Synthesis and Characterization of Copper Nanoparticles using Dragon Fruit Peel (Hylocereus costaricensis) Extract Bio-Reductor

Sintesis dan Karakterisasi Nanopartikel Tembaga dengan Bioreduktor Limbah Kulit Buah Naga (*Hylocereus costaricensis*)

Ani Qomariyah*, Hanim Istatik Badi'ah

Department of Medical Laboratory Technology, Banyuwangi Institute of Health Sciences
Jl. Letkol Istiqlah No. 109, Banyuwangi, Indonesia

*Corresponding author: ani.qomariyah@stikesbanyuwangi.ac.id

Diterima: 26 Agustus 2024, Direvisi: 5 November 2024, Diterbitkan: 09 Desember 2024

ABSTRACT

The green chemistry technique was carried out for the very first time to synthesize copper nanoparticles (Cu-NPs) by applying $CuSO_4$ as a precursor and red dragon fruit peel extract as a reducing agent. The extracting procedure of red dragon fruit peel was conducted by maceration technique with solvent of methanol. Cu-NPs were produced through green chemistry by the reduction method. Cu-NPs were prepared by combining $CuSO_4$ solution with red dragon fruit peel extract in the compositions of 1:1, 1:2, 1:3, 1:4, and 1:5. The successfully synthesized Cu-NPs were analyzed using Scanning Electron Microscopy (SEM), Particle Size Analyzer (PSA), and UV-Visible Spectrophotometer. The variation in the volume of reducing agent affect the maximum wavelength produced. The optimum concentration of reducing agent (1:5) shows the highest intensity at 650 nm. The optimum pH for the synthesis of copper nanoparticles (Cu-NPs) with dragon fruit extract was 6. Cu-NPs were stable at 20 minutes to 1 hour. From the SEM figure of Cu-NPs, it can be observed that the particles are of round shape. Volume or weight analyzes of Cu-NPs employing PSA provided particle diameters between 80 and 120 nm with an approximate distribution of 100 nm.

***Keywords**: Bio-Reductor; Copper Nanoparticles; Dragon Fruit Peel*

ABSTRAK

Teknik *green chemistry* dilakukan untuk pertama kalinya untuk mensintesis nanopartikel tembaga (Cu-NP) dengan menggunakan $CuSO_4$ sebagai prekursor dan ekstrak kulit buah naga merah sebagai agen pereduksi. Prosedur ekstraksi kulit buah naga merah dilakukan dengan teknik maserasi dengan pelarut metanol. Cu-NP diproduksi melalui green chemistry dengan metode reduksi. Cu-NP dibuat dengan cara mengkombinasikan larutan $CuSO_4$ dengan ekstrak kulit buah naga merah dengan komposisi 1:1, 1:2, 1:3, 1:4, dan 1:5. Cu-NP yang berhasil disintesis dianalisis dengan menggunakan *Scanning Electron Microscopy* (SEM), *Particle Size Analyzer* (PSA), dan Spektrofotometer UV-Visible. Variasi volume agen pereduksi mempengaruhi panjang gelombang maksimum yang dihasilkan. Konsentrasi agen pereduksi optimum (1:5) menunjukkan intensitas tertinggi pada 650 nm. pH optimum untuk sintesis nanopartikel tembaga (Cu-NP) dengan ekstrak buah naga adalah 6. Cu-NP stabil pada 20 menit hingga 1 jam. Dari gambar SEM Cu-NP, dapat diamati bahwa partikelnya berbentuk bulat. Analisis volume atau berat Cu-NP yang menggunakan PSA memberikan diameter partikel antara 80 dan 120 nm dengan perkiraan distribusi 100 nm.

***Kata kunci:** Bio-Reduktor; Nanopartikel Tembaga; Kulit Buah Naga*

INTRODUCTION

Recently, nanoparticles have gained more attention in various applications (Ingle et.al., 2014). The nanoparticles are nanoscale particles, which are approximately 1-100 nm in diameter. Applications of nanoparticles in human life such as in the environmental field (Athanassiou et.al., 2006), biomedicine (Ingle et.al., 2014), antimicrobial (El Zowalaty et.al., 2013; Cioffi et.al., 2005), sensors (Putri et.al., 2023), catalysis (Qomariyah et.al., 2021)., Chung et.al., 2013), electronics (Sampath et.al., 2014), agriculture (Moznuzzaman et.al., 2021) and in other fields. Various kinds of nanoparticles for formalin sensors that have been used are copper oxide nanoparticles (CuO/Cu_2O NPs) (Nuryono et.al., 2019; Zayyoun et.al., 2016), ZnO micro-octahedron assembled nanoparticles (Atha et.al., 2012), and two-dimensional (2D) SnO_2 nanosheets and one-dimensional (0D) Au nanoparticles (Moznuzzaman et.al., 2021). Nanoparticles that have been used for formalin sensors are sensitive but costly. Therefore, it is necessary to develop a low-cost, simple, and stable formalin detection.

Nanoparticles can be made by synthesizing using chemicals, but this can cause the production of chemical waste and is environmentally hazardous. So that the manufacture of copper nanoparticles can be conducted by utilizing plants as reducing agents, namely by biosynthesis or green synthesis methods (Shende et.al., 2015). The conditions for selecting a good bioreductor are having an -OH group bound to a secondary C atom that can reduce copper ions to copper metal and compounds that have an -OH group itself will undergo oxidation (Sinha et.al., 2015). Various kinds of natural bioreductors to synthesize copper nanoparticles have been used including by utilizing clove flower extract (Elmosallamy et.al., 2021), ketapang leaves (Alam et.al., 2023), areca nut shell waste extract (Some et.al., 28). Although these studies used synthesized raw materials from environmentally friendly natural materials, they did not obtain practical and accurate bio-reductors. For this reason, the utilization of natural materials for copper nanoparticle bio-reductors that produce good quality is still being developed.

The type of plant that contains reductant material that is quite abundant is red dragon fruit (*Hylocereus costaricensis*) (Haruna et.al., 2022). Red dragon fruit has high antioxidants (Zayyoun et.al., 2016). Usually, what is utilized from dragon fruit is only the contents and the peel is thrown away. However, based on the research before, red dragon fruit peel is rich in antioxidant sources in the form of vitamin

C, flavanoids, tannins, alkaloids, steroids, and saponins (Denby et.al., 2016). Therefore, the dragon fruit peel has the potential to be applied as a bio-reductors in the copper nanoparticle synthesis.

Dragon fruit production in the Banyuwangi Regency reached 28,819 tons with a land area of 1,152 hectares in 2014 (the BPS Banyuwangi Regency). The production increased compared to 16,631 tons in 2013 with a land area of 678 hectares. Dragon fruit production centers in Banyuwangi are in Bangorejo, Pesanggaran, Siliragung, Tegaldlimo and Purwoharjo sub-districts. Bangorejo contributes 39% of the total dragon fruit production in Banyuwangi or equivalent to 11,000 tons per hectare with a land area of 449 hectares (Hanifa et.al., 2023). With the abundance of dragon fruit plants in Banyuwangi, the resulting dragon fruit peel waste is also abundant.

In this study, the green synthesis of Cu nanoparticles (Cu-NPs) using dragon fruit peel waste as a bioreductor was carried out. The successfully synthesized Cu-NPs were analyzed using Scanning Electron Microscopy (SEM), Particle Size Analyzer (PSA), and UV-Visible Spectrophotometer.

METHODOLOGY

Equipment and Materials

The equipment used in this research are UV-Visible Spectrophotometer Genesys 10S, Fourier Transform-Infra Red Spectroscopy (FT-IR) (Shimadzu IRPrestige21), Scanning Electron Microscopy (SEM) (Hitachi FLEXSEM 100), Particle Size Analyzer (PSA) (Shimadzu type SALD-7500nano), oven (Nabertherm KTR 4500), centrifuge (Hitachi), magnetic stirrers, mortar and pestle, and glassware. The materials needed in this research are dragon fruit waste (*Hylocereus polyrhizus*) from the waste of fruit juice traders in Banyuwangi Regency, East Java, Aquademin or Aquademineralisata, Copper (II) Sulphate ($CuSO_4$) 0.03 M (Merck), Sodium Citrate (Merck), Sodium hydroxide (NaOH) 1 M (Merck), Hydrochloric acid (HCl) (Merck), Tricarboxcylic acid / TCA (Merck)

Synthesis of Copper Nanoparticles with Dragon Fruit Peel Extract

1. **Cu-NPs Synthesis with Variation of $CuSO_4$ and Dragon Peel Extract Volume Ratio**

The volume of dragon fruit peel extract was varied with volume ratio of $CuSO_4$ and dragon fruit peel extract (DFP) 1:1, 1:2, 1:3, 1:4, and 1:5. Then, this mixture was named with Cu-DFP (1:1), Cu-

DFP (1:2), Cu-DFP (1:3), Cu-DFP (1:4), and Cu-DFP (1:5). Five beakers were filled with 38 mL of distilled water, 0.03 M $CuSO_4$ was poured in, and the solution was then homogenized. The pH was then measured at an initial pH of 4.5. Subsequently, approximately 5 drops of NaOH were added to achieve a pH of 6. The mixture was stirred in an ice bath for 15 minutes and analyzed using the UV-Visible Spectrophotometer in the wave length range of 400 – 800 nm. A dragon fruit peel extract without copper nanoparticle was also tested.

2. Cu-NPs Synthesis with pH Variation

In this work, three mixtures were prepared, each containing 38 mL of distilled water and 0.03 M $CuSO_4$ with the best volume ratio. Then, the mixture was stirred until it was evenly distributed. Next, 4 mL of red dragon fruit extract was added to the solution as a reducing agent. Each solution was conditioned at varying pH values (6, 9, and 12) with the addition of 1 M NaOH. At pH 6, three drops of 1 M NaOH were added, five drops at pH 9, and 20 drops at pH 12. The mixture was stirred for 15 min in a container containing ice cubes. The absorbance was then measured using the UV-visible Spectrophotometer with a wavelength of 400-800 nm. The highest absorbance was used to determine the maximum pH.

3. Stability Observation of Cu Nanoparticles

In this study, 38 mL of distilled water was added to 0.03 M $CuSO_4$ with the best volume ratio in three beaker glasses and homogenized. Subsequently, the beaker glass was labeled with a specified time variation. A red dragon peel reducer was added to each beaker to the best volume ratio. Next, the pH was measured at an initial pH of 4.5. Approximately 5 – 20 drops of NaOH were added so that the pH was until same with the result of the best pH. The mixture was stirred in an ice bath for 15 minutes and storage at room temperature for 20 minutes, 30 minutes, 1 hour, 1 day, and 10 days. Then, if the time reached, it analyzed using the UV-Visible Spectrophotometer.

Characterization of Cu Nanoparticles

The best result of Cu-NPs synthesis then was characterized using Scanning Electron Microscopy (SEM) and Particle Size Analyzer (PSA).

DISCUSSION

Synthesis of Copper Nanoparticles with Dragon Fruit Peel Extract

Based on the results of the synthesis of copper nanoparticles (Cu-NPs) with dragon fruit extract, the presence of secondary metabolites such as phenolics acted as electron donors to Cu metal. During the copper nanoparticle (Cu-NPs) synthesis process, a color change occurred when the extract solution was mixed with the $CuSO_4$ solution. This color change is a strong indication of the formation of Cu-NPs. The reduction of Cu metal by dragon fruit extract was possible in the presence of phenolic compounds, resulting in the reduction of Cu^{2+} to Cu^0 [24]. This is illustrated in Figure 1. These phenolic components consist of hydroxyl groups that can chelate metals. The metal binding capability of phenolic compounds is attributed to the highly nucleophilic characteristic of the aromatic chain. Flavonoids are a major group of polyphenolic compounds that efficiently chelate and decrease metallic ions into nanoparticles (Sinha et.al., 2015).

The absorbance measurement of the wavelength was carried out by utilizing the UV-Visible Spectrophotometer. to prove that the reduction reaction occured. The formation of copper nanoparticles was indicated by the formation of absorbance peaks at the wavelength of 200-650 nm.

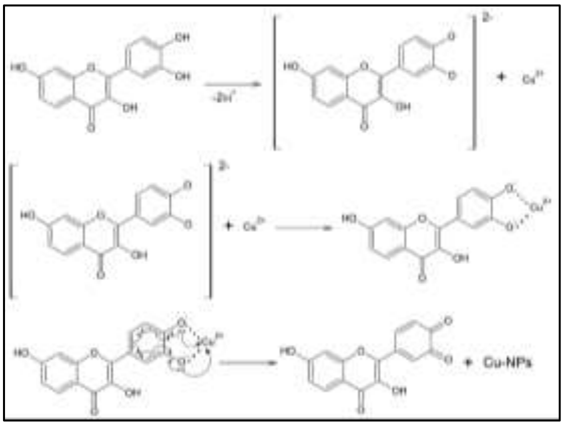

Figure 1. The prediction of the reaction mechanism for the formation of copper nanoparticles

Cu-NPs Synthesis with Variation of $CuSO_4$ and Dragon Peel Extract Volume Ratio

The volume of dragon fruit peel extract was varied with volume ratio of $CuSO_4$ and dragon fruit peel extract (DFP) 1:1, 1:2, 1:3, 1:4, and 1:5. This was done to examine the effect of reducing agent concentration on the formation of copper nanoparticles (Cu-NPs). In Figure 2, it appears that the solution from the left to the right becomes darker in red. This affects the color of the resulting solution, where the greater the volume of reducing agent, the more concentrated the color of the solution, which is expected that the more volume of reducing agent, the more Cu nanoparticles will be formed.

Figure 2. From the left to the right: Cu-DFP (1:1), Cu-DFP (1:2), Cu-DFP (1:3), Cu-DFP (1:4), and Cu-DFP (1:5)

Measurements of colloidal copper nanoparticles using a UV-Visible Spectrophotometer were carried out in the wavelength range of 400-800 nm. The change in peak intensity is related to the concentration of reducing agent. The higher the reducing agent concentration, the higher the intensity. The characteristics of the formation of copper nanoparticles by UV-Visible Spectrophotometer analysis can be observed from the formation of the absorbance spectrum at a wavelength of 200-650 nm (Qomariyah et.al., 2023). Maximum wavelengths that are further to the right (in the region of more than 700 nm) indicate that a nanoparticle size is getting smaller. In this study, the maximum wavelength was 650 nm for variations of $CuSO_4$ and dragon fruit peel extract of 1:5. As the concentration of the reducing agent increases, the maximum wavelength shifts to the right (Figure 3). Visually, this is also indicated by the darker color of the solution (Figure 2). This shows that the variation in the volume of the reducing agent affect the maximum wavelength produced. This finding is consistent with previous work that used a dragon fruit extract for Cu-NPs synthesis. The optimum concentration of the reducing agent shows the highest intensity (Figure 3).

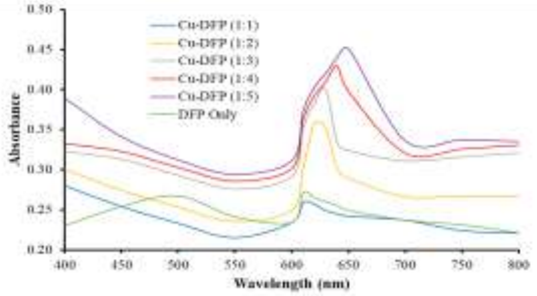

Figure 3. UV-Visible Spectra of Cu-NPs with Variation of $CuSO_4$ and Dragon Peel Extract Volume Ratio

Cu-NPs Synthesis with a pH Variation

The $CuSO_4$ solution was mixed with the dragon fruit extract. Then, 1 M of sodium hydroxide was poured to vary the pH with a pH variation of 4, 6, 8, 10, 12. The purpose of pH variation was to calculate the optimum pH for the formation of copper nanoparticles (Cu-NPs). As shown in Figure 4, the color of the resulting solution with different pH values did not experience a significant color difference.

Figure 4. Cu-NPs with a pH variation of 4, 6, 8, 10, and 12

Based on the results of measurements using a UV-Visible Spectrophotometer, it can be observed that with pH variation, the absorbance formed is also different. The highest absorbance is obtained at pH = 6 (Figure 5). Thus, the optimum pH for the formation of copper nanoparticles (Cu-NPs) with dragon fruit extract was 6. The pH of reducing compounds and capping agents can affect the copper ion reduction process into nanoparticles. The phenolic functional group from dragon fruit extract can be deprotonated to form a group a new functional unit that is negatively charged under alkaline conditions. The phenolic groups can remove H^+ to form a conjugate base (Zayyoun et.al., 2016). Negatively charged functional groups can bond with Cu^+ through electrostatic interactions or coordination covalent bonds as in Figure 1. The advantage of the dragon fruit peel extract in the bio-synthesis of copper nanoparticles can save valuable materials used and reduce the waste produced, because dragon fruit extract has two functions simultaneously as a reducing agent and a capping agent.

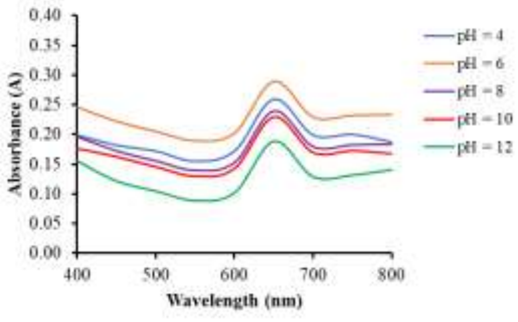

Figure 5. The effect of pH to the bio-synthesis of Cu-NPs

At pH of 6, the absorbance value is the highest, with the absorbance peak obtained at a wavelength of 650 nm. In accordance with the phase diagram of the formation of copper species, at lower pH, copper will exist in the form of Cu^{2+} (Sinha et.al., 2015). While at higher pH, copper will exist in the form of $Cu(OH)_2$. At a pH of about 6, a copper is in its metal form, Cu, which in this case will also be reinforced by the formation of reducing agents. This result agree with the previous study (Haruna et.al., 2022). Copper in the form of Cu^{2+} and in the form of $Cu(OH)_2$, will be more difficult to observe with UV-Visible Spectrophotometer because flavonoid compounds in dragon fruit extract are difficult to interact with these species. This causes the intensity observed at low and high pH to decrease (Figure 5).

p.ISSN:2354-9610,e.ISSN:261-5081
Vol.9,No.2,Hal.40-51(Desember 2024)

The Stability Observation of The Cu Nanoparticles

The synthesis of copper nanoparticles (Cu-NPs) using dragon fruit extract was carried out by varying the reaction time to determine the effect of reaction time on the formation of copper nanoparticles (Cu-NPs). Reaction time is also related to the stability of the nanoparticles (Some et.al., 2021). Reaction times were analyzed using the UV-Visible Spectrophotometer after the storage process nanoparticles. The stability of nanoparticles can be expressed in terms of aggregation. Aggregation occurs when the nano-structures experience clustering due to interactions between the particles nearby. Thus, the stability of the nanoparticles depends on the prevention aggregation process. This prevention can be modified using a capping agent. The capping agent can be an anion or a polymer. Nanoparticles are otherwise not aggregation occurs when the solution does not experience extreme color changes and no precipitate appears. The longer the storage time nanoparticles and no aggregation occurs, the better the stability.

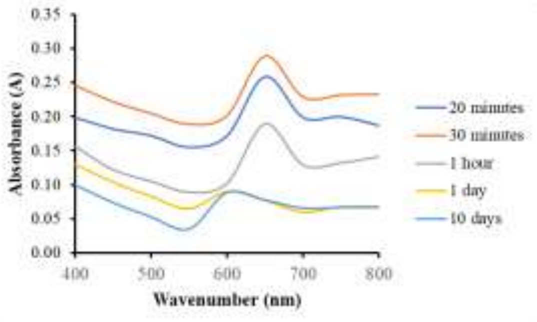

Figure 6. The stability observation of Cu-NPs

In Figure 6, it is shown that at 20 minutes, 30 minutes, and 1 hour, the peak wavelength is the same at 650 nm. This shows that at these times Cu-NPs are stable. However, when allowed to stand for 1 to 10 days, it can be seen that the peak wavelength has shifted to the left. This shifting of the wavelength to the left indicates an increasing particle size. This result is due to the longer time the particles can agglomerate. Furthermore, it can also be seen that in the Cu-NPs immersion from 1 to 10 days, there is a decrease in absorbance. This is because the presence of nanoparticles in the solution will decrease because of the agglomeration.

Characterization of Copper Nanoparticles

The nanoparticle morphology of Cu was investigated by SEM (Figure 8). Based on the Scanning Electron Microscopy (SEM) figure of Cu nanoparticles, it could be observed that the particles were round in shape, while the tenorite nanoparticles morphology in the earlier study was stem-shaped. A reducing agent that has a concentration that is higher than the ideal concentration is able to swiftly decrease Cu^+ ions. This may speed up particle growth and lead to aggregation, which results in larger copper nanoparticles and a wider range of copper nanoparticle sizes. So, in the image of the SEM analysis results, the particle size is not uniform, and there are particles that are more than 100 nm in size due to aggregation.

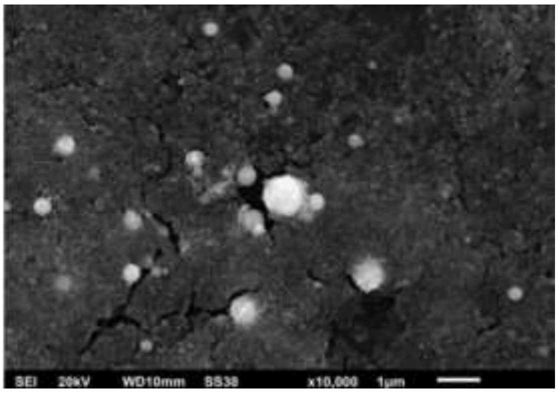

Figure 8. The SEM image of copper nanoparticles

To enhance the results of SEM analysis, particle size analysis using Particle Size Analyzer (PSA) was conducted. The particle size distribution analysis of the sonicated nanocrystals was conducted by dynamic light scattering method (via 632 nm Laser input energy). It was found that in the prepared samples, the particles had a broad size distribution, but were mainly dispersed in a tight range, as demonstrated in Figure 9. The analysis of the volume or weight of the samples gave a particle distribution between 80 and 120 nm with an approximate distribution of 100 nm. Nevertheless, this does not exclude the probability of smaller particles since light scattering from larger particles will depress the intensity of smaller particles existing in the sample.

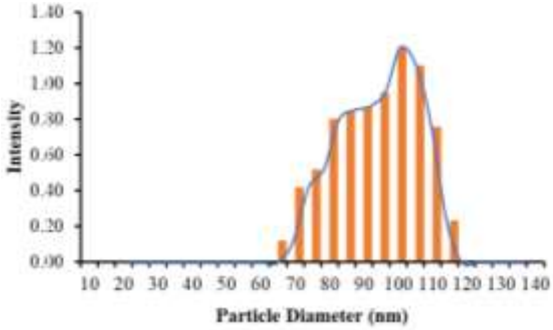

Figure 9. The diagram of copper nanoparticle size

CONCLUSION

Cu-NPs were produced through green chemistry by the reduction method. Cu-NPs was synthesized by mixing $CuSO_4$ solution with the red dragon fruit peel extract in the ratio of 1:1, 1:2, 1:3, 1:4, and 1:5. The best composition (1:1) showed the highest absorbance of 650 nm on UV-Visible Spectrophotometer analysis and the particle size was obtained as 100 nm using PSA. The Cu-NPs obtained were round shape with a stability time of 20 minutes to 1 hour.

ACKNOWLEDGEMENT

We would like to express our gratitude to the Directorate General of Vocational Higher Education, the Ministry of Education, Culture, Research and Technology, Republic of Indonesia for the granting of a novice lecturer research grant with the contract number 199/SPK/D.D4/PPK.01.APTV/VI/2023.

REFERENCES

N. Taprab and Y. Sameenoi, Rapid screening of formaldehyde in food using paper-based titration, *Analytica Chimica Acta*, 1069, (2019), 66–72, https://doi.org/10.1016/j.aca.2019.03.063.

L. Zhang *et al.*, High sensitive and selective formaldehyde sensors based on nanoparticle-assembled ZnO micro-octahedrons synthesized by homogeneous precipitation method," *Sensors and Actuators B: Chemical*, 160, 1, (2011), 364–370, https://doi.org/10.1016/j.snb.2011.07.062.

R. K. Mishra, A. Kushwaha, and P. P. Sahay, Influence of Cu doping on the structural, photoluminescence and formaldehyde sensing properties of SnO_2 nanoparticles, *RSC Adv.*, 4, 8, (2014), 3904–3912, https://doi.org/10.1039/C3RA43709D.

N. S. Al-Radadi and A. M. Abu-Dief, Silver nanoparticles (AgNPs) as a metal nano-therapy: possible mechanisms of antiviral action against COVID-19, *Inorganic and Nano-Metal Chemistry*, (2022), 1–19, May 2022, https://doi.org/10.1080/24701556.2022.2068585.

M. N. Descamps *et al.*, Real-time detection of formaldehyde by a fluorescence-based sensor, *Procedia Engineering*, 5, (2010), 1009–1012, https://doi.org/10.1016/j.proeng.2010.09.280.

L. Fappiano, F. Carriera, A. Iannone, I. Notardonato, and P. Avino, A Review on Recent Sensing Methods for Determining Formaldehyde in Agri-Food Chain: A Comparison with the Conventional Analytical Approaches, *Foods*, 11, 9, (2022), 1351, https://doi.org/10.3390/foods11091351.

U. S. Akshath, L. Sagaya Selvakumar, and M. S. Thakur, Detection of formaldehyde in food samples by enhanced chemiluminescence, *Anal. Methods*, 4, 3, (2012), 699, https://doi.org/10.1039/c2ay05608a.

H. Yulianti, R. Hastuti, and D. S. Widodo, Ekstraksi dan Uji Kestabilan Pigmen Betasianin dalam Kulit Buah Naga (Hylocereus polyrhizus) Serta Aplikasinya Sebagai Pewarna Tekstil, *J. Kim. Sains Apl.*, 11, 3, (2008), 84–89, https://doi.org/10.14710/jksa.11.3.84-89.

M. Justo Alonso *et al.*, Evaluation of low-cost formaldehyde sensors calibration," *Building and Environment*, 222, (2022), 109380, https://doi.org/10.1016/j.buildenv.2022.109380.

P. K. Khanna, P. More, J. Jawalkar, Y. Patil, and N. Koteswar Rao, Synthesis of hydrophilic copper nanoparticles: effect of reaction temperature, *J Nanopart Res*, 11, 4, (2009), 793–799, https://doi.org/10.1007/s11051-008-9441-9.

A. P. Ingle, N. Duran, and M. Rai, Bioactivity, mechanism of action, and cytotoxicity of copper-based nanoparticles: A review, *Appl Microbiol Biotechnol*, 98, 3, (2014), 1001–1009, https://doi.org/10.1007/s00253-013-5422-8.

E. K. Athanassiou, R. N. Grass, and W. J. Stark, Large-scale production of carbon-coated copper nanoparticles for sensor applications, *Nanotechnology*, 17, 6, (2006), 1668–1673, https://doi.org/10.1088/0957-4484/17/6/022.

M. El Zowalaty, N. A. Ibrahim, M. Salama, K. Shameli, M. Usman, and N. Zainuddin, Synthesis, characterization, and antimicrobial properties of copper nanoparticles, *IJN*, (2013), 4467, https://doi.org/10.2147/IJN.S50837.

N. Cioffi *et al.*, Copper Nanoparticle/Polymer Composites with Antifungal and Bacteriostatic Properties, *Chem. Mater.*, 17, 21, (2005), https://doi.org/10.1021/cm0505244.

S. E. Putri *et al.*, Biosynthesis of Copper Nanoparticles Using Hylocereus costaricensis Peel Extract and their Photocatalytic Properties, *Karbala International Journal of Modern Science*, 9, 2, (2023), https://doi.org/10.33640/2405-609X.3300.

D. Mott, J. Galkowski, L. Wang, J. Luo, and C.-J. Zhong, Synthesis of Size-Controlled and Shaped Copper Nanoparticles, *Langmuir*, 23, 10, (2007), 5740–5745, https://doi.org/10.1021/la0635092.

A. Qomariyah, N. Nuryono, and E. S. Kunarti, Recovery of Gold in Au/Cu/Mg System from SH/Fe_3O_4@SiO_2 as a Magnetically Separable and Reusable Adsorbent, *Indo. J. Chem. Res.*, 9, 1, (2021), 26–34, https://doi.org/10.30598//ijcr.2021.9-ani.

P.-R. Chung, C.-T. Tzeng, M.-T. Ke, and C.-Y. Lee, Formaldehyde Gas Sensors: A Review, *Sensors*, 13, 4, (2013), 4468–4484, https://doi.org/10.3390/s130404468.

M. Sampath, R. Vijayan, E. Tamilarasu, A. Tamilselvan, and B. Sengottuvelan, Green Synthesis of Novel Jasmine Bud-Shaped Copper Nanoparticles, *Journal of Nanotechnology*, (2014), 1–7, https://doi.org/10.1155/2014/626523.

Md. Moznuzzaman, Md. R. Islam, and I. Khan, Effect of layer thickness variation on sensitivity: An SPR based sensor for formalin detection, *Sensing and Bio-Sensing Research*, 32, (2021), 100419, https://doi.org/10.1016/j.sbsr.2021.100419.

N. Nuryono, A. Qomariyah, W. Kim, R. Otomo, B. Rusdiarso, and Y. Kamiya, “Octyl and propylsulfonic acid co-fixed Fe_3O_4@SiO_2 as a magnetically separable, highly active and reusable solid acid catalyst in water,” *Molecular Catalysis*, 475, (2019), 110248, https://doi.org/10.1016/j.mcat.2018.11.019.

N. Zayyoun, L. Bahmad, L. Laânab, and B. Jaber, The effect of pH on the synthesis of stable Cu2O/CuO nanoparticles by sol–gel method in a glycolic medium, *Appl. Phys. A*, 122, 5, (2016), 488, https://doi.org/10.1007/s00339-016-0024-9.

D. H. Atha *et al.*, Copper Oxide Nanoparticle Mediated DNA Damage in Terrestrial Plant Models, *Environ. Sci. Technol.*, 46, 3, (2012), 1819–1827, https://doi.org/10.1021/es202660k.

S. Shende, A. P. Ingle, A. Gade, and M. Rai, Green synthesis of copper nanoparticles by Citrus medica Linn. (Idilimbu) juice and its antimicrobial activity, *World J Microbiol Biotechnol*, 31, 6, (2015), 865–873, https://doi.org/10.1007/s11274-015-1840-3.

T. Sinha and M. Ahmaruzzaman, Green synthesis of copper nanoparticles for the efficient removal (degradation) of dye from aqueous phase, *Environ Sci Pollut Res*, 22, 24, (2015), 20092–20100, https://doi.org/10.1007/s11356-015-5223-y.

A. Elmosallamy, M. El-zaidy, and S. Hussein, Green Synthesis of Silver Nanoparticles Using Mangifera Indica L. (Musk) Peels Extract and Evaluation of Its Cytotoxic Activities, *Egypt. J. Chem.*, 12, 3, (2021), https://doi.org/10.21608/ejchem.2021.109739.5004.

T. Alam, R. Ardiansyah, S. Maulidayanti, D. Azvara, F. O. Purnomo, and D. Annas, Tyrosinase Inhibitory of Silver Nanoparticles Synthesized using Morus Nigra Leaves Extract, *J. Kim. Sains Apl.*, 26, 3, (2023), 85–90, https://doi.org/10.14710/jksa.26.3.85-90.

S. Some, S. Das, R. Mondal, M. Gangopadhyay, and G. K. Basak, Medicinal Plant Extract Mediated Green Synthesis of Metallic Nanoparticles: A Review, *IJPE*, 7, 02, (2021), 119–132, https://doi.org/10.18811/ijpen.v7i02.02.

C. A. Haruna, W. A. Malik, M. Y. S. Rijal, A. H. Watoni, and L. O. A. N. Ramadhan, Green Synthesis of Copper Nanoparticles Using Red Dragon Fruit (Hylocereus polyrhizus) Extract and Its Antibacterial Activity for Liquid Disinfectant, *J. Kim. Sains Apl.*, 25, 10, (2022), 352–361, https://doi.org/10.14710/jksa.25.10.352-361.

K. J. Denby *et al.*, The mechanism of a formaldehyde-sensing transcriptional regulator, *Sci Rep*, 6, 1, (2016), 38879, https://doi.org/10.1038/srep38879.

N. L. Hanifa, A. Afifah, D. K. Wijaya, N. Nurmazaya, and A. Qomariyah, Acid and Base modified Pectin from Orange Peel as an Effective Bio-adsorbent for Pb(II) and Cr(VI) from Textile Industry Wastewater, *Indo. J. Chem. Res.*, 10, 3, (2023), 149–156, https://doi.org/10.30598//ijcr.2023.10-qom.

A. Qomariyah, Perbandingan Metode Mohr Dan Volhard Dalam Penetapan Kadar Klorida Air Sungai Pangpang Desa Tapanrejo, *JITK*, 8, 3, (2023), https://doi.org/10.31942/inteka.v8i3.8217.