Inkalindo Environmental Journal (IEJ)
Website: inkalindo-journal.or.id

Vol. 1, no. 1 (2), pp. 15-32

Fabrication and Application of the NaOH-activated Sorbent from Gayo Arabica Coffee Shells for Adsorption of Lead Metal (Pb) in Liquid Waste

Pembuatan dan Aplikasi Sorben Cangkang Kopi Arabika Gayo Teraktivasi NaOH untuk Adsorpsi Logam Timbal (Pb) dalam Limbah Cair

Mariana, Dinda Fathira, Risna Safitri, and Syawaliah Muchtar

Universitas Syiah Kuala, Banda Aceh 23111, Indonesia

Corresponding author: mariana_hasyim@yahoo.com

Abstract

Indonesia is a developing country with a high level of environmental pollution, especially heavy metal pollution from industrial waste such as Pb(II). One of several environmentally-friendly separation methods that can be used to reduce levels of Pb(II) is adsorption by using waste-based biosorbent. In this study, we report the fabrication of low-cost and green adsorbent from Gayo Arabica coffee shell waste. The fabricated adsorbent is activated by NaOH to further improve its performance and is applied for the removal of Pb(II) in liquid waste. The resulting adsorbents are characterized using Scanning Electron Microscopy (SEM) to determine the morphological structure, Fourier Transform Infra-Red Spectrophotometer (FTIR) to determine the functional groups, and X-Ray Diffraction, (XRD) to determine the crystalline structure. The results show that the characterization of the two types of adsorbents meet the quality requirements according to SNI 06-3730-1995. The initial concentration of Pb(II) solution used is 300 mg/L, contact time (0, 30, 60, 90, 120 and 150 minutes) and type of activator (0.5 M NaOH and without activator). The initial concentration of Pb(II) before and after adsorption is tested using AAS. The analysis results obtained show that the maximum absorption capacity that can be carried out by the adsorbent is 271,577 mg/g and an efficiency of 90% at the equilibrium time of 120 minutes using an adsorbent NaOH 0.5 M. It is also revealed that the adsorption process of Pb(II) by coffee shell sorbent follows isotherm Langmuir model.

[*Indonesia merupakan negara berkembang dengan tingkat pencemaran lingkungan yang tinggi, terutama pencemaran logam berat seperti Pb(II) dalam limbah industri. Salah satu metode yang digunakan untuk menurunkan kadar logam berat timbal Pb(II) yang ramah lingkungan adalah metode adsorpsi dengan menggunakan adsorben cangkang kopi. Penelitian ini bertujuan untuk memperoleh karakterisasi adsorben dari cangkang kopi yang dipengaruhi oleh proses aktivasi kimia terhadap penyerapan logam berat timbal Pb(II). Adsorben yang dihasilkan dilakukan karakterisasi menggunakan Scanning Electron Microscopy (SEM) untuk mengetahui struktur morfologi, Fourier Transform Infra-Red Spectrophotometer (FTIR) untuk mengetahui gugus fungsi, dan X-Ray Diffraction (XRD) untuk mengetahui struktur kristalin. Hasil penelitian menunjukkan bahwa karakterisasi kedua jenis adsorben memenuhi syarat mutu sesuai SNI 06-3730-1995. Konsentrasi awal larutan Pb(II) yang digunakan yaitu 300 mg/L, waktu kontak (0, 30, 60, 90, 120 dan 150 menit) dan jenis aktivator (NaOH 0,5 M dan tanpa aktivator). Konsentrasi awal logam Pb(II) sebelum dan sesudah adsorpsi diuji menggunakan AAS. Hasil analisa yang diperoleh menunjukkan bahwa kapasitas penyerapan maksimum yang mampu dilakukan oleh adsorben yaitu 271,577 mg/g dan efisiensi sebesar 90% pada waktu kesetimbangan 120 menit dengan menggunakan adsorben aktivator NaOH 0,5 M. Proses adsorpsi logam berat timbal (Pb) oleh adsorben cangkang kopi mengikuti persamaan Langmuir.*]

Keywords: adsorption; coffee shell; Pb metal; biosorbent; adsorbent activation

I. Introduction

Indonesia is a developing country with a high level of environmental pollution, especially in producing heavy metals as waste. Heavy metals are a form of inorganic material that often causes serious problems, however, among various kinds of environmental pollution, water pollution is a problem that always catches the attention of many parties considering the impact it causes can have negative consequences for the lives of living things, including humans (Tchounwou et al., 2012).

Lead metal ion (Pb) is one of the heavy metals whose presence in the environment can come from the mining industry in the form of tailings, namely a metal ore processing process with a concentration ranging from 200-500 mg/L. This value is very high in relation to the Class I water quality standard, namely 0.03 mg/L (Ucun et al., 2003).

Aceh Province, to be precise in Central Aceh District, is the best quality coffee producer where the coffee shells after harvesting are immediately disposed of into the environment as waste. This waste continues to increase with the increase in coffee production in Indonesia. Based on this, the coffee shell can be transformed into activated carbon, so that it is expected to have more value than just waste from coffee production.

II. Literature Review

a. Adsorption

Adsorption is the process of collecting soluble substances (soluble) in solution by the surface of the absorbent object where a physical chemical bond occurs between the substance and its absorption (Sawyer et al., 1978). The adsorption process is described as the process of molecules leaving a solution and sticking to the surface of the absorbent due to physical and chemical bonds. According to Nasrudin (2005), adsorption is a process by which fluid molecules touch and attach to a solid surface. Meanwhile, according to Suryawan (2004), adsorption is a physical phenomenon that occurs when gas or liquid molecules are brought into contact with a solid surface.

Adsorption is a phenomenon related to surfaces where interactions between liquid or gas molecules and solid molecules are involved. This interaction occurs because of the attractive forces of atoms or molecules covering the surface. The adsorption capacity of activated carbon depends on the type of pore and the number of surfaces that may be used to adsorb (Yu et al., 2019).

Adsorption is a process that occurs when a fluid (liquid or gas) is bound to a solid and finally forms a film (thin layer) on the surface of the solid. According to Husin and Rosnelly, (2007), the absorption mechanism starts with the diffusion of the adsorbate molecules through the film around the adsorbent, followed by the movement of the adsorbate molecules through the pores and then the binding of the adsorbate molecules by the adsorbent surface.

b. Activated Carbon

Carbon is a porous solid produced from burning materials containing carbon elements. Carbon has a surface that is still covered by hydrocarbon deposits which make carbon less efficient in absorption, while activated carbon is carbon that has a surface structure that does not deposit hydrocarbons and has gone through an activation process, where activation is divided into two, namely physical activation and chemical activation. Physical activation is carried out with the help of heat, steam and CO_2 gas, while chemical activation is carried out by immersion in a chemical solution (Meisrilestari et al., 2013). The purpose of the activation process is to enlarge the pores with a surface area of activated carbon generally ranging from 300 - 3000 M2/g and this pore area is closely related to the pore structure of the activated carbon so that the absorption process is better and this depends on the activation method used. used. Activated carbon is also a porous material containing 87-97% carbon and the rest is hydrogen, oxygen, sulfur and other materials (Jorgetto et al., 2015).

Activated carbon contains 5 to 15 percent water, 2 to 3 percent ash and the rest consists of carbon. Carbon which is now widely used is in the form of granules (granular) and powder form (flour). The amount of activated carbon

absorption is strongly influenced by the state of the pores that are formed (Nurdiansah & Susanti, 2013). Activated carbon is used in the adsorption system because activated carbon has a large surface area and high absorption capacity (El-Bahy and El-Bahy, 2016).

Activated carbon is generally made from various materials that contain carbon. Such as bone, seed coat, hard and soft wood, bark, corn cobs, sawdust, rice husk, and coconut shell are examples of basic materials that are often used. Other materials that can also be used are refinery waste, peat soil, coal, cassava waste, and vegetable fiber. The production of activated carbon includes two main stages, namely the carbonization process of the raw material and the activation process of the carbonized material. Carbonization is the process of breaking down organic cellulose into carbon elements accompanied by the removal of non-carbon elements, which takes place at temperatures around 500-900° C (Zhou et al., 2015).

c. Coffee Shell

The existence of coffee shells is still agricultural waste. This waste continues to increase with the increase in coffee production in Indonesia. Based on this, the coffee shell can be made into activated carbon, so that it is expected to have more value than just waste from coffee production. The waste produced from the coffee processing process consists of the skin of the fruit (pericarp), pulp and the skin of the coffee beans, which are commonly called coffee shells. The coffee waste ranges from 50-60 percent of the harvest. Coffee shell waste has a hard texture and functions as a protector of coffee beans (Syabriana, 2018). Coffee shells are an inexpensive and easy to obtain material that can be used to reduce levels of heavy metal lead (Pb) in industrial wastewater.

The content or characteristics of coffee endocarp (shell) can be seen in Table 1 as follows.

Table 1. Coffee shell characteristics

Component	Percentage (%)
Cellulose	53,19
Hemicellulose	20,17
Lignin	28,58

Source: Forest Products Research and Development Center, 2018

d. Lead Metal

Lead is a chemical element in the periodic table which has the symbol Pb with atomic number 82. The heavy metal lead (Pb) occurs naturally in the earth's crust. Lead (Pb) can also come from the results of human activities, which is 300 times more than the natural Pb found in the earth's crust. In addition, lead (Pb) can also be sourced from industrial waste in the form of Pb (II) ions. Waste from the mining industry, metal dyes, the electricity industry, and the petroleum

industry contains undesirable amounts of Pb (II) ions with concentrations ranging from 200-500 mg/L (Ucun et al., 2003). This value is very high in relation to water quality standards based on Government Regulation Number 82 of 2001 concerning Water Quality Management of 0.03 mg/L.

III. Methods

a. Materials and Tools

The tools used in this study were Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), Surface Area Analyzer (SAA), Atomic Absorption Spectrophotometry (AAS), X-Ray Fluorescence (XRF), hot plate and stirrer, muffle furnace, 100-120 mesh mechanical sieve, and desiccator. While the materials used were Gayo Arabica coffee shells, NaOH (s) 0.5 M, Pb (NO3) 2, 0.1 N iodine solution, 1% starch indicator, 0.1 N sodium thiosulfate and distilled water.

b. Making Activated Carbon from Coffee Shells

The coffee shells were washed and dried in the sun then carbonized at 350 ° C for 120 minutes using a muffle furnace until carbon formed. The carbon is crushed using a mortal and pestle, then sieved using a 100-120 mesh sieve. Furthermore, the chemical activation process was carried out by immersing in 250 mL of 0.5 M NaOH solution and 25 grams of activated carbon with a stirring speed of 250 rpm for 3 hours. Then each mixture was filtered and washed with distilled water until the pH was neutral. After the neutral pH of the adsorbent is dried using an oven dryer with a temperature of 110 ° C until its weight is constant, this is done to remove the remaining water on the activated carbon.

c. Adsorbent Characterization

The resulting adsorbent was characterized using Scanning Electron Microscopy (SEM) to determine the morphological structure, Fourier Transform Infra-Red Spectrophotometer (FTIR) to determine functional groups, X-Ray Diffraction (XRD) to determine crystalline structure, X-Ray Fluorescence (XRF) to determine the chemical composition and concentration and Surface Area Analyzer (SAA) to determine the surface area of the adsorbent.

d. Water Content

1 gram of activated carbon is put into a weighed porcelain dish. The plates were put in an oven at 105 ° C for 3 hours then cooled in a desiccator and weighed.

$$Water\ content\ (\%) = \frac{(a-b)}{a} \times 100\% \qquad (1)$$

Where, a is the weight of the initial carbon (g), and b represents the weight of dry carbon (g)

e. Ash Content

2 grams of activated carbon is put into a weighed porcelain dish. The plates were put into the muffle furnace at 600 ° C for 6 hours then cooled in a desiccator and weighed.

$$Ash\ content\ (\%) = \frac{a}{b} \times 100\% \qquad (2)$$

Where, a is the weight of ash (g), and b is the weight of initial dry carbon (g)

f. Absorption of iodine

As much as 0.15 grams of activated charcoal is put into a dark, closed place. Then 25 mL of 0.1 N iodine solution was put into a container then shaken for 15 minutes then filtered. A total of 10 mL of the filtrate was titrated with 0.1 N sodium thiosulfate solution. If the yellow color of the solution is almost gone, a 1% starch indicator is added. Titration is continued until the exact blue color disappears.

$$Iod\ absorption\ \left(\frac{mg}{g}\right) = \frac{\left\{10 - \left(\frac{N \times V}{0{,}1}\right)\right\}}{S} \times 12{,}69 \times 2{,}5 \qquad (3)$$

Where, V is the required sodium thiosulfate solution, N is the normality of the sodium thiosulfate solution, S is the weight of carbon (g), and 12.69 is the amount of iodine which corresponds to 1 ml of 0.1 N sodium thiosulfate solution.

g. Adsorption Test Against Artificial Waste Pb (NO3) 2

Artificial waste of Pb (NO3) 2 with variations in initial concentrations of 200, 300 and 500 mg/L each as much as 100 ml was contacted with 0.1 gram of adsorbent measuring 100-120 mesh, with variations in contact time 0, 30, 60, 90, 120 and 150 minutes and the type of adsorbent NaOH activator 0.5 M and without activator with a stirring speed of 250 rpm. After contact with the adsorbent, artificial waste Pb (NO3) 2 was measured the concentration of Pb (NO3) 2 using AAS.

IV. Results

a. Adsorbent characterization

Characterization of activated carbon from coffee shells can be seen in Table 2.

Table 2. Characterization of activated carbon from coffee shells

Parameter	SNI Quality Standards No. 06-3730-1995*	Adsorbent Type	Analysis results
Water content	Max. 15%	Activator NaOH 0,5 M	1 %
		No Activator	4 %
Ash content	Max. 10%	Activator NaOH 0,5 M	3,5 %
		No Activator	4 %
Iodine Absorption	Min. 750 mg/g	Activator NaOH 0,5 M	1628,6 mg/g
		No Activator	994,05 mg/g

(**Source: SNI No. 06-3730-1995*)

b. Scanning Electron Microscope (SEM) Analysis

The Scanning Electron Microscope (SEM) characterization was carried out to see the surface morphology of the adsorbent. SEM analysis results can be seen in Figure 1.

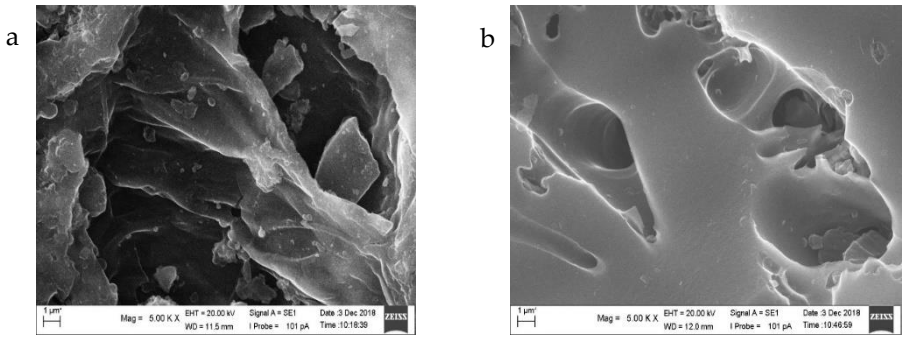

Figure 1. The results of adsorbent characterization using SEM (a) without activator; (b) 0.5 M NaOH activator with a magnification of 5000 times

c. Surface Area Analyzer (SAA) Analysis

Characterization of the Surface Area Analyzer (SAA) using the Brunauer, Emmet, and Teller (BET) method aims to determine the surface area of the adsorbent. The results of surface area analysis can be seen in Table 3.

Table 3. Result of surface area activated carbon from coffee shell

Adsorbent Type	Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Size (Å)
No Activator	3,0438	0,0075	98,5269
Activator NaOH 0,5 M	12,238	0,054	177,261

d. Fourier Transform Infra-Red (FTIR) Analysis

The Fourier Transform Infra-Red (FTIR) characterization was carried out to see the functional groups contained in the adsorbent from the coffee shell with a

variety of activators (without activator and 0.5 M NaOH activator). The results of FTIR analysis can be seen in Figure 2.

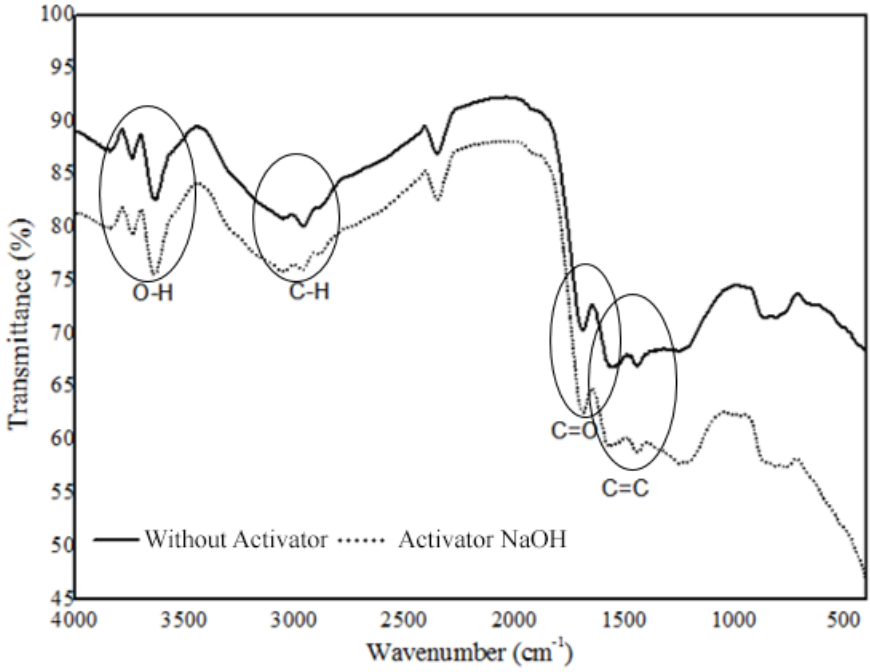

Figure 2. FTIR spectrum for adsorbent without activator and activator of 0.5M HCl

Tabel 4. FTIR spectra readings on adsorbent from coffee shell

Functional groups	Bond	*Wavenumbers range* (cm^{-1})		
		Reference*	**No Activator**	**Activator NaOH 0,5 M**
H_2O	O–H	4000-3400	3620 dan 3743	3645 dan 3743
CH_4	C–H	3000-2700	2964	2970
Aromatic	C=C	1690-1450	1649-1452	1649-1450
Aldehydes, Ketones, Carboxylic Acids	C=O	1900-1650	1693	1693

*Source: * Ma et al., 2015*

e. X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF) Analysis

Characterization of X-Ray Diffraction (XRD) aims to determine the crystalline structure of the adsorbent from the coffee shell which is characterized by peaks at an angle of 2θ. The results of XRD analysis can be seen in Figure 3.

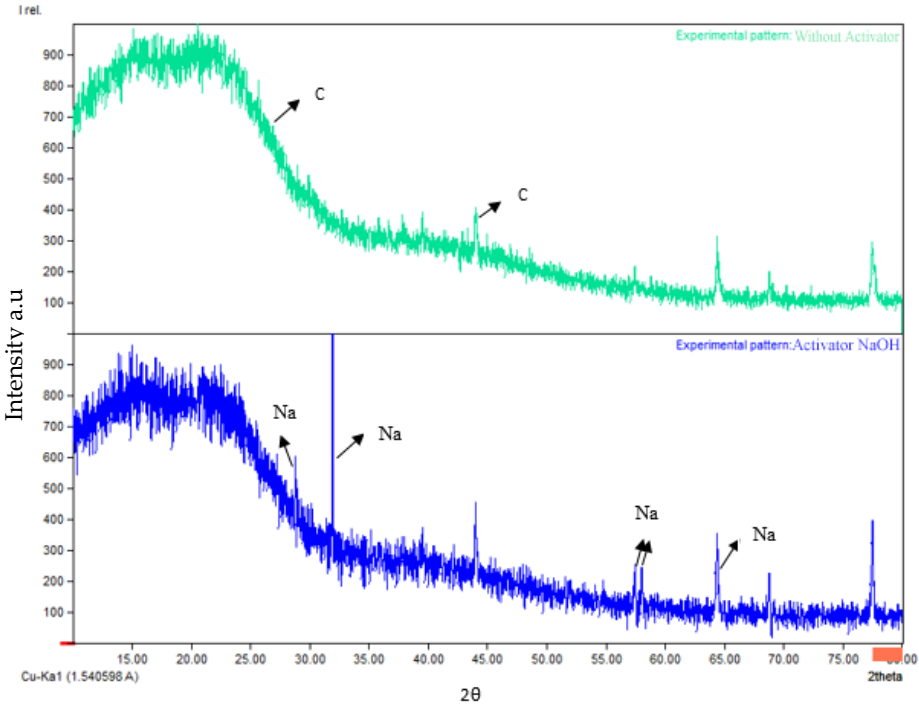

Figure 3. XRD patterns for adsorbent without activator and activator of 0.5 M NaOH

Table 5. XRF Analysis Data

Component	% By weight	
	No Activator	Activator NaOH 0,5 M
SiO_2	2,6	3
P_2O_5	3,2	4,3
K_2O	37,4	32
CaO	38,9	44,8
TiO_2	0,67	-
MnO	0,55	0,79
Fe_2O_3	10,2	12,1
NiO	0,2	1,1
CuO	0,9	2,3
Yb_2O_3	0,4	-
SO_3	3,2	-
BaO	0,2	-
Re_2O_7	1,4	-

f. Effect of Contact Time on Efficiency and Absorption Capacity of Pb (II) Metal

The efficiency of adsorbent absorption is influenced by several factors, namely, contact time, initial concentration, adsorbent dose and pH of the solution to be absorbed (Tan et al. 2012). Contact time is one of the factors that influence the adsorption process. Determination of the optimum contact time for adsorption aims to determine the time required by the activated carbon adsorbent from the coffee shell to absorb the maximum lead metal ion (Pb). The relationship between contact time and absorption efficiency of Pb (II) metal and absorption capacity can be seen in Figure 4 and Figure 5.

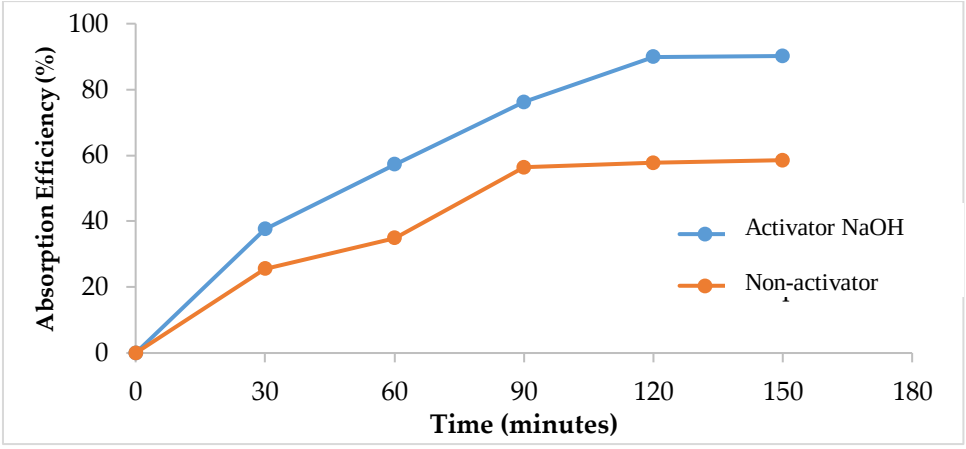

Figure 4. Effect of contact time on absorption efficiency of Pb (II) metal at the initial concentration of adsorbate 302.22 ppm

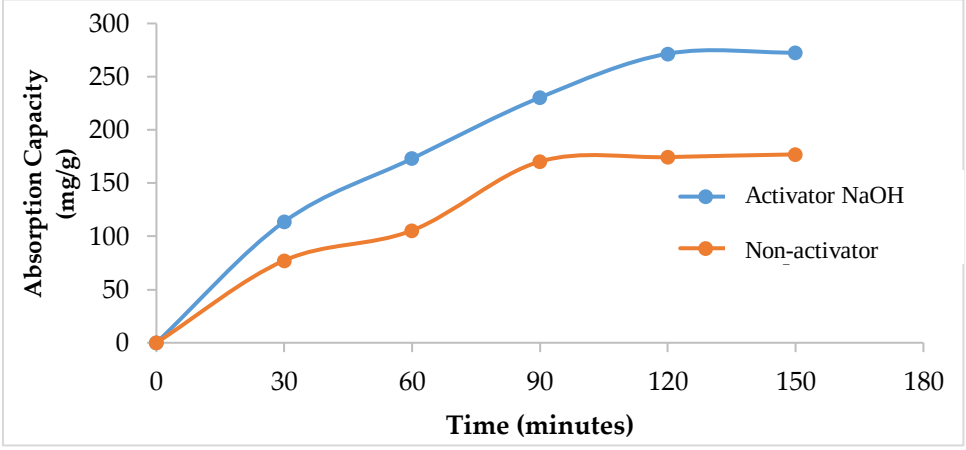

Figure 5. Effect of contact time on absorption efficiency of Pb (II) metal at the initial concentration of adsorbate 302.22 ppm

g. Effect of Activator Type on Efficiency and Absorption Capacity of Pb (II) Metal

The effect of the activator in the chemical activation process of the adsorbent greatly affects the ability of the adsorbent to absorb Pb metal. The activator used is basic NaOH. The presence of the activator gives a different effect, causing differences in the ability of the adsorbent to absorb Pb metal. The relationship between the type of activator on the efficiency and absorption capacity of Pb metal can be seen in Figure 6 and Figure 7.

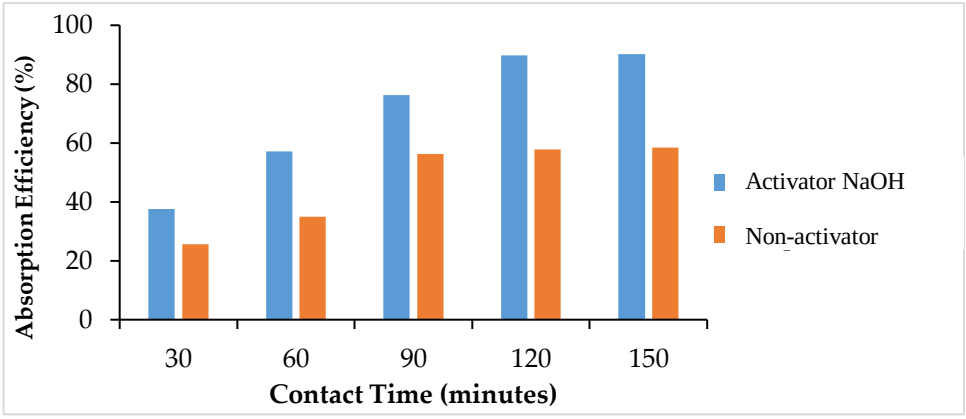

Figure 6. Effect of activator types on the absorption efficiency of Pb (II) metal at the initial concentration of adsorbate 302.22 ppm

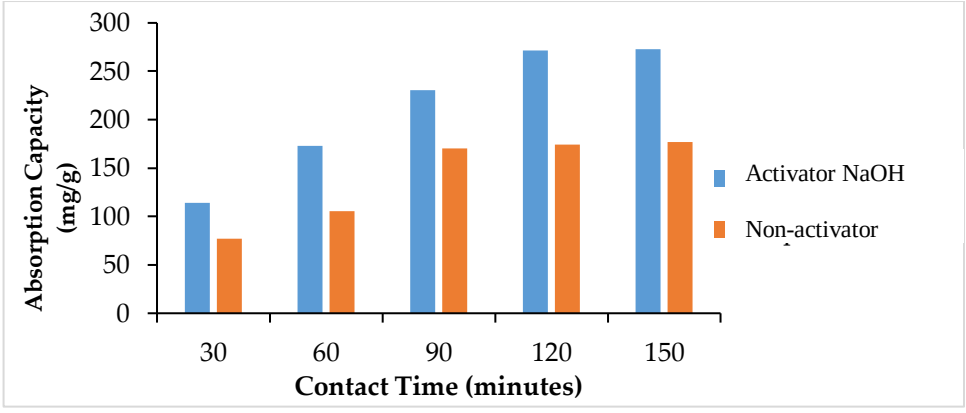

Figure 7. Effect of the type of activator on the absorption capacity of Pb (II) metal with an initial concentration of 302.22 ppm of adsorbate

h. Adsorption Isotherm

The Langmuir adsorption isotherm of Pb (II) metal can be obtained by making a curve of the relationship between Ce to Ce/Qe. The graph of Langmuir isotherm equation for adsorbent using NaOH activator can be seen in Figure 8.

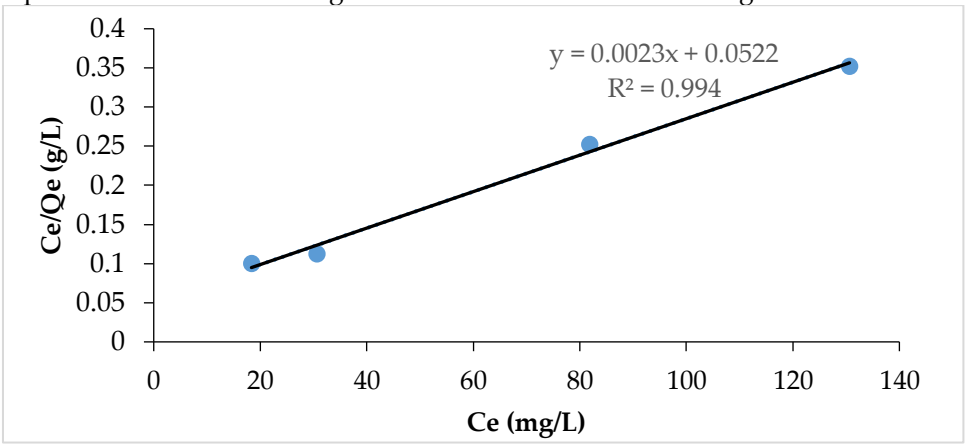

Figure 8. Langmuir isotherm model for Pb (II) absorption using NaOH activator adsorbent

The Freundlich adsorption isotherm of Pb (II) metal can be obtained by constructing a correlation curve between log Ce to log Qe. The graph of Freundlich's isotherm equation for adsorbent using NaOH activator can be seen in Figure 9.

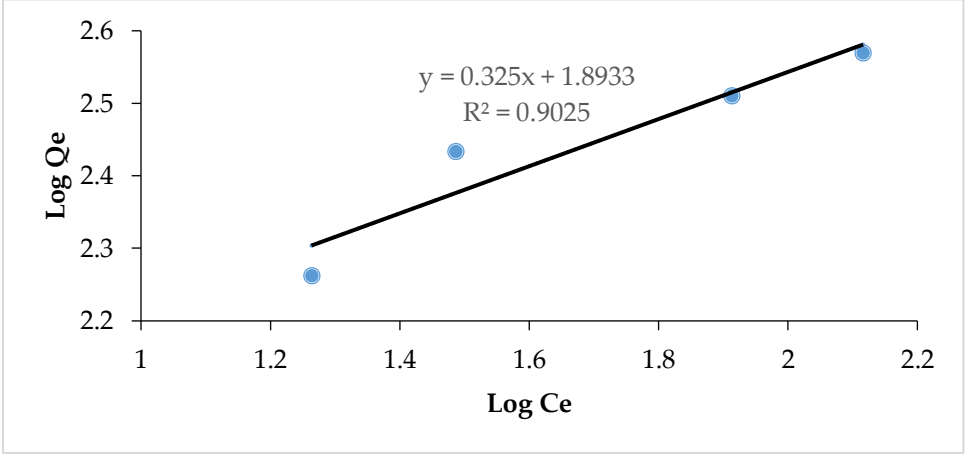

Figure 9. Freundlich isotherm model for Pb (II) absorption using NaOH activator adsorbent

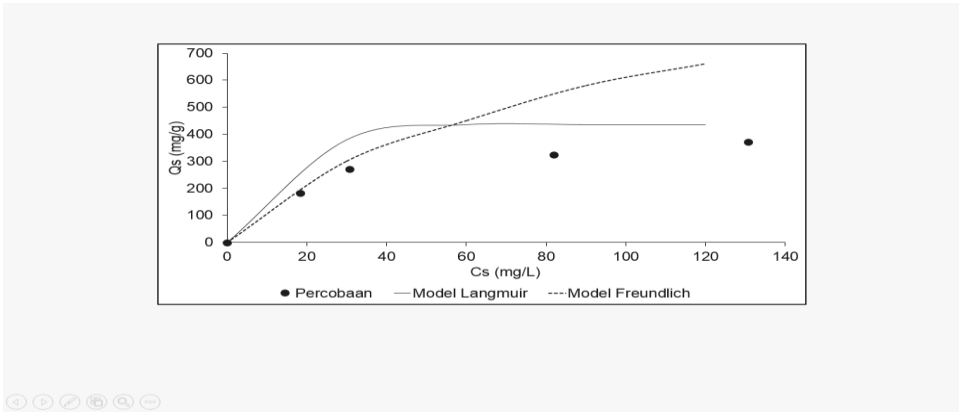

Figure 10. Comparison of Freundlich and Langmuir isotherm models with experimental results

Based on the equations obtained from the two isotherm models, the maximum absorption capacity (q_m) and absorption rate constant (KL/KF) can be calculated as in Table 6.

Table 6. Calculation Results of Adsorption Isotherms

Isotherm Langmuir			**Isotherm Freundlich**		
q_m	**K_L**	**R^2**	**1/n**	**K_F**	**R^2**
434,783	0,044	0,994	3,077	0,277	0,9025

V. Discussions

a. Adsorbent characterization

Table 2 shows the results of the analysis of activated carbon, showing that the moisture content, ash content and absorption of iodine have met the quality standards for activated carbon based on SNI No. 06-3730-1995. The activated carbon produced in this study is very good for use as an adsorbent in reducing Pb (II) metal.

b. Scanning Electron Microscope (SEM) Analysis

Based on Figure 1, it can be seen that the difference in surface morphology of coffee shell activated carbon with variations without activator and 0.5 M NaOH activator. Adsorbents without using an activator still have impurities that fill and cover the pores. The high ash content causes some of the pores on the adsorbent surface to be still covered with ash. Meanwhile, adsorbent using 0.5 M NaOH solution activator, the surface of the adsorbent pores is clean and not filled with impurities that cover the surface.

c. Surface Area Analyzer (SAA) Analysis

Table 3 shows that the activation treatment results in a larger surface area and pore volume, activation using 0.5 M NaOH activator can dissolve some of the inorganic compounds that cover the pores so that the pores open and more pores are formed. The more pores that are formed, the larger the surface area.

From the BET test data results also showed that the average pore diameter for the adsorbent without activator was 98.5269 Å while the adsorbent using 0.5 M NaOH activator was 177.261 Å. From these data shows that the adsorbent without activator and using an activator is classified as mesoporous. According to Mariana and the research team, said that the diameter of the mesoporous lies in the range of 20-500 Å (Mariana et al., 2018).

d. Fourier Transform Infra-Red (FTIR) Analysis

Based on Table 4, it can be seen that, the absorption of -OH, CH, C = C and C = O groups dominates the two coffee shell adsorbent samples either without activator or using 0.5 M NaOH activator. From the results obtained, there is a decrease in the absorption peak in the carbon sample. Active after chemical activation. This shows that the activation process affects the absorption intensity in the wavelength region and results in changes to the functional group structure (Hanum et al., 2017).

e. X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF) Analysis

Based on Figure 3 shows the results of X-ray diffraction on the coffee shell adsorbent sample. (Khalil et al., 2013) reported that activated carbon exhibits a very irregular microcrystalline structure in which the microcrystals of graphite are randomly oriented. It can be seen that in the adsorbent without activator with a carbonization process at 350oC for 120 minutes, there is carbon (C) in the area 2θ = 26.28o (d = 3.3887 Å) and 44.27o (d = 2.0443 Å). The few sharp peaks on the adsorbent without activator indicate that this is an amorphous structure (Das et al., 2015).

In the NaOH activator adsorbent, there are wide peaks because the reflection from the plane can be seen clearly. The sharp peaks are produced due to better layer alignment which is characteristic of the crystal structure (Das et al., 2015). The XRD pattern of NaOH activator adsorbent contained several sharp peaks in the region 2θ = 28.77o (d = 3,1005 Å); 32.10o (d = 2.7863 Å); 57.82o (d = 1.5935 Å); 58.44o (d = 1.5781 Å) and 64.37o (d = 1.4461 Å) which are caused by the presence of sodium (Na). The sharpness of the peaks indicates that the Na presented is relatively large, although it is still in the micro range.

f. Effect of Contact Time on Efficiency and Absorption Capacity of Pb (II) Metal

Figure 4 shows that the longer the contact time between the adsorbate and the adsorbent, the higher the absorption efficiency until equilibrium occurs. Based on the experimental results, the absorption efficiency for the initial concentration of 302.22 mg/L with a contact time of 30, 60, 90, 120 and 150 minutes was obtained using the NaOH activator adsorbent, respectively, 37.7; 57.3; 76.2; 89.9 and 90.2% while without activator are 25.6; 34.9; 56.3; 57.7 and 58.6%.

The adsorption capacity shows the ratio of the amount of adsorbate absorbed by the adsorbent (Tan et al., 2012). The relationship between contact time and absorption capacity can be seen in Figure 5. Based on Figure 5, it can be seen that the absorption capacity increases with the increase in contact time between the adsorbate and the adsorbent. The longer the contact time, the concentration of Pb (II) metal absorbed will increase until equilibrium occurs. Based on the experimental results, it was found that the absorption capacity for the initial concentration of 302.22 mg/L with contact times of 30, 60, 90, 120 and 150 minutes using NaOH activator adsorbent were 113.78; 173.03; 230.39; 271.58 and 272.56 mg/g while using adsorbent without activator were 77.29; 105.49; 170.26; 174; 44 and 176.97 mg/g. At the beginning of contacting the adsorbate with the NaOH activator adsorbent, the adsorbate absorption rate was very large, namely at 30 to 120 minutes while at 120 minutes to 150 minutes (te) there was a balance of absorption.

Based on this, it shows that the optimum contact time of NaOH activator adsorbent in the absorption of Pb metal ions is achieved at 120 minutes. Meanwhile, using adsorbent without activator, the optimum contact time for the absorption of Pb metal ions was achieved at 90 minutes. The longer the contact time, the more adsorbed metal will cause the more opportunities for activated carbon to come in contact with the metal bound in the activated carbon pores until the contact time needed is enough to adsorb the metal (Zikra & Yenti, 2016).

g. Effect of Activator Type on Efficiency and Absorption Capacity of Pb (II) Metal

Figure 6 shows that the adsorbent that has the greatest removal efficiency is the adsorbent using NaOH activator, the absorption efficiency is obtained for the initial concentration of 302.22 mg/L with contact times of 30, 60, 90, 120 and 150 minutes using the NaOH activator adsorbent respectively. Contributing is 37.7; 57.3; 76.2; 89.9 and 90.2% while without activator are 25.6; 34.9; 56.3; 57.7 and 58.6%. This is due to the effect of chemical activation using NaOH activator which can release impurities in the adsorbent so that the pores of the active site widen.

The adsorption capacity shows the ratio of the amount of adsorbate absorbed by the adsorbent (Tan et al., 2012). The relationship between the type of activator

and absorption capacity can be seen in Figure 7. Based on Figure 7, it can be seen that the type of activator greatly affects the absorption capacity of Pb (II) metal. The type of activator used was NaOH and without activator, it was found that the absorption capacity for the initial concentration of 302.22 mg/L with contact times of 30, 60, 90, 120 and 150 minutes using NaOH activator adsorbent were 113.78; 173.03; 230.39; 271.58 and 272.56 mg/g while using adsorbent without activator were 77.29; 105.49; 170.26; 174; 44 and 176.97 mg/g. It can be concluded that the adsorbent activated using NaOH activator provides greater absorption ability of Pb (II) metal compared to adsorbent without activator.

In this study, the type of chemical activation affected the adsorbent's ability to absorb adsorbate. Activators that provide alkaline conditions are much more efficient than those without using activators. Barbosa et al. (2016) obtained the results that the adsorbent with alkaline activator (KOH) has the best absorption ability compared to without activator with adsorption capacity values, respectively, 435 and 17.2 mg/g.

h. Adsorption isotherm

The adsorption isotherm model is determined to determine the interaction between the solution and the adsorbent and the optimum ability that can be achieved by the adsorbent. The adsorption isotherms commonly used are Langmuir and Freundlich isotherms. This equilibrium model test is intended to determine the appropriate equilibrium to be used in an adsorption process. Determination of the equilibrium model can be done by looking at the value of the highest determinant coefficient (R2) from the graphs produced from each adsorption isotherm plot. The Langmuir adsorption isotherm of Pb (II) metal can be obtained by making a curve of the relationship between Ce to Ce/Qe. Graph of Langmuir isotherm equation for adsorbent using NaOH activator can be seen in Figure 8. While the Freundlich adsorption isotherm of Pb (II) metal can be obtained by making a curve of the relationship between log Ce to log Qe. The graph of Freundlich's isotherm equation for adsorbent using NaOH activator can be seen in Figure 9.

Based on Figure 8 and Figure 9, it can be seen that the adsorption of Pb (II) metal by coffee shell activated carbon tends to follow the Langmuir isotherm model. This can be seen from the determinant coefficient (R2) of the Langmuir isotherm model, which is 0.994, higher than the determinant coefficient of the Freundlich isotherm model, which is 0.9025. This shows that there is an active site on the surface of the adsorbent that can absorb one molecule. The bond between the adsorbent and the adsorbate can occur physically and chemically. The bond must be strong so that the molecules that have been adsorbed along the surface are maintained (Oscik, 1982). In the Langmuir isotherm the active sites on the adsorbent surface are homogeneous, where the adsorbent can only adsorb one Pb (II) metal ion for each active site and there is no interaction

between Pb (II) metal ions at adjacent active sites (Muslim et al. , 2015). Based on the equations obtained from the two isotherm models, the maximum absorption capacity (qm) and absorption rate constant (KL/KF) can be calculated as in Table 5.

VI. Conclusion

From the research that has been done, it can be concluded as follows. The optimum contact time of adsorbent using NaOH activator to absorb Pb (II) metal was achieved at 120 minutes, while using adsorbent without activator was achieved at 90 minutes. The type of activator greatly affects the efficiency and absorption capacity of activated carbon in absorbing Pb (II) metal. The best type of activator is the adsorbent with NaOH activator showing the greatest efficiency and absorption capacity. In the variation of the type of activator, the highest absorption capacity was 271.577mg/g using 0.5M NaOH activator and at 120 minutes. Adsorption isothermal model used coffee shell adsorbent against Pb (II) metal following the Langmuir isothermal model.

Disclosure and Conflicts of Interest

There is no conflict of interest

References

Das, D., Samal, D. P., & Meikap, B. C. (2015). Preparation of activated carbon from green coconut shell and its characterization. *Journal of Chemical Engineering & Process Technology*, *6*(5), 1-7.

El-Bahy, S. M., & El-Bahy, Z. M. (2016). Synthesis and characterization of polyamidoxime chelating resin for adsorption of Cu (II), Mn (II) and Ni (II) by batch and column study. *Journal of environmental chemical engineering*, *4*(1), 276-286.

Hanum, F., Gultom, R. J., & Simanjuntak, M. (2017). Adsorpsi Zat Warna Metilen Biru dengan Karbon Aktif dari Kulit Durian Menggunakan KOH dan NAOH sebagai Aktivator. *Jurnal Teknik Kimia USU*, *6*(1), 49-55.

Husni, H., & Rosnelly, C. M. (2007). Studi Kinetika Adsorpsi Larutan Logam Timbal (Pb) Menggunakan Karbon Aktif dari Batang Pisang. *Jurnal Hasil Penelitian Industri*, *20*(1), 1-10.

Jorgetto, A. D. O., da Silva, A. C., Wondracek, M. H., Silva, R. I., Velini, E. D., Saeki, M. J., ... & Castro, G. R. (2015). Multilayer adsorption of Cu (II) and Cd (II) over Brazilian Orchid Tree (Pata-de-vaca) and its adsorptive properties. *Applied Surface Science*, *345*, 81-89.

Khalil, H. P. S., Jawaid, M., Firoozian, P., Rashid, U., Islam, A., & Akil, H. M. (2013). Activated carbon from various agricultural wastes by chemical activation with KOH: preparation and characterization. *Journal of Biobased Materials and Bioenergy*, *7*(6), 708-714.

Mariana, Marwan, Mulana, F., Yunardi, Ismail, T. A. & Hafdiansyah, M. F. (2018). Activation and Characterization Of Waste Coffee Grounds As Bio-Sorbent. *Iop Conference Series: Materials Science and Engineering,* 334**,** 012029.

Meisrilestari, Y., Khomaini, R., & Wijayanti, H. (2013). Pembuatan arang aktif dari cangkang kelapa sawit dengan aktivasi secara fisika, kimia dan fisika-kimia. *Konversi*, *2*(1), 45-50.

Nasruddin, M. (2005). *Dynamic Modeling and Simulation of Two-Bed Silicagel Water Adsorption Chiller*, Mainz.

Nurdiansah, H., & Susanti, D. (2013). Pengaruh Variasi Temperatur Karbonisasi dan Temperatur Aktivasi Fisika dari Elektroda Karbon Aktif Tempurung Kelapa dan Tempurung Kluwak Terhadap Nilai Kapasitansi Electric Double Layer Capacitor (EDLC). *Jurnal Teknik ITS*, *2*(1), F13-F18.

Oscik, J. 1982. *Adsorption*. New York: John Willey & Sons.

Sawyer, C. N., McCarty, P. L., & Parkin, G. F. (1978). Chemistry for environmental engineers. *Environmental Management*, *3*, 0-0.

Suryawan, B. (2004). Karakteristik Zeolit Indonesia sebagai Adsorben Uap Air. *Disertasi. FT Universitas Indonesia, Jakarta*.

Syabriana, M. (2018). Produksi Bioetanol Dari Limbah Kulit Kopi Menggunakan Enzim Zymomonas Mobilis Dan Saccharomyces Cereviseae. *Jurnal Serambi Engineering*, *3*(1).

Tan, K. A., Morad, N., Teng, T. T., Norli, I., & Panneerselvam, P. (2012). Removal of cationic dye by magnetic nanoparticle (Fe3O4) impregnated onto activated maize cob powder and kinetic study of dye waste adsorption. *APCBEE Procedia*, *1*, 83-89.

Tchounwou P.B., Yedjou C.G., Patlolla A.K., Sutton D.J. (2012) Heavy Metal Toxicity and the Environment. In: Luch A. (eds) *Molecular, Clinical and Environmental Toxicology*. pp 133-164. Experientia Supplementum, vol 101. Springer, Basel. https://doi.org/10.1007/978-3-7643-8340-4_6.

Ucun, H., Bayhana, Y. K., Kaya, Y., Cakici, A., & Algur, O. F. (2003). Biosorption of lead (II) from aqueous solution by cone biomass of Pinus sylvestris. *Desalination*, *154*(3), 233-238.

Yu, F., Yang, C., Zhu, Z., Bai, X., & Ma, J. (2019). Adsorption behavior of organic pollutants and metals on micro/nanoplastics in the aquatic environment. *Science of the Total Environment*, *694*, 133643.

Zhou, Y., Zhang, L., & Cheng, Z. (2015). Removal of organic pollutants from aqueous solution using agricultural wastes: a review. *Journal of Molecular Liquids*, *212*, 739-762.

Zikra, N. R. Y. & Yenti, S. R. (2016). Adsorpsi Ion Logam Pb Dengan Menggunakan Karbon Aktif Kulit Durian Yang Teraktivasi. *Jom FTEKNIK 3*(1), 1-8.