Characterization and utilization of coconut coir and bentonite-based adsorbents for removal of lead metal ion from hazardous liquid waste

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Abstract. Adsorbent is one of the most commonly used materials because of its high adsorption effectiveness. However, adsorption with one type of adsorbent causes a lower adsorption efficiency. This study aims to determine the characterization of adsorbents from coconut coir and bentonite-based adsorbents and the combined adsorbent from coconut coir charcoal and bentonite and to examine the adsorption capacity of lead metal ion on these adsorbents. The types of adsorbents used in this study were coconut coir charcoal without activation, coconut coir charcoal with activation, pure bentonite, bentonite with activation, and combination of activated coconut coir charcoal: activated bentonite with mass ratio of 70:30. The research was initiated with pyrolysis of coconut coir at temperature of 400°C, then activated chemically with 0.3 M HCl solution. The resulting adsorbents were characterized using Scanning Electron Microscopy (SEM) to determine the morphological structure, Fourier Transform Infra-Red Spectrophotometer (FTIR) to determine the functional groups, X-Ray Diffraction (XRD) to determine the crystalline structure. Then the adsorption of lead metal ions was carried out by using these adsorbents. The results showed that the best adsorption efficiency is by adsorbent combination of activated coconut coir charcoal: activated bentonite with mass ratio of 70:30. The adsorption efficiency of lead metal ions using activated coir adsorbents: activated bentonite (70:30) is 35.0%. The activated coconut coir charcoal: activated bentonite with mass ratio of 70:30 has the largest adsorption capacity of lead metal ions which is 182.71 mg/gr.

1. Introduction
Coconut coir that is a waste from coconut plantations is available in large quantities and is easily found in Indonesia [1], can be used as sorbent because it contains quite high lignin, cellulose and hemicellulose and has a porous structure.According to research by Etim et al, the results of testing coconut coir ash (CCD) against methylene blue in aqueous solution were very effective to reduce the levels of methylene blue and the material was also inexpensive compare to other materials [2]. Furthermore, the results of research conducted by Tan et al stated the results of KOH adsorption: by impregnated charcoal can adsorb 191.73 mg / g from a solution of 2,4,6 TCP [3].Bentonite has a layer
structure that has the ability to swell and has cations that can be exchanged with others. Although bentonite clay functions as adsorption, its adsorption capacity is still limited. These deficiencies can be regulated through the activation process by using acid solutions such as HNO$_3$, HCl and H$_2$SO$_4$ [4]. The use of bentonite together with coconut coir to produce a novel adsorbent would be an alternative way to form adsorbent with higher sorbent surface reactivity. In this study the use of adsorbents from coconut coir and bentonite-based adsorbents and the combination between activated charcoal from coconut coir and activated bentonite was performed to have the combined adsorbent with the best adsorption capacity. The adsorbent obtained was tested for adsorption capacity by using lead metal ion solution.

2. Method

2.1. Materials and tools

The tools used in this study are Fourier Transform InfraRed Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), hot plates and stirrers, tube furnaces, muffle furnaces, digital scales, mechanical sieves 100-200 mesh and desiccator. While the materials used are coconut coir, bentonite, HCl 0.3 M, Pb(NO$_3$)$_2$ solution and distilled water.

2.2. Carbonization process of coconut coir

Coconut coir was put into the tube furnace and then carbonized at 400 °C for 2 hours [6]. Then the coconut charcoal was cooled for 24 hours. Then it was ground and sieved using a 100-200 mesh sieve [5,6].

2.3. Bentonite activation process

Bentonite originating from BlangDalam Village, Nisam Sub-District, Aceh Utara was washed with water to remove soil and dirt, then dried, milled and sieved to particle size of 100-200 mesh. Subsequently bentonite was put into an erlenmeyer and activated by the addition of HCl at temperature of 110 °C and an activation time of 30 minutes.

2.4. The mixing and carbonization process

Activated charcoal from coconut coir and activated bentonite was mixed with mass ratio of 70:30. The adsorbents were then dissolved in distilled water with a ratio of 10: 1 (liquid:solid) and stirred using a stirrer for 2 hours. After stirring, the sorbents were put in oven for 4 hours at temperature of 110 °C to remove moisture content. Next, the dried materials were put in a muffle furnace and heated at temperature of 800 °C for 2 hours [7]. After the carbonization process the material was stored in a desiccator.

2.5. Adsorbent characterization

The produced adsorbent was characterized using Scanning Electron Microscopy (SEM) to determine the morphological structure, Fourier Transform Infra-Red Spectrophotometer (FTIR) to determine the functional group and X-Ray Diffraction (XRD) to determine the crystalline structure.

2.5.1. Water content. Two grams of combined adsorbents were put into a weighted porcelain cup. The cup was put into the oven at temperature of 105°C for 3 hours then cooled in a desiccator and weighed. The formula of moisture content can be seen on Equation 1.

\[
\text{Moisture Content (\%)} = \frac{a - b}{a} \times 100\% \quad (1)
\]

Where :

a = initial carbon weight (g)
b = dry carbon weight (g)
2.5.2. Ash content. Two grams of combined adsorbents were put into a weighted porcelain cup. The cup was put into the muffle furnace and heated at 600°C for 6 hours then cooled in a desiccator and weighed. The formula of ash content can be seen on Equation 2.

$$\text{Ash Content (\%)} = \frac{a}{b} \times 100\%$$ (2)

Where:

- \(a\) = ash weight (g)
- \(b\) = initial dry carbon weight (g)

2.5.3. Adsorption of lead metal ion. One hundred ml of 1000 mg/L artificial Pb(NO₃)₂ waste solution was contacted with 0.5 gram of adsorbent with variation of contact time 30, 60, 90, 120 and 150 minutes while stirring at speed of 250 rpm. After being contacted with adsorbents, the concentration of artificial Pb(NO₃)₂ waste solution was measured using AAS. The formula of percentage of adsorption and adsorption capacity can be seen on Equation 3 and 4 respectively.

$$\text{adsorption (\%)} = \frac{\text{initial concentration of adsorbate} - \text{final concentration of adsorbate}}{\text{initial concentration}} \times 100\%$$ (3)

$$\text{adsorption Capacity} = \frac{\text{initial concentration of adsorbate} - \text{final concentration of adsorbate}}{\text{the amount of adsorbent}} \times \text{solution vol}$$ (4)

3. Result and discussion

3.1. Characterization on of prepared adsorbents

The analysis showed that the activated carbon from coconut coir was activated HCl 0.3 M and without activator has met the quality standard of activated carbon according to SNI No. 06-3730-1995. Initial characterization of prepared adsorbents to see the water content and ash content of each adsorbent can be seen in Table 1.

| No. | Type of Adsorbent | Water content | Quality Standard SNI No. 06-3730-1995 | Ash Content | Quality Standard SNI No. 06-3730-1995 |
|-----|-------------------|---------------|---------------------------------------|-------------|---------------------------------------|
| 1.  | Coconut Coir      | 5 %           | Max 15%                               | 1.84%       | Max 10%                               |
| 2.  | Coconut Coir Charcoal | 6.5%       | Max 15%                               | 1.73%       | Max 10%                               |
| 3.  | Activated Coconut Coir Charcoal | 7 % | Max 15%                               | 2.09%       | Max 10%                               |
| 4.  | Purified Bentonite | 4.3%          | Max 15%                               | 0.53%       | Max 10%                               |
| 5.  | Activated Bentonite | 7.5%          | Max 15%                               | 2.32%       | Max 10%                               |
| 6.  | Activated Coconut Coir Charcoal: Activated Bentonite (70:30) | 3.5% | Max 15%                               | 1.84%       | Max 10%                               |

Table 1 shows the analysis results of prepared adsorbents, showing that the water content and adsorption of iodine met the quality standards of activated charcoal based on SNI No. 06-3730-1995. The highest water content was found in activated bentonite by 7.5%, while the lowest water content was found in activated coconut coir charcoal: bentonite (70:30) was by 3.5%. This is due to the chemical activation of the bentonite and the washing process with water. Water in the activation and washing solution enters the bentonite, causing the water content in the bentonite to increase. Whereas, the activated coconut coir charcoal adsorbent: activated bentonite (70:30) that is physically activated at a temperature of 800 °C, the water in the adsorbent would evaporate causing a decrease of water content compared to previous adsorbent. According to research by Abdul Ghani et al, the water content is influenced by various processes such as stirring, size reduction and combustion [8], a low water content would improve carbon quality because the adsorption of activated carbon against gases or liquids is higher. Then the highest ash content was found in sample of activated bentonite that was
2.32%, while the lowest ash content was found in activated coconut coir charcoal: activated bentonite (70:30) as much as 0.53%. This is because in activated bentonites the use of chemicals as activators often results in contamination of the activated charcoal produced. Generally, activators leave unwanted remnants, for example substances that are not soluble in water at the time of washing.

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

![SEM photographs of (a) pure coconut coir, (b) coconut coir charcoal without activation, (c) coconut coir charcoal with activation, (d) pure bentonite (e) bentonite with activation and (f) activated coconut coir charcoal: activated bentonite (70:30) by magnification 2000 times.](image-url)
Coconut coir charcoal with chemical activation of HCl has a more regular pore distribution with a greater number of pores than without chemical activation. In addition, in coconut coir charcoal with HCl activation has much higher visible surface pores compared to coconut coir charcoal without activation. This is because activation with HCl is more able to dissolve impurities so that more pores are formed, and the adsorbate adsorption process becomes more higher than without activation which has fewer number of pores. Carbon pores without activation, was still covered by some impurities. Coconut coir charcoal activated by HCl solution shows a change with appearance of the number of open pores [9].

In Figure 1 (d) pure bentonite shows that the pore morphology is still closed, in Figure 1 (e) bentonite with activation begins to appear open pores, and in Figure 1 (f) activated coconut coir charcoal: activated bentonite (70:30) the open pores became larger. This shows that chemical activation in bentonite can open pores bigger than in pure bentonite. The pore morphology of activated coconut coir charcoal: activated bentonite (70:30) is greater than coconut coir adsorbent types and bentonite so that the distribution of activated coconut coir : activated silica (70:30) is more regular with more pores than the type of adsorbent coconut coir and bentonite [8].

3.3. Fourier Transform Infra-Red (FTIR)
Characterization of Fourier Transform Infra-Red (FTIR) was conducted to determine the functional groups or components contained in the adsorbent of activated coconut coir charcoal: activated bentonite. The results of the FTIR analysis can be seen in Figure 2.

![FTIR spectrum for several adsorbents.](image)

**Figure 2.** FTIR spectrum for several adsorbents.

| Functional Groups | Bond | Wavenumbers Range (cm⁻¹) | Reference | Activated Coconut Coir Charcoal | Activated Bentonite | Activated Coconut Coir Charcoal: Activated Bentonite (70:30) |
|-------------------|------|---------------------------|-----------|-------------------------------|------------------|---------------------------------------------------------------|
| CH₄               | C–H  | 3000-2700                 | -         | -                             | -                | -                                                             |
| Aldehyde, Keton,  | C=O  | 1900-1650                 | 1653      | 1859,37                       | 1840,04          |                                                                |
| Carboxyl acid     | Si–O–Si | 1130-1000       | 1016,48  | 1082,06                       | 1100,37          |                                                                |
| SiO₂              |      |                          | Source: Ma et al. (2015). |                  |                  |                                                                |

**Table 2.** IR Interpretation of several prepared adsorbents.
Based on Table 2 the FTIR spectrum of activated coconut coir charcoal: activated bentonite shows the shifting of wave numbers. This shows that the activation process affects the absorption intensity at the wavelength. Coconut coir adsorbent has several functional groups which are suitable for the structure of activated carbon in general which contains C-H, C = O, and Si-O-Si which are used as active groups to absorb adsorbate.

3.4. X-rays diffraction (XRD) analysis

The characterization of XRD aims to determine the crystalline structure of the coconut coir and bentonite-based adsorbents at an angle of 2θ. The following analysis test results using XRD for 5 types of adsorbents in Figure 3.

![XRD profile for several prepared adsorbents](image)

**Figure 3.** XRD profile for several prepared adsorbents.

Figure 3 shows that the sharp peak region is a characteristic of silicon oxide (SiO$_2$) and the reflection of XRD results also shows crystalline form. The success of chemical activation in coconut coir and bentonite adsorbents can be studied through testing of coconut coir charcoal samples before activation and after chemical activation, pure bentonite and bentonite after chemical activation, and the combination of coconut coir and bentonite adsorbent by using X-Ray Diffraction (XRD) to see the composition level that affects the adsorbent. Coconut coir charcoal without activation shows a peak at 2θ namely: 22.46° (d = 3.95537 Å) indicating the present of SiO$_2$, then coconut coir charcoal with activation shows a peak at 2θ namely: 23.16° (d = 3.90052 Å) which shows the present of SiO$_2$. On sample of pure bentonite shows peak at 2θ namely: 19.68° (d = 4.43469 Å) which shows SiO$_2$ and on bentonite with activation shows peak at 2θ namely: 20.01° (d = 4.43469 Å) which shows SiO$_2$ and on coconut coir: bentonite shows a peak at 20 namely: 23.82° (d = 3.73253 Å) which shows SiO$_2$. Activation of coconut coir charcoal decreases a peak intensity of coconut coir charcoal compared to coconut coir charcoal before activation at the diffraction angle from 2θ namely: 22.46° (d = 3.95537 Å) to 2θ namely: 23.16° (d = 3.90052 Å). The new diffraction angle shows that the activation of coconut coir charcoal causes coconut coir charcoal to be more amorphous compared to before activation. The activation process which involves chemical activation and high temperature heating causes a change in the structure of the carbon aromatic compound bonds and the partial breakdown of the double bonds between carbon atoms into a single bond. This is largely due to the decomposition of oxygen-containing bonds as well as the removal of carbon atoms due to the effect of pressure which makes the existing layers fragmented.
Table 3. The composition of each adsorbents.

| Type of Adsorbent                                      | Composition (%) |  
|-------------------------------------------------------|-----------------|
|                                                        | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ |
| Coconut coir charcoal                                  | 51.3    | 34.5        | 14.3        |
| Activated coconut coir charcoal                        | 61.3    | 28.9        | 9.8         |
| Pure bentonite                                         | 43.5    | 34          | 22.5        |
| Activated bentonite                                    | 81.4    | 14.3        | 4.3         |
| Activated coconut coir charcoal: activated bentonite   | 73.5    | 20.6        | 5.8         |

From these compositions, it can be seen that after activation process, the composition change of SiO$_2$, Al$_2$O$_3$ and Fe$_2$O$_3$ occurred, the amount of silica composition increased for both samples of activated coconut coir charcoal and activated bentonite. The activators are useful for increasing pore volume on the surface of the adsorbent. The amount of silica composition for samples of combination activated coconut coir charcoal and activated bentonite is between the value of activated coir charcoal composition and activated bentonite.

3.5. The effect of adsorbent types on adsorption efficiency and adsorption capacity of lead metal ion

In this study the adsorption process of lead metal ion solution by prepared adsorbents was measured by using an AAS tool. Figure 4 shows that adsorption efficiency increase with increasing of the contact time until reaching optimum contact time. After the optimum contact time is achieved, the adsorption efficiency value decreases significantly. However, for sample of activated coconut coir charcoal: activated bentonite (70:30) after the optimum contact time is reached the adsorption efficiency value decreases and after that tends to be constant. The highest adsorption efficiency value for lead metal ion as much as 35 % was obtained after 90 minutes contact time for sample of activated coconut coir charcoal: activated bentonite (70:30). Table 3 also show that the SiO$_2$ content found in sample of activated coconut coir charcoal: activated bentonite (70:30) is higher than in sample of activated coconut coir charcoal and it is slightly below the activated bentonite. From the XRD results, the silica content found in sample of activated coconut coir charcoal: activated bentonite (70:30) is as high as 73.5%. Silica plays an important role in the adsorption process because it has good adsorption and ion exchange capabilities [9]. Besides, the presence of greater Al$_2$O$_3$content in sample of activated coconut coir charcoal: activated bentonite (70:30) makes the ability of this adsorbent better than other adsorbents.

![Figure 4](image-url)

**Figure 4.** Relationships among contact time (minute), types of adsorbent and adsorption efficiency.
Adsorption capacity shows the ratio of the amount of adsorbate that be able be adsorbed by the adsorbent. The relationship between the type of adsorbent and the adsorption capacity can be seen in Figure 5.

![Figure 5](image_url)

**Figure 5.** Relationships among contact time (minute), type of adsorbents and adsorption capacity.

Figure 5 shows that adsorption capacity will increase with increasing of contact time between adsorbent and lead metal ion, and then after reaching the optimum adsorption time there is a decrease in lead adsorption and tends to decrease. The optimum adsorption time of lead metal ion by the adsorbent is 90 minutes. The highest adsorption capacity was 182.71 mg/g. Figure 5 show that the type of adsorbent and contact time affect significantly the adsorption capacity, and for the effect of contact time, the adsorption capacity would decrease after 90 minute of adsorption process.

4. Conclusion
Characterization of coconut coir, coconut coir charcoal, pure bentonite, activated bentonite, and activated coconut coir charcoal: activated bentonite (70:30) indicated that the water content and ash content have met the activated carbon quality standard based on SNI No. 06-3730-1995. SEM characterization indicated that activated coconut coir charcoal: activated bentonite (70:30) has the largest pore surface compared to coconut coir and bentonite types adsorbent. FTIR characterization showed that the absorption of the C−H, C=O, and Si−O−Si groups dominates the five adsorbents. From the XRD test results, the silica content in sample of activated coconut coir charcoal: activated bentonite (70:30) was 73.5%.

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