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Pemanfaatan Limbah Belimbing Wuluh, Kulit Jeruk, dan Bayam sebagai Sumber Asam Organik: Studi Konsentrasi Asam dan Potensi sebagai Agen Reduktor

Utilization of Averrhoa bilimbi, Orange Peel, and Spinach Waste as a Source of Organic Acids: A Study on Acid Concentration and Potential as a Reducing Agent

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ABSTRAK

Limbah buah dan sayuran mengandung asam organik yang masih dapat dimanfaatkan, menawarkan potensi baru sebagai agen reduktor dalam aplikasi kimia ramah lingkungan. Sampel yang digunakan dalam penelitian ini meliputi limbah belimbing wuluh, kulit jeruk, dan bayam, yang diketahui mengandung asam organik. Penelitian ini bertujuan untuk mengoptimalkan proses pelarutan asam organik dari sampel-sampel tersebut serta mengidentifikasi potensinya sebagai agen reduktor. Penelitian ini menggunakan metode pengeringan dan pelarutan limbah belimbing wuluh, kulit jeruk, dan bayam. Sampel dikeringkan pada suhu 60°C, lalu dilarutkan dalam akuabides dengan variasi waktu dan suhu. Konsentrasi asam organik dianalisis secara alkalimetri dan permanganometri untuk mengukur asam total dan asam reduktor. Hasil penelitian menunjukkan bahwa variasi waktu dan suhu pelarutan memengaruhi konsentrasi asam organik yang terlarut dari sampel limbah. Konsentrasi tertinggi dicapai pada waktu pelarutan 90 menit dan suhu 60°C, di mana waktu dan suhu yang melebihi batas ini justru menurunkan konsentrasi asam terlarut. Identifikasi kualitatif menunjukkan bahwa belimbing wuluh dan bayam mengandung asam oksalat dan asam askorbat, sementara kulit jeruk mengandung asam sitrat dan asam askorbat. Data ini menegaskan potensi sampel sebagai agen reduktor, terutama pada kondisi pelarutan optimal.

ABSTRACT

Fruit and vegetable waste contains organic acids that can still be utilized, offering new potential as reducing agents in environmentally friendly chemical applications. The samples used in this study include Averrhoa bilimbi, orange peel, and spinach waste, known to contain organic acids. This study aims to optimize the extraction process of organic acids from these samples and identify their potential as reducing agents. The method involves drying and dissolving the waste samples, which were dried at 60°C and then disbanded in aquabidest with varying times and temperatures. The concentration of organic acids was analyzed using alkalimetry and permanganometry to measure total acids and reduce acids. The results show that variations in dissolution time and temperature influence the concentration of dissolved organic acids in the waste samples. The highest concentration was achieved at a dissolution time of 90 minutes and a temperature of 60°C, with concentrations decreasing at longer times and higher temperatures. Qualitative identification indicates that Averrhoa bilimbi and spinach contain oxalic and ascorbic acids, while orange peel contains citric and ascorbic acids. These findings highlight the potential of these samples as reducing agents, especially under optimal dissolution conditions.

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1. INTRODUCTION

Fruit and vegetable waste is a source of organic matter that is often underutilized and can become an environmental problem if not properly managed. On the other hand, the demand for environmentally friendly chemicals continues to rise, especially in applications requiring natural reducing agents. Particular fruit and vegetable waste contains organic acids, such as oxalic acid, ascorbic acid, and citric acid. [1]–[3], which are potentially used in various chemical processes. Utilizing this waste helps reduce environmental pollution and provides a safer and more sustainable alternative to conventional chemicals.

Previous research has shown that certain types of fruit and vegetable waste contain significant levels of organic acids. Averrhoa bilimbi (bilimbi) contains notable amounts of oxalic and ascorbic acids. [1], while the orange peel is rich in citric and ascorbic acids, which contribute to its antioxidant activity [4]. Additionally, spinach contains a high level of oxalic acid, making it a potential source of organic acids. [5]. These organic acids offer added benefits as natural reducing agents that can be applied in various environmentally friendly chemical processes. Studies have shown that spinach (*Amaranthus spp.*) contains significant levels of oxalic acid. Spinach is a commonly consumed vegetable in Indonesia. It contains oxalic acid, a compound that can bind with minerals such as calcium, forming insoluble compounds that may affect mineral absorption in the body. [6]. The oxalic acid content in green spinach (*Amaranthus gangeticus*) and red spinach (*Amaranthus spinosus*) varies, with concentrations reaching thousands of ppm, depending on the sample's processing and storage conditions. [7]. The high oxalic acid content in spinach makes it a potential source of organic acids for various chemical applications, including as a natural reducing agent in environmentally friendly processes.

The amount of organic acids that can be extracted from the waste of Averrhoa bilimbi, orange peel, and spinach highly depends on the extraction conditions. Extraction time and temperature are crucial factors influencing the solubility of organic acids in water. Insufficient extraction time may lead to incomplete dissolution, while excessive time can result in degradation or re-binding of the dissolved acids. Similarly, higher extraction temperatures can accelerate the extraction process but may cause evaporation or degradation of organic acids at certain levels [8]–[10]. Therefore, this study optimizes extraction time and temperature to achieve the most efficient conditions for extracting organic acids. Although the utilization of fruit and vegetable waste as a source of organic acids has been widely studied, research exploring its potential as a reducing agent remains limited. Previous studies have primarily focused on extracting and characterizing organic acids without further evaluating their reducing capability in chemical applications. Therefore, this study introduces a novel approach by assessing the effectiveness of organic acids derived from waste as a more environmentally friendly natural reducing agent.

2. METHOD

Materials and Equipment

This study utilized laboratory equipment, including an analytical balance, drying oven, beaker glass, Erlenmeyer flask, hot plate with a magnetic stirrer, digital thermometer, volumetric pipette, measuring cylinder, filter paper, and pH meter. The primary materials used in this study included dried waste samples of *Averrhoa bilimbi*, orange peel, and spinach, which were obtained from Yogyakarta, and distilled water. The chemical reagents used were NaOH (e-Merck p.a), $KMnO_4$ (e-Merck p.a), $H_2C_2O_4$ (oxalic acid, e-

Merck p.a), $Na_2C_2O_4$ (sodium oxalate, e-Merck p.a), $AgNO_3$ (e-Merck p.a), $FeCl_3$ (e-Merck p.a), and $CaCl_2$ (e-Merck p.a).

Sample Preparation and Extraction Process

Averrhoa bilimbi, orange peel, and spinach were dried using an oven dryer at 60°C for ±1 hour and then ground before extraction. A total of 5 grams of sample was dissolved in 100 mL of aquabidest with varying extraction times (30, 60, 90, and 120 minutes) at room temperature. The extraction process was also carried out at different temperatures (30°C, 60°C, 90°C, and 120°C) to evaluate the effect of temperature on the solubility of organic acids. A hot plate with a magnetic stirrer maintained homogeneous mixing during extraction.

Identification and Quantification of Organic Acids

The identification of organic acids was carried out using qualitative tests, including precipitation tests with $AgNO_3$ and $CaCl_2$ to detect oxalic acid, redox tests with methylene blue to detect ascorbic acid, and complexometric tests with $FeCl_3$ to detect citric acid. The concentration of organic acids in the extracted solution was analyzed using alkalimetric titration with NaOH to determine total acids and permanganometric titration with $KMnO_4$ to determine reducing acids. The results of these identification and analysis processes were used to determine the optimal extraction conditions and evaluate the potential of organic acids as reducing agents.

3. RESULT

The analysis results indicate that variations in extraction time affect the concentration of total and reducing acids dissolved in the samples. The acid concentration increases with longer extraction times until it reaches a maximum value, after which changes occur at longer durations. The data on the concentration of total and reducing acids at different extraction times are presented in Figure 1.

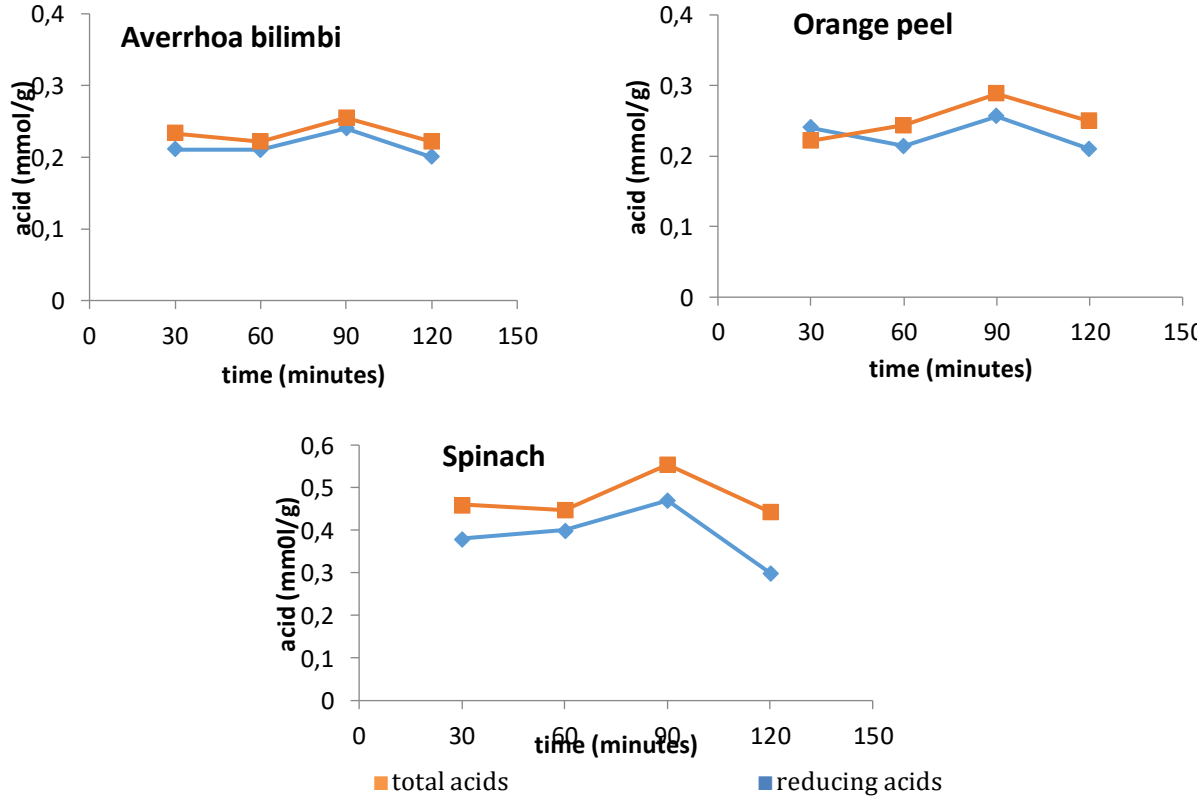

Figure 1. Effect of Extraction Time on the Dissolved Acid Concentration in Averrhoa bilimbi, Orange Peel, and Spinach

After determining the optimal extraction time, temperature optimization was carried out to evaluate its effect on the amount of dissolved organic acids. The analysis results indicate that variations in extraction temperature influence the concentration of total and reducing acids in the samples. The acid concentration increases with rising temperature until it reaches a maximum value, then changes at higher temperatures. The data on the concentration of total and reducing acids at different extraction temperatures are presented in **Figure 2.**

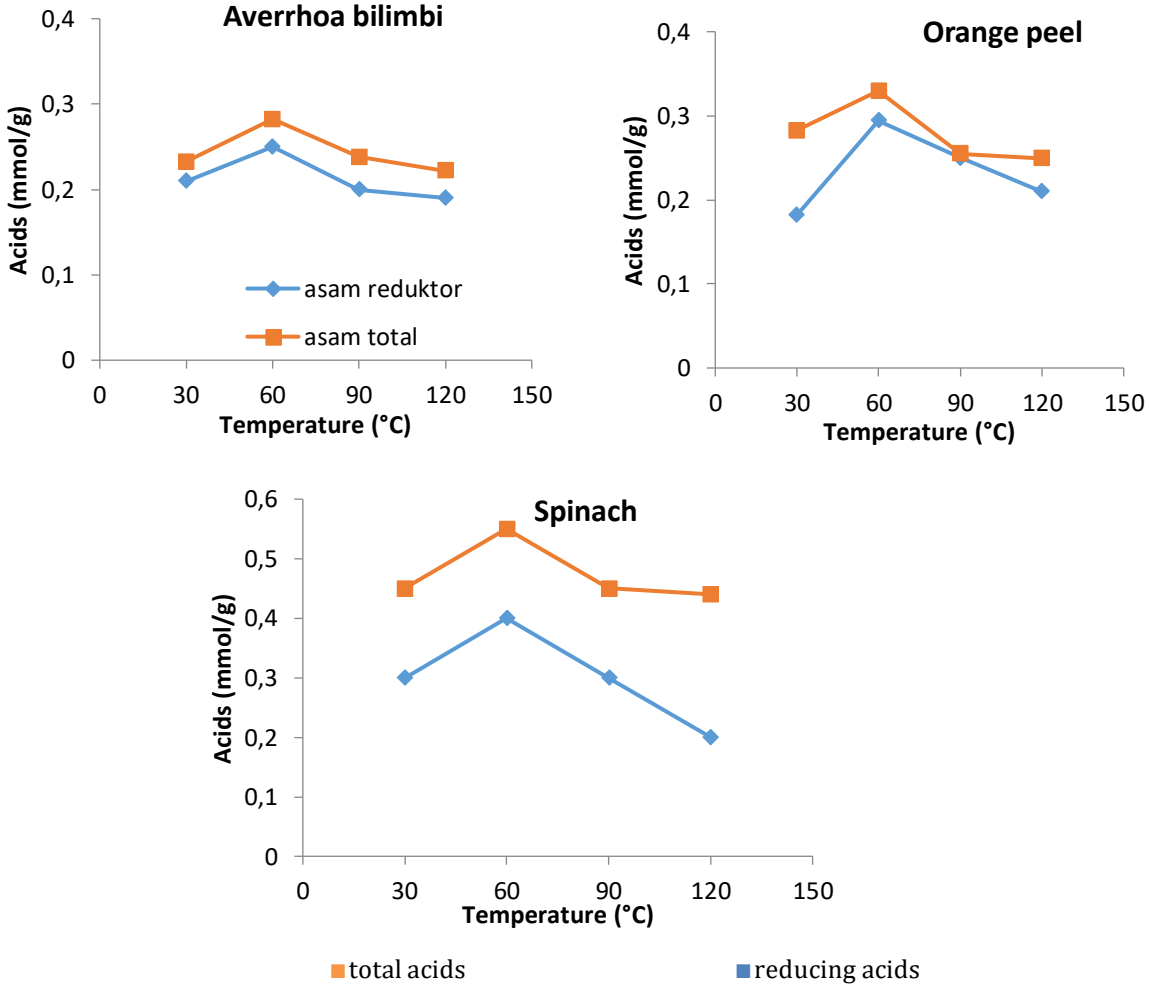

Figure 2. Effect of Extraction Temperature on the Dissolved Acid Concentration in Averrhoa bilimbi, Orange Peel, and Spinach

The identification of organic acids in Averrhoa bilimbi, orange peel, and spinach was conducted using qualitative tests. The presence of oxalic acid was determined through precipitation tests with $AgNO_3$ and $CaCl_2$, ascorbic acid was identified using a redox reaction with methylene blue, and citric acid was detected via an complexometric response with $FeCl_3$. The results of these qualitative tests are presented in Table 1.

Table 1. Identification of Oxalic Acid, Ascorbic Acid, and Citric Acid in Averrhoa bilimbi, Orange Peel, and Spinach

Sample	Oxalic Acid	Ascorbic Acid	Citric Acid
Averrhoa bilimbi	Present	Present	Not Detected
Orange Peel	Not Detected	Present	Present
Spinach	Present	Present	Not Detected

The concentration of total and reducing acids in *Averrhoa bilimbi*, orange peel, and spinach was determined using alkalimetric and permanganometric titration methods. Total acid concentration represents the overall organic acid content in the sample while reducing acid concentration indicates the fraction of acids capable of acting as reducing agents. The percentage of reducing acid relative to total acid was also calculated to assess the potential reducing capability of each sample. The results of this analysis are presented in **Table 2.**

Table 2. Concentration of Total and Reducing Acids

Sample	Total Acid Concentration (M)	Reducing Acid Concentration (M)	Reducing Acid/Total Acid (%)
Averrhoa bilimbi	0.0141	0.0128	90.78
Orange Peel	0.0164	0.0147	89.63
Spinach Leaves	0.0277	0.0193	69.67
Spinach Stems	0.0185	0.0128	69.18

4. DISCUSSION

This study demonstrated that the extraction time and temperature significantly influence the solubility of organic acids from Averrhoa bilimbi, orange peel, and spinach. The results indicate that optimal conditions maximize acid extraction while minimizing potential degradation, highlighting the efficiency of controlled extraction parameters.

In addition to optimizing the extraction conditions, this study highlights the presence of reducing acids in Averrhoa bilimbi, orange peel, and spinach, distinguishing it from previous research that primarily focused on total organic acid content. The percentage of reducing acids relative to total acids varied among the samples, with Averrhoa bilimbi exhibiting the highest proportion (90.78%), followed by orange peel (89.63%), spinach leaves (69.67%), and spinach stems (69.18%). These results indicate that while all samples contain organic acids, their ability to act as reducing agents differs significantly.

The high proportion of reducing acids in Averrhoa bilimbi and orange peel suggests that these samples possess more significant potential as natural lowering agents. This is likely attributed to specific organic acids that play a role in redox reactions. Ascorbic acid, detected in all samples, is well known for its reducing properties. Oxalic acid, found in Averrhoa bilimbi and spinach, also reduces potential. Citric acid, identified only in orange peel, is not typically considered a potent reducing agent, further supporting the varying reducing capabilities observed in this study.

These findings provide new insights into the potential application of organic acid-rich plant waste as environmentally friendly reducing agents. Unlike previous studies that focused solely on extraction and characterization, this study emphasizes the functional role of these acids in redox processes. This distinction highlights the importance of identifying organic acids in fruit and vegetable waste and assessing their specific chemical behavior for practical applications.

Previous research has demonstrated the reducing capabilities of ascorbic and oxalic acids. For instance, a study by Putri et al. (2016) investigated the influence of ascorbic and oxalic acids on reducing Au(III) ions under UV irradiation. The results indicated that both acids effectively enhanced the reduction process, with optimal conditions at a molar ratio of 2:3 (Au(III): organic acid) and a pH of 3. Ascorbic acid exhibited a stronger effect under UV irradiation, while oxalic acid was more effective without UV exposure [11].

Additionally, ascorbic acid is an antioxidant by donating electrons, thereby neutralizing reactive oxygen species. This electron donation capability underscores its

role as a reducing agent in various biochemical processes [12]. These studies corroborate our findings, reinforcing the potential of utilizing plant-derived organic acids as natural reducing agents in various applications.

This study identified the organic acid content in *Averrhoa bilimbi*, orange peel, and spinach and compared the findings with existing literature. In this study, *Averrhoa bilimbi* and spinach contained oxalic acid and ascorbic acid, while orange peel contained ascorbic acid and citric acid.

Previous literature states that oxalic acid is the predominant organic acid present in *Averrhoa bilimbi* [13]. Additionally, *Averrhoa bilimbi* is known to contain citric acid at concentrations ranging from 92.6 to 133.8 mg/100 g [14]. However, in this study, citric acid was not detected in *Averrhoa bilimbi*, while oxalic acid was identified.

This discrepancy may be due to differences in extraction methods, environmental growing conditions, or the ripeness of the fruit at the time of sampling. Genetic variations and analytical techniques may also influence the identification of organic acid content.

Previous literature states that one of the major components in oranges is organic acids, such as citric acid, tartaric acid, and ascorbic acid (vitamin C). The ascorbic acid content in oranges reaches 27 mg per 100 grams or 53 mg per 100 grams of mandarin orange juice. The peel of sweet oranges (Citrus sinensis) contains approximately 1.4% citric acid [3], [15], [16]. These findings are consistent with our study, which detected the presence of citric acid and ascorbic acid in orange peel. Spinach contains oxalic acid, which can be a reducing agent. Spinach also contains ascorbic acid (vitamin C), which acts as an antioxidant and a natural reducing agent [5], [7], [17]. These findings align with our study, which detected the presence of oxalic acid and ascorbic acid in spinach.

This study's findings indicate that Averrhoa bilimbi, orange peel, and spinach contain organic acids with potential as natural reducing agents. This discovery has significant implications across various fields, including environmental sustainability, industrial applications, and green chemistry.

The presence of ascorbic and oxalic acid in these samples suggests their potential use as eco-friendly reducing agents in chemical processes. Utilizing plant-derived extracts as natural reducing agents aligns with the principles of green chemistry, offering a sustainable alternative to synthetic chemicals. Research has demonstrated that plant extracts, rich in phytochemicals such as polyphenols, saponins, and terpenoids, can effectively act as reducing and stabilizing agents in nanoparticle synthesis [18]. Furthermore, the concept of waste valorization is supported by these findings. Extracting valuable compounds from fruit and vegetable waste can reduce environmental pollution and promote a circular economy. Studies have shown that agricultural waste extracts can serve as natural reducing agents, contributing to sustainable nanoparticle synthesis [19].

The identified organic acids, particularly ascorbic acid, are recognized in the food and pharmaceutical industries for their antioxidant properties. Their application as natural antioxidants can enhance product preservation and contribute to health benefits. Additionally, oxalic acid's reducing capabilities may have potential applications in pharmaceutical formulations. The efficiency of extraction methods plays a crucial role in obtaining these bioactive compounds. Ultrasound-assisted extraction (UAE) has been identified as an advanced and efficient technique for enhancing the extraction of bioactive compounds from plant materials [20]. Implementing such green extraction methods can improve yield and maintain the integrity of the compounds, making them more viable for industrial applications.

In summary, this study provides insights into the organic acid content of certain plant materials and highlights their potential applications as natural reducing agents and antioxidants. Adopting sustainable extraction and utilization practices can significantly advance environmental sustainability and industrial processes.

5. CONCLUSION

This study demonstrates that bilimbi fruit, orange peel, and spinach contain organic acids with potential as natural reducing agents. Extraction optimization showed that the best conditions were 90 minutes and 60°C, with organic acid concentrations decreasing at higher temperatures. Bilimbi fruit and orange peel exhibited a higher proportion of reducing acids than spinach, indicating their more significant potential as reducing agents. These findings support the utilization of fruit and vegetable waste as a sustainable source of natural chemicals for various industrial applications.

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7. REFERENCES

[1] R. R. Samsudin, "Bioaktif Belimbing Wuluh (Averhoa bilimbi (Linn.)) Terhadap Kadar Formalin Dalam Tahu," *J. Muhammadiyah Med. Lab. Technol.*, vol. 1, no. 2, p. 88, 2018, doi: 10.30651/jmlt.v1i2.1541.

[2] F. Fahrudin, D. R. Haribowo, F. Hamida, H. I. Wardhana, and F. Mirliana, "Aktivitas Herbal Antidepresan Kombinasi Biji Salak dan Kulit Jeruk Terhadap Mencit yang Diperlakukan Tail Suspension Test (TST)," *J. Biotek Medisiana Indones.*, vol. 10, no. 2, pp. 143–154, 2022, doi: 10.22435/jbmi.v10i2.5827.

[3] A. Deasy Rosita Dewi, "Aktivitas Antioksidan Dan Antibakteri Ekstrak Kulit Jeruk Manis (Citrus sinensis) Dan Aplikasinya Sebagai Pengawet Pangan," *J. Teknol. dan Ind. Pangan*, vol. 30, no. 1, pp. 83–90, 2019, doi: 10.6066/jtip.2019.30.1.83.

[4] R. Wiradimadja, W. Tanwiriah, and D. Rusmana, "Effect of starfruit (Averrhoa bilimbi L.) giving in the diet on the performance, carcass and income over feed cost native chicken," *Ziraa'ah*, vol. 40, no. 2, pp. 86–92, 2015.

[5] H. Fitriani, N. Nurlailah, and D. Rakhmina, "Kandungan Asam Oksalat Sayur Bayam," *Med. Lab. Technol. J.*, vol. 2, no. 2, p. 51, 2016, doi: 10.31964/mltj.v2i2.95.

[6] H. Fitriani, N. Nurlailah, and D. Rakhmina, "Kandungan Asam Oksalat Sayur Bayam," *Med. Lab. Technol. J.*, vol. 2, no. 2, pp. 51–55, 2016.

[7] A. Puspitasari and A. Mahayana, "Determination of Oxalid Acid in Green Spinach (Amaranthus Gangeticus) An Red Spinach (Amaranthus Spinousus) Using Spectrophotometry Method," *Jurnal Kimia dan Rekayasa*, vol. 2, no. 1. pp. 32–38, 2021. doi: 10.31001/jkireka.v2i1.24.

[8] R. Nurlaila, A. Muarif, M. Meriatna, M. Masrullita, and I. Ishak, "Pengaruh Suhu dan Waktu Ekstraksi dalam Proses Pembuatan Pektin dari Kulit Buah Sukun dengan Pelarut Asam Sitrat," *J. Sci. Appl. Technol.*, vol. 7, no. 2, p. 65, 2023, doi: 10.35472/jsat.v7i2.1105.

[9] Miksusanti, Elfita, and S. Hotdelina, "Aktivitas Antioksidan dan Sifat Kestabilan Warna Campuran Ekstrak Etil Asetat Kulit Buah Manggis (Garcinia mangostana L.)

dan Kayu Secang (Caesalpinia sappan L.)," *J. Penelit. Sains*, vol. 15, no. 2, pp. 60–69, 2012.

[10] N. W. A. Yuliantari, I. W. R. Widarta, and I. D. G. M. Permana, "Pengaruh Suhu dan Waktu Ekstraksi Terhadap Kandungan Flavonoid dan Aktivitas Antioksidan Daun Sirsak (Annona muricata L.) Menggunakan Ultrasonik The Influence of Time and Temperature on Flavonoid Content and Antioxidant Activity of Sirsak Leaf (Annona mur," *Media Ilm. Teknol. Pangan*, vol. 4, no. 1, pp. 35–42, 2017.

[11] R. P. Putri, E. T. Wahyuni, and A. Suratman, "Pengaruh Asam Askorbat dan Asam Oksalat Pada Reduksi Ion Au(III) Oleh Adanya Sinar UV," Universitas Gadjah Mada, 2016.

[12] A. Adawiah, D. Sukandar, and A. Muawanah, "Aktivitas Antioksidan dan Kandungan Komponen Bioaktif Sari Buah Namnam," *J. Kim. Val.*, vol. 1, no. November, pp. 130–136, 2015, doi: 10.15408/jkv.v0i0.3155.

[13] M. Muzaifa, "Perubahan Komponen Kimia Belimbing Wuluh (Averrhoa bilimbi L.) Selama Pembuatan Asam Sunti," *J. Teknol. Pertan. Andalas*, vol. 22, no. 1, p. 37, 2018, doi: 10.25077/jtpa.22.1.37-43.2018.

[14] A. Aseptianova and E. H. Yuliany, "Penyuluhan Manfaat Belimbing Wuluh (Averrhoa bilimbi Linn.) sebagai Tanaman Kesehatan di Kelurahan Kebun Bunga, Kecamatan Sukarami, Palembang," *Abdihaz J. Ilm. Pengabdi. pada Masy.*, vol. 2, no. 2, p. 52, 2020, doi: 10.32663/abdihaz.v2i2.910.

[15] T. W. Kurniawan and W. Deglas, "Pemanfaatan Kulit Buah Jeruk Mandarin (Citrus reticulata) Dalam Pembuatan Permen Jelly Dengan Variasi Konsentrasi Bubuk Agar," *Agrofood*, vol. 1, no. 2, pp. 1–5, 2019.

[16] Yulianis et al., "Analisa Vitamin C Kulit Jeruk Manis (Citrus Sinensis (L.) Osbeck) dengan Spektrofotometri Uv-Visible," *J. Katalisator*, vol. 3, no. 2, pp. 135–144, 2020.

[17] *et al.*, "Changes in postharvest quality of organic spinach during storage after heatshock and hydrocooling treatment," *J. Keteknikan Pertan.*, vol. 04, no. 1, pp. 53–58, 2016, doi: 10.19028/jtep.04.1.53-58.

[18] F. Khan, M. Shariq, M. Asif, M. A. Siddiqui, P. Malan, and F. Ahmad, "Green Nanotechnology: Plant-Mediated Nanoparticle Synthesis and Application," *Nanomaterials*, vol. 12, no. 4, 2022, doi: 10.3390/nano12040673.

[19] F. Rodríguez-Félix *et al.*, "Trends in Sustainable Green Synthesis of Silver Nanoparticles Using Agri-Food Waste Extracts and Their Applications in Health," *J. Nanomater.*, vol. 2022, 2022, doi: 10.1155/2022/8874003.

[20] A. G. Demesa, S. Saavala, M. Pöysä, and T. Koiranen, "Overview and Toxicity Assessment of Ultrasound-Assisted Extraction of Natural Ingredients from Plants," *Foods*, vol. 13, no. 19, pp. 1–13, 2024, doi: 10.3390/foods13193066.