Eco-Friendly Synthesis of Gold Nanoparticles through *Gracilaria* sp Seaweed Extract for Foam Height Stability in Liquid Hand Soap Formulations

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ABSTRACT

Gold nanoparticles (G-NPs) were successfully synthesized using *Gracilaria sp* seaweed extract. Visually, color changes from purple-blue to ruby red and then finally to pink. UV-Vis spectrophotometer showed the optimum condition of G-NPs at 531 nm wavelength with an absorbance value of 1.1. The fourier transform infrared (FTIR) spectroscopy shows the absorption peak of functional groups at the *Gracilaria sp* seaweed extract like hydroxyl group (-OH), aromatic (C=C), alkane (C-H), and amine (C-N) at the wavenumbers of 3356, 1613, 1456, and 1182 cm⁻¹, respectively. The X-ray diffraction (XRD) shows the crystallinity peaks of G-NPs at 20: 38.3°, 44.1°, 64.8°, and 77.8° with miller indices of (111), (200), (220), and (311). The Particle size analyzer (PSA) shows the distribution and particle size average of G-NPs was 11.8 nm. Analysis of particle zeta charge (PZC) confirms the total charge of inter-particles was -24.7 mV. The transmission electron microscopy (TEM) images shows the G-NPs was spherical shape with a particle size was 20 nm. The hand soap@G-NPs have a pH of 6.0 and foam height stability of 4.1 cm for 10 min.

Keywords: Biosynthesis, Gold nanoparticles, Gracilaria sp seaweed, Foam height stability

INTRODUCTION

Gold nanoparticles (G-NPs) are material that has a particle size variation from 1-100 nm. The physical properties of gold nanoparticles can be visually observed in the change of color before and after the reduction reaction of Au^{3+} ions to Au^{0} [1]. The morphological shape and particle size variation of gold colloids is a new potential at the development of nanomaterial science. Previous research reported the color of gold colloids like ruby red, purple-blue, and pink-red [2-4]. Gold nanoparticles have the morphological shapes such as hexagonal, triangular, rod, pentagonal, and truncated triangular with particle size of 10-40 nm [5]. Gold colloid can be applied as a drug delivery, catalyst, bactericidal activity, detection with melamine, and sensing tool for the lateral flow immunoassay development [6-10]. The usage of a capping agent has an effect on the particle size stability of gold colloids. The previous studies reported that the synthesis of gold nanoparticles successfully carried out using the natural plant media as a capping agent and reduction Au^{3+} ions to Au^{0} such as latex from *Heavea brasiliensis, Lilium casa blanca, Lysimachia christinae, Curcuma mangga,* Vanillin, *Terminalia mantaly, Bauhinia tomentosa* Linn, *Achillea wilhelmsii, Fusarium solani,* fruit

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extracts, and *Fritillaria cirrhosa* [11-21]. In this research, we reported that the synthesis of gold nanoparticles using *Gracilaria sp* seaweed.

The phytochemical test of *Gracilaria sp* seaweed extract showed the content of secondary metabolites such as alkaloids and flavonoids. These compounds are the derivative groups of polyphenols which can act as reducing Au^{3+} ions to Au^{0} . Furthermore, the gold colloid formed can function as a color of the cosmetic product [22-25]. In cosmeceuticals science, hand soap is one of the cosmetic products that is needed in everyday life. The hand soap can be applied as an antiseptic and antibacterial. Hand soap is included in personal care liquid products that are widely produced because it is more practical and has an attractive shape compared to solid soap. The parameters test such as viscosity, pH, the color of liquid soap, and foam stability produced after the formulation process greatly affect the physical properties of hand soap products [26-31]. Some previous research reported, the color agent for hand soap products uses congo red, methyl orange, and methylene blue. This compound is very dangerous for environmentally [32-34]. Therefore, we propose the use of the color agents in the hand soap formula by green approach.

The synthesis of G-NPs as support materials of the hand soap formula was carried out at room temperature. The *Gracilaria sp* seaweed extract can function as a natural bio-reducing, stabilized agent, and capping agent in the synthesis of G-NPs. The color changes of gold colloids after and before reaction were investigated. The hand soap@G-NPs was formed in the analysis using UV-Vis, FTIR, XRD, PSA, PZC, and TEM. The pH, foam height stability, and color liquid soap were carried out to report the physical properties of hand soap@G-NPs.

EXPERIMENT

Chemicals

The samples of *Gracilaria sp* seaweed were obtained from the South Lampung area, Indonesia. Gold metal (Purity: 99%) was purchased from PT Antam (Jakarta, Indonesia), HCl (Purity: 37%), HNO₃ (Purity: 65%), sodium sulfate (Purity: 99%) was purchased from Merck (Darmstadt, Germany). Sodium laureth sulfate (SLS, Purity: 95%), cocamidopropyl betaine (CAPB, Purity: 35%), glycerin (Purity: 99%), methanol (Purity: 95%), n-hexane (Purity: 99%), and ethyl-acetate (Purity: 99%) were obtained from Sigma-Aldrich (Missouri, United States).

Procedure reaction

Preparation of Gracilaria sp seaweed extract

25 g Gracilaria sp seaweed were cleaned and dried at room temperature for 7 days. The dried of Gracilaria sp seaweed was grounded to obtain a fine powder. The fine powder of Gracilaria sp seaweed was macerated using 200 mL methanol for 7 days and filtered and then evaporated. The Gracilaria sp seaweed extract was partitioned using n-hexane, ethyl-acetate, and water. The methanol and water fraction was carried out a phytochemical tests to determine of secondary metabolites compound in the Gracilaria sp seaweed extract. The water fraction was prepared with various concentrations at 0.01%, 0.02%, and 0.03% (w/v). Then, the optimum condition at water fraction used to reducing of Au³⁺ ions to Au⁰.

Eco-friendly synthesis of G-NPs

10 mL of HAuCl₄ solution (9×10^{-4} M) were reacted with 0.5 mL of *Gracilaria sp* seaweed extract (0.01%). The reducing reaction of Au³⁺ to Au⁰ ions was observed at room temperature for 1 h. The color changes of gold colloid was observed from purple-blue to ruby

red and then finally to pink. The same treatment for the extract at concentrations of 0.02% and 0.03%.

Formulation of hand soap@G-NPs

1 mg of sodium sulfate powders was added to 2 g of SLS gel and then was stirred for 20 min. After homogeneous, was added 1 mL CAPB and 0.5 mL glycerin to the mixture. Slowly treatment, was added about 50 mL of G-NPs to the mixture and was stirred for 1 h. The hand soap@G-NPs formula was further characterized and foam stability test.

Instrumentation

Gold colloid formed were observed using UV-Vis spectrophotometer (Shimadzu 2600) at 200-800 nm wavelength. The Fourier Transform Infrared spectroscopy (FTIR Perkin-Elmer) characterization to determine the functional group of in the *Gracilaria sp* seaweed extract at 4000-400 cm⁻¹ wavenumbers. The crystallinity and crystallite size of G-NPs were analyzed using X-ray Diffraction spectroscopy (XRD Shimadzu 7000) at diffraction angles (2θ): 20-80°. The Particle Size Analyzer (PSA Malvern ZEN 1600) with dynamic light scattering system to determine of the particle size of G-NPs and hand soap@G-NPs. The total charge of interparticle on G-NPs was analysis using Particle Zeta Charge (PZC Malvern ZEN 1600). The particle size and morphological of G-NPs were analyzed using Transmission Electron Microscopy-Selected Area Electron Diffraction (TEM-SAED JEM 1400) with an electron beam energy of 350 keV.

RESULT AND DISCUSSION

The maceration process of *Gracilaria sp* seaweed produced a dark green solution that indicated the all secondary metabolites can be attracted to methanol solvent. The phytochemical test of methanol and water fractions shows the positive (+) for flavonoid compounds. Furthermore, the water fraction was used as a medium in the synthesis of G-NPs. The all results of the phytochemical test as shown in Table 1. The flavonoid compounds contained in *Gracilaria sp* seaweed extract can function as a natural bio-reducing for Au³⁺ ions to Au⁰ [35].

	Fraction			
Bioactive compound	Methanol	N-hexane	Ethyl acetate	Water
Flavonoids	+	+	+	+
Alkaloids	+	+	-	-
Steroids	-	-	-	-
Tannins	-	-	-	-
Triterpenoids	+	-	+	+

Table 1. The active compound in Gracilaria sp seaweed extract

Fig. 1. shows the color changes of gold colloids at various concentrations of *Gracilaria sp* seaweed extract. Visually, the color changes of gold colloids occur from purple-blue to ruby red and then finally to pink by increasing the gold colloid concentration, respectively. A significant ruby red color was seen in the addition of *Gracilaria sp* seaweed extract with a concentration of 0.02% as shown in Fig. 1b. These results indicated the gold colloid was prepared successfully by *Gracilaria sp* seaweed extract.



Figure 1. Gold colloid images using *Gracilaria sp* seaweed extract with various concentration of (a) 0.01%, (b) 0.02%, and (c) 0.03%.

The UV-Vis spectrophotometer to determine the absorption peaks (λ_{max}) and absorbance value of gold colloids. Fig. 2. shows a series of UV-Vis spectrums of gold colloid with various concentrations of *Gracilaria sp* seaweed extract. The gold colloid has an absorption peak at 537 (0.01%), 531 (0.02%), and 535 (0.03%) nm wavelength with an absorbance value of 1.3, 1.1, and 0.9. The *Gracilaria sp* seaweed extract with 0.02% concentration is an optimum condition for the synthesis of G-NPs, because the G-NPs have absorption peaks at the smallest. The previous research reported, gold nanoparticles have a surface plasmon resonance (*SPR*) phenomenon that shows at a wavelength range of 500-600 nm [36]. The G-NPs with optimum condition (extract: 0.02%) were further analyzed using FT-IR, XRD, PSA, PZC, and TEM-SAED.



Figure 2. UV-Vis spectrum of gold colloid with various concentrations of *Gracilaria sp* seaweed extract.

FTIR spectroscopy to determine the functional groups contained in secondary metabolites in *Gracilaria sp* seaweed extract and vibration mode of G-NPs were formed. Fig. 3. shows the FT-IR spectra of *Gracilaria sp* seaweed extract and vibration mode peaks of G-

NPs. The *Gracilaria sp* seaweed extract has functional groups like hydroxyl (-OH), aromatic (C=C), alkane (C-H), and amine (C-N) at 3356, 1613, 1456, and 1182 cm⁻¹ wavenumbers, respectively as shown in Fig. 3a. The Au metals have vibration mode at the absorption peaks of 512 cm⁻¹ wavenumbers. The interaction between the functional groups in *Gracilaria sp* seaweed extract with G-NPs at the reducing process, causing the decrease and absorption peaks shift of G-NPs spectrum as shown in Fig. 3b. On the other hand, the loss of absorption peaks at the ranges of 3000-4000 cm⁻¹ wavenumbers (Fig. 3b) was indicates strong interaction at the –OH ions with G-NPs. Furthermore, the functional group of -OH is thought from phenolic derivated in contained of flavonoid compound of *Gracilaria sp* seaweed extract. The functional group of -OH be through oxidation and form a radical electron. The radical electron used as a reducing source of Au³⁺ to Au⁰ ions [37].



Figure 3. FTIR spectra of (a) Gracilaria sp seaweed extract and (b) green of G-NPs.

XRD spectroscopy was used to analysis of crystallite size, diffraction peaks, and crystallinity of G-NPs as shown in Fig. 4. The G-NPs have diffraction peaks at the angles (2θ) : 38.3° , 44.1° , 64.8° , and 77.8° with miller indices of (111), (200), (220), and (311), respectively. This results correspond with the literature of JCPDS card (No. 04-0784). On the other hand, G-NPs have a crystal structure of face-centered cubic (FCC) lattice with the coordination number of atom was 12 [38-39]. The crystallite size of G-NPs can be determine using the Debye Scherrer's equation [40]:

$$D = \frac{K\lambda}{\beta cos\theta} \tag{1}$$

D is mean of particle size, K is constant value (0.9), λ is wavelength of X-ray, and β is full widht at half maximum intensity theta of the Bragg angle. After calculated, the crystallite size average of G-NPs is 15 nm. According to XRD diffraction angle, G-NPs were successfully synthesized using the green method by utilizing of *Gracilaria sp* seaweed extract.



Figure 4. XRD patterns of G-NPs.

PSA and PZC analysis to determine of particles distribution, particles size average, and inter-particle total charge of G-NPs using dynamic light scattering (DLS) system. Fig. 5. shows the PSA and PZC spectra of G-NPs. The G-NPs have a two peaks with particle size is 7.4 and 16.23 nm. The distribution and particle size average of G-NPs was 11.8 nm as shown in Fig. 5a. Apart from as a natural bioreductor, secondary metabolites in contained at *Gracilaria sp* seaweed extract can be function as a capping agent of gold colloid. The G-NPs with a very negative (-30 mV) or positive (+30 mV) are high stability [41-42]. The G-NPs were synthesized by *Gracilaria sp* seaweed extract have PZC value is -24.7 mV as shown in Fig. 5b. The predicted of the charge prevents particle agglomeration due to inter-repulsion similar on the particle surface. The capping agent has a function as a protective of particle size to be agglomerated. The G-NPs were synthesized using *Gracilaria sp* seaweed extract has a high stability which can be observed of the repulsion inter-particles.



Figure 5. (a) PSA and (b) PZC spectra of G-NPs.

The TEM-SAED images to determine of the morphology, particle size and diffraction pattern of G-NPs. The G-NPs has a spherical shape with 300.000x magnification as shown in Fig. 6a. The particle size average of G-NPs was 20 nm. Fig. 6b. shows the SAED pattern of G-NPs crystal by the presence of a ring circle according to JCPDS data of gold, namely of (111), (200), (220), and (311). This results of SAED data correspond with XRD that the indicated the crystal structure of G-NPs was face-centered cubic (FCC) [43]. Gold has a higher density than the capping agent of *Gracilaria sp* seaweed extract. From the TEM-SAED images, G-NPs were capped using the functional groups containing secondary metabolites of *Gracilaria sp* seaweed extract so that has a particle distribution of even.



Figure 6. (a) TEM image and (b) SAED of AuNPs.

For the liquid hand soap application using the G-NPs that the optimum condition of *Gracilaria sp* seaweed extract (0.02%). Fig. 7. shows the foam height stability of liquid hand soap. For the stirred of 5 min (A), hand soap and hand soap@G-NPs have foam height stability of 4.6 and 4.7 cm, respectively as shown in Fig 7a.



Figure 7. Foam height stability images of (a) hand soap and (b) hand soap@G-NPs.

The journal homepage www.jpacr.ub.ac.id p-ISSN : 2302 – 4690 | e-ISSN : 2541 – 0733 After stirred continuous for 10 min (B), the changes of foam heght occurs to 2.6 and 4.1 cm, respectively as shown in Fig. 7b. The presence of G-NPs have the effect on the foam height stability in liquid hand soap. This results indicated, the particles of gold insert to bubble of foam in hand soap by physics interaction. Furthermore, we reported the pH of hand soap@G-NPs was 6.0 that the according with Indonesian National Standard (SNI) [28-29]. From this results, can be concluded the G-NPs to function at the foam height stability in liquid hand soap formulations. On the other hand, hand soap@G-NPs has potential for antibacterial application in the future.

CONCLUSION

G-NPs were successfully synthesized by natural bio-reductor with utilization of *Gracilaria sp* seaweed extract. Gold colloid has a ruby red color. Based on the UV-Vis spectrum, the optimum condition of *Gracilaria sp* seaweed extract were used of 0.02% with the 531 nm wavelength and absorbance value of 1.1 for G-NPs. FTIR spectrum showed the vibration mode of Au was 512 cm⁻¹ wavenumbers. XRD pattern showed the crystallite size of G-NPs was 15 nm with a crystal structure of FCC. PSA spectrum shows the distribution and particle size average of G-NPs was 11.8 nm. PZC spectrum showed the inter-particle charge value of -24.7 mV. TEM images shows the G-NPs is spherical shape with a particle size of 20 nm. The hand soap@G-NPs have a pH of 6.0 and foam height stability of 4.1 cm for 10 min.

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