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The Effect of Concentration of Citric Acid Solution on Extraction of Pectin from Watermelon Albedo

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Abstract. Watermelon albedo or the white flesh of watermelon rind contains pectin with high enough content. In this study was conducted the extraction of pectin from watermelon albedo by the liquid-solid extraction method. The citric acid solution was used as a solvent with concentrations varied by 4%, 7%, and 10%. The research steps include the pretreatment of raw material, the extraction, the posttreatment of extraction, and the analysis of pectin. The pretreatment aimed to reduce water content and reduce the size of raw material. The extraction process was the main process in which pectin dissolution occurred in the citric acid solvent. Furthermore, the posttreatment of extraction aimed to obtain pectin solid with the addition of ethanol. The final step was the analysis, including pectin yield, moisture content, methoxyl content, galacturonic acid content, and pectin functional group. Based on research obtained, an increase in the concentration of citric acid increased pectin yield, methoxyl content, and galacturonic acid content. The moisture content of pectin decreased with the increasing concentration of citric acid. Pectin yield, moisture content, methoxyl content, galacturonic acid content resulted from 10% concentration of citric acid solvent are 8.356%, 19.748%, 7.029%, and 69.048%, respectively. Based on FTIR analysis, the functional groups contained in pectin are hydroxyl group, methyl group, carbonyl group, and ether group. This functional groups are main constituents of pectin structure.

Keywords: *watermelon albedo, citric acid, extraction*

Abstrak. Albedo semangka atau daging putih dari kulit semangka mengandung pektin dengan kadar yang cukup tinggi. Pada penelitian ini dilakukan ekstraksi pektin dari albedo semangka dengan metode ekstraksi padat cair. Larutan asam sitrat digunakan sebagai pelarut dengan konsentrasinya divariasikan sebesar 4%, 7%, dan 10%. Tahapan penelitian meliputi perlakuan awal bahan baku, ekstraksi, perlakuan akhir ekstraksi, dan analisis pektin. Perlakuan awal bertujuan untuk mengurangi kandungan air bahan baku dan memperkecil ukuran bahan baku. Proses ekstraksi merupakan proses utama, yang mana terjadi pelarutan pektin dalam pelarut asam sitrat. Selanjutnya, perlakuan akhir ekstraksi bertujuan untuk memperoleh padatan pektin dengan penambahan etanol. Tahap akhir adalah analisis meliputi rendemen pektin, kadar air, kadar metoksil, kadar asam galakturonat, dan gugus fungsional pektin. Berdasarkan penelitian diperoleh bahwa dengan peningkatan konsentrasi asam sitrat meningkatkan rendemen pektin, kadar metoksil dan kadar asam galakturonat. Kadar air pektin menurun dengan bertambahnya konsentrasi asam sitrat. Rendemen pektin, kadar air, kadar metoksil, dan kadar asam galakturonat pektin dengan konsentrasi pelarut asam sitrat 10% masing-masing 8,356%; 19,748%; 7,029%; dan 69,408%. Berdasarkan analisis FTIR, gugus fungsional yang terkandung dalam pektin adalah gugus hidroksil, gugus metil, gugus karbonil, dan gugus eter. Gugus-gugus fungsional tersebut merupakan konstituen utama dari struktur pektin.

Kata kunci: *albedo semangka, asam sitrat, ekstraksi*

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INTRODUCTION

Pectin is a material that belongs to a complex heteropolysaccharide. In general, pectin is found in the primary cell wall and the middle lamella of plant tissue (Mellerowicz & Sundberg, 2008). Pectin is composed of galacturonic molecules that bind to α-(1-4) glycoside bonds, thus forming galacturonic acid (Aji et al., 2017). Some carboxyl groups of pectin polymers are esterified by methanol (methylation) into methoxyl groups (Akhmalludin & Kurniawan, 2009). Pectin with a high methoxyl content can form gels in the presence of sugar and acid conditions, whereas a low methoxyl content can form gels in the presence of divalent ions, such as calcium (Clarissa et al., 2019).

Pectin can be extracted from by products of fruits, which is waste from processing the fruits (Dalal et al., 2019). One example of fruits that produce considerable waste is watermelon. Watermelon consists of 3 parts, namely the outer layer (exocarp), the middle layer or white flesh (mesocarp) and inner flesh (endocarp) (Syalom et al., 2020).

Mesocarp or watermelon albedo is a white layer of watermelon and has not been widely used because of its sour taste (Maulani et al., 2014). Based on Effendi and Wardatun (2012), every 5.2 kg of watermelon produced a watermelon rind of 2.2 kg. Moreover, based on the Central Statistics Agency, watermelon production in Indonesia in 2020 is 560,317 tons. So, the production of watermelon albedo is about 221,410 tons per year (it was assumed that the amount of watermelon albedo is equal to the watermelon rind due to the small amount of exocarp). According to Singh (1975) in Campbell (2006), the content of pectin in watermelon albedo is about 13%. With high enough pectin content, watermelon albedo can be used as a raw material to obtain pectin.

Pectin from the rind of the fruit can be extracted conventionally with an acidic solvent. Some researchers have extracted pectin from watermelon albedo, such as Campbell (2006), Maulani et al. (2014), Petkowich et al. (2016), and Hidayah et al. (2020). The acid solvents used by the four researchers were nitric acid, hydrochloric acid, and acetic acid. Among the four researchers, no one has extracted pectin from watermelon albedo using a citric acid solvent by conventional method Ishartani et al. (2020) successfully extracted pectin from watermelon albedo by other method which was microwave assisted extraction.

Based on Nurhaeni et al. (2018), among three types of solvents (citric acid 5%, hydrochloric acid 5%, and acetic acid 5%), it was known that citric acid solvent produces the highest yield in extracting pectin from rind and rags of *cempedak* fruit, which was 38.85%. Thus, this study was carried out by extracting pectin from watermelon albedo with citric acid solvent by conventional method to determine its effectiveness in extracting pectin. In addition, variations in citric acid concentration were done to determine the effect of citric acid concentration on the yield and properties of pectin produced.

MATERIAL AND METHODS

Materials

The materials used were red watermelon albedo obtained from fruit seller located in Cihanjuang Village West Bandung Regency, citric acid, aqua dest, 95% ethanol, filter paper, aluminum foil, sodium hydroxide, hydrochloric acid, sodium chloride, and PP indicator.

Instrumentation

The equipment used was a blender, sieve with the size of 10 mesh, a set of reflux tools, thermometer, oven, analytical scale, vacuum pump, Buchner funnel, mortar and pestle, desiccator, volumetric flask, volumetric pipette, burette, beaker glass, and Erlenmeyer flask. Figure 1 showed a set of reflux tools used in the extraction process.

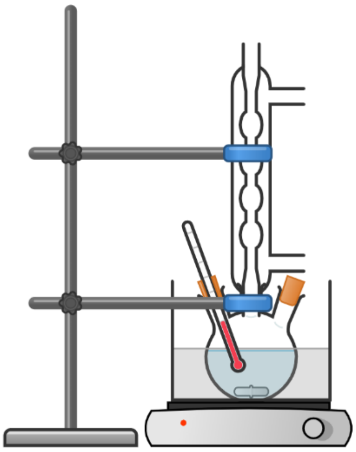


Figure 1. A set of reflux tools

Procedure

Pretreatment of raw material

The procedure of pretreatment was done using method written by Maulani et al. (2014) with slight modification. The pretreatment steps of watermelon albedo include the washing process, the reducing the size process, the drying process, the reducing the size process, and the screening process. Watermelon albedo was washed with water and then reduced size by using the blender. The drying process was conducted with the help of sunlight for four days and then the reducing the size of dry watermelon albedo until the powder was obtained. The end of pretreatment was screened by a sieve with the size of 10 mesh.

Furthermore, the moisture content of watermelon albedo powder was analyzed by heating watermelon albedo powder in the oven at a temperature of 105 °C for 2 hours. The amount of water contained in watermelon albedo powder was determined by reducing the weight of watermelon albedo powder before and after heating.

Pectin extraction

The procedure of extraction was done using method written by Madjaga et al. (2017) and Nurhaeni et al. (2018) with slight modification. Five grams of watermelon albedo powder was entered into the reflux tool, and added citric acid solution. The extraction process was carried out at a temperature of 90 °C, for 60 minutes and stirred with a stirrer. In this study, the concentration of the citric acid solution was varied by 4%, 7%, and 10% (citric acid weight/aqua dest weight).

Posttreatment of extraction

The procedure of posttreatment was done using method written by Madjaga et al. (2017) and Nurhaeni et al. (2018) with slight modification. The result of the extraction process was separated between filtrate and solid residue with the help of a vacuum pump. The filtrate was precipitated by adding 95% ethanol with a volume ratio of 1:1.5 and left for 24 hours. Then, the solid was separated by filtrate and repeatedly washed with ethanol. Finally, the solid was dried in the oven for 8 hours at 40 °C.

Analysis of pectin

1. Moisture content

The analysis procedure of moisture content was done using method written by Nurhaeni et al. (2018). 0.1 grams of pectin was heated in the oven at 105 °C for 2 hours. Furthermore, pectin was cooled in a desiccator and weighed until it was obtained a constant weight.

2. Methoxyl and galacturonic content

The analysis procedure of methoxyl and galacturonic content was done using method written by Devianti et al. (2019). 0.1 grams of pectin was moistened with 1 ml of 95% ethanol, then dissolved with 20 ml of aqua dest. The process of dissolving pectin was carried out at a temperature of 40 °C for 1 hour with stirring. Furthermore, 0.2 grams of NaCl was added to the mixture and given a PP indicator of 3 drops. Titration was done using a NaOH solution of 0.1 N until the solution turned pink and did not change when shaken for 30 seconds. V1 symbolized the volume of the titrant. Furthermore, the solution that has been titrated was added 10 ml of NaOH solution of 0.25 N and stirring for 1 hour at room temperature and closed. After that, the mixture was added 10 ml of HCl solution of 0.25 N and titration with NaOH solution of 0.1 N. V2 symbolized the number of titrants required for titration.

$$\text{Methoxyl content} = \frac{\text{V2} \times \text{Mtitrant} \times 31}{\text{mass of sample}} \quad (1)$$

$$\text{Galacturonic content} = \frac{(\text{V1+V2}) \times 176 \times 100}{\text{mass of sample}} \quad (2)$$

3. Identification of functional groups

Analysis of the pectin functional group was conducted using the Fourier Transform Infrared Spectroscopy (FTIR) tool.

RESULT AND DISCUSSION

Raw Material

The raw material used in this study was the watermelon albedo. Figure 2 showed the watermelon albedo after the pretreatment process. The moisture content of watermelon albedo after the pretreatment process was 12.26%.

Figure 2. Watermelon albedo

Pectin Extraction

Pectin can be obtained from watermelon albedo by the solid-liquid extraction method. Solid-liquid extraction is the process of separating solute from components that are insoluble to certain solvents. In this study, the solvent used in the pectin extraction was a citric acid solution. Citric acid concentrations varied by 4%, 7%, and 10%. The yield, moisture content, methoxyl content, and galacturonic content of pectin products were as follows.

Pectin yield

Pectin yield is a comparison of the weight of extracted pectin with the weight of raw materials. Figure 3showed the pectin yield, and it can be known that the pectin yield was affected by the concentration of citric acid. The greater the concentration of citric acid used, the greater the pectin yield. It was because higher concentrations of citric acid contain more hydrogen ions (H^+) that will break the bonds between protopectin and compounds contained in the cell wall of watermelon albedo (Maulani et al., 2014) and hydrolysis of protopectin into pectinate (pectin) (Aji et al., 2017). This reaction caused pectin to dissolve in a citric acid solution.

The study obtained 6.63%, 7.79%, and 8.36% yields for citric acid concentrations of 4%, 7%, and 10%, as shown in Figure 3. This yield was still relatively low compared to the pectin content in watermelon albedo based on Singh (1975) in Campbell (2006), which was 13%. It occurred because pectin dissolved in water and evaporated together with water during pretreatment.

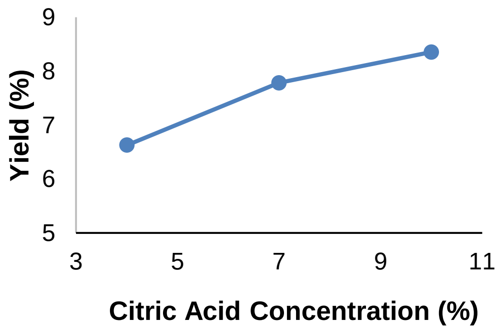


Figure 3. Pectin yield (%) against variations in citric acid concentration (%)

Moisture Content

The moisture content of pectin affects the quality of the product. High moisture content causes the product to have poor quality. In this study, pectin was dried at 40 °C for 8 hours. The drying process at low temperatures aimed to prevent the degradation of pectin. Figure 4 showed the tendency of moisture content against variations in citric acid concentrations. All pectins have a moisture content between 19% to 25%. The moisture content of pectin did not meet the requirements of the International Pectin Procedures Association (IPPA), in which the moisture content of pectin must be less than 12% (IPPA in Susanti et al., 2021). The relatively high moisture content was due to less drying time.

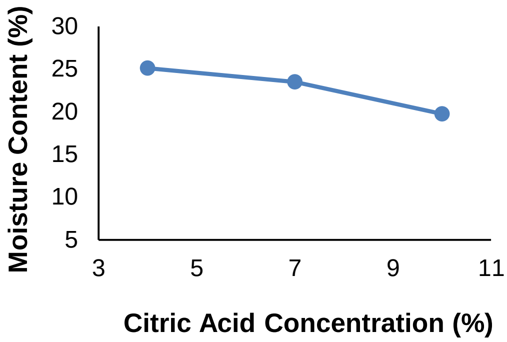


Figure 4. Moisture content (%) against variations in citric acid concentration (%)

Methoxyl Content

The methoxyl content indicates methoxyl the number of carboxyl groups esterified by methanol. Methoxyl content affects the texture of pectin gel. The higher the methoxyl content, the easier it dissolves in water. According to the International Pectin Procedures Association (IPPA) in Susanti et al. (2021), the type of pectin is divided into two based on its content, namely pectin with high methoxyl content and pectin with low methoxyl content. The high methoxyl content is more than 7.12%, while the low methoxyl content is 2.50 - 7.12%. The methoxyl content of this study is in the range of 6% to 7%, which is pectin with a low methoxyl content. Based on Figure 5, the greater the concentration of citric acid used, the greater the methoxyl content. It is due to more free carboxyl groups being esterified.

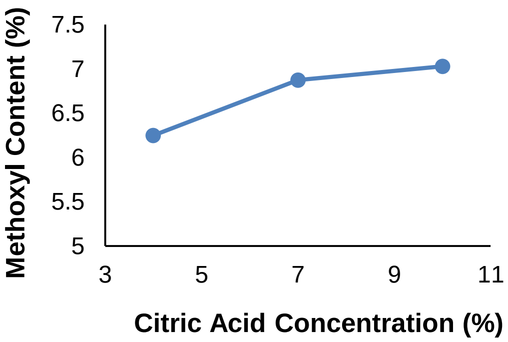
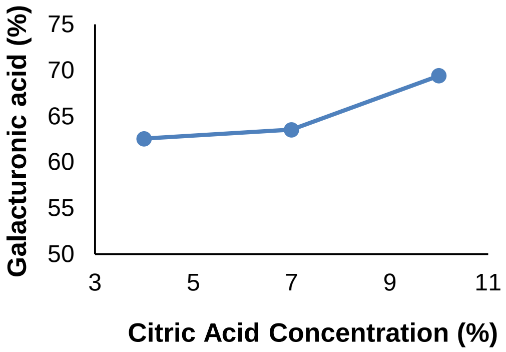


Figure 5. Methoxyl content (%) against variations in citric acid concentration (%)

Galacturonic Acid Content

D-galacturonic acid is the primary component of pectin (Maulani et al., 2014). Based on Figure 6, galacturonic acid content was getting more significant with increasing concentrations of citric acid. It is due to the process of hydrolysis of protopectin into pectin. Based on the IPPA in Susanti et al. (2021), the galacturonic acid content is at least 35%. All pectin products meet the requirement.



Gambar 6. Galacturonic acid content (%) against variations in citric acid concentration (%)

Functional Groups of Pectin

Pectin extracted with a 10% citric acid solvent was tested with FTIR. Testing was done to identify the pectin functional group. Figure 7 showed the spectrum of pectin. Based on Figure 7 known that pectin contains -OH or hydroxyl group (3,270 cm^{-1}), $-CH_3$ or methyl group (2,936 cm^{-1}), carbonyl group (1,732 cm^{-1}), and ether group (1,085 cm^{-1}). It indicated that the identified functional groups are appropriate when compared to the pectin structure.

This result was supported by the results of previous research related to pectin extraction. Based on Nurmila et al. (2019) and Megawati & Ulinuha (2015) obtained -OH or hydroxyl group at the wavelength of 3,448.72 and 3,430,82 cm^{-1}, $-CH_3$ or methyl group at the wavelength of 2,926.01 and 2,928.05 cm^{-1}, carbonyl group at the wavelength of 1,743.65 and 1,639.08 cm^{-1}, as well as ether group at the wavelength of 1,145 and 1,044.37 cm^{-1}. Furthermore, Pavia et al. (2009) explained that -OH or hydroxyl group, $-CH_3$ or methyl group, carbonyl group, and ether group are at the wavelength range of 3,200 – 3,650 cm^{-1}, 2,840 – 3,000 cm^{-1}, 1,630 – 1,850 cm^{-1}, and 1,000 – 1,260 cm^{-1}.

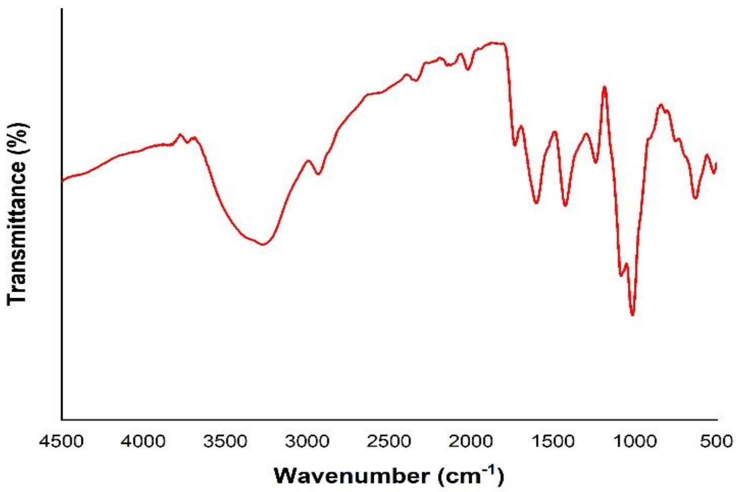


Figure 7. The spectrum of pectin derived from watermelon albedo

CONCLUSION

Pectin was successfully extracted from watermelon albedo with a citric acid solvent. The method used was solid-liquid extraction (conventional method). An increase in the concentration of citric acid from 4% to 10% obtained an increase in pectin yield, methoxyl, and galacturonic acid content. Meanwhile, the moisture content of pectin decreased with the increasing concentration of citric acid. Pectin yield, moisture content, methoxyl content, and galacturonic acid content of pectin extracted using the citric acid concentration of 10% were 8.356%, 19.748%, 7.029%, and 69.408%, respectively. FTIR analysis showed the functional groups contained in pectin ware contains hydroxyl group, methyl group, carbonyl group, and ether group.

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