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GREEN EXTRACTION TECHNIQUE TO SEPARATE TANNIN FROM COFFEE HUSK WASTE USING NATURAL DEEP EUTECTIC SOLVENT (NADES)

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ABSTRACT

Natural deep eutectic solvent (NADES) is the green solvent for the extraction of tannic acid from coffee husk waste. The NADES used was based on a choline chloride compound combined with glycerol, glucose, citric acid, and proline. The research results show that the best composition of NADES solvent used choline chloride and proline (1:1) with an extraction yield of 5.45 mg TAE g^{-1} and a tannin concentration in NADES of 272.28 mg/L. The optimum extraction conditions were obtained at the addition of 40% water, extraction time of 30 minutes, the ratio of sample and solvent (1:30), and temperature at 80°C with the extraction yield obtained were 7.11; 8.11; 9.16; 22.83 mg TAE/g, respectively. This research supports green technology in extracting active compounds from coffee skin waste so that it can be applied further and is safe for use in pharmaceuticals and food.

Keywords: Green Extraction, NADES, Coffee Husk, Choline Chloride, Tannin.

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INTRODUCTION

Tannins are natural polyphenols that are abundant, easily extracted, and soluble in water.[1] The main property of tannins is to form insoluble complexes with alkaloids, gelatin, and other proteins and can be classified as hydrolyzed and condensed substances.[2,3] Tannins are secondary metabolites known for their antioxidant activity and provide various health benefits for the body.[4] In this study, the tannins were obtained from the extraction of coffee husk waste. Many coffee husks from the agroindustry end up in landfills since they have no commercial value. Approximately 0.18 tons of coffee husks are produced per ton of fresh coffee.[5] Therefore, it is very important to develop solutions to reduce the waste of coffee husks. Coffee husk has the potential to be used in this study since it is known to contain secondary metabolites such as caffeine, tannins, and polyphenols.[6,7] The utilization of coffee husk waste is expected to reduce the environmental impact as well as to support the concept of a circular bioeconomy. Extraction methods have been widely used to separate the active substances, namely, Soxhlet,[8] maceration, homogenate-assisted extraction,[9] ultrasound-assisted extraction,[10] microwave-assisted extraction,[11] supercritical fluid extraction,[12] and pressurized liquid extraction.[13] The main challenge of tannin extraction in this study is to utilize economically viable waste that can selectively extract the target compound using a minimal amount of non-toxic solvent. Recent developments in the field of green chemistry reveal that the use of green solvent techniques such as NADES is increasing exponentially.[14] NADES is a mixture formed from various hydrogen bond donors (HBD) and hydrogen bond acceptors (HBA).[15] When compared with conventional organic solvents, NADES provides many advantages such as non-toxic, thermal stability, non-volatile, and sustainable green properties.[16,17] NADES has been widely used to extract several bioactive compounds in plants, such as pectin from manganese skins,[18] lignin from grape stems,[19] anthocyanins from Aronia melanocarpa,[20] antioxidants from *Corylus avellana* L.,[21] polyphenols from mate tea leaves,[22] and saponins from *Trillium govanianum*.[23] In this study, NADES was used to extract tannin from coffee husk waste. NADES is made by mixing quaternary ammonium salt, and choline chloride (HBA), with a variety of HBD compounds

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derived from glycerol, glucose, citric acid, and proline compounds. Then selected pairs of HBA and HBD compounds that are effective and efficient form a close bond that helps break down coffee skin waste to extract tannin compounds. In addition, the optimum extraction conditions were determined by the ratio of the amount of water in NADES, extraction time, ratio of the number of samples to NADES, and temperature. From the literature study, there is still no specific research on green extraction techniques to extract tannin from coffee husk waste using NADES as a green solvent. The results of this study are expected to support green technology for the isolation of active substances and be applied in the food and pharmaceutical industries. From the literature study, there is still no specific research on green extraction techniques to extract tannin from coffee husk waste using NADES as a green solvent. The purpose of this study is to extract tannin compounds from coffee husks using NADES. The results of this study are expected to support green technology for the isolation of active substances and be applied in the food and pharmaceutical industries.

EXPERIMENTAL

Sample Preparation

The sample is coffee husk waste which has been dried and mashed at a size of 20 mesh. Samples were stored in plastic containers to avoid contact with air and sunlight.

NADES Preparation

NADES was prepared with a certain mole composition ratio according to HBA and HBD. This study used HBA compounds from choline chloride with various HBD compounds from sugar, organic acids, and amino acids. The mole ratio of HBA and HBD is 1:1. The HBD compounds used in this study were glycerol, glucose, citric acid, and proline. The NADES was prepared by heating a solid-liquid mixture and a solid-solid mixture at a temperature of 100-150°C with constant stirring. Stirring was done with a range of 30-120 minutes until a clear solution was formed.[24] The mixture was cooled to room temperature and carried out the characteristics of the NADES mixture made.

Extraction of Active Substances from Coffee Husk Using NADES

Extraction of the active substance from coffee husks using NADES was carried out by mixing 0.5 g of dry sample with 10 mL of NADES stirred at a speed of 120 shakers/minute at room temperature for 30 minutes in an Eppendorf tube. The mixture was filtered to obtain the supernatant and measured using a spectrophotometer.

Extraction Parameter Optimization

The extraction was carried out to select the best experimental conditions for the separation of tannin compounds in coffee husks. The influencing factors are the type of NADES component, the amount of water in NADES, the extraction time, the ratio of the number of samples to NADES, and temperature. The effect of adding water is done by varying the amount of water (20, 30, 40, 50, and 60%). Extraction time was varied for 30, 60, 90, 120, and 150 minutes. Moreover, the ratio of the number of samples to the NADES solvent was carried out in a ratio (1:10, 1:15, 1:20, 1:25, and 1:30). The extraction temperature was varied at 40, 50, 60, 70, and 80°C.

Analysis of the Tannin Content

500 µL of the extract was dissolved (1:10), stirred, and mixed with 2.5 mL of Folin Ciocalteu. After 3 minutes, 2 mL 75 % sodium carbonate was added. The mixture was incubated in a dark room for 2 hours. Absorbance was measured at a wavelength of 720 nm. Tannin content was determined based on the tannic acid calibration curve which shows mg tannic acid equivalent (TAE)/L extract.

RESULTS AND DISCUSSION

Tannin Extraction with NADES Solvent

The NADES solvent prepared was used for the extraction of tannins from coffee husk waste. Extraction results were analyzed for tannin content using standard tannic acid. The NADES used were coded NADES 1 (glycerol), NADES 2 (glucose), NADES 3 (citric acid), and NADES 4 (proline). The yield of tannin extraction from coffee husk waste in NADES can be seen in Fig.-1. Based on Fig.-1, it can be seen that the amount of tannin extracted using NADES can be expressed as extraction yield. NADES based

on choline chloride with an HBD group of glycerol, glucose, citric acid, and proline compounds were 1.09, 2.08, 2.28, and 5.45 mg/g respectively. Optimum extraction was obtained with the composition of NADES as choline chloride and proline. The successive extraction efficiency was obtained with the composition of choline chloride with proline > citric acid > glucose > glycerol.

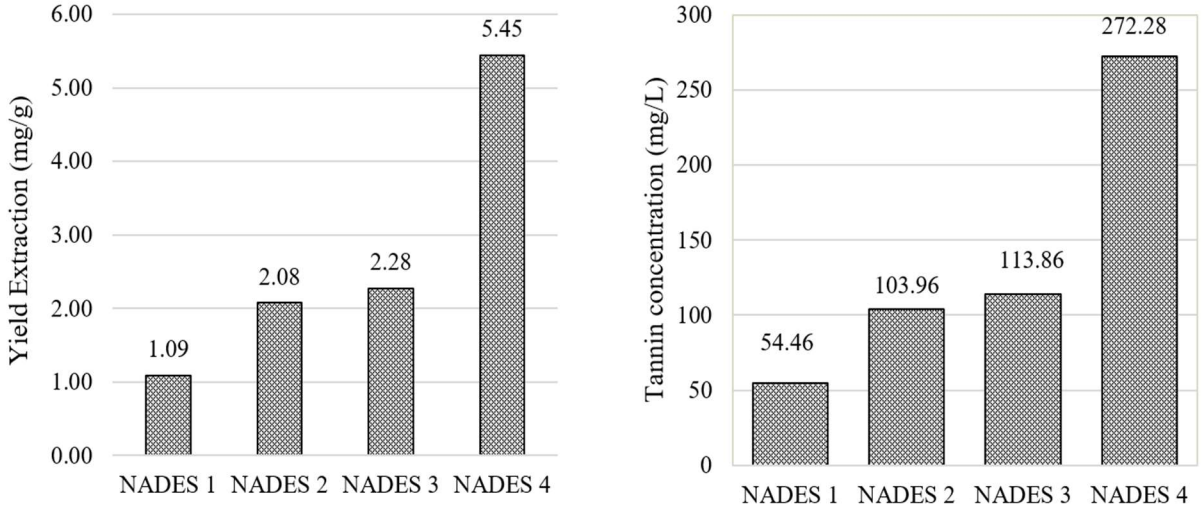

Fig.-1: Extract of Tannin from Coffee Skin using NADES

The concentration of tannin extracted in NADES using choline chloride with HBD glycerol, glucose, citric acid, and proline obtained levels of 54.46; 103.96; 113.86; and 272.28 mg/L. Choline chloride-based NADES with a combination of proline forms stronger hydrogen bonds in forming a stable solution,[25] so that it can extract more tannin compounds. The selection of the most suitable NADES as a solvent is very important to maximize the extraction of the target compound with minimal influence on its bioactive properties.[22] In this study, NADES 4 (based on choline chloride and proline) became the best solvent for tannin extraction.

Effect of Adding Water on Tannin Extraction

This study used varied amounts of water addition (20, 30, 40, 50, and 60%). The effect of adding water on tannin extraction using NADES can be seen in Fig.-2.

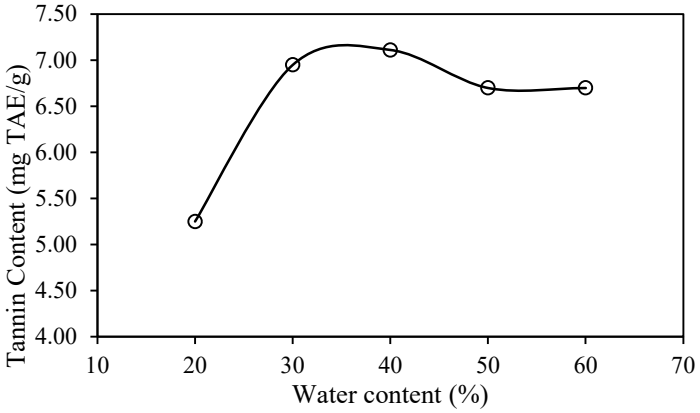

Fig.-2: Effect of Adding Water on Tannin Extraction using NADES

The addition of 20% water resulted in 5.25 mg tannin acid equivalent (TAE)/g as tannin acid. Furthermore, the addition of water up to 40% increased the extraction efficiency to 7.11 mg TAE/g. The addition of water to NADES can reduce the viscosity, increase the polarity, and increase the extraction efficiency of the target compound.[16] However, if there is an excess of water, it can reduce the extraction efficiency due to the breaking of the intermolecular hydrogen bond structure in NADES.[24] This is evident

from the addition of 50-60% water which decreased extraction efficiency to 6.70 mg TAE/g. Therefore, the optimum water addition in this study was 40%.

Effect of Time on Tannin Extraction Using NADES

The effect of time on the tannin extraction using NADES is shown in Fig.-3. The use of different times aims to obtain a balance in the extraction process. The time variations in this study were 30, 60, 90, 120, and 150 minutes.

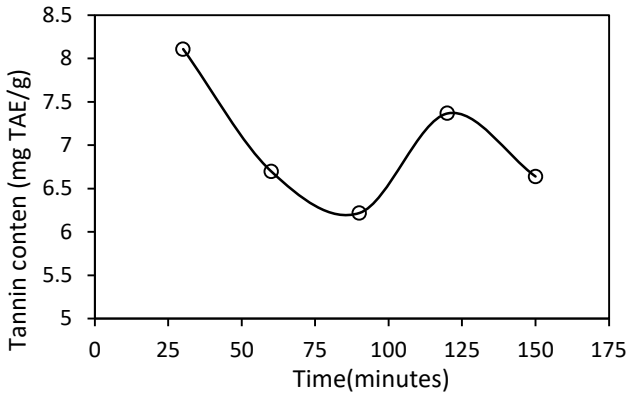

Fig.-3: Effect of Time on the Tannin Extraction using NADES

The extraction for 30 minutes obtained a yield of 8.11 mg TAE/g. Extraction efficiency decreased with increasing extraction time. After 90 minutes, the efficiency decreased to 5.14 mg TAE/g. A prolonged extraction process can damage the structure of bioactive compounds.[25] However, the extraction for 120 minutes decreased the efficiency to 7.37 mg TAE/g. The desorption of the target compound in the solvent increased the efficiency from 90 minutes to 120 minutes. After 150 minutes, the efficiency fell back to 6.64 mg TAE/g. The effect of time on the tannin extraction using NADES indicates a fluctuating pattern. This was due to the extraction and desorption processes. We considered 30 minutes of extraction time to be sufficient to obtain optimum extract results of tannin compounds. a relatively short extraction process is known to be effective in stabilizing NADES to maximize the extraction of the target compound.[21] Too long an extraction time is certainly not practical in terms of economy and workload.

Effect of Sample/Solvent Ratio on Tannin Extraction Using NADES

The effect of the sample/solvent ratio on tannin extraction using NADES can be seen in Fig.-4.

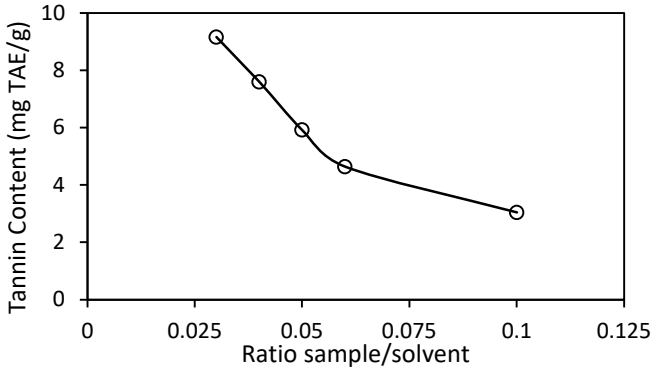

Fig.-4: Effect of Sample/Solvent Ratio on Tannin Extraction using NADES

The sample/solvent ratio used in the study was varied in comparison at 1:10 (0.10 g/mL), 1:15 (0.06 g/mL), 1:20 (0.05 g/mL), 1:25 (0.04 g/mL), and 1:30 (0.03 g/mL). The effect of the sample/solvent ratio on tannin extraction using NADES can be seen in Fig.-4. It shows that the smaller sample/solvent ratio

causes the efficiency of tannin extraction to increase. This result is in accordance with the principle of mass transfer, where an adequate mass transfer can be achieved when the sample size is smaller than the solvent.[21] The optimum sample/solvent ratio in this study was obtained at the composition of 1:30 or 0.03 g/mL with a yield of 9.16 mg TAE/g.

Effect of Temperature on Tannin Extraction Using NADES

The temperatures used in the study varied from 40, 50, 60, 70, and 80°C. The effect of temperature on tannin extraction using NADES is shown in Fig.-5.

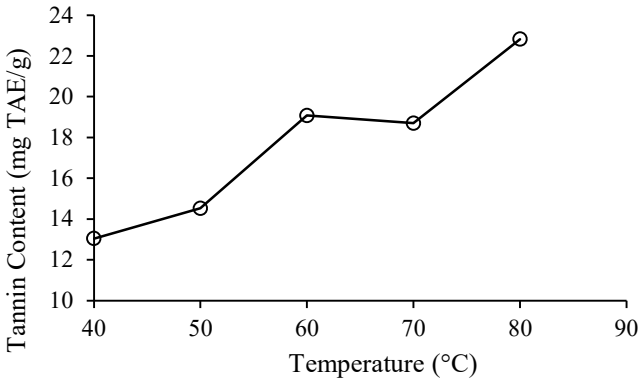

Fig.-5: Effect of Temperature on Tannin Extraction using NADES

Figure-5 shows that the higher the extraction temperature, the greater the amount of tannin extracted. Heating from 40-80°C increased the extraction yield from 13.03 to 22.83 mg TAE/g. Increasing the temperature is known to decrease the viscoelastic properties of NADES and can also reduce surface tension, thereby increasing matrix penetration which generally increases the solubility of the target compound, i.e., tannin.[21] The maximum extraction results in this study were obtained at a temperature of 80°C. The maximum extraction temperature of 80°C because heating at higher temperatures can cause the degradation of bioactive compounds.[22]

CONCLUSION

The green extraction technique using a combination of green solvents (NADES) has succeeded in extracting active compounds from coffee husk waste. The results show that NADES based on choline chloride and proline was the best solvent combination since it proved effective in extracting tannin compounds from coffee husk waste with the highest extraction yields and tannin concentrations of 5.45 mg/g and 272.28 mg/L. Extraction of tannins using NADES proved to be influenced by the composition of water addition, extraction time, sample/solvent ratio, and temperature. The optimum extraction conditions were obtained at the addition of 40% water, extraction time of 30 minutes, the ratio of sample and solvent (1:30), and temperature at 80°C with the extraction yield obtained were 7.11; 8.11; 9.16; 22.83 mg TAE/g, respectively. This research supports green technology for the isolation of active substances so that they can be applied further and are safe for use in the food industry.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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