The Effect of Demineralization Stage of Agar’s Solid Waste on the Characterization of Activated Carbon

R Febrianto1, Sudarno2, R Kusdarwati2
1Aquaculture, Faculty of Fisheries and Marine, Universitas Airlangga, Surabaya, Indonesia
2Department of Fish Health Management and Aquaculture, Faculty of Fisheries and Marine, Universitas Airlangga, Surabaya, Indonesia

Correspondence author: darnosudarno1@gmail.com

Abstract: Agar’s solid waste contains quite high amount of crude fiber at 38.05%, so it can be used as activated carbon. Activated carbon is carbon whose configuration of carbon atoms is freed from bonding with other elements. The effectiveness of activated carbon as an adsorbent is seen from the ash content. High level of ash in a material can reduce the ability of activated carbon in the adsorption process, making it undesirable in the manufacture of activated charcoal. Demineralization using HCl solution can affect the decrease in ash content. This study used the experimental method of pre-post test and the analysis was carried out using the associated T-Test (paired T-Test). Pre-test was conducted using 0% HCl or without demineralization and Post-test was conducted using 5% HCl. Study results show that there is no effect on the characteristics of ash content, volatile substances, pure activated carbon, yield and there is effect on water content. It indicates that demineralization process using 5% HCl on the yet optimum material does not have tangible impact on the resulted ash content and characteristics of activated carbon.

Keywords: Demineralization, characterization, activated carbon, agar’s solid waste

1. Introduction

Agar is a commodity that has long existed and is known in Indonesia. Agar is a polysaccharide compound obtained from the processing of rhodophyceae (red algae) seaweed which has agarophyte compounds, as well as Gracillaria sp. (Sari, 2013). Gracillaria verrucosa is one type of rhodophyceae used as agar because it has a higher agarose content compared to agarpectin (Riswanti, 2013). The agar processing industry produces quite a lot of solid waste. Kim et al. (2007) stated that the companies are able to produce solid waste at 65-75% of the amount of raw material used for each production cycle. Solid waste of agar contains quite high crude fiber amounted to 38.05%, so that it can be used as activated carbon (Faujiah, 2012).

Activated carbon is carbon whose configuration of carbon atoms is freed from bonding with other elements. Activated carbon is made through three stages, namely dehydration, carbonation, and activation. Dehydration aims to eliminate water content from the material. In carbonation process, decomposition of raw material of carbon will occur with the break of chemical bonds and depolymerization, resulting in new bond. Activation process is performed by soaking charcoal in an activator solvent, enabling the activator to diffuse into the charcoal’s pores. Activator solvent will be adsorbed by charcoal that will dissolve tar and inorganic minerals (Danarto and Samun, 2008). Activator and time are determinant to the making of activated carbon. If the activation time used is too fast, activator material will not be completely detached...
from activated carbon, while if it is too long, the structure will be damaged (Sani, 2011).

The effectiveness of activated carbon as an adsorbent is also seen from the ash content. In the study conducted by Faujiah (2012), activated carbon with ZnCh activator has 68.21% ash content. The high ash content in a material may reduce the ability of activated carbon in adsorption process, making it undesirable in the making of active charcoal (Suwilin, 2007). Agar’s processing, which uses chemicals such as CaO or NaOCl in the bleaching process as well as a number of acid and alkaline solution in the extraction process, is assumed to cause the high level of ash in agar’s solid waste. On the basis of such issue, it is necessary to conduct demineralization stage on agar’s solid waste materials. Demineralization aims to eliminate minerals in the agar’s solid waste and examine the characteristics in the resulted activated carbon.

2. Material and methods
2.1 Place and Time of Research
This study was conducted from March to August 2017 in Laboratory of Education, Faculty of Fisheries and Marine, Universitas Airlangga, Surabaya.

2.2 Materials and Tools
Tools required in this study are electric furnace, oven, hot plate, pH paper, beaker glass, Erlenmeyer flask, stirring stick, measuring cup, analytical scales, porcelain cup, desiccators, crucible tongs, thermometer, volume pipette, drop pipette, rubber bulb, burette and support stand. Materials used in this study are zinc chloride (ZnCl2), 5% HCl, aquades, and agar’s solid waste obtained from PT. Kappa Carrageenan Nusantara, Pasuruan District, East Java.

3. Research Procedure
Making activated carbon refers to the method used by Faujiah (2012) which has been modified; 20 grams of agar solid waste with demineralization and without demineralization, both dried and carbonated at a temperature of 400°C for 10 minutes until charcoal is generated. The charcoal is then added with ZnCl2 activator at 40 mL volume with 4 M concentration. Samples were soaked in ZnCl2 activator for 10 hours at room temperature, then filtered using filter paper and the residue was collected. Residue was washed many times using aquades until it reached neutral pH. Sample was dried for 3 hours in an oven at 105°C temperature, then cooled in a desiccator. The produced activated carbon was then characterized.

3.1 Characterization of Activated Carbon
a. Ash Content
Ash content testing in activated carbon refers to the method applied by Association of Official Analytical Chemist (AOAC) (2005), in which cup was cleaned and dried in an oven for 30 minutes at 105°C temperature, then put in the desiccator and scaled. Five grams of sample was scaled and put into ignition furnace (600°C) for 6 hours. The cup was put in the desiccator and scaled. Ash content was determined using the following formula:

\[
\text{Ash content (\%) = \frac{\text{weight of ash}}{\text{weight of sample}} \times 100}\%
\]

b. Volatile Substance Content
Analysis of volatile substance content was conducted based on American Society for Testing and Material (ASTM) (1999) method, in which 1 gram of sample was put in the porcelain cup with recorded dry weight, then heated in the furnace at 950°C for 10 minutes. Calculation of volatile substance content used the following formula:
Volatile substance content (%) = \( \frac{B - A}{100\%} \)

Description:  
A = Weight of empty cup (gram)  
B = Weight of cup with sample (gram)  
C = Weight of cup with dried sample (gram)

c. Analysis of Pure Activated Carbon Content  
Content of bound or pure activated carbon was determined in accordance with Indonesian National Standard (1995) with the following calculation:  
Pure activated carbon content (%) = \( 100\% - (B + C) \)

Description:  
B = Volatile substance content (%)  
C = Ash content (%)

d. Yield Calculation  
Activated carbon yield is the weight of activated carbon resulted compared to the total raw material. Activated carbon yield was determined according to Indonesian National Standard (1995) with the following equation:  
\[ \text{Yield} \times 100\% = \frac{\text{Weight of activated carbon}}{\text{Weight of raw material}} \]

e. Water Content Analysis  
Testing the water content of activated carbon refers to the method applied by Association of Official Analytical Chemist (AOAC) (2005), in which an empty cup and dried in an oven for ±30 minutes at 105°C temperature, then put in the desiccator for 15 minutes and scaled. Five grams of sample was scaled and put in the cup and dried for 6 hours at 105°C temperature. The cup was put in the desiccator for 30 minutes and re-scaled. Water content was determined by the following formula:  
\[ \text{water content(\%)} = \frac{B - C}{B - A} \times 100\% \]

Description:  
A = Weight of empty cup (gram)  
B = Weight of cup with sample (gram)  
C = Weight of cup with dried sample (gram)

3.2 Data Analysis  
The collected data was then analyzed using SPSS 16.0 software (SPSS, Inc., Chicago, IL) and Dependent T-Test (Paired T-Test). Prior to the T-Test, data normality testing was conducted to identify if the data distribution is normal or not. Data analysis results of characteristics of activated carbon was compared with Indonesian National Standard (SNI) in terms of activated carbon.

4. Results and Discussion

4.1 Results  
The effect of using HCl on the demineralization process may increase the value of pure activated carbon and yield, and may reduce the value of ash content, water content and content of volatile substances. This value can be seen in Figure 1 to Figure 5.
4.2 Discussion

Ash content is one of the impurity components that can affect the quality of activated carbon. Ash content is the remaining mineral left behind when carbonated. Figure 1 shows a decrease in ash content in activated carbon with demineralization process. It is because the use of HCl in the demineralization process can eliminate minerals contained in the materials. The high level of ash in both samples exceeds the value of Indonesian National Standard (SNI), of which the level of ash in activated powder carbon is 10%. The time of soaking and given concentration of activator can also influence ash levels. In Prastiwi’s (2014) research, the more time of activation the higher the ash level due to the more time of activation the more pores opened.

The concentration of ZnCh solution as an activator can expand the surface of activated charcoal because more pores are also produced (Faujiah, 2012). In the formation of pores, a combustion process occurred on the surface of the activated carbon which produces ash, so that the more pores
produced, the higher the ash content (Pambayun et al. 2013). The activator substances that are not washed perfectly during neutralization can also increase the activated charcoal ash content produced (Verla et al. 2012).

The analysis of levels of volatile substances aims to determine the levels of substances that have not evaporated at the temperature of the carbonation and activation process but evaporate at 950°C. There is a decrease in the level of volatile substances on activated carbon with the addition of demineralization process in Figure 2. Testing the level of volatile substances is highly necessary because the data was used to calculate the levels of pure activated carbon in the sample. The value of volatile substances has met the SNI-06-3730-1995 standard because it is less than 25%.

The volatile substance content in the study results is lower when compared to Faujiah’s (2012) study, which stated that the volatile substances content of activated carbon from agar solid waste uses a 4M ZnCl₂ activator at 7.33%. The optimal activation time affects the level of volatile substances. In Prastiwí’s (2014) study of activated carbon with different concentrations of ZnCl₂ activators, optimal results were obtained at the activation time of 20 hours. This was also stated in the Rasjidin’s (2006) study, that the decrease in volatile substance levels along with the duration of activation time was a result of the activator substances used being increasingly absorbing, coating and protecting the surface of activated carbon from heat.

Testing the level of pure activated carbon aims to determine the amount of pure activated carbon remaining after the carbonation process. Pure activated carbon is the amount of activated carbon bound in charcoal (Prastiwí, 2014). There is an increase in the pure activated carbon level in activated carbon by the demineralization process in Figure 3. In the results of the study, the levels of pure activated carbon from both samples are not in accordance with SNI-06-3730-1995 which calls for at least 65% for pure activated carbon in powder form. High and low levels of pure activated carbon depend on the ash content and the level of volatile substances. The higher the ash content and the level of volatile substances, the lower the level of pure activated carbon (Zaqyyah, 2017).

The activated carbon yield is one of the parameters used to determine the final weight of activated carbon produced from the initial raw material. Faujiah (2012) stated that yield is usually considered for the economic side of a material. The average yield value is 88.50% for the yield of activated carbon with the addition of the demineralization process and 88.89% in the yield of activated carbon without the addition of the demineralization process (Figure 4). This is in accordance with the research conducted by Faujiah (2012), in which the yield of activated carbon from agar-agar solid waste with ZnCl₂ activator is 87.19% and in Prastiwí’s research (2014) claiming that the yield of activated carbon from solid waste is 95.83-97.01%. The high yield is caused by the type of activator. As an activator agent, ZnCl₂ is more suitable for maintaining heat in the carbonation process of palm fronds so as to prevent further oxidation of carbon (Esterlita and Herlina, 2015).

Determination of water content aims to learn the hygroscopic nature of charcoal. The presence of water in charcoal is related to the hygroscopic nature of the charcoal itself, that charcoal has a great affinity for water (Khairani et al., 2015). Through the water content testing, it can be seen how much water can be evaporated so that the water bound to the activated carbon does not cover the pore of the activated carbon itself. There is a decrease in the water content of the activated carbon by the demineralization process (Figure 5). The loss of water molecules in the activated carbon causes the pores in the activated carbon to increase. The larger the pores, the larger the surface area of activated carbon (Herlandien, 2013).

The water content of activated carbon in the study meets the standards of SNI-0603730-1995, which states that the maximum value of water content of powdered activated carbon does not exceed 15%. Water content in activated carbon is influenced by the water content that is bound to the material that has evaporated during the process of dehydration and also carbonation. High water content can reduce the active adsorption of charcoal against liquids and gases (Wijayanti, 2009).

5. Conclusion and suggestions
From the results of the study, it can be concluded that the demineralization stage using 5% HCl in
agar-agar solid waste material does not affect the ash content of the activated carbon produced. The yield, moisture content, volatile substances, and pure activated carbon tests were carried out to learn the different characteristics of activated carbon with the demineralization stage and without the demineralization stage. The demineralization stage of agar solid waste using 5% HCl only affects the water content and has no effect on yield, volatile substances and levels of pure of activated carbon. Th researchers suggest that research should be conducted on the optimal concentration of HCl at the time of demineralization of agar-agar solid waste materials in order to provide a decrease in ash content that is consistent with the standards and to use the optimal concentration of ZnCh activator for activated carbon activation.

6. References
[1] Association of Official Analytical Chemist [AOAC]. 2005. Official Method of Analysis of The Association of Official Analytical of Chemist. Arlington (US): The Association of Official Analytical Chemist, Inc.
[2] American Society for Testing and Material [ASTM]. 1999. ASTM D 4607-94: Standard Test Method for Determination of Iodine Number of Activated Carbon. Philadelphia (US) : American Society for Testing and Material.
[3] Danarto, Y. C. dan T. Samun. 2008. Pengaruh Aktivasi Karbon dari Sekam Padi pada Proses Adsorpsi Logam Cr (IV): Jurusan Teknik Kimia. 7(1) : 13-16.
[4] Esterlita, M.O. dan Herlina, N. 2015. Pengaruh Penambahan Aktivator ZnCh, KOH, Dan H3PO4 Dalam Pembuatan Karbon Aktif Dari Pelepas Aren (Arenga pinnata). Jurnal Teknik Kimia. 4(1) : 47-52.
[5] Faujiah, F. 2012. Pemanfaatan Karbon Aktif dari Limbah Padat Industri Agar -agar Sebagai Adsorben Logam Berat dan Bahan Organik dari Limbah Industri Tekstil. Skripsi. Fakultas Perikanan dan Ilmu Kelautan Institut Pertanian Bogor. 61 hal.
[6] Herlandien, Y.L. 2013. Pemanfaatan Arang Aktif Sebagai Adsorben Logam Berat dalam Air Lindi di TPA Pakusari Jember. Skripsi. Fakultas Matematika dan Ilmu Pengetahuan Alami Universitas Jember. 84 hal.
[7] Khairani, F., Itnawati dan Bali, S. 2015. Potensi Arang Aktif dari Limbah Tulang Kambing sebagai Adsorben Ion Besi (III), Kadmium (II), Fluorida dan Sulfat Dalam Larutan. JOM FMIPA. Universitas Riau. 2(1) : 107-115.
[8] Kim .G.S, Myung .K.S, Kim .Y.J, Oh .K.K, Kim .J.S, Ryu .H.J and K. H. Kim. 2007. Methode of Producing Biofuel Using Sea Algae. Seoul (KR): World Intelectual Property Organization.
[9] Pambayun, G. S., Remigius, Y. E. Yulianto, M. Rachimoellah., dan Endah, M.M. Putri. 2013. Pembuatan Karbon Aktif dari Arang Tempurung Kelap da dengan Activator ZnCh dan Na2CO3 sebagai Adsorben untuk Mengurangi Kadar Fenol dalam Air Limbah. Journal Teknik POMITS. 2(1). ISSN:2337-3539.
[10] Prastiwi, A. D. 2014. Penggunaan ZnCl2 Sebagai Aktivator Karbon Aktif Dari Limbah Padat Agar Dan Aplikasinya Sebagai Adsorben Pada Limbah Cair Industri Tahu. Skripsi. Fakultas Perikanan dan Ilmu Kelautan Instituts Pertanian Bogor. 52 hal.
[11] Rasjidin, I. 2006. Pembuatan Karbon Aktif dari Tempurung Biji Jambu Mede (Anacardium occidentale) sebagai Adsorben pada Pemurnian Minyak Goreng Besak. [skripsi]. Bogor (ID): Institut Pertanian Bogor.
[12] Riswanti, F. H., Moch, Amin, A., dan Agustono. 2013. Pengaruh Medium yang Tercemar Organoklorin (Endosulfan) terhadap Dominansi Plankton pada Media Air yang Terpapar Logam Berat Cr. Jurnal Ilmiah Perikanan dan Kelautan. 5(1): 1-4.
[13] Sani. 2011. Pembuatan karbon aktif dari tanah gambut. Jurnal Teknik Kimia. 5(2): 400-406.
[14] Sari, W. T., Sudarno., dan Alamsjah, A. 2013. Pengaruh Biofilter Rumput Glacilaria sp. terhadap Dominasi Plankton pada Media Air yang Terpapar Logam Berat Cr. Jurnal Ilmiah Perikanan dan Kelautan. 5(1): 1-3.
[15] Standar Nasional Indonesia (SNI). 1995. SNI-06-3730-1995: Karbon Aktif Teknis, Badan Standar Nasional. Jakarta.
[16] Suwilin. 2007. Efektifitas Arang Aktif Kayu Sengon (Paraserianthes Falcatoria L. Nielsen) dan Tempurung Kelapa (Coconus Nucifera L.) Untuk Pemurnian Minyak Goreng Bekas. Skripsi. Fakultas Kehutanan, Institut Pertanian Bogor.

[17] Verla, A.W., Horsfall. M., Verla E.N., Spiff, A.I. and O.A. Ekpete. 2012. Preparation and characterization of activated carbon from fluted pumpkin (Telfairia occidentalis Hook.F) seed shell. Asian Journal of Natural and Applied Sciences. 1(3): 39-50.

[18] Wijayanti, D. S. 2009. Karakteristik Briket Arang dari Serbuk Gergaji dengan Penambahan Arang Cangkang Kelapa Sawit. Skripsi. Fakultas Pertanian. Universitas Sumatra Utara. 48 hal.

[19] Zaqqyah, K. 2017. Karakterisasi Karbon Aktif dari Limbah Padat Industri Agar-Agar dengan Konsentrasii Aktivator Yang Berbeda. Skripsi. Fakultas Perikanan dan Kelautan. Universitas Airlangga, Surabaya.