IOP Conference Series: Earth and Environmental Science

The application of activated carbon from coconut shell and zeolite as adsorbents on coffee decaffeination using the Swiss Water Process (SWP)

To cite this article: S Saloko *et al* 2020 *IOP Conf. Ser.: Earth Environ. Sci.* **443** 012067

IOP Conf. Series: Earth and Environmental Science **443** (2020) 012067 doi:10.1088/1755-1315/443/1/012067

The application of activated carbon from coconut shell and zeolite as adsorbents on coffee decaffeination using the Swiss Water Process (SWP)

S Saloko, Y Sulastri, Murad and S Wahyuni

Faculty of Food Technology and Agroindustry, Mataram University
Jl. Majapahit No. 62 Mataram, Indonesia 83126

Email: s_saloko@unram.ac.id

Abstract. The purpose of this study was to assess the effect of coconut shell activated carbon and zeolite as adsorbents with various concentrations in coffee decaffeination process using Swiss Water Process (SWP). This research used a completely randomized design (CRD) with 2 factors i.e. the type of adsorbent (coconut shell activated carbon and zeolite) and adsorbent concentration (5%, 10% and 15%) with three replications. The parameters tested were chemical quality (moisture content, ash content, antioxidant activity and caffeine content), physical quality parameter (colour) and organoleptic parameters (aroma and taste). The results showed that the interaction between the type of adsorbent and adsorbent concentration only contributed significantly to the caffeine content. Treatment using zeolite adsorbent with a concentration of 15% is the best treatment with the highest caffeine content reduction with moisture content 4.59%; ash content 4.77%; antioxidant activity 23.58%; the caffeine content 0.68%; ºHue value 47.06; L* value 10.34; aroma scoring 3.25 (a rather strong coffee aroma); aroma hedonic 3.35 (a bit like); taste scoring 3.05 (slightly bitter) and taste hedonic 3.2 (a bit like).

1. Introduction

Coffee (*Coffea* spp.) is a tropical plant that grows in Indonesia. This plant has long been cultivated with a fairly high economic value. Coffee is a popular beverage, with a high consumption rate alongside water and tea. Coffee obtains from the fruit of the coffee plant (*Coffea* spp.) under the family of Rubiaceae and belongs to genus Coffea. Coffee plants originated from Africa continent and have around 70 species from the genus Coffea, but only two species have economic value, namely Robusta (*Coffea canephora*) and Arabica (*Coffea arabica*) [1].

Coffee is popular not only because of its distinctive flavour, but also because of its benefit as an antioxidant like polyphenols that could stimulate brain performance. However, coffee also has several shortcomings. The caffeine content is the main problem of coffee consumption. Caffeine with an excessive consumption rate can increase muscle tension, stimulates the work of the heart, and increase gastric acid secretion work [2].

Coffee contains two main components, caffeine and cafeol. The caffeine content in Robusta coffee beans ranged from 1.5% to 2.6%, while the Arabica coffee beans ranged from 0.9% to 1.4% [3]. Reduced levels of caffeine (decaffeination) in coffee needs to be done until it reaches the safe limit of

150 mg per day or about 2 to 3 cups. The caffeine content can be decreased by decaffeination process [4].

Decaffeination is a process to reduce the levels of caffeine in coffee so that the consumers can enjoy the flavour and taste without any side effects. The aim of decaffeination is to reduce the levels of caffeine, psychological effects and to ensure the safety of consumers [5]. There are many methods that could be applied to reduce the levels of caffeine in coffee. One of the methods that are currently being used at the industry of low caffeine coffee is the Swiss Water Process. This method is one of the most secure methods for caffeine extracting process using activated charcoal as the adsorbent. Activated charcoal designated to capture the molecules of caffeine that works as the producer of low caffeine coffee. The concentration used in the coffee industry ranged between 5–20% [6].

Activated charcoal itself consists of several types based on its raw materials, including activated charcoal which derived from coconut shell. Coconut shell is a waste product of coconuts. The coconut industry is still largely focused on coconut meat processing as the primary outcome. By products such as coconut shell is still done traditionally on a small scale, sometimes even becomes a waste of coconuts product. At low caffeine coffee processing industry, coconut shells can be used as a raw material of activated charcoal which serves as an adsorbent of caffeine in coffee decaffeination process.

In addition to coconut shell activated charcoal, other adsorbent material that has a high absorption rate is zeolite. Zeolite is a unique adsorbent, since it has a very small size and uniform shape compared to other adsorbents such as activated carbon or silica gel, and thus the zeolite only able to absorb the molecules with a diameter equal to or smaller than the diameter of the gap cavity, whereas molecules diameter larger than the zeolite pores are retained and will only cross between particles. Zeolite pore size ranges from 3 to 15 Å [7]. Since zeolites have a large surface area, they are known as a selective adsorbent with high adsorption effectiveness [8].

The existence of zeolite in Indonesia are very abundant, however its use are still very minimal. The use of zeolite as an adsorbent is on the purification of used cooking oil and absorbing copper metal ions (Cu^{2+}) on waste water. Zeolite with a percentage of 2% within 100 minutes is the most effective adsorbent of used cooking oil. The use of zeolite to absorb the caffeine compounds has never been done before. Based on the description above, research has been carried out on the application of activated carbon from coconut shell and zeolite as adsorbent on coffee decaffeination using Swiss Water Process.

2. Materials and methods

2.1. Materials and tools

Materials used in this research are Robusta coffee beans that have been dried, derived from Goa Hamlet, Bentek Village, Gangga Subdistrict, North Lombok Regency, West Nusa Tenggara Province, Indonesia. Other materials include water, charcoal coconut shell, zeolite, Calcium Chloride ($CaCl_2$), 1 M HCl, methanol solution, distilled water, DPPH (2.2-difenil -1-picryhidrazy) and caffeine standard 10 ppm; 25 ppm and 50 ppm.

The tools used in this study is a 60 mesh sieve, mortar iron, cabinet dryer, oven drying MEMMERT type UNB 400, Oven COSMOS CO-9919, spectrophotometer UV-Vis, High Performance Liquid Chromatography (HPLC), Chromameter (MSEZ User Manual), cooker, steamer pans, coffee roaster (rotisserie coffee beans), KIRIN blender, filter paper, glass, basin, baking sheet, filter, spoon, bottle packaging, secondary packaging, furnace electricity, analytical scales, desiccators, baker glass 150 mL, volumetric flask, volumetric pipette, erlenmeyer, porcelain cup, test tube, test tube rack, aluminium foil, label paper, stopwatch and tissue.

2.2. Method

The method used in this study is an experimental method implemented in the laboratory. Trial design used in this study is Completely Randomized Design (CRD) with two factors. First factor is the type of Adsorbent (A) which consists of 2 levels treatments which are the coconut shell activated charcoal and zeolite. Second factor is the concentration of the adsorbent (K) which consists of 4 levels of treatment: 0%, 5%, 10% and 15%. Data from the observations were analyzed for variance at the level of 5% using Co-stat software. If there are any significant difference, further testing is therefore needed using the Honestly Significant Different (HSD) with 5% significance [9]. The parameters analyzed in this study including moisture content, ash content, antioxidant activity, caffeine content, colour and organoleptic (aroma and taste).

2.3. Implementation of research

2.3.1. Adsorbent preparation

2.3.1.1 *Size uniformity.* The coconut shell activated charcoal and zeolite adsorbent are pureed into powder, uniform in size using a sieve with size of 60 mesh.

2.3.1.2 *Coconut shell charcoal activation.* The activation process begins with washing the charcoal using distilled water and then filters it to dry using filter paper. After that, immerse it into 25% ($CaCl_2$) solution for 12 hours. The comparison of solvent to coconut shell activated charcoal is 2:1. After that, use distilled water to wash the material until it can be separated and dry using the oven at 200ºC for 3 hours.

2.3.1.3 *Zeolite activation.* The activation process begins with washing the zeolite using distilled water, after that filter it with filter paper to dry. Then zeolite was soaked using HCl 1 M with a 2:1 ratio of solvent and zeolite. Immersion was done for 3 hours and rinsed with distilled water until the dirt or ingredients are separated, and then dried it at 200ºC for 3 hours.

2.3.2. Decaffeination process

2.3.2.1 Preparation of raw materials. Raw materials used in this study was 3000 g Robusta coffee varieties that have been dried in advance and obtained from Hamlet Cave, Bentek Village, District Gangga, North Lombok, West Nusa Tenggara.

2.3.2.2 Sorting. Sorting is the selection stage, to separate the coffee beans from dirt, foreign objects or broken coffee, to standardize the size of coffee so that it will be easier to unify the quality of the roasted coffee produced.

2.3.2.3 *Weighing.* Coffee beans are weighed with digital scales as many as 2100 g for all treatments and 100 g for each treatment.

2.3.2.4 Extraction. A 100 g Coffee beans extracted into 280 mL of boiled water with a temperature of 100ºC for 3 hours to extract its flavour and caffeine. The coffee beans are then separated from the soaking water to produce the extracts of caffeine and coffee flavour. The adsorbent (coconut shell activated charcoal and zeolite) with concentration of 0%, 5%, 10% and 15% are added into the extract for caffeine adsorption. After that the extract and adsorbent are separated using filter paper.

2.3.2.5 *Half drying.* Coffee beans are dried using cabinet dryer with a temperature of 55ºC for 2 hours. Timing and temperature are obtained based on the results of preliminary research where half drying was done with the heating. This process maximizes the absorption of coffee bean flavour back into the coffee beans.

2.3.2.6 *Immersion.* Water from the extraction process is used in the immersion process. The water has been extracted by caffeine but still contains the flavour of coffee, this process restores the flavour that lost in the coffee beans using cabinet dryer with a temperature of 75ºC for 2 hours to reabsorb the extracts.

2.3.2.7 *Drying.* Drying the coffee beans was intended to evaporate the water content in the grain toward the equilibrium moisture content. Reduction of moisture content of materials is done so that the developments of microorganisms and enzyme activities that can cause spoilage inhibited and help maximize the roasting process. Drying in this study conducted by using a dryer (cabinet dryer) with a temperature of 55ºC for 3 hours.

2.3.2.8 *Roasting.* The coffee roasting process aims to develop the aroma and taste of the coffee with several characteristics, to facilitate the process of grinding and to extract the coffee. Roasting is done using a coffee roasting machine with a roasting temperature of 250° C for 0.5 hour.

2.3.2.9 *Pulverization.* Pulverization of roasted coffee beans is done using a blender. After that, it was uniformly sized with a 60 mesh sieve. The size of the coffee powder will affect the taste and the aroma of the coffee. In general, the smaller size, the better aroma and taste.

2.3.2.10 *Brewing.* In the process of coffee brewing, all aspects of both the volume of water used and the temperature of the brewing water must be observed. In this process, 200 mL of water with a temperature of 90ºC was mixed with coffee powder with a dose of 8 g, and then stirred until it dissolved.

2.3.2.11 Analysis. The analysis of coffee decaffeination includes moisture content, ash content, antioxidant activity, caffeine content, colour and organoleptic test consisting of aroma and taste.

3. Result and discussion

3.1. Moisture content

Moisture content is the amount of water contained in the material which is expressed in percent. Moisture content is also one of the most important characteristics of food which determines the freshness and durability of the food, high moisture content will easily calls bacteria, molds and yeast to multiply, so that changes will occur in food ingredients [10]. The moisture content parameter is a measurement of the water content in a material which aims to provide a minimum limit or range of the amount of water in the material [11].

The results of analysis of variance at the level of 5% showed that the interaction of the type and the concentration of adsorbent did not give any significant effect on the moisture content of decaffeinated coffee powder. The detailed result can be seen in figure 1.

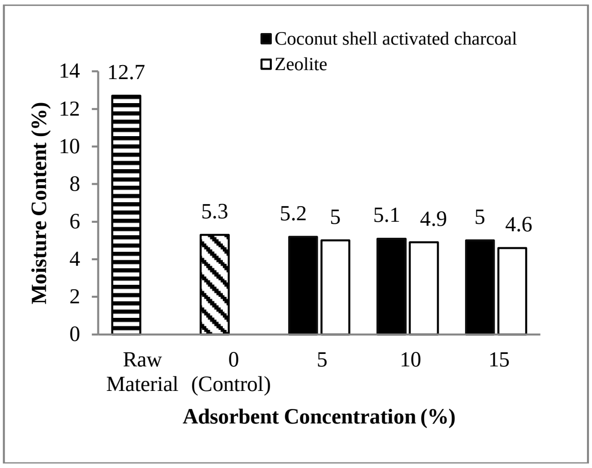

Figure 1. The influence of concentration and type of adsorbent on the moisture content of robusta coffee decaffeinated powder.

Based on figure 1, the treatment on different types of adsorbents i.e. coconut shell activated charcoal and zeolite had no significant effect on the water content of Robusta coffee decaffeinated. However, the treatment on different adsorbent concentrations had a significant effect on the water content of Robusta decaffeinated coffee. The moisture content produced in the treatment of the type of coconut shell activated charcoal adsorbent concentrations of 5%, 10% and 15% in succession is 5.20%; 5.11% and 5.02%. Moisture content in the treatment of zeolite adsorbent concentrations of 5%, 10% and 15% in succession are 5.02%; 4.87% and 4.59%. The results of the analysis also found that the initial Moisture content of raw materials was 12.72% and the moisture content of the control treatment was 0% (K0) with adsorbent of 5.27%.

The moisture content of each treatment had no significant effect on each other because the decaffeination process of the adsorbent used both hydrophobic coconut shell activated charcoal and hydrophobic zeolite. According to [12], non-polar adsorbents are hydrophobic adsorbents; this adsorbent will absorb adsorbents other than water. One of the non-polar adsorbents is activated carbon, while the zeolite adsorbent depends on the Si: Al ratio. Since the Si: Al ratio is low; zeolites are hydrophilic and have a high affinity for water and other polar compounds. Conversely, when the Si: Al ratio is high, zeolite will become hydrophobic and adsorbs non-polar compounds [13].

In this study, yellowish white zeolite that belongs to the type of mordenite zeolite was used, this type of zeolite is known for having the highest Si content among other natural zeolite. The same temperature and time of roasting are also causing impact that explains why the moisture content in each different treatment in this study provides the same moisture content. However, a significant decrease in moisture content occurs in Robusta coffee beans that have not gone through any process with ground coffee produced after going through the decaffeination and roasting process.

After going through a series of processes, the moisture content of raw materials was decreased from 12.72% to 4.59%. The main factor was the roasting processed that use a high temperature and caused evaporation. This is in line with what was revealed by [14], that the heating process can cause the moisture contained in the material to evaporate. The higher heating temperature, the higher number of waters in the material that will evaporate and lower the moisture content.

The moisture content produced by decaffeination of the coffee powder on all treatments ranged between 4.59%-5.20% and has already fulfil the Indonesian National Standard 01–3542–2004 which regulates the quality of ground coffee.

3.2. Ash content

Ash content is a mixture of inorganic components or minerals contained in a food ingredient. The ash content of a food product illustrates the amount of burning minerals into substances that cannot be

evaporated [15]. Determination of ash content is closely related to the mineral content contained in a material. If the minerals contained in food are high, then the ash content will also be high [14].
The results of analysis of variance at the level of 5% showed that the interaction of the type and concentration of the adsorbent did not give a significant effect on the ash content of decaffeinated ground coffee produced. The detailed result can be seen in figure 2.
Based on figure 2, the treatment on different types of adsorbents i.e. coconut shell activated charcoal and zeolite adsorbent had no significant effect on the ash content of Robusta decaffeinated coffee powder. The treatment of different adsorbent concentrations of 5%, 10% and 15% also had a significant effect on the ash content of decaffeinated coffee powder. Ash content produced in the treatment of the type of coconut shell activated charcoal adsorbent concentration of 5%, 10% and 15% in succession, among others, 4.75%; 4.46% and 5.02%. The ash content in the treatment of zeolite adsorbent concentrations of 5%, 10% and 15% respectively is 5.15%; 5.12% and 4.77%. The results of the analysis also found that the initial ash content of raw materials was 5.13% and the ash content of the control treatment was 0% (K0) with adsorbent of 4.66%.

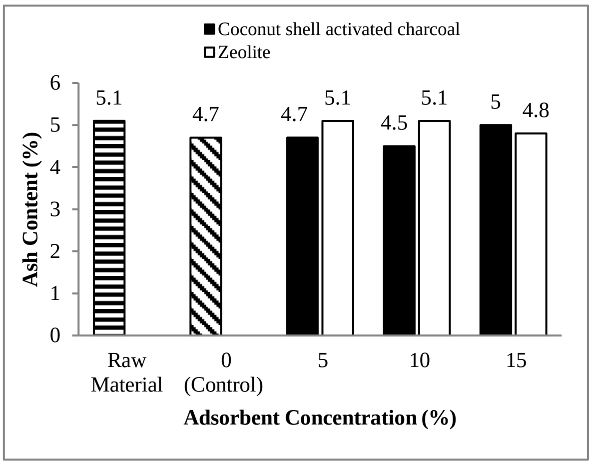

Figure 2. Type and concentration of adsorbents effect on the ash content of robusta coffee decaffeinated powder.

Ash content produced in the Robusta decaffeinated coffee powder of A1K1 treatment (Coconut shell active charcoal adsorbent with a concentration of 5%), A1K2 (Coconut shell active charcoal adsorbent with a concentration of 10%), A1K3 (Coconut shell activated charcoal adsorbent with a concentration of 15%), and A2K3 (15% zeolite adsorbent) has met the Indonesian National Standard 01–3542–2004 which regulates the quality requirements of ground coffee, with a maximum ash content of 5% b/b. The treatment of A2K1 (adsorbent zeolite with a concentration of 5%) and A2K2 (adsorbent zeolite with a concentration of 10%) produced a slightly higher ash content than the Indonesian National Standard 01–3542–2004, the ash content was 5.15% in the A2K1 treatment (Zeolite adsorbent with a concentration of 5%) and 5.12% in the A2K2 treatment (zeolite adsorbent with a concentration of 10%).
Higher ash content tends to be found in the use of zeolite as an adsorbent. Zeolite used as an adsorbent that contributes to the increase of ash content because zeolite itself is formed from mineral compounds which is one of the factors that could increase the ash content, where the higher the mineral content of the material the higher the ash content. This is in line with the research of [16], in his study of the effect of the use of zeolite on rations; it was found that a higher level of zeolite (5.0 and 7.5%) will increase the ash content in the ration which resulted in a decrease in digestibility. High ash levels due to a high mineral content, dirt or the rest of the epidermis can also affect the ash content in the coffee beans [17].
Ash content is the amount of minerals contained in the material, where the minerals contained in coffee are potassium, calcium, magnesium, and non-metallic minerals namely phosphorus and Sulphur

[3]. In this study, it can be concluded that the factors which cause the high ash content are the process of sorting and other processes that leave residues, the use of adsorbents and the raw material of the coffee beans themselves, each coffee bean has a different level of ash because each region can produce a different seed.

3.3. Antioxidant activity

Antioxidants are a compound that neutralizes free radicals, it able to remove, clean and withstand reactive oxygen or free radicals in the body [18]. Antioxidants in the food is essential for maintaining the quality of the product, preventing rancidity, changes in nutritional value, changes in colour and aroma, and other physical damage caused by oxidation reactions [19]. The antioxidant activity is expressed as the arrest of radical treatment formulations, measured using the DPPH (2.2-diphenyl-1-pikrihidrazil) [20]. The principle of this analysis is that the antioxidant compounds in the sample reacts with radical DPPH and DPPH, colour decay will fade as measured by spectrophotometer at a wavelength of 517 nm. Determination by spectrophotometer at a wavelength of 517 nm is the determination of residual DPPH that were not caught by the antioxidants in the sample.
Results of analysis of variance at the level of 5% indicate that the interaction of the type and concentration of the adsorbent did not give a significant effect on the antioxidant activity of Robusta coffee decaffeination powder produced. The detailed result can be seen in figure 3.

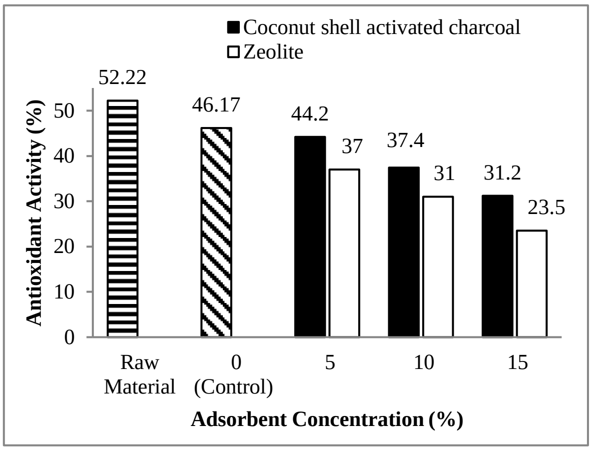

Figure 3. Adsorbent type and concentration effect on the antioxidant activity of robusta decaffeinated coffee powder.

Based on figure 3, the antioxidant activity produced in the treatment on Robusta coffee decaffeinated powder are ranged from 23.58 to 44.19%. The highest antioxidant activity value is in the treatment of A1K1 (Adsorbent of coconut shell activated charcoal with a concentration of 5%) of 44.19% and the lowest value in the treatment A2K3 (Adsorbent zeolite with a concentration of 15%) is 23.58%. Based on the results of a further 5% HSD test, the antioxidant activity in the treatment of coconut shell activated charcoal adsorbent type was different from the treatment of zeolite adsorbents.
Treatment of coconut shell activated charcoal adsorbent type resulted in a higher antioxidant activity compared with other types of zeolite adsorbent. It was caused by the absorption of each adsorbent which cause the absorption of its compounds, including antioxidants. Some examples of antioxidant compounds found in coffee are caffeine, polyphenols, flavonoids, proanthocyanidin, coumarin, chlorogenic acid and tocopherols [21]. This is in line with the statement of [22], stating that the adsorption ability of an adsorbent is influenced by several factors, one of them is the nature of the adsorbent in the form of pore structure. Pore structure relates to the surface area, the smaller the pores as a result of a greater surface area, the more the speed of adsorption.
According to [23], the average diameter of a pore is 21.6 Å, while according to IUPAC, porous materials can be classified based on the size of its pores: material microporous (pore diameter < 20 Å),

Mesoporous materials (pore diameter 20–50 Å) and macropores material (diameter > 500 Å). Therefore, the activated charcoal and zeolite are included in the mesoporous and microporous material. It can also be concluded that the adsorbent types of zeolite have a higher absorption of antioxidant compounds compared to the adsorbent types of coconut shell activated charcoal. The results of a further test in HSD 5% referred in this study shows that the treatment of carbon activated coconut shell to become adsorbent (A1) is higher than that of the treatment to become zeolite (A2).
Based on the results of a further test of HSD 5%, the antioxidant activity in the treatment of different adsorbent concentration gives a significant effect. The treatment of the adsorbent concentration increases the ability to capture free radicals DPPH. The results obtained proved that the higher the concentration of adsorbent, the lower the antioxidant activity. This is consistent with the ability of the adsorbent that is able to absorb the compounds exist in one form of antioxidant coffee extract such as caffeine, polyphenols, flavonoids, proanthocyanidin, coumarin, chlorogenic acid and tocopherols. The higher the concentration of adsorbent used, the more the percentage of absorbed compounds. This proves that the higher the antioxidant activity in the treatment, the lower the concentrations of the adsorbent. Further test of HSD 5% in the treatment also shows a similar result.
In this study, the antioxidant activity of the initial raw material Robusta coffee beans used has 52.22% of antioxidant, hereinafter the control variable without the use of adsorbent (K0) is reduced to 46.17%. According to Handy et al., (2016), a high temperature is one factor that is decreasing in the antioxidant activity, where bioactive components such as flavonoids, tannins, and phenols damaged at temperatures above 50ºC could undergo a structural change.

3.4. Caffeine ingredients

Caffeine is the alkaloid found in coffee beans, guarana seed, tea leaf (theine) and cola fruit. Based on the FDA (Food Drug Administration) the permitted caffeine dose is 100–200 mg/day, while according to SNI 01–7152–2006, the maximum limit of caffeine in foods and beverages is 150 mg/day or 50 mg/serving. Each type of coffee contains different caffeine dose, the Robusta coffee contains 2.473% caffeine while Arabica coffee contains 1.994% caffeine [24].
Results of the analysis of variance in the level of 5% indicate that the interaction between type and concentration of adsorbent gives a significant effect on the caffeine content of coffee powder produced. Impact of the type and concentration of the adsorbent on the caffeine content can be seen in figure 4.

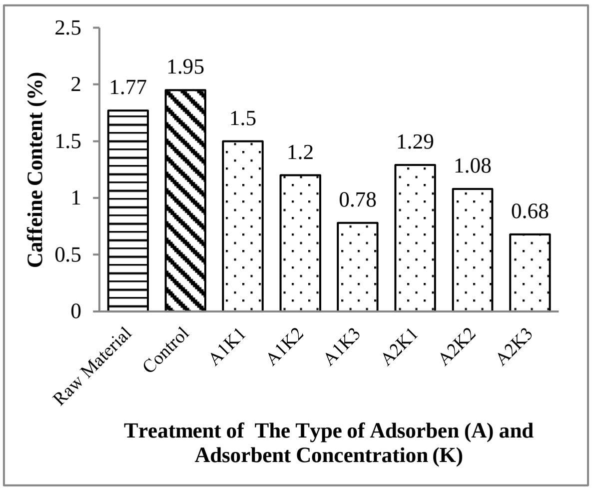

Figure 4. Interaction of treatment of adsorbent types and adsorbent concentration (A*K) against caffeine content parameters.

Information:
A1K1: Coconut shell active charcoal adsorbent with 5% concentration

A1K2: Coconut shell active charcoal adsorbent with 10% concentration
A1K3: Coconut shell active charcoal adsorbent with 15% concentration
A2K1: Zeolite adsorbent with 5% concentration
A2K2: Zeolite adsorbent with 10% concentration
A2K3: Zeolite adsorbent with 15% concentration

Based on figure 4, the caffeine content produced by all combinations with the adsorbent in Robusta decaffeinated coffee powder was collected from 0.68% - 1.50% while that of commercial ground coffee containing caffeine increased by 1.09% - 2.20%. The highest caffeine content in A1K1 training (Adsorbent of coconut shell activated charcoal with a concentration of 5%) was 1.50% and the lowest value on maintenance of A2K3 (Adsorbent zeolite with a concentration of 15%) was 0.68%. The results of the analysis also obtained the initial caffeine content of raw materials, which is 1.77% and the caffeine content of the control arrangement of the adsorbent concentration of 0% (K0) is 1.95%.

Based on the results of the 5% HSD test, it was found that the caffeine content of the coconut shell activated charcoal active adsorbent was significantly different from the treatment of zeolite adsorbents. The treatment of coconut shell active charcoal adsorbent produced a higher caffeine content compared to the type of zeolite adsorbent. This was caused by the difference in the absorption of each adsorbent to the caffeine compound. The results of a further HSD 5% test in the caffeine content shows that the content of activated charcoal in the coconut shell (A1) is 1.17%, while in the zeolite (A2) is 1.02%. Based on the explanation, it can be seen that the zeolite adsorbent has a higher absorption capacity of caffeine compounds than the adsorbent of coconut shell activated charcoal. This difference in absorbency could be caused by the differences in pore size and surface area of each adsorbent.

Caffeine has a molecular density of 1.23 g/cm^3 [25]. According to [7], zeolite is a unique adsorbent, because it has a very small and uniform pore size compared to the other adsorbents such as activated carbon and silica gel. Therefore, zeolites are only able to absorb molecules with the same or smaller diameter than the diameter of the cavity gap, while molecules with larger diameters of zeolite pores will be held back and will only cross between particles. Zeolites contain molecular scale pores and cavities with a size range of 3–15 Å, whereas for carbon or activated charcoal, according to [23] the average pore diameter size is 21.6 Å. According to IUPAC, porous material can be classified based on its size, i.e. microporous material (pore diameter < 20 Å), mesopore material (pore diameter 20–50 Å) and macrospore material (diameter > 500 Å), therefore carbon or activated charcoal categorized as mesoporous material and zeolites as micropore material. Based on the explanation, the smaller the pore diameter of the adsorbent, the greater the surface area and the absorption capacity possessed. This is in line with [26] research on the comparison of zeolite and activated charcoal absorption in the Pb metal adsorption process showed that the absorption of zeolite against Pb metal was greater at 99.03% compared to activated charcoal, which was 65.57%. Zeolite as an adsorbent is selective and has a high absorption capacity. Likewise, with [27], the study was a comparison of the absorption of activated charcoal, zeolite and silica gel against heavy metals in leach ate. The results of the comparison of absorption in each adsorbent were 1.3: 2.2: 1.0. The biggest reduction was by zeolite with a doubling of silica gel which causes the decrease in the heavy metal Fe.

Based on the results of the 5% HSD test, the caffeine content of the different adsorbent concentrations gave a significant effect. The treatment of the adsorbent concentration had an effect, which is the ability to capture caffeine compounds. Evidence in the results obtained is the higher the concentration of the adsorbent, the caffeine content decreases. This is in line with the ability of the adsorbent that is able to absorb the compounds in coffee extract, one of which is caffeine compounds. The higher the concentration of the adsorbent used, the more the absorbed compounds will be, this is what causes a decrease in the higher caffeine content in the treatment of higher concentrations of adsorbents. The results of the 5% HSD test on the treatment of the concentration of the adsorbent decreases in line with the increasing concentration of the adsorbent used.

The caffeine content produced by Robusta decaffeinated coffee powder in all treatments was ranged between 0.68% - 1.50%. The results of the analysis of the caffeine content produced fulfil the

Indonesian National Standard 01–3542–2004 which regulates the quality requirements of ground coffee to be at maximum of 2% b/b.

3.5. Colours
Colour is the term for all sensations that arise from the retinal activity of the eye and is associated with the mechanism of nerves when something reaches the eye. The nature of vision or appearance of a product is the first characteristic observed by consumers while other properties will be valued later. Colour is included in appearance. Therefore, colour is one of the most important sensory quality elements [36]. Colour analysis was carried out using the Chromameter Minolta CR 300 tool. Colour analysis was carried out to determine the white degree or brightness of coffee powder based on L* values and candied colour schemes based on values a and b.

3.5.1. L value.* Lightness (L) shows the brightness interval at the appearance of a material. The results are in the form of numbers ranging from 0–100. The smaller the number, the darker the appearance of the material and vice versa. The results of analysis of variance at the level of 5% showed that the interaction of the type and concentration of adsorbent did not give a significant effect on the value of L* at the decaffeinated ground coffee produced. The detailed results are explained in figure 5 below.

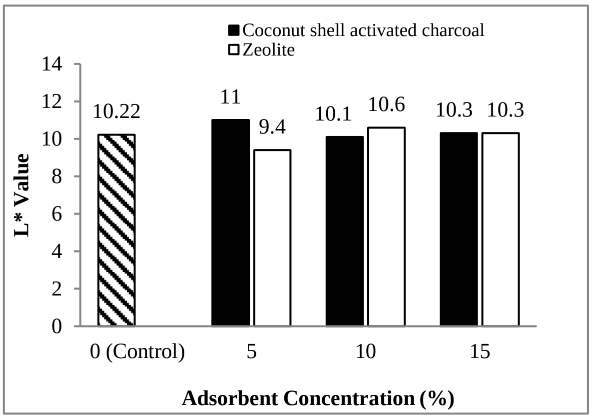

Figure 5. The influence of type and concentration of adsorbent against *L** value of robusta coffee decaffeinated powder.

Based on figure 5, the average colour of the L* value in coffee powder was ranged from 9.41 to 11.03. Based on the graph, the treatment of different types of adsorbents: adsorbent of coconut shell activated charcoal and zeolite adsorbent gave a significant effect on the L* value of Robusta decaffeinated coffee powder. The treatment of different adsorbent concentrations of 5%, 10% and 15% also had a significant effect on the L* value of Robusta decaffeinated coffee powder. The value of L* produced in the treatment of the coconut shell activated charcoal adsorbent with the concentrations of 5%, 10% and 15% respectively is 11.03; 10.12 and 10.34. The L* value in the treatment of zeolite adsorbent concentrations of 5%, 10% and 15% in succession, among others are 9.41; 10.59 and 10.34. The results of the analysis also obtained an L* value in the control treatment of 0% (K0) adsorbent and concentration of 10.22.
A low L* value (dark) can be caused by a Maillard reaction that occurs between a primary amine group of proteins and reducing sugars which produce a brownish yellow colour called melanoidin [37]. The Maillard process occurs in coffee beans due to the high temperature in the roasting process that obtained a dark coloured coffee.

3.5.2. Degree of hue value. Degree of hue is the dominant spectrum colour according to its wavelength which is expressed based on the values of a and b. Colour descriptions based on °Hue values are divided into 10 groups: red, yellow red, yellow, yellow green, green, blue green, blue purple and red purple. The results of the variance analysis at the level of 5% showed that the interaction adsorbent type concentration did not have a significant effect on the value of ºHue decaffeinated ground coffee produced. The effect of type and concentration of adsorbent on the value of ºHue Robusta coffee decaffeinated powder can be seen in figure 6.

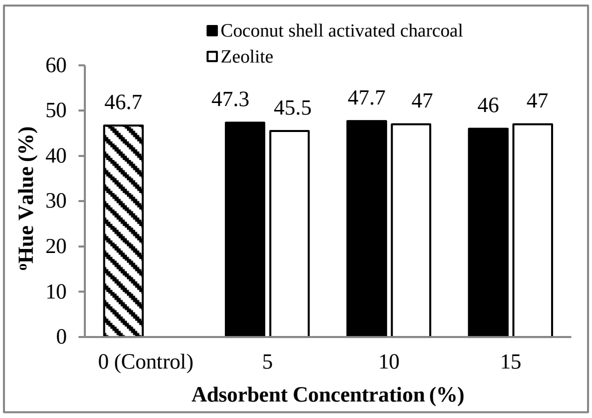

Figure 6. The influence of type and concentration of adsorbent against degree of hue value of robusta coffee decaffeinated powder.

Based on figure 6, it shows that the average ºHue value of coffee powder ranges from 45.56 to 47.75. Based on the graph, the treatment of different types of adsorbents, namely the adsorbent of coconut shell activated charcoal and zeolite adsorbent had a significant effect on the value of ºHue decaffeinated Robusta coffee. The treatment of different adsorbent concentrations of 5%, 10% and 15% also gave a significant effect on the ºHue value of Robusta decaffeinated coffee powder. The ºHue value produced in the treatment of coconut shell activated charcoal adsorbent concentration of 5%, 10% and 15% is 47.26; 47.75 and 46.03 respectively. ºHue in the treatment of zeolite adsorbent concentrations of 5%, 10% and 15% are 45.56; 46.94 and 47.06. The results of the analysis also obtained a ºHue values in the control treatment of 0% (K0), which is 46.67.

The mean colour of the ºHue value of the main treatment of Robusta decaffeinated coffee powder in this study ranged from 45.56 to 47.75. This shows that the coffee powder produced is in the vulnerable red colour of ºHue value. Roasting is one process that plays an important role in the formation of colour in coffee. The colour is produced because of the Maillard reaction which results in the emergence of carbonyl compounds (reduction groups) and amino groups. Maillard reaction is a non-enzymatic browning reaction that produces complex compounds with a high molecular weight. In this reaction, condensation occurs between amino acids or proteins with sugar [28].

3.6. Aroma

Aroma is a value contained in products that can be directly enjoyed by consumers [29] states that the aroma of a product in many ways determines the smell of a product; even the aroma or smell is more complex than taste. Sensory sensitivity is usually higher than sensory taste. Even the food industry considers odour testing to be very important because it can quickly provide results for the assessment of a product. The results of the diversity analysis at the level of 5% showed that the interaction of the type of adsorbent and the concentration of the adsorbent had no significant effect on the organoleptic aroma of the hedonic method and scoring. The detailed result can be seen in figure 7.

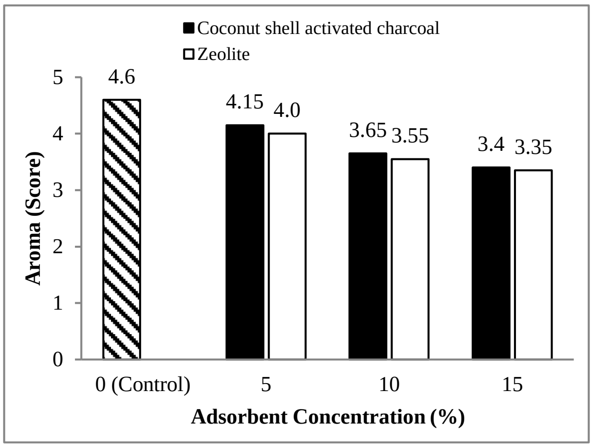

Figure 7. The effect adsorbents type and concentration on organoleptics aroma of robusta coffee decaffeinated powder using hedonic method.

Based on figure 7, overall, the panellists gave a value of 3.35 (rather like) - 4.60 (very like) on each treatment for the aroma organoleptic test of the hedonic method. The hedonic aroma value given tends to decrease in line with the increasing concentration of the adsorbent. The highest value was obtained in the control treatment with a value of 4.60 and the lowest value was obtained in the A2K3 treatment (15% zeolite adsorbent) with a value of 3.35. The effect of the type and concentration of the adsorbent on organoleptic Robusta decaffeinated coffee powder scoring method can be seen in figure 8.

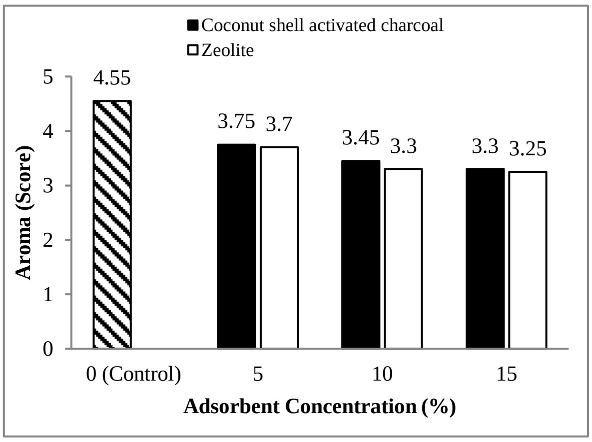

Figure 8. The effect of type and concentration of adsorbents on organoleptic aroma of robusta coffee decaffeinated powder using scoring method.

Based on figure 8, overall, the panellists gave a score of 3.25 (the aroma of coffee was rather strong) - 4.55 (the aroma of coffee was very strong). The scent value of the scoring given also decreases in line with the increasing adsorbent concentration. The highest value obtained was in the control treatment with a value of 4.55 and the lowest value was obtained in the treatment of A2K3 (15% zeolite adsorbent) with a value of 3.25. This is caused by the ability of the adsorbent to absorb aroma-giving compounds in coffee such as caffeol. The higher the concentration of the adsorbent, the more compounds are absorbed so that the aroma of the coffee produced will disappears. This is in line with the statement of [30], that activated carbon has the ability to absorb odours, colours, gases and metals, as well as zeolite adsorbents. [31] stated that the commercial application of zeolite adsorption ability is to eliminate odours.

According to [32], the aroma formation that is typical to coffee is caused by the caffeine and other coffee-forming compounds. The aroma formation also depends on the formation of compounds that are volatile and do not evaporate. Volatile acids are formed due to the degradation of carbohydrate, protein and fat compounds in the final stages of the pyrolysis process. The results of the organoleptic analysis of aromas produced can meet the Indonesian National Standard 01–3542–2004 which regulates the quality requirements of ground coffee.

3.7. Taste

Taste is a reaction caused by the stimulation of olfactory receptor cells and salivary glands to a material that enters the mouth. Taste is one of the factors that influence consumer acceptance of a product [33].The results of the variance analysis at the level of 5% showed that the interaction between the type and the concentration of the adsorbent had no significant effect on the organoleptic taste of the hedonic and scoring method. The effect of the type and concentration of the adsorbent on the organoleptic taste of Robusta coffee decaffeinated powder using hedonic method can be seen in figure 9.

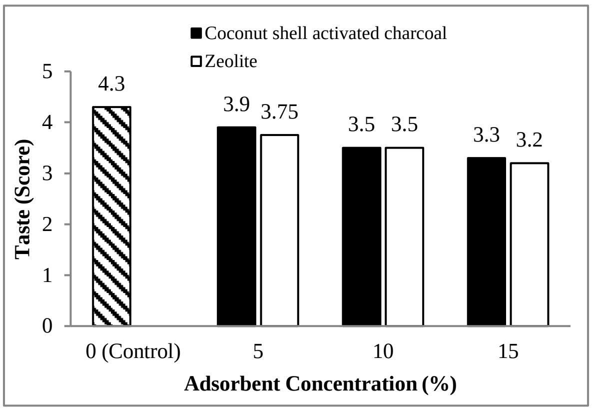

Figure 9. The effect of type and concentration of adsorbents on the organoleptic taste of robusta coffee decaffeinated powder using hedonic method.

Based on figure 9, overall, the panellists gave a score of 3.20 (rather like) - 4.30 (likes) in each treatment for the organoleptic test of the taste of the hedonic method. The hedonic taste value given decreases as the adsorbent increases. The highest value was obtained in the control treatment with a value of 4.30 and the lowest value was obtained in the treatment of A1K3 (adsorbent of coconut shell activated charcoal concentration of 15%) with a value of 3.20. The effect of the type and concentration of the adsorbent on the organoleptic taste of Robusta decaffeinated coffee powder using scoring method can be seen in figure 10.

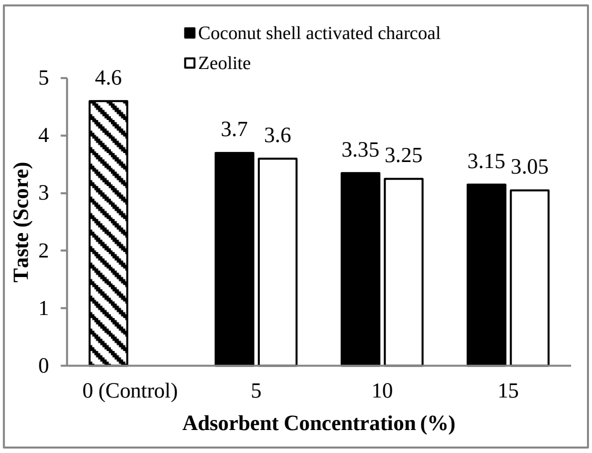

Figure 10. The effect of type and concentration of adsorbents on organoleptic taste of robusta coffee decaffeinated powder using scoring method.

Based on figure 10, overall, the panellists gave values ranging from 3.05 (somewhat bitter) - 4.60 (very bitter) in each treatment. The value of the taste of the scoring given also decreases as the adsorbent increases. The highest value was obtained in the control treatment with a value of 4.60 and the lowest value was obtained in the treatment of A2K3 (15% zeolite adsorbent) with a value of 3.05. The results of the taste organoleptic analysis produced can meet the Indonesian National Standard 01–3542–2004 which regulates the quality requirements of ground coffee.
[34] states that the taste in coffee is influenced by the results of degradation of several compounds such as carbohydrates, alkaloids, chlorogenic acid, volatile compounds, and trigonelline. In the roaring process, there is a lot of caffeine loss due to degradation. Caffeine has a strong bitter taste besides chlorogenic acid and trigonelline. Caffeine contributes as much as 10% in the formation of bitter taste. Chlorogenic acid decomposes as much as 50% during roasting and will disappear in the degree of "heavy roast" roasting. Whereas trigonelline is only 15% decomposed for each degree of roasting. This decomposition event occurs in the pyrolysis stage. Pyrolysis occurs when temperatures reach 200ºC. According to [35], the bitter taste of coffee extract was caused by the content of minerals along with the breakdown of crude fibre, chlorogenic acid, caffeine, tannin, and other organic and inorganic compounds. Therefore, the taste in coffee is influenced by the degree of roasting and the type of coffee and how it is processed.

4. Conclusions
Based on the analysis of the research, there are several conclusions that can be made:
- The interaction between type and concentration of the adsorbent gives a significant effect on the parameters of caffeine content, but did not give a significant effect on the parameters of the moisture content, ash content, antioxidant activity, ºHue value, L* value, organoleptic aroma (Hedonic and scoring method) and organoleptic taste (Hedonic and scoring method),
- The treatment of the type of coconut shell activated carbon adsorbent (A1) and zeolite (A2) provides a significant effect on the parameters of antioxidant activity and caffeine content, but not on the parameters of moisture content, ash content, ºHue value, L* value, organoleptic aromas (Hedonic and scoring method) and organoleptic taste (Hedonic and scoring method),
- The treatment of the adsorbent concentration of 5%, 10% and 15% gives a significant effect on the parameters of antioxidant activity, caffeine content, organoleptic of aroma (hedonic and scoring method) and organoleptic taste (hedonic and scoring method), but not on the parameters of moisture content, ash content, ºHue value and L* value.
- The best treatment was the use of the adsorbent in the process of coffee decaffeination methods, which is swiss water treatment types of zeolite adsorbent with a concentration of

15% (A2 K2) with the highest caffeine reduction. In this treatment, the robusta coffee powder produced has 4.59%; moisture content 4.77%; ash content, 23.58%; the antioxidant activity, 0.68% caffeine content, 47.06 ºHue value, 10.34 L* value, aroma scoring of 3.25 (a rather strong coffee aroma), aroma hedonic of 3.35 (a bit like), taste scoring of 3.05 (slightly bitter) and a taste of hedonic of 3.20 (a bit like).

References

[1] Rahadian D 2011 Proses Dekafeinasi Kopi 10 [Online]. Available: https://rahadiandimas.staff.uns.ac.id/files/2011/10/Proses-Dekafeinasi-Kopi.pdf. [Accessed 01 2018]
[2] Mulato S, Widyotomo S and Lestari H 2001 Water Extraction of Caffeine in Robusta Coffee Using a Fixed Bed Column *Pelita Perkebunan* **17**(2) 97–109
[3] Clarke R J and Macrae R 1985 *Coffee Volume 2 Technology* **24** 3 397
[4] BPOM, KETENTUAN POKOK PENGAWASAN SUPLEMEN MAKANAN 2004. [Online]. Available: https://asrot.pom.go.id/img/Peraturan/Keputusan%20Kepala%20BPOM%20No.%20HK.00.05.23.3644%20tentang%20Ketentuan%20Pokok%20Pengawasan%20SM.pdf. [Accessed 01 2018]
[5] Widyotomo S, Mulato S, Purwadaria H K and Syarief A M 2009 Decaffeination Process Characteristic of Robusta Coffee in Single Column Reactor Using Ethyl Acetate Solvent, *Pelita Perkebunan*, **25(**2) 101–25
[6] Eugen B 1939 Process for decaffeinating coffee United States of America Patent U S2198859A
[7] Khairinal andTrisunaryati W 2000 Dealuminasi Zeolit Alam Wonosari dengan Perlakuan Asam dan Proses Hidrotermal *Seminar Nasional Kimia V II I* (Yogyakarta)
[8] Newsam 1991 Zeolites *Solid State Chemistri* (Carindon Press)
[9] Hanafiah 2003 *Design of Theory and Application Trial* (Jakarta: PT Raja Grafindo Persada)
[10] WinarF G 1997 *Kimia Pangan dan Gizi* (Jakarta: Gramedia Pustaka Utama)
[11] Guntarti A 2015 Penentuan parameter NON spesifik Ekstrak Etanol Kulit Buah Manggis (Garcinia Mangostana) pada Variasi asal daerah, *Jurnal Farmasains* **2**(5) 202–7
[12] Kurniawan D 2016 Pemanfaatan Media Bambu Sebagai Adsorbent Penyerap Logam Timbal (Pb) Dengan Perbandingan Tanpa Aktivasi Dan Aktivasi Dengan Asam Sitrat (Yogyakarta: Universitas Islam Indonesia)
[13] Yuliusman Y, Purwanto W W and Nugroho Y S 2013 Pemilihan Adsorben Untuk Penjerapan Karbon Monoksida Menggunakan Model Adsorpsi Isotermis Langmuir, *Reaktor: Chemical Engineering Journal* **14** 3 225–33
[14] Winarno 2008 Kimia Pangan dan Gizi: Edisi Terbaru (Jakarta: Gramedia Pustaka Utama)
[15] Sandjaja andAtmarita 2009 Kamus Gizi Pelengkap Kesehatan Keluarga, (Jakarta: PT Kompas Media Nusantara)
[16] Sulastri 2007 Pengaruh Penggunaan Zeolit dalam Ransum terhadap Konsumsi Ransum, Pertumbuhan, dan Persentase Karkas Kelinci Lokal Jantan, *Zeolite Journal of Indonesia* **6**(1) 38–42
[17] C Erna 2012 Uji Aktivitas Antioksidan dan Karakteristik Fitokimia pada Kopi Luwak Arabika dan Pengaruhnya terhadap Tekanan Darah Tikus Normal dan Tikus Hipertensi (Universitas Indonesia Jakarta: Fakultas Matematika dan Ilmu Pengetahuan Alam)
[18] Aqil F, Ahmad I and Mehmood Z 2006 Antioxidant and Free Radical Scavenging Properties of Twelve Traditionally Used Indian Medicinal Plants *Turk. J. Biol.* **30** 177–83
[19] Winarsi H 2007 Antioksidan alami dan radikal bebas potensi dan aplikasinya dalam kesehatan (Yogyakarta: Kanisius)
[20] Saloko S 2014 Nanoenkapsulasi Asap Cair dalam Kitosan dan Maltodekstrin Menggunakan Teknik Spray Drying (Yogyakarta: Universitas Gadjah Mada)

[21] Harahap M R 2017 Identifikasi Daging Buah Kopi Robusta (Coffea robusta) Berasal Dari Provinsi Aceh., *Journal of Islamic Science and Technology* **3**(2) 201–10
[22] Sembiring M T and Sinaga T S 2003 Arang Aktif Pengenalan dan Proses Pembuatannya (Medan: Universitas Sumatera Utara)
[23] Allport H B 1997 Activated Carbon *Encyclopedia of Science and Technology* (New York: Mc Graw Hill Book Company)
[24] Elina and Hartono 2009 Penetapan Kadar Kafein Dalam Biji Kopi Secara Kromatografi Cair Kinerja Tinggi *Biomedic Journal* **2**(1) 72–80
[25] Mumin A, Kazi F A, Zainal A and Zakir H 2006 Determination and Characterization of Caffeine in Tea, Coffee, and Soft Drink by Solid Phase Extraction and High Performance Luquid Chromatography (S PE –H P L C) *Malaysian Journal of Chemistry* **8**(1) 45–51
[26] Heltina D, Wijaya D S K and Rahmi N 2006 Perbandingan Daya Jerap Zeolit Aktif Dan Arang Aktif Pada Proses Adsorpsi Logam Pb (Universitas Riau, Pekanbaru)
[27] Larasati A I, Susanawati L D and Suharto B 2016 Efektivitas Adsorpsi Logam Berat Pada Air Lindi Menggunakan Media Karbon Aktif, Zeolit, Dan Silika Gel Di Tpa Tlekung, Batu *Jurnal Sumberdaya Alam dan Lingkungan* **1**(1) 44–8
[28] Jing H and Kitts D D 2002 Chemical and Biochemical Properties of CaseinSugar Maillard Reaction Product *Food Chem. Toxicol.* **40**(7) 1007–15
[29] Soekarto 1985 Penilaian Organoleptik (untuk Industri Pangan dan Hasil Pertanian), (Jakarta: Bharata Karya Aksara)
[30] Ramdja A F, Halim M and Handi J 2008 Pembuatan karbon aktif dari pelepah kelapa (Cocusnucifera) **15**(2)1–8
[31] Whitelaw M 2003 Zeolite: A cyber interview,. [Online]. Available: www.markw.com/zeointvw.htm. [Accessed 13 03 2019]
[32] Sivetz M 1972 *How Acidity Affects Coffee Flavour* (Westport: Connecticut: The A VI Publishing Company Inc)
[33] Winarno 2002 Kimia Pangan dan Gizi (Jakarta: Gramedia)
[34] Sari L I 2001 Mempelajari Proses Pengolahan Kopi Bubuk (Coffea canephora) Alternatif dengan Menggunakan Suhu dan Tekanan Rendah, (Bogor: Institut Pertanian Bogor)
[35] Jacob M B 1951 The Chemistry and Technology of food Product (New York: Interscience Publ. Inc.)
[36] Kramer and Twigg 1983 Mutu Produk Secara Organoleptik diterjemahkan oleh Adia (Jakarta: Universitas Indonesia Press)
[37] Makfoeld D 2002 Kamus Istilah Pangan dan Nutrisi (Yogyakarta: Penerbit Kanisius)

Acknowledgments
Authors thank to The Ministry of Research, Technology and Higher Education of the Republic of Indonesia for research funding through student joint research program.