

Microwave-assisted extraction of pectin from cocoa peel

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Abstract: Pectin is a polymer of d-galacturonate acids linked by β -1,4 glycosidic bond. This study isolates pectin from cocoa peel (*Theobroma cacao*) using citric acid as solvent by microwave-assisted extraction method. Cocoa peels (moisture content of 10%) with citric acid solution (pH of 1.5) irradiated by microwave energy at various microwave power (180, 300, 450 and 600 W) for 10, 15, 20, 25 and 30 minutes respectively. Pectin obtained from this study was collected and filtrated by adding 96% ethanol to precipitate the pectin. The best results obtained from extraction process using microwave power of 180 Watt for 30 minutes. This combination of power and time yielded 42.3% pectin with moisture content, ash content, weight equivalent, methoxyl content and galacturonate levels were 8.08%, 5%, 833.33 mg, 6.51% and 58,08%, respectively. The result finding suggested that microwave-assisted extraction method has a great potency on the commercial pectin production.

1. Introduction

Cocoa plant (*Theobroma cacao*), native plant in Indonesia, contributes to economic growth from industrial sector. Chocolate industry utilizes cocoa bean to produce chocolate and disposes cocoa peel as solid waste. Increasing the demand of cocoa bean lead to accumulation of cocoa peel in the environment and disposal of cocoa bean become serious problem. Previous study found that cocoa peel is a source of pectin, so that the peel has a benefit to for pectin production. Pectin may be found as a fiber component in the lamella layer and primary cell wall of cocoa plant [1]. Pectin is popular polysaccharide used as gelling, stabilizing and thickening agent in food industry [2]. It consists of d-galacturonic acid backbone linked by α -(1.4) glycosidic bond. Some carboxyl groups of pectin polymer esterified into methoxyl groups [3].

Pectin isolation commonly carries out by extraction of strong or weak acids [4]. Extraction may proceeds by various methods such as soxhlet extraction, maceration and stirring extraction. Recently, Wang S, et al. (2007) and Shkodina, O.G, et al. (1998) reported microwave-assisted extraction [5] and enzymatic method [6] to extract pectin from plants. Acid method carries out at high temperature using sulfuric, phosphoric, nitric, hydrochloric and citric acids [7]. In addition, microwave-assisted extraction (MAE), a technique to extract dissolved materials in plant by microwave energy, is introduced to improve the extraction method. The technology is suitable for the removal of thermolable dielectric materials such as cocoa. This method proved effectively reduces extraction timeless energy and solvent consumption, higher yields, higher accuracy and precision [8]. Lefsih, K et al.(2017) and Swamy, G.J and Muthukumarappan, K (2017) reported laboratory scale application of microwave-assisted extraction to extract pectin from *Opuntia ficus indica* [3] and banana peels [5].



Instead of extraction at high temperature, others reported utilization of microwave energy for heating and sterilization process [9, 10, 11]. Sarah et al. (2014) evaluated heating performance method for conventional heating and microwave heating using palm fruit sample [11]. Microwave heating proved more effective as compare to conventional heating, because microwave energy generates heat instantly from water molecule re-orientation inside plant during heating process [12]. Microwave energy creates instant and rapid heating to facilitate temperature required for extraction process.

In this study, microwave-assisted extraction method used to extract pectin from cocoa peel. Qiu et al. (2010) reported parameters associated with yield and pectin quality during extraction process such as pH, temperature, and extraction time, agitation and solid to liquid ratio [7]. In the case extraction process by microwave irradiation, level of microwave power during extraction process also taken into consideration instead of previous parameters

2. Materials and Methods

Material used in this study was *Theobroma cacao* from Pangkalan Brandan and Galang, Sumatera Utara. The chemicals used were citric acid, ethanol, silver nitrate solution, distill water, sodium chloride, sodium hydroxide and phenolphthalein. Experimental rig to extract pectin from cocoa peel is an erlenmeyer in a domestic microwave oven Samsung model ME731K with frequency of 2450 MHz and 800 Watt.

2.1. Pretreatment

Prior to the experiment, the cocoa fruit was cleaned upon arrival from plantation by putting the fruits inside basin filled full with lime ash solution to remove the gums. The cocoa fruit was cut into cocoa slices with dimension of 2x2x0.5 cm and sun dried for approximately 8 hours, and another 4 hours using conventional oven at temperature of 40°C. Then, the dried cocoa slices was blended (Miyako model BL-151PFAP No 34060052217) to reduce cocoa size into smaller particles size (60 mesh).

2.2. Extraction process

Cocoa peels powder (moisture content of 10%) diluted with citric acid solution (pH 1.5). The powder was placed inside a microwave cavity and irradiated by microwave energy at various microwave power (180, 300, 450 and 600 W) for 10, 15, 20, 25 and 30 minutes respectively. The extract was then filtered by using filter paper (Whatman no 2) to obtain the filtrate. Furthermore, the filtrate was stirred and heated at temperature of 95°C until the volume was reduced up to 50% of filtrate. The filtrate was cooled and pectin precipitation was carried out by adding acidified ethanol. The precipitated pectin was washed using ethanol to obtain pectin and remove chloride, and dried in an oven at temperature of 40°C for approximately 8 hours. The dried pectin was ready for further quality assessment such as moisture and ash content [13], equivalent weight [14], methoxyl content and galacturonate content [15].

3. Results and Discussion

The performance of microwave-assisted extraction method for pectin production was indicated by yield and quality of pectin in accordance to International Pectin Producers Association (IPPA) Quality Standard [16] at various extraction time and microwave power.

3.1. Effect of extraction time and microwave power on yield of pectin

Figure 1 shows relationship between extraction time and yield of pectin. In general, prolonged extraction time, associated with longer heating period, and increment of microwave power increased yield of pectin. Prior to the extraction by microwave irradiation, the cocoa suspension was heated to maximum temperature before attaining constant temperature. Prolonged heating in this case occurred at constant temperature. During heating period, extraction of pectin from cocoa peel occurred due to the increase of temperature. The presence of acid facilitated the release of pectin from tissue cell wall of cocoa powder. Similar phenomena reported by Nurdjanah and Usmiati for pectin extraction from

pumpkin [...]. Elevating extraction temperature increased kinetic energy of sample solution and facilitated solvent diffusion into the tissue cells of pumpkin. In other words, elongated heating period would attain high temperature, the greater time and temperature extraction process, so that greater pectin was produced [17].

Figure 1 shows increment of microwave power from 180 to 450 Watt increase the yield of pectin. Additional microwave power will reduce the yield of pectin due to excessive time and temperature of extraction process destroyed the pectin [17]. The best extraction time to obtain 42.3% yield of pectin was 30 min at microwave power of 300 Watt. Increment of microwave power indicates more heat delivered into cocoa suspension, thus causing more pectin substances to be extracted.

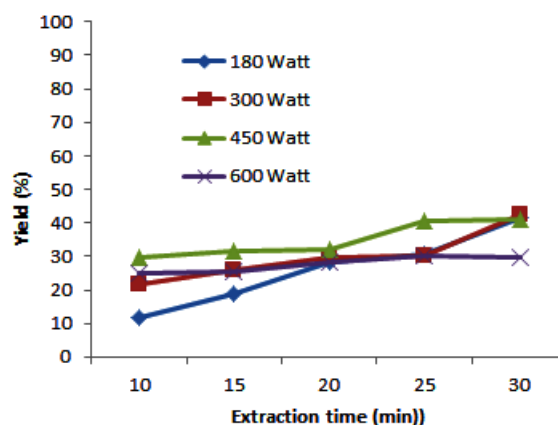


Figure 1. Effect of extraction time to yield of pectin at various microwave power

3.2 Effect of extraction time and microwave power on quality of pectin

Figure 2, Figure 3 and Figure 4 show relationship between extraction time and microwave power on the quality of pectin. Figure 2 illustrate that moisture content reduced with increment of microwave power and extraction time. Prolonged extraction process from 10 to 30 min at constant microwave power along with the increment of microwave power from 180 to 600 Watt reduced the moisture content. Moisture affects shelf life of pectin, in which higher water content causes susceptibility to microbial activity and reduces the quality of pectin. Moisture content in pectin observed ranged between 8.08 to 11.88% which was still below the allowed maximum moisture on IPPA standard [16].

Ash content represents mineral content of pectin, such as potassium, sodium, magnesium and iron. Ash content indicates pectin purity level, in which high pectin purity indicated by low ash content. The level of ash in pectin flour is influenced by the presence of inorganic material residues contained in cocoa peel, extraction methods and pectin insulation [19]. Figure 2b indicates that ash content increased with the extended of extraction period. Higher ash content was obtained at increment of microwave power from 180 to 450 Watt. Elevated power which also illustrated higher temperature and extraction period resulted in higher pectin ash content. The prolonged extraction time promoted hydrolysis of protopectin producing more calcium and magnesium contents of pectin [20]. In general, ash content in this study ranged from 1-5% or below IPPA standard. Maximum allowance ash content in pectin according to IPPA standard is 10% [16].

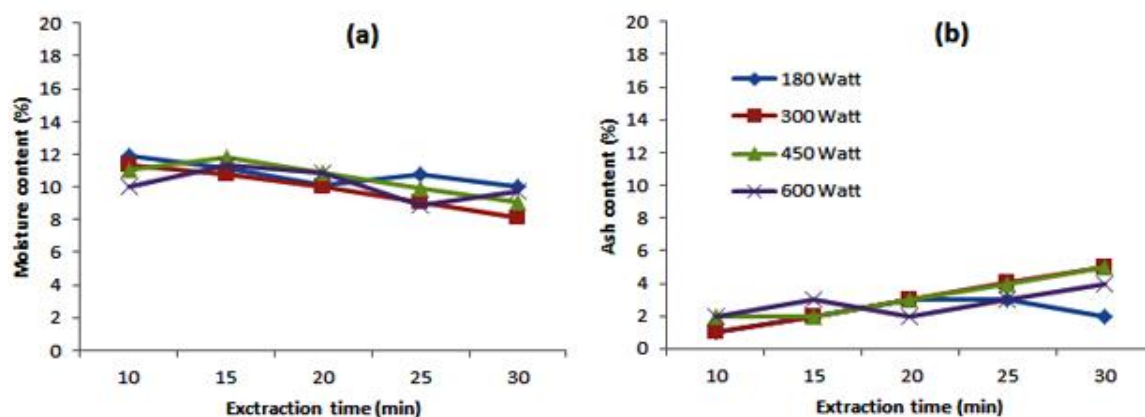


Figure 2. Effect of extraction time to moisture (a) and ash content(b) at various microwave power

Figure 3 shows relationship between equivalent weight and extraction time. Pectin equivalent weight represents anhydrouronic acid content and degree of esterification. This study observed extraction of pectin from cocoa peel assisted by microwave irradiation should occurred less than 21 min. The increase of extraction time yielded more pectin equivalent weight, indicating that greater pectin released from cocoa peel was resulted at the first 20 min of extraction time. However, lengthened extraction duration from 20 to 30 min reduced the pectin equivalent weight. This study suggests that pectin extraction period more than 20 min responsible for pectin degradation or pectin de-polymerization into pectic acid which was denoted by greater un-esterified galacturonate acid. In this microwave treatment, increment of microwave power from 180 to 200 Watt increased equivalent weight. However, increasing microwave power greater than 200 Watt resulted in lower equivalent weight. The equivalent weight of pectin ranged between 800 to 3000 mg, above IPPA standard (600-800 mg) [16]. Plant characteristic, raw material quality and extraction method are suggested for high pectin equivalent weight in this study as compared to IPPA standard. The results suggested that extraction should carried out at 300 Watt for 30 min to obtain pectin with equivalent weight meet the IPPA standard. Pectin equivalent weight resulted from this process combination was 833.33 mg.

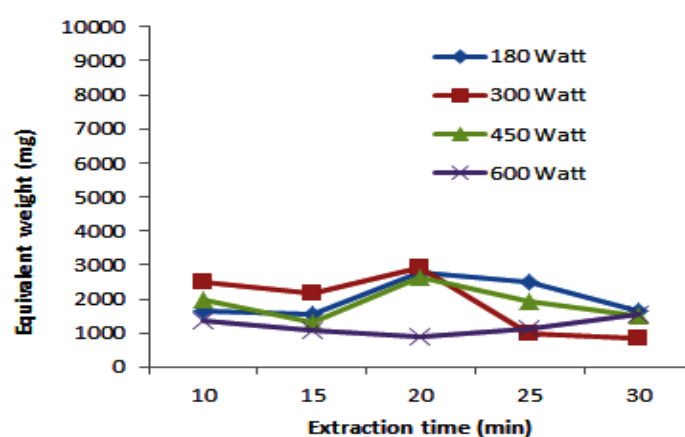


Figure 3. Effect of extraction time to equivalent weight of pectin at various microwave power

Figure 4.a shows relationship between methoxyl number and extraction time. Methoxyl number represents free esterified carboxyl group in the pectin and influences the gel formation. High Methoxyl (HM) pectin can form gels in the presence of sugars and acids in certain comparisons, whereas Low Methoxyl (LM) pectin can form gel in the absence of sugars [21]. Methoxyl number increased at

longer extraction time at constant microwave power due to hydrolysis of methyl ester group with the present of acid. The increase of microwave power from 180 to 300 Watt improved the methoxyl number, while prolonging extraction duration from 300 to 450 and 600 Watt decreased the methoxyl content. However, all methoxyl content obtained in this study ranged between 2.5 to 7.12% , which meet the IPPA standard for LM content (2.5 to 7.2%) [16].

Galacturonate levels as well as the charge of pectin molecules play an important role in determining the functional properties of the pectin solution and affecting the structure and texture of the gel formation [22]. In addition to the methoxyl content, gel strength is also associated with the levels of galacturonate acid in the pectin. Galacturonate acid levels represent the amount of pectin present in pectin flour. High galacturonate acid indicates strong bonds in the pectin during gel formation [23]. Figure 4.b shows galacturonate levels increased along with the longer of extraction time at constant microwave power. According to the Food Chemical Codex [24], the acceptable amount of galacturonate content is not less than 65%. In this study, galacturonate content ranged between 22 to 58.08%. To obtain pectin with galacturonate specification meets pectin quality requirements, pectin extraction should be carried out more than 20 min using power of 450 and 600 Watt.

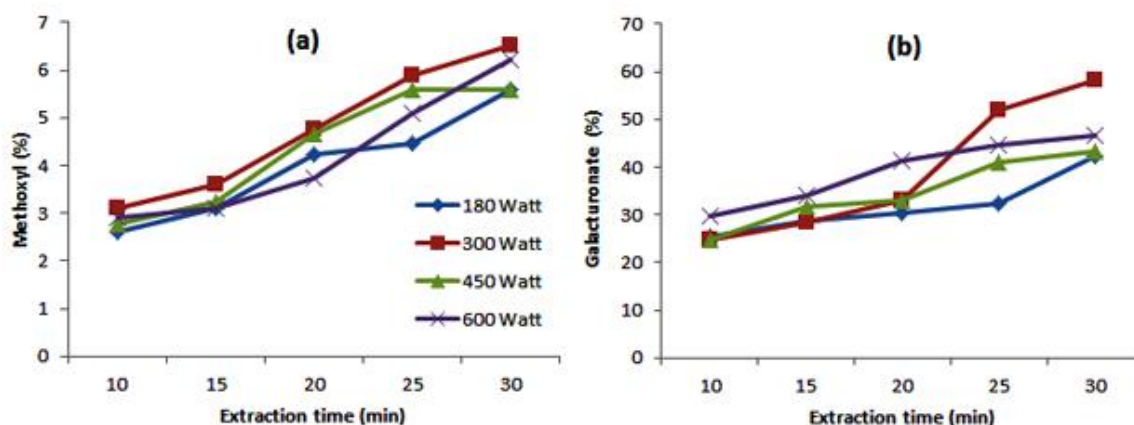


Figure 4. Effect of extraction time to galacturonate and methoxyl content at various microwave power

Overall pectin quality resulted from this study is tabulated in Table 1.

Table 1. Pectin quality as compared to IPPA standard

Quality factor	This study	IPPA [16]
Methoxyl content (low) (%)	2.5 - 7.12	2.5 – 7.2
Levels of galactic acid (%)	22 - 58.08	Min 35
Drying losses (moisture content) (%)	8.08 - 11.8	Max 12
Ash content (%)	1-5	Max 10
Equivalent Weight (mg)	800 - 3000	600 - 800

4. Conclusions

Pectin extraction from cocoa peel using microwave-assisted method was influenced by microwave power and extraction time. In addition, microwave power was associated with extraction temperature. This study concludes that extraction time and microwave power affect yield of pectin and pectin quality, in which the increment of microwave power and extraction time result in greater yield, methoxyl content and galacturonate content in pectin. On the contrary, it reduced moisture content, while the ash content and equivalent weight was fluctuated. The best pectin extraction by microwave

irradiation can be conducted at microwave power of 300 Watt for 30 min. This combination of power and time produce pectin (yield of 42.3%) with moisture content of 8.08%, ash content of 5%, equivalent weight of 833.33 mg, methoxyl content of 6.51% and galacturonate level of 58.08%. Overall, quality of pectin resulted in this study meet criteria established by IPPA [16], except for the equivalent weight.

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