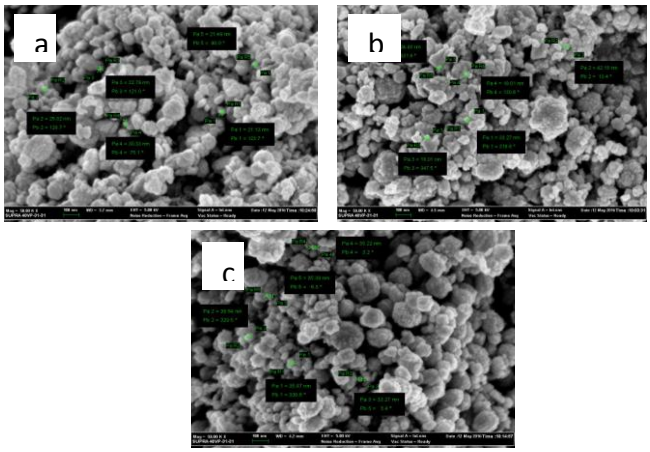

Fig. 2: FESEM images of ZnONPs synthesized at temperatures of a) 60ºC b) 70ºC and c) 80ºC

The elemental analysis from Fig. 3 a), b) and c) confirmed the presence of zinc and oxygen at different synthesis temperature. Highest percentage of Zinc and Oxygen were identified at temperature of 60ºC.

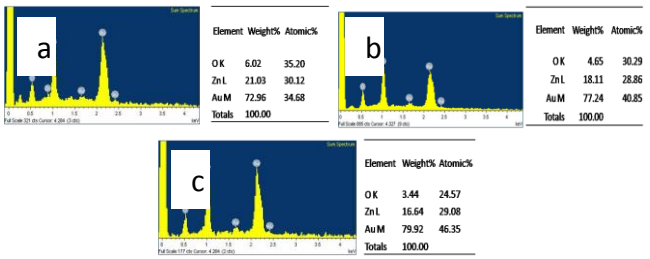

Fig. 3: EDX of ZnONPs synthesized at temperature of a) 60ºC, b) 70 ºC and c) 80 ºC

3.3 XRD analysis

The XRD patterns of ZnONPs synthesized at 60ºC, 70ºC and 80ºC are shown in Fig. 4 a), b) and c) respectively. The reflection peaks at 2 θ = 31^0, 34^0, 36^0, 47^0, 56^0, 62^0 and 67^0 correspond to (100), (002), (101), (102), (110), (103) and (112) reflection planes of zinc oxide hexagonal structure respectively. There are no other characteristic impurities peaks present which also confirmed that the product obtained is in pure phase and also are crystalline in nature because of the presence of high intensity narrow peaks. The narrow and strong diffraction peaks indicate the crystalline nature of zinc oxide, which is consistent with the XRD pattern of ZnONPs in this study. The size of ZnONPs was obtained by Debye – Scherrer's equation. The average sizes of ZnONPs at synthesis temperature of 60ºC, 70ºC and 80ºC was 16.25 nm, 17.15 nm and 17.39 nm respectively as listed in Table 2.

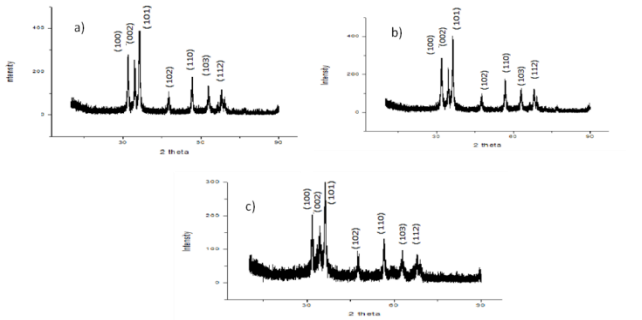

Fig. 4: XRD pattern of ZnONPs synthesized at a) 60ºC, b) 70ºC and c) 80ºC.

Table 2: Crystallite size of ZnONPs at synthesis temperature of 60ºC, 70ºC and 80ºC

Zinc oxide nanoparticles at 60ºC		
2Θ (deg)	Phase (hkl)	Size (nm)
31.777	100	11.42
34.432	002	11.50
36.264	101	14.96
47.553	102	18.00
56.612	110	18.71
62.877	103	19.30
67.969	112	19.86
16.25		

Zinc oxide nanoparticles at 70ºC		
2Θ (deg)	Phase (hkl)	Size (nm)
31.699	100	17.12
34.382	002	17.24
36.182	101	17.33
47.459	102	14.39
56.463	110	18.69
62.760	103	15.43
67.805	112	19.84
17.15		

Zinc oxide nanoparticles at 80ºC		
2Θ (deg)	Phase (hkl)	Size (nm)
31.768	100	17.11
34.422	002	11.49
36.254	101	17.33
47.540	102	18.00
56.595	110	18.70
62.858	103	19.30
67.948	112	19.86
17.39		

3.4 Flavonoid Test

Flavonoid is a major compound in the plant kingdom and is believed to play a role in the process of biosynthesis in reducing metallic ion and its stabilization. This study is an initiative of using the phytochemical compound within *Pandanus amaryllifolius.* Screening and presence of flavonoid compound in *Pandanus amaryllifolius* leaf extract was confirmed by using Harbone method. Pale yellow precipitates, yellow precipitates and black precipitates were observed in the clear solution after a few minutes of stirring the solution of lead II acetate, sodium hydroxide test, and ferric chloride respectively. The results of flavonoid test by using *Pandanus amaryllifolius* leaves extract were constructed as shown in Table 3. "+" symbol is used as a symbol to signify the presence of flavonoid in the leaves extract. These results were in line with the previous research using root extract of *Zigiber officinale* [21]. However, the extensive mechanism responsible for biosynthesis of ZnONPs is yet unclear.

Table 3: Flavonoids test for *Pandanus amaryllifolius* leaves extract

Name of test	Observation	Result
Lead acetate	Pale yellow precipitate	+
Sodium hydroxide	Deep yellow precipitate	+
Ferric chloride	Black precipitate	+

3.5 Corrosion measurement-weight loss method

From Table 4, it can be understood that the highest percentage of corrosion inhibition efficiency;79.34% was contributed by coupon C (ZnONPs synthesized at 60ºC). Coupon B was soaked with the mixture of HCl and *Pandanus amaryllifolius* leaf extract to determine the ability of *Pandanus amaryllifolius* leaf extract alone as corrosion inhibitor. The result show that it can perform the inhibiton although its percentage was small. The inhibition was believed to form a protective layer on the metal surface and reduced the corrosion rate of the mild steel. Coupon C, D and E were all soaked in the solution of HCl mixed with ZnONPs.

Table 4: Corrosion rate and corrosion inhibition efficiency of ZnONPs at different parameters

Coupon	Solution	Weight loss (mg)	Corrosion rate (mm/yr)	Inhibition efficiency (%)
A	1M HCl (Blank)	392	6.679	-
B	1M HCl + 2 mL *Pandanus amarllyfolius* extract	142	2.419	63.78
C	1M HCl + 1.5 g ZnONPs (60ºC)	81	1.380	79.34
D	1M HCl + 1.5 g ZnONPs (70ºC)	86	1.465	78.07
E	1M HCl + 1.5 g ZnONPs (80ºC)	122	2.079	68.87

From Fig. 5, there is an increment in inhibition efficiency from Coupon A to Coupon B which is about 63 %. Inhibition efficiency also improved to Coupon C from Coupon B with 24.38 % and Coupon C also recorded the largest inhibition efficiency value. But, there were downturn for Coupon D and Coupon E in the inhibition efficiency. This was related to the particle size of ZnONPs. Small size of ZnONPs has a large surface area so it covers more space than the bigger sized particle. It also has better binding capabilities to the surface of mild steel because it only needs small energy to be bound to the mild steel surface and remains longer to protect the surface from corrosion.

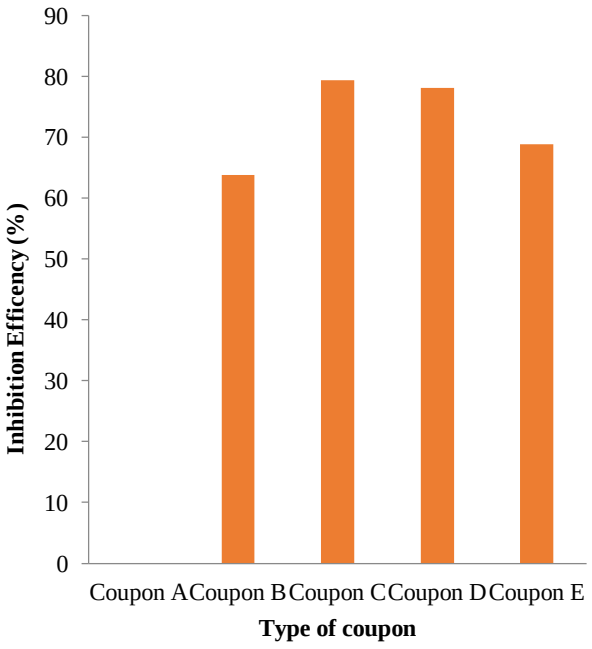

Fig. 5: Graph of inhibition efficiency with respect to type of coupon

4. Conclusions

The ZnONPs were successfully synthesized using *pandanus amaryllifolius* leaf extract as reducing agent. It was understood that flavonoids of the extract could be responsible constituents for the efficient formation of the ZnONPs. In addition, our study successfully demonstrates the effect of synthesis temperature on variation of particle size of ZnONPs which greatly influenced the corrosion inhibition. A good corrosion inhibition efficiency of mild steel at 79.43 % was also successfully investigated at synthesis temperature of 60ºC with particle size of 16.25 nm. Hence there is enhanced need to tap these bio resources towards development of advanced materials that could be useful for other potential applications.

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