Preparation and Characterization of Activated Carbon from Gayo Coffee Shell as an Adsorbent for Removal of Lead (Pb) in Liquid Waste

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Abstract. Adsorption been a popular low-cost and environmentally friendly method that can be used to reduce heavy metals in wastewater especially with the use of biomass-sourced sorbents. In this study, the adsorbent was prepared from the coffee shell. The Performance of the prepared adsorbent was studied on the adsorption of Pb(II). The initial concentration of Pb(II) solution used was 300 mg/L and contact time was varied to 0, 30, 60, 90, 120 and 150 minutes. The characteristics of the sorbent were studied in terms of moisture content, ash content, and adsorption of I2. Further characterizations of the coffee shell sorbent were also carried out using Scanning Electron Microscopy (SEM), Fourier Transform Infra-Red Spectrophotometer (FTIR), X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF) and Surface Area Analyzer (SAA). The characterization results showed that the prepared sorbent meets the quality requirements according to SNI 06-3730-1995. The results from the adsorption process revealed that the maximum absorption capacity that can be performed by sorbent was 170.26 mg/g at the equilibrium time of 90 minutes. In conclusion, the coffee shell can be a potential biomass material to prepare adsorbent with high removal performance of heavy metal.

1. Introduction
Indonesia is one of developing countries with high pollution issues particularly in terms of water pollution. Water pollution is defined as a condition which living things, substances, energy or other components presence in the water, causing the quality of the water to be polluted. These inputs are often referred to as pollutant elements, which practically sourced from routine discharges, such as liquid waste discharges. One of common water pollutants is heavy metal such as lead (Pb) [1-3].

In the environment, Pb is usually resulted from mining activities especially during the processing of metal ore with concentrations ranging from 200-500 mg/L [3, 4]. This concentration is considerably very high to be discharged into the environment. According to class I water quality standards, the safe Pb content in water is not more than 0.03 m/L [5].

Adsorption is a separation process that has been rapidly adopted for remediation of contaminants in water and wastewater [6, 7]. Absorbents such as activated carbon plays an
important role as an efficient material in this process. However, the producing cost of activated carbon is still expensive; for that reason, many researchers have begun to look for alternative adsorbents made from local and natural sources. Natural-source such as those from plant-based materials can be used as a source to fabricate sorbent for removal of heavy metals from water and wastewater systems [8, 9].

Aceh Province precisely the Central Aceh Regency is one of big producer of highest quality coffee in Indonesia. The farming and production activities of coffee generate a huge load of waste. In most case, those generated wastes especially in the form of coffee shell are directly loaded into the environment as waste without further treatment or use. These wastes continue to grow with the growing production of coffee in Indonesia. Based on this, in this study, coffee shells are utilized to prepare activated carbon with the aim to add more economical and environmental values to the coffee-sourced waste. To the best of our knowledge and based on literature study, the utilization of coffee shells especially those from Gayo arabica coffee is for the first time reported in this work. In earlier work [10], we have performed a similar study by utilizing coffee ground as a bio-sorbent. The coffee shell can be used as a sorbent source due to its organic components such as cellulose, hemicellulose, and lignin. According to Pope [11], materials containing lignin, hemicellulose, and cellulose can be used as raw material for sorbent production due to their effectiveness in absorbing metals in liquid waste. The detailed content or characteristics of coffee endocarp (shell) can be seen in Table 1.

| Component   | Percentage (%) |
|-------------|----------------|
| Cellulose   | 53.19          |
| Hemicellulose| 20.17          |
| Lignin      | 28.58          |

In detail, this paper reports the preparation of low-cost adsorbent from the shell of Gayo Arabica coffee. The basic characteristics of the prepared adsorbent are evaluated through several analysis. The performance of adsorbent is also tested in adsorption of Pb-containing artificial wastewater solution.

2. Experimental

2.1 Materials
The shell of Gayo Arabica coffee was obtained from Aceh Tengah regency, Indonesia, and used as the main material in sorbent preparation. The other supporting materials were Pb(NO₃)₂ (Pudak Scientific, Indonesia) as an artificial contaminant sample. In addition, Iodine solution (Sigma Aldrich, USA) (0.1 N), the starch indicator (1%) (LabChem, Pennsylvania, USA), sodium thiosulfate (The Science Company, Colorado, USA) (0.1 N) and distilled water were also used in this work.

2.2 Preparation of Activated Carbon Sorbent from Coffee Shells
The coffee shell was washed and sun-dried then carbonized at 350°C for 120 minutes using a muffle furnace until the carbon was formed. The resulting carbon was crushed using mortar and pestle, then sifted using a 100-120 mesh sieve.

2.3 Characterizations of the Sorbent
The prepared activated carbon sorbent from this research was characterized using Scanning Electron Microscopy (SEM, FEI, Inspect-s50, Japan), Fourier Transform Infra-Red
Spectrophotometer (FTIR, Shimadzu, IRPrestige21, Japan), X-Ray Diffraction (XRD, PanAnalytical, E’xpert Pro, UK), X-Ray Fluorescence (XRF, PanAnalytical, Minipal 4, UK), Surface Area Analyzer (SAA, Nova, Quantachrome, USA) to study the morphological structure, observe the functional groups, investigate the crystalline structure, analyze the chemical composition as well as concentration, and determine the surface area of sorbent, respectively. In addition, some other characterizations were also carried out, as follows:

2.3.1 Water content. 1 gram of sorbent was put into a porcelain dish which has been weighed. The dish was placed into an oven at a temperature of 105°C for 3 hours. Following that, the dried sorbent was cooled down in a desiccator and weighed again.

\[
\text{Water content (\%)} = \frac{a-b}{a} \times 100
\]

where \(a\) and \(b\) represent the initial and dried weights of the sorbent (g), respectively.

2.3.2 Ash content. 2 grams of sorbent was placed into a porcelain dish and weighed. The cup was put into a muffle furnace at 600°C for 6 hours then cooled in a desiccator and weighed.

\[
\text{Ash content} = \frac{a}{b} \times 100 \ %
\]

where \(a\) and \(b\) are the respective weight of ash and initial dried carbon (g).

2.3.3 Absorption of iodine. 0.15 gram of sorbent was put into a sealed container. Then, 50 mL of 0.1 N iodine solution was added in the container then shaken for 15 minutes then filtered. A total of 10 mL of filtrate was titrated with 0.1 N sodium thiosulfate solution. If the yellow color of the solution was almost gone, 1% starch indicator was added. Titration continues until the blue color is gone.

\[
\text{Absorption of iodine (mg/g)} = \left\{ \frac{10 \left( \frac{N \times V}{S} \right)}{0.1} \right\} \times 12.69 \times 2.5
\]

Where, \(V\) is the volume of used sodium thiosulfate solution, \(N\) for sodium thiosulfate concentration, \(S\) represents the mass of carbon (g), and 12.69 is the equivalent of iodine to 1ml of 0.1 N sodium thiosulfate solution.

2.4 Adsorption Test on Artificial Pb(NO₃)₂ Wastewater. Initially, artificial wastewater solution was prepared in 1000 ppm by dissolving 0.799 gram of Pb(NO₃)₂ into 500 ml of deionized water then diluted into 200, 300 and 500 mg/L as varying initial concentrations. A total of 100 ml sample was contacted with 0.1 gram sorbent with a different contact time of 0, 30, 60, 90, 120 and 150 minutes, the process was carried out with a stirring speed of 250 rpm. The concentration of Pb(NO₃)₂ in feed solution and after adsorption was measured Pb using Atomic absorption spectrometer (AAS).

3. Results and Discussion

3.1 Water and ash content and

The activated carbon sorbent from the coffee shell was characterized in terms of water content and ash content, as well as adsorption of iodine, the results can be seen in Table 2. The results of analysis which presented in Table 2 indicate that the prepared activated carbon sorbent has the water content, ash content and absorption capacity of iodine that meet the quality standards of activated carbon.
based on SNI No. 06-3730-1995. These results confirm that the prepared adsorbent in this study can be used for application in the reduction of Pb (II) metal.

Table 2. Characteristics of activated carbon sorbent from the coffee shell

| Parameter       | SNI Standard No. 06-3730-1995* | Analysis results |
|-----------------|---------------------------------|------------------|
| Water Content   | Max. 15%                        | 4 %              |
| Ash Content     | Max. 10%                        | 4 %              |
| Iodine Adsorption | Min. 750 mg/g                  | 994.05 mg/g      |

3.2 Scanning Electron Microscope (SEM) Analysis

The Scanning Electron Microscope (SEM) analysis was carried out to study the surface morphology of the activated carbon sorbent prepared from the coffee shell. The SEM imaging result is shown in Fig. 1.

Based on Fig. 1, it is seen that the sorbent has a porous surface with large size of pores. It is reported that sorbent with a porous surface is advantageous for the adsorption as it provides more contact area [10].

3.3 Surface Area Analyzer (SAA) Analysis

The surface area of the sorbent was determined by means of Surface Area Analyzer (SAA) using the Brunauer, Emmet, and Teller (BET) method. Results of analysis can be seen in Table 3.

Table 3. Analysis results of the surface area of coffee shell activated carbon sorbent

| Surface Area (m²/g) | Pore Volume (cm³/g) | Pore Size (Å) |
|---------------------|---------------------|---------------|
| 3.0438              | 0.0075              | 98,5269       |

Table 3 shows that the sorbent has pores with an average diameter of 98.5269 Å. These results indicate that sorbent is classified as a mesoporous material. As reported by Mariana et al. [10], the mesoporous material has a diameter ranging of 20-500 Å.
3.4. Fourier Transform Infrared (FTIR) Analysis
With the aim to observe the chemical functional groups contained in coffee shell sorbent, the analysis was carried out by means of FTIR instrument. The IR spectra result is provided in Fig. 2.

![Figure 2. IR Spectra of activated carbon sorbent from the coffee shell](image)

From Fig. 2, it can be observed that there are several peaks that distinguish the spectra of the prepared sorbent. The peaks are representing the presence of –OH group, C-H, C = C and C = O which mostly contributed from the organic components contained in the coffee shell. Detailed information on spectra reading is given in Table 4.

| Functional group                  | Remarks    | Wavenumber (cm⁻¹) | Reference [12] | This study |
|-----------------------------------|------------|-------------------|----------------|------------|
| H₂O                               | O–H        | 4000-3400         | 3620 and 3743  |
| CH₄                               | C–H        | 3000-2700         | 2964           |
| Aromatic                          | C=C        | 1690-1450         | 1649-1452      |
| Aldehyde, Ketone, Carboxylic acid | C=O        | 1900-1650         | 1693           |

3.5 X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF) Analysis
The X-Ray Diffraction (XRD) analysis aims to determine the crystalline structure of the coffee shell sorbent which is characterized by peaks at an angle of 2θ. The results of the XRD analysis can be seen in Fig. 3.

Fig. 3 shows the results of XRD pattern of coffee shell sorbent. According to Khalil et al. [13], activated carbon showed an irregular microcrystalline structure in which microcrystals of graphite were randomly oriented. Their result is consistent with the finding in this study, as seen in the sorbent which carbonized at 350°C for 120 minutes, carbon (C) is detected in the 2θ area of 26.28° (d = 3.3887 Å) and 44.27° (d = 2.0443 Å). The small but sharp peak in the XRD pattern indicates an amorphous structure of the sorbent [14].
Figure 3. XRD pattern of coffee shell sorbent

Table 5. XRF Analysis Data

| Komponen | % Weight |
|----------|----------|
| SiO₂     | 47.32    |
| Al₂O₃    | 10.46    |
| Fe₂O₃    | 8.87     |
| MgO      | 8.84     |
| SO₃      | 0.16     |
| K₂O      | 0.45     |
| CaO      | 11.54    |
| Na₂O     | 0.07     |
| P₂O₅     | 0.161    |
| TiO₂     | 0.377    |
| Mn₂O₃    | 0.163    |
| CrO₃     | 0.078    |

3.6 Effect of Contact Time on Pb (II) Metal Absorption Capacity

Contact time is one of the factors affecting the adsorption process. Determination of the optimum contact time for adsorption aims to determine the time needed by the coffee shell sorbents to absorb the maximum lead (Pb) ion. The relationship between contact time and the adsorption efficiency of Pb (II) metal is shown in Fig. 4.

Based on Fig. 4, it can be seen that the absorption capacity increases with increasing contact time between the adsorbate and sorbent. By prolonging the contact time, the absorbed Pb (II) metal increase until the equilibrium occurs. Based on the results of the experiment, it is 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 are 77.29; 105.49; 170.26; 174.44 and 176.97 mg/g, respectively. At the beginning of the process, the absorption rate is very large, especially in the first 30 minutes until minute 90, and from minute 90th until minute 150th (te) in which the absorption equilibrium occurs. Based on this, it can be concluded that the optimum contact time of activated carbon in Pb metal
ion absorption is achieved at 90 minutes. Longer contact time resulted in more adsorbed Pb due to the increasing chance of activated carbon to intersect and contact with the Pb particles and the particles adhered to the surface of the sorbent [15].

![Figure 4. Effect of contact time on adsorption capacity of Pb (II) metal at the initial concentration of adsorbate 302.22 ppm](image)

### 4. Conclusion
Preparation of activated carbon sorbent from Gayo Coffee Shell has been conducted. Characterization results show that the water content, ash content, and absorption of iodine have met the quality standards of activated carbon based on SNI No. 06-3730-1995. Result of SEM imaging confirms that the sorbent has a structure with a lot of pores formed. BET characterization result indicates that the coffee shell sorbent is classified as mesopore. The FTIR characterization results show that the –OH, C-H, C = C, and C = O functional groups dominate the chemical composition of the activated carbon sorbent from the coffee shell. The XRD characterization reveals a slight sharp peak which is the indication of the amorphous structure. The equilibrium time was achieved at 90 minutes of operation time with an absorption capacity of 170.26 mg/g. From the overall results, it can be concluded that the coffee shell waste has a high potential to be utilized as an adsorbent material.

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