Determination Of The Effects Of pH and Adsorption Isotherm Of Pb(II) Metal Ions by Using Activated Carbon From Spent Coffee Grounds

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Abstract. Caffein, tannin, and polyphenol contents in a substance is an important parameter to determine the hazardous level of the substance. This makes the spent coffee ground considered as a hazardous waste. Lead, on the other hand, is considered as toxic heavy metal because of its ability to pollute water ecosystem. In this study, the spent coffee ground was activated by activated carbon then it was used to adsorb lead ion [Pb(II)]. The effect of pH and the adsorption type of the activated carbon used to adsorb lead ion were studied. Several steps such as brewing, drying, and carbonizing under a specific condition were used to obtain the samples of spent coffee ground. The samples were then activated chemically by using HCl and then washed by using deionized water, and dried. The result shows that the moisture content of the activated carbon from the spent coffee ground was 11.32 ± 0.03%, and its pores size formed was 8.50 ± 4.11 nm. The maximum amount of adsorption was occurred at pH 3 and it followed the Langmuir type of adsorption isotherm. The maximum adsorption capacity was 4.97 ± 0.16 mg/gr for each gram of adsorbent which was the activated carbon from the spent coffee ground.

Keywords: Spent Coffee Ground; Activated Carbon; pH; SEM; Adsorption Isotherm

1. INTRODUCTION

Coffee consumption has become a primary need for young generation nowadays. Many local coffee-shop sellers are available everywhere. In 2016 the national coffee consumption was 250 thousand tons, based on the research conducted by the Ministry of Agriculture. Its growing rate was 10.54% each year [1]. The coffee consumption will reach 370 thousand tons in 2021 [2]. There are roughly 1500 local coffee shops in Jabodetabek nowadays [3].

In contrary, the development of the waste treatment from the coffee waste cannot match with the huge development rate of the local coffee shops. Based on the report from Dr. Amanda Cameron, 3000 tons of coffee waste can be produced each year. 90% of it was disposed to landfills, and the rest was collected by the organic waste processors or composting customers [4]. The caffeine, tannin, and polyphenol content, coffee grounds can be toxic. Furthermore, in order to reduce coffee waste, oxygen in large quantities is needed. Therefore, coffee waste can be utilized further in making oil, biochar, and bioactive compounds [5]. Waste coffee ground is a cheap and easy material to be used as an organic adsorbent material to be transformed into activated carbon or bioactive compound [6].

Heavy metals pollution can be found in water bodies and their contamination in aquatic ecosystems is intensively related to the release of heavy metals by domestic, industrial, and other human activities. According to [7], heavy metals that have entered into waters will be diluted and spread by mortar or turbulence and ocean currents. Some examples of toxic heavy metals to humans are Lead, Arsenic, Copper, Cadmium, Nickel, Mercury, and Zinc.

Lead is a common metal for human activities. It is widely used as batteries, cables, paints, gilding, industrial pesticides, and anti-pollution materials in gasoline [8–9]. The huge usage of Pb in non-food industries may often poison living things. Most Lead on earth enter the natural aquatic system and accumulate, which can eventually enter the bodies of animals and humans [10].

One of the effective ways to treat lead waste is by adsorption process. Adsorption is chosen because it is a simple method and uses adsorbent of natural materials from unused biomass remnants such as spent coffee grounds. Based on [11], research states that if the particle size of coffee grounds is bigger than 200 µm (mesh), then it can eliminate 87% of lead metal ions. According to [12], it is stated that stirring speed of 90 rpm for 30 minutes of time contact are the optimum speed and time such that the activated carbon can adsorb heavy metals. Based on [13], it has been determined that the adsorption capacity based on the pH of Cu and Cr metals can be used as a reference with the same condition.

This study aims to use spent coffee grounds (Robusta) as active carbon compound. These active carbon compounds from spent coffee grounds will be focused on the effect of pH on the amount of Pb(II) metal ions and type of isotherm adsorption of Pb(II) metal ions on the activated carbon from Spent coffee ground (Robusta).

2. LITERATURE REVIEW

According to [14], spent coffee ground is possible to turn into bio-active compound. The content of waste coffee ground is listed in Table 1.

Table 1. The content of waste coffee ground

No	Parameter	Composition (%)
1	Total Carbon	47.8 – 58.9
2	Total Nitrogen	1.9 – 2.3
3	Protein	6.7 – 13.6
4	Ash	0.43 – 1.6
5	Cellulose	8.6
6	Total Lignin	–

Activated carbon is a porous solid that contains 85-95% of carbon, produced from materials that contain carbon by heating it at high temperatures and can be used as an adsorbent [15–21]. It is used as a filter molecule in purification of water, liquids and gases and in food manufacturing process. It can be used as catalysts in the removal of sulfur and nitrogen in the industry [16].

Adsorbents are defined as solids that can absorb specific components of a fluid phase [22] or substances or materials that can bind and maintain liquids or gases in them [23]. Several types of commercial adsorbents that have been used are zeolite, silica gel, and activated alumina [24].

Adsorption is the event of attaching an atom or molecule to a substance on the surface of another substance due to the imbalance of force in the surface. Adsorbed substances are called adsorbates, and adsorption agents are called adsorbents. The adsorption process is described as a process of molecules leaving solutions and sticking to the surface of absorbent substances due to physical and chemical bonds [25–30].

The adsorption isotherm is an adsorption process that takes place at a fixed temperature. Adsorption isotherm shows a relationship between the amount of substance adsorbed by the weight of activated charcoal and dissolved concentrations at a certain or fixed temperature [31]. The isotherm model used in this study is Langmuir and Freundlich [32–33]. The application of the isotherm curve obtained by the correlation equation used to determine the maximum adsorption capacity, equilibrium constant, and adsorption energy.

The toxicity properties of heavy metals can be grouped into three groups, namely high, medium, and low toxic. High toxic heavy metals consist of elements Pb, Hg, Cu, Cd, and Zn. Moderately toxic is composed of elements Cr, Ni, and Co, while low toxic consists of elements Fe and Mn. The presence of heavy metals in waters are dangerous, both directly to the life of the organism and its effects indirectly on human health.

Poisoning caused by Pb metal compounds can occur due to the inclusion of these metal compounds into the body. The process of entering Pb can be through several ways, namely through breathing, oral (through food and drink) and penetration of the skin layer [34–41]. Lead is one of the metals that was first melted and used for industrial use.

Batch methods for adsorption studies are usually carried out with several Erlenmeyer glasses containing solutions with certain substances which will be adsorbed on certain variations. In each tube, several adsorbents were added with the same weight. Then the solution and adsorbent in the tube are stirred using a magnetic stirrer at a specific time, and after that, it is filtered, and the solution concentration is analyzed. The difference in adsorbate concentration before and after adsorption is considered as the concentration of adsorbate adsorbed by the adsorbent [42].

Scanning Electron Microscopy (SEM) is one type of electron microscope that uses electron beams to describe the surface shape of the material. The working principle of SEM is to describe the surface of an object with a beam of electrons reflected with high energy. The surface of the irradiated object will reflect the electron beam. But of all the reflected electron beams, there is one electron beam that is reflected at high intensity. The detector contained in SEM will detect the highest intensity electron beam reflected by objects. Electrons can reach resolutions up to 0.1-0.2 nm [43] but the microscope type of light is only able to reach a resolution of 200 nm. The difference of the optical and SEM image is shown in Figure 1 [44].

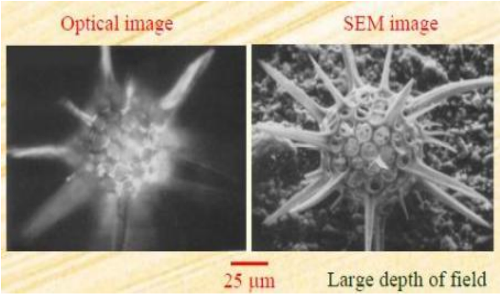


Figure 1. Difference between optical and SEM image

Atomic Absorption Spectroscopy (AAS) absorbs light by atoms. Atoms absorb light at a certain wavelength, depending on the character of the element. The basic principle of AAS is the interaction between electromagnetic radiation and samples. AAS is a very appropriate method to analyze substances at low concentrations. AAS is based on the emission and absorption of atomic vapour [45].

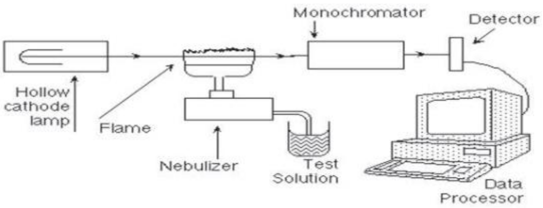


Figure 2. AAS instrumentations

Absorption follows the Lambert-Beer law, i.e. the absorbance is directly proportional to the flame length that the light goes through and the atomic concentration of the atom in flame. Both of these variables are difficult to determine, but the flame length can be made constant so that the absorbance is only directly proportional to the concentration of the analyze in the sample solution. The techniques of analysis are calibration curves. The quantitative aspects of the spectrophotometric method are explained by the Lambert-Beer law. AAS Instrument is shown in Figure 2 [46].

3. METHODOLOGY

The research methodology is shown in the Figure 3 below.

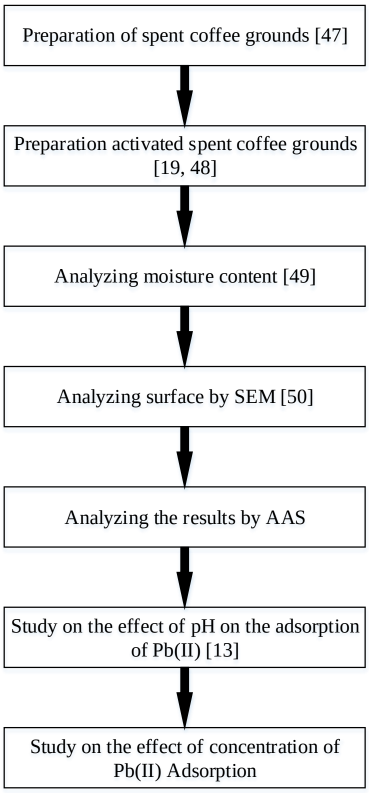


Figure 3. The block diagram of the preparation of spent coffee grounds

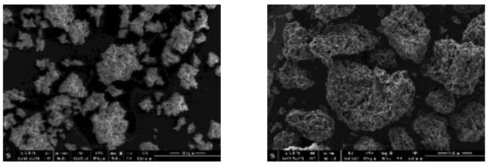
4. RESULT

The value of water level shows that a lot of water which covers the pores of activated charcoal. The lower the water content removal, the more places in the pore that can be occupied by the adsorbate so that the adsorption takes place optimally [49]. The experiment to determine moisture content removal is done thrice and its average value is listed on the Table 2. The operation temperature is 110°C. The moisture content removal of the activated carbon has met the maximum standard set by the Indonesian Industry Standard (SNI) of 15% so that means the activated carbon from the spent coffee grounds is suitable to use as an adsorbent.

Table 2. Average percentage of moisture content removal and its standard deviation

Average percentage	11.32
Standard deviation	0.03

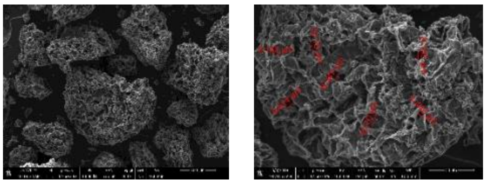
The morphological characterization process of the adsorbent was carried out by analyzing the spent coffee grounds before and after the activation process of carbonization using SEM. The result with 200× magnification is shown in Figure 4.



(a) (b)

Figure 4. Morphology of the spent coffee ground (a) before and (b) after activation with 200 magnification

From figure 4a, it can be seen that the particle size of the coffee pulp is not uniform since it has not been smoothed to 100 mesh. Figure 4b shows us that after being grinded using a 100 mesh filter, the particles are almost at the same size, which is around 100 microns in diameter. There are also some uncertain particles formed that might be some organic compounds or tars because the carbonization process is destroyed or discredited due to activation using HCl, so only carbon compounds are separated from the coffee grounds. Furthermore, the result with 1000× magnification is shown in Figure 5.



(a) (b)

Figure 5. Morphology of the spent coffee ground (a) before and (b) after activation with 1000 magnification

From figures 5, the result of activated carbon from spent coffee grounds has changed to form pores with an average size from seven randomly taken samples are about 8.50±4.11 nm while for the un-activated spent coffee ground has no pores.

One of the important parameters in the adsorption of metal ions is pH (acidity level). Determination of the effect of pH aims to determine the pH value, which gives the highest percent removal of spent coffee ground from Pb(II) metal ions. This research was carried out at variations in pH 3, 5, and 7, with initial concentration 5 mg/L. Each variation is repeated thrice. According to [51], testing at pH bigger than seven is not possible because it is the limit for Pb(II) metal precipitating as a form of $Pb(OH)_2$ and the precipitating process for Pb(II) is very fast at pH bigger than 7. The result is shown in Table 3.

Table 3. Effect of pH on the %-removal of Pb(II) ion

pH	**%-Removal**	**Standard Deviation**
3	85.44	0.27
5	74.43	2.66
7	53.03	3.16

It can be seen that increasing pH can reduce the amount of Pb(II) metal adsorbed by spent coffee grounds. At pH 3, spent coffee grounds can adsorb Pb(II) ion by 85±0.3% then followed by a decreasing amount of Pb(II) metal adsorbed at pH 5 by 74±2.7% and by 53±3.2% at pH 7. This process can be influenced by the presence of metal ion exchange reactions with functional groups contained in the spent coffee grounds as adsorbent. Based on [52], if the solution is too alkaline, it can be caused by Pb^{2+} tends to form into $Pb(OH)_2$ so that the interaction with activated carbon surface from spent coffee ground decreases.

Adsorption equilibrium is a condition where there is no change in the concentration of the adsorbate either in the liquid phase or in the adsorbent [53]. This research was conducted at pH 3 with the initial concentration 5, 30, 90, and 120 mg/L, to learn its effect on the adsorption capacity (Q_e [=] mg/g). Every variation is done thrice. The result is shown in Table 4.

Table 4. Effect of initial concentration on the adsorption capacity

Concentration (mg/L)	**Average Q_e (mg/g)**	**Standard Deviation**
5	0.21	0.00
30	1.08	0.02
90	2.23	0.03
120	2.42	0.01

As seen on Table 4, the higher the concentration the bigger the adsorption capacity is. It can also be concluded that the surface of activated carbon from spent coffee grounds has not reached saturation point so that the adsorption process of Pb(II) metal can still be able to run. This is because the higher the concentration of Pb(II), the more Pb(II) molecules interact with the adsorbent, which is activated carbon from spent coffee grounds so that the adsorption capacity increases.

Adsorption isotherm shows a relationship between the amount of substance adsorbed by the weight of activated carbon and dissolved concentrations at a specific or fixed temperature [31]. Isotherm Langmuir and Freundlich are widely used to describe mineral adsorption processes [54]. Isotherm Langmuir assumes that the adsorption process is monolayer and the adsorption sites are all the same. On the other hand, the Freundlich model assumes that surface adsorption is heterogeneous with sites that have different adsorption energy. Adsorption capacity, equilibrium constant, and adsorption energy can be obtained through the correlation equation produced from the isotherm curve.

This research is conducted to determine the proper equilibrium model. It depends on the value of the coefficient of determination (R^2) presented in Table 5 and Table 6 below. The R^2 values for Langmuir isotherm are obtained by plotting $1/Q_e$ as y-axis and $1/C_e$ as x-axis, while The R^2 values for Freundlich isotherm are obtained by plotting log Q_e as y-axis and log C_e as x-axis, where Q_e is the adsorption capacity and C_e is the concentration at equilibrium. Every variation is done thrice. Q_m is the maximum adsorption capacity in mg/g, K_L is the Langmuir constant, n is intensity of adsorption, and K_F is the Freundlich constant. The suitable equilibrium model is the one with higher R^2 [55].

Table 5. Value of R^2, Q_m, and K_L of Langmuir Isotherm

Var.	R^2	Q_m	K_L
1	0.9998	5.1466	0.0087
2	0.9999	4.8285	0.0092
3	0.9999	4.9407	0.0090

Table 6. Value of R^2, K_F, and n of Freundlich Isotherm

Var.	R^2	K_F	n
1	0.9868	0.0660	1.2837
2	0.9895	0.0652	1.2857
3	0.9885	0.0657	1.2872

It can be seen from the tables above that the adsorption results of Pb(II) by carbon active from spent coffee ground more likely to follow the Langmuir isotherm whose its R^2 value is greater than that of Freundlich isotherm.

Langmuir Isotherm illustrates that the adsorbent and adsorbate form a single layer, the surface of the adsorbent is homogeneous, and the absorption that occurs does not exceed the active site of the activated carbon. The Q_m parameter is the maximum adsorption capacity of an adsorbent in mg/g. While the K_L is a constant that shows the bond energy between solutes and adsorbents [56]. The $K_L > 1$ indicates a strong level of affinity [57]. Table 5 shows that the Q_m values are 5.1466, 4.8285 and 4.9407 mg/gr. However, the K_L value obtained is much less than 1 which means that the affinity that occurs in the Pb metal adsorption process with activated carbon from the spent coffee ground is very weak.

From Table 6, the K_F values obtained are 0.0660, 0.0652, and 0.0657, and the values n are 1.2837, 1.2857, and 1.2872. In general, the higher the K_F value, the higher the adsorption capacity [58]. The value of n is a measure of the deviation of the adsorption linearity which is generally used to determine the true level of adsorption. If its value is 1 then the adsorption that occurs is linear. If the value for $n < 1$, then it is a chemical adsorption, but if the value for $n > 1$, then it is physical adsorption [59]. At the value of $n > 1$, it can be identified that the absorption of the adsorbent to the adsorbate used is proper [60].

Deciding that the Langmuir isotherm is more suitable, the next step is to learn about the adsorption energy. Table 7 shows the result about adsorption energy during this research. This is done for each variation to obtain its average value and standard deviation. Adsorption energy is calculated by the following formula: $E_{ads} = -RT \ln (K_L)$.

Table 7.

Average adsorption energy (kJ/mol)	11.68
Standard deviation	0.07

The adsorption energy of Pb(II) ion with activated carbon from the spent coffee ground is too low then it is categorized as physical adsorption. Based on [28], physical adsorption occurs when the related adsorption energy is less than 20 kJ/mol and is caused by the appeal of Van der Walls and is reversible. The bonding is reversible which means that the bond is temporary, so that Pb(II) ion can be rereleased from the activated carbon from spent coffee ground. The possibility of forming chemical bonds or chemisorption in this research is very small or even impossible, because the resulted adsorption energy is very small and cannot reach the energy of 100 kJ/mol.

5. CONCLUSION

This objective of this research is to use spent coffee grounds (Robusta) as active carbon compound. The effect of pH and initial concentration are studied, as well as the surface morphology of the activated carbon obtained from the spent coffee ground. From the observational data that has been analyzed and discussed, conclusions can be taken as follows:

1. Moisture content of the activated carbon from the spent coffee ground obtained in this research, which was activated at 500˚C for 2 hours, and using HCl was 11.32 ± 0.03%.
2. From SEM analysis, it can be seen that the pores of activated carbon from spent coffee grounds can be formed after being activated. The average pore size was 8.50 ± 4.11 nm from seven pores was taken randomly.
3. The effect of pH on Pb(II) ion adsorption using activated carbon from coffee grounds as adsorbent; it was found at pH 3 produced the highest removal of Pb(II) in solution which was 85.44 ± 0.27% average.

4. Activated carbon from the spent coffee ground as much as 1 gram for 5, 30, 90, and 120 mg/L of Pb(II) concentration has not reached saturation point so that the adsorption process of Pb(II) metal can still be able to run.
5. The result of Pb(II) heavy metal adsorption isotherm with activated carbon from spent coffee ground refers to the type of Isotherm Langmuir, which has a maximum adsorption capacity of 4.97 ± 0.16 mg/gr average.
6. In this study, physical adsorption that occurs in the process of Pb(II) heavy metal adsorption with activated carbon from the spent coffee ground which produces average energy of 11.68 ± 0.07 kJ/mol and the bond reaction is reversible.

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