INTRODUCTION

From time to time, the world’s population continues to grow significantly. This condition causes an increase in anthropogenic activity, which increases pollution in the environment. Industrial, mining, agricultural, and household activities are examples of anthropogenic activities that generate waste and contribute significantly to environmental pollution (Gupta et al., 2012). The waste produced typically contains hazardous chemicals such as organic waste, inorganic waste, and other chemical substances that will eventually pollute the soil and waters. The heaviest metals are found in liquid waste from industrial and mining activities (Rabie et al., 2019).

Heavy metal waste is extremely hazardous to humans, and some of it is even toxic. Heavy metals can build up in the human body as a result of various food chains (Meena et al., 2008). Mercury (Hg), arsenic (As), cadmium (Cd), iron (Fe), and radioactive compounds are the heavy metals that have the most negative effects on humans, affect the organs of the body, and cause poisoning. One of the most dangerous heavy metals is mercury (Rocha et al., 2012). As a result, environmental pollution caused by these heavy metals must be addressed immediately in order to avoid even more dangerous effects on human life and to avoid long-term consequences (Abdel Salam et al., 2011).

Many researchers have developed methods to remove mercury from water, such as ion...
exchange, membrane filtering, chemical precipitation, and active carbon adsorption. Adsorption is the most widely used of these methods (Rabie et al., 2019). Adsorption is defined as the adhesion of an adsorbate (adsorbed substance) to the surface of an adsorbent (substance that adsorbs). Adsorption is a popular, simple, and widely used method. The process is simple, and the adsorbent used can be re-absorbed, either for reuse or to remove the compounds contained in the adsorbate. Similarly, in terms of the availability of readily available adsorbent materials in nature, the adsorption method is a popular method for removing mercury metal ions from water (Rabie et al., 2019).

Adsorbents used in the adsorption process are typically organic. Organic adsorbents have several advantages, including the fact that they are readily available in nature, do not require a large investment, are simple, and, most importantly, do not harm the environment. Activated carbon is one of the most commonly used natural adsorbents and one of the best adsorption alternatives. The raw material can be obtained from a variety of agricultural or plantation waste, including coconut shells, durian peels, rice husks, and others. Cocoa shell is one of several natural ingredients that can be used as raw materials for activated carbon. So far, very little research has been conducted on the adsorption of mercury ions using adsorbents derived from the pyrolysis of cocoa shells. The study focused on the ability of cocoa shell to act as a biosorbent for Hg and Ni metal ions (Yetri et al., 2018). The cocoa shell adsorbent used in this study was chemically activated with 0.6 M nitric acid. The adsorbent used in this study was derived from the pyrolysis of cocoa shells without any chemical activation. Additionally, the adsorbent material was characterized and used to reduce mercury ions. The goal of this study was to characterize the adsorbents produced by pyrolysis of cocoa shells and their application in mercury ion reduction.

**EXPERIMENTAL PROCEDURE AND METHODOLOGY**

**Materials**

The materials used in this study were cocoa shells, Hg(NO₃)₂ 1000 mg-Hg/L; NaOH 0.1 N; HNO₃ 0.05 N; iodine, and aquadest with a conductivity < 1 µS/cm. The equipment used includes a pyrolysis reactor, AAS (Agilent Technologies, Type 200 Series AA.), shaker (Yamato type SA400), pH meter, beaker glass, volumetric flask, porcelain cup, glass funnel, pipettor (Eppendorf), spatula, filter paper (Whatman 42), 100-mesh mechanical sieve, analytical balance (MS204TS/00), magnetic stirrer, electric oven (DHG 9053A), muffle furnace (Isuzu model EPTR-26R), spectrophotometer FTIR Prestige-21 (Shimadzu), and SEM JEOL-JSM6510 LA.

**Pyrolysis of Cocoa shells**

After washing and drying, the cocoa shells were placed in the pyrolysis reactor for 1.5 hours at 300 °C, 340 °C, and 380 °C, respectively. Pyrolysis produces activated charcoal, tar, and liquid smoke. Pyrolysis activated charcoal was cooled to room temperature and stored in a desiccator. The activated charcoal was then ground and sieved through a mechanical sieve with a mesh size of 100.

**Adsorption of mercury ion**

100 ml of 2 ppm mercury solution was placed in a separators funnel, then 1 gram of adsorbent was added and shaken at 180 rpm for contact times of 15, 30, 45, 60, 75, and 90 minutes at pH 7. At each contact time interval, 10 ml of sample was collected, filtered, and the filtrate AAS analyzed.

**Characterization of adsorbent from pyrolysis of cocoa shells**

Scanning electron microscopy (SEM) was applied to study the morphological structure, while X-ray diffraction (XRD) analysis was used to determine the crystal structure, and the adsorbent functional groups were analyzed using Fourier transform infrared (FTIR).

**Water content**

1 gram of adsorbent was weighed and put into a porcelain cup that had been weighed, then put into an oven at 115 °C for 3 hours. It was then cooled in the desiccator until reached room temperature before being weighed. Water content in the adsorbent was obtained through calculation using the following equation:

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

where:

- \( a \) – initial adsorbent weight (g);
- \( b \) – weight dry of adsorbent (g).
Ash content

The adsorbent was weighed at 2 grams and put into a porcelain cup that had been weighed. Then put it in the muffle furnace at 800–900 °C for 2 hours. It was then cooled in the desiccator until it reached room temperature before being weighed. The ash content in the adsorbent was obtained through calculation using the following equation:

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

where: $b$ – ash weight (g); $a$ – initial dry carbon weight (g).

Iodine absorption

In a closed container, 0.15 gram of the adsorbent was placed, and 50 ml of a 0.1-N iodine solution was added. The mixture was then shaken for 15 minutes before being filtered. Existing filtrate was diluted to 10 ml and titrated with a 0.1 N thiosulfate solution. If the solution turns yellow, add 1% starch solution. Solution was then titrated again until the blue color vanished and iodine adsorption was calculated using the equation as follow.

$$\text{Iodine absorption = } \frac{A - B \times N (\text{Na}_2\text{S}_2\text{O}_3) \times 12.69 \text{ fp}}{\alpha}$$ \tag{3}

where: $A$ – volume of iodine solution (mL), $B$ – volume of solution (Na$_2$S$_2$O$_3$) used (mL), $N (\text{Na}_2\text{S}_2\text{O}_3 \text{ H}_2\text{O})$ – concentration of (Na$_2$S$_2$O$_3$) (N), $\alpha$ – mass of carbon (g), $N (\text{iodin})$ – concentration of iodine (N), fp – dilution factor, 12.69 – iodine constant for 1 mL 0.1 N natrium thiosulphate solution.

Adsorption parameters selection

The adsorption parameters were selected based on factors that affect to adsorption capacities, including contact time between adsorbate and adsorbent, solution pH, and pyrolysis temperature of the adsorbent preparation. According to the findings of Suhendrayatna et al. (2019) and Muslim et al. (2022), the contact time between adsorbate and adsorbent has a significant impact on adsorption. Jia et al. (2019) and Hassan et al., (2020) concluded that the pyrolysis temperature would increase the pore size, so it has a significant impact on adsorption. According to the findings of Xu et al. (2022), the adsorption capacities were related to solution pH. In this study, the adsorption parameters varied were the contact time between the adsorbate and the adsorbent, the solution pH, and pyrolysis temperature of the adsorbent preparation (Xu et al., 2022).

RESULT AND DISCUSSION

Physical characteristics of adsorbents

In this study, the adsorbent was obtained from the pyrolysis of cocoa shells. After washing and drying the cocoa shells, they were placed in the pyrolysis reactor for 1.5 hours at 300 °C, 340 °C, and 380 °C. The pyrolysis process generates activated charcoal, tar, and liquid smoke (Desvita et al., 2021). After reaching a room temperature-activated charcoal was stored in a desiccator. Figure 1 shows cocoa shells before pyrolysis, after pyrolysis, and adsorbent produced by pyrolysis of cocoa shells after being crushed and sieved with a 100-mesh mechanical sieve. According to Hasan et al. finding’s biochar produced by

![Figure 1](image-url)
low-temperature pyrolysis is suitable for use as an adsorbent to adsorb ionic contaminants. Biochar produced by high-temperature pyrolysis is better suited for absorbing organic contaminants (Hassan et al., 2020). In this study, activated charcoal pyrolysis were used to absorb mercury ions at low temperatures ($\text{Hg}^{2+}$).

Table 1 shows the physical characteristics of adsorbent, including water content, ash content, and iodine absorption. The adsorbent meets the requirements specified in SNI 06-3730-1995 for technical activated charcoal.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>The quality standard of Activated Carbon based on SNI 06-3730-1995</th>
<th>Analysis results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Before pyrolysis (300°C)</td>
</tr>
<tr>
<td>Water content</td>
<td>Max 15%</td>
<td>25%</td>
</tr>
<tr>
<td>Ash content</td>
<td>Max 10%</td>
<td>8.5%</td>
</tr>
<tr>
<td>Iodine absorption</td>
<td>Min 750 mg/g</td>
<td>255 mg/g</td>
</tr>
</tbody>
</table>

Table 1. Result of analysis of water content, ash content, and iodine absorption of adsorbent

The adsorbent’s water content was low, far below the maximum required value. This means that water molecules were still bound to the adsorbent, although in small amounts. The ash content and iodine absorption capacity analysis results were also in accordance with the SNI standards. This shows that activated charcoal prepared from cocoa shells meets the requirements for use as an adsorbent.

Morphological characteristics

SEM was used to examine the adsorbent’s micromorphology. The adsorbent’s surface morphology has a significant impact on the adsorption process. Adsorption will be improved due to the large pore size and surface area. SEM analysis was performed at magnifications of 1000 and 3000 times. Figure 2 shows the SEM analysis results for cocoa shell before and after pyrolysis.

Figure 2 shows that before pyrolysis, the particle size of the cocoa shells was larger and...
lumpy, whereas after pyrolysis, the particle size found smaller and spreads out. This demonstrated that the pyrolysis process in cocoa shells could decompose organic matter and break down the cocoa shell composition into gas, liquid, and solid phases (charcoal). Impurities were removed during the pyrolysis process by evaporating gas and liquid, yielding active charcoal (the solid phase) with high porosity and small particle size. A large surface area indicates a small particle size, making it easier to interact with metals. This results was consistent with the findings of other researchers (Misran et al., 2022; Lestari et al., 2017).

**X-Ray diffraction (XRD) analysis**

The crystal structure of each material was determined by XRD analysis of cocoa shells before and after pyrolysis. The technique of X-ray diffraction was widely used to determine the degree of crystallinity of various materials. Other polymers are non-crystalline, whereas cellulose polymers (various organic matter) are crystalline (Salah Omer et al., 2022). Figure 3 depicts the results of the XRD analysis. Figure 3 shows that there were high and wide peaks at an angle of 2θ: 15° to 22° in the material before pyrolysis. It was made of an amorphous carbon structure (Yusuff et al., 2022). Likewise, the XRD results after pyrolysis, but with a more sloping peak. The peaks in the XRD results after pyrolysis show an orderly structure, with close spacing without sharp peaks indicating that the activated carbon formed was amorphous. The OH groups of various organic materials will produce an orderly crystal structure (Salah Omer et al., 2022).

**Fourier transform infra-red (FTIR) analysis**

FTIR analysis examines the resulting spectrum to determine the chemical functional groups present in the cocoa shell prior to pyrolysis. This chemical functional group was identified using FTIR in the 500-4000 cm⁻¹ range. Figure 4 depicts the FTIR spectra. Table 2 shows the absorption peaks at each wavelength, as well as an analysis of possible functional groups.

Figure 4 shows an example, the obtained spectra show slightly different analysis results between cocoa shells before and after pyrolysis. The presence of OH groups (hydroxyl) and OH stretching was evidenced by the presence of absorption peaks that were characteristically sharp and wide at wave numbers 3815 and 3329 cm⁻¹ in the spectra of cocoa shell before pyrolysis. The presence of aromatic compounds in the activated carbon was identified by a decrease in the absorption peak (Mohideen et al., 2011). In the FTIR wave spectrum before pyrolysis absorption peaks also appeared at the numbers 1735 cm⁻¹ to 1527 cm⁻¹ indicating the presence of C-O and C-C groups which were typical groups found in activated carbon.
After pyrolysis, the OH group (stretching) was no longer present in the cocoa shell spectra. This was most likely because the pyrolysis process evaporates the water content of the cocoa shell. According to other studies, the lower hydrogen and oxygen content of biochar after pyrolysis may be due to dehydration, carbonization during activation, or the pyrolysis process itself (Jabar et al., 2022). After pyrolysis, the spectral results showed a reduction in the peaks for each functional group. This was most likely due to the pyrolysis process’s evaporation of volatile substances (Jabar et al., 2022).

Furthermore, it can be concluded that the adsorbents produced by pyrolysis of cocoa shells contain O-H, C-O, C-C, C=H groups as active groups for mercury ion absorption. According to Jia et al. (2019), the number of carbon groups obtained in pyrolysis charcoal was consistent with the fact that pyrolysis charcoal is mostly composed of carbon. Other studies have found that the adsorption capacity of mercury ions with natural adsorbents was determined not only by the pore size of the adsorbent, but also by the surface chemical properties. The presence of functional groups O-H, C-O, C-C, C=H, particularly those containing oxygen, increases the adsorption capacity of biosorbents for mercury ions (Jia et al., 2019).

**Adsorption of mercury ions**

The contact time in this study ranged from 0 to 15, 30, 45, 60, 75, and 90 minutes. Figure 5 depicts a graph of the effect of contact time on the absorption capacity of mercury ions. Figure 5 shows that the absorption capacity of mercury ions increased as contact time increases. Contact times of 15 to 60 minutes resulted in significant increased in absorption capacity, namely 0.055 mg/g, 0.074 mg/g, 0.096 mg/g, and 0.099 mg/g.

<table>
<thead>
<tr>
<th>Functional groups</th>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-H (Hydroxyl)</td>
<td>4000–3400</td>
<td></td>
</tr>
<tr>
<td>O-H stretches</td>
<td>3500–3200 (Mentari et al., 2018)</td>
<td>3329</td>
</tr>
<tr>
<td>C≡C</td>
<td>2450–2345</td>
<td></td>
</tr>
<tr>
<td>C=O Ketones</td>
<td>1700–1500</td>
<td></td>
</tr>
<tr>
<td>C=O Lignin</td>
<td>1700–1500</td>
<td></td>
</tr>
<tr>
<td>C-O Carboxylic acid</td>
<td>1250–1000</td>
<td></td>
</tr>
<tr>
<td>C-O-C</td>
<td>1000–500</td>
<td></td>
</tr>
<tr>
<td>O-H Polysaccharides</td>
<td>1000–500</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4. FTIR Spectra of cocoa shell before and after pyrolysis

Table 2. FTIR characterization results of cocoa shell before and after pyrolysis

<table>
<thead>
<tr>
<th>Functional groups</th>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-H (Hydroxyl)</td>
<td>3815</td>
<td>3936; 3712; 3635</td>
</tr>
<tr>
<td>O-H stretches</td>
<td>3329</td>
<td>-</td>
</tr>
<tr>
<td>C≡C</td>
<td>2937; 2900</td>
<td>2873; 2833</td>
</tr>
<tr>
<td>C=O Lignin</td>
<td>2362</td>
<td>2355</td>
</tr>
<tr>
<td>C=O Ketones</td>
<td>1735; 1608; 1527</td>
<td>1573</td>
</tr>
<tr>
<td>C-O Carboxylic acid</td>
<td>1101; 1060</td>
<td>1076; 1047; 1004</td>
</tr>
<tr>
<td>C-O-C</td>
<td>1060; 916; 862; 821; 777; 665; 619; 588; 501</td>
<td>950; 873; 827; 788; 759; 694; 617; 572; 534; 516</td>
</tr>
</tbody>
</table>
It then increased gradually over 60 minutes, reaching equilibrium with an absorption capacity of 0.106 mg/g at 90 minutes. According to the findings of Suhendrayatna et al. (2019), the contact time between the adsorbate and the adsorbent has a significant impact on adsorption (Suhendrayatna et al., 2019). In the study of Muslim, et al., (2022) obtained the same results, with the adsorption capacity increasing sharply in the first 60 minutes, then gradually increasing at 60 and 70 minutes until reaching an equilibrium time of 90 minutes (Muslim et al., 2022).

Several researchers reported that mercury removal was carried out by adsorption processes using various adsorbents. Park et al. (2018) reported the mercury adsorption process using sulfurized wood biochar (SWB) and pristine wood biochar (WB). The research result showed that mercury adsorption was well described by pseudo second order model. The maximum adsorption capacities of SWB and WB were found at 107.5 and 57.8 mg/g (Park et al., 2018). The adsorption kinetics model that occurred in this study was also a pseudo-second-order model with the adsorption capacities was 0.106 mg/g. In next research, adsorbent can be chemically activated to increase adsorption capacities. In another study, Lelifajri et.al. (2021) have used magnetic sulfonated chitosan composite beads as an adsorbent for reducing mercury ions. Results shown that the highest adsorption capacities was 0.65 g (at a composition of sulfonated chitosan of 56.5%) (Lelifajri et al., 2021). One of the main parameters in the adsorption process is the adsorption capacity which describes the performance of the adsorbent applied in the adsorption process. Table 3 presents a comparison of the adsorption capacity values of various types of natural adsorbents. When compared to absorbents from other activated carbon-based natural materials that have been reported in previous studies, adsorbent from the pyrolysis process produced in this study are classified that

**Table 3. Hg (II) ion adsorption capacity by adsorbent based on natural materials**

<table>
<thead>
<tr>
<th>Adsorbent-based on natural materials</th>
<th>Adsorption capacity</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bambo (Bambusa vulgaris var. striata)</td>
<td>218.08 mg/g</td>
<td>(Mistar et al., 2019)</td>
</tr>
<tr>
<td>Coconut shell</td>
<td>3.02 mg/g</td>
<td>(Goel et al., 2004)</td>
</tr>
<tr>
<td>Bambusa vulgaris var. striata</td>
<td>248.05 mg/g</td>
<td>(González &amp; Pliego-Cuervo, 2014)</td>
</tr>
<tr>
<td>Rice straw</td>
<td>0.11 mmole/g</td>
<td>(Goel et al., 2004)</td>
</tr>
<tr>
<td>Rice husks</td>
<td>1.30×10³ mol.dm⁻³</td>
<td>(Khalid et al., 1999)</td>
</tr>
<tr>
<td>ZnCl₂-modified walnut shells</td>
<td>151.5 mg/g</td>
<td>(Zabibi et al., 2009)</td>
</tr>
<tr>
<td>Palm bunches and rice husks</td>
<td>10.01 mg/g</td>
<td>(Suhendrayatna et al., 2019)</td>
</tr>
<tr>
<td>Modified natural zeolite</td>
<td>9–26 mg/g</td>
<td>(Inglezakis et al., 2023)</td>
</tr>
<tr>
<td>Magnetic sulfonated chitosan composite beads</td>
<td>0.65 g</td>
<td>(Lelifajri et al., 2021)</td>
</tr>
<tr>
<td>Sulfurized Wood Biochar (SWB)</td>
<td>107.5 mg/g</td>
<td>(Park et al., 2018)</td>
</tr>
<tr>
<td>Pristine wood biochar (WB)</td>
<td>57.8 mg/g</td>
<td>(Park et al., 2018)</td>
</tr>
<tr>
<td>Peanut and sheanut shells</td>
<td>98.20–100 %</td>
<td>(Duwiejuah et al., 2022)</td>
</tr>
<tr>
<td>Cocoa shell</td>
<td>0.106 mg/g</td>
<td>This Study</td>
</tr>
</tbody>
</table>
has a relatively low adsorption capacity (0.106 mg/g). When compared to absorbents from other activated carbon-based natural materials that have been reported in previous studies, adsorbent from the pyrolysis process produced in this study is classified as adsorbents that have a relatively low adsorption capacity (0.106 mg/g). The differences in adsorption capacity is due to the fact that each natural material has different characteristics of its constituent elements, such as the type of functional group and its preparation method.

Adsorption kinetics

Adsorption kinetics is the rate at which a solute in a solution is released onto the solid surface of an adsorbent at a given dose, temperature, flow rate, and pH (William Kajumba et al., 2019). The amount of mercury ion adsorbed by the adsorbent per unit of time is also defined as adsorption kinetics. It can be determined by tracking the amount of mercury ions adsorbed by the adsorbent over time. It was presented as a mercury adsorption rate constant (Muslim et al., 2015). There are two processes at work during the adsorption process: physical adsorption and chemical adsorption.

Figure 6 depicts an adsorption kinetics graph based on pseudo-first-order equations. The pseudo-first-order kinetics model was based on the assumption that the adsorption process is reversible or physical.

Based on Figures 6 and 7, it is possible to conclude that the adsorption kinetics model that occurs in this study was a pseudo-second-order model. The larger PSO correlation coefficient is 0.9929, while the smaller PFO correlation coefficient is 0.8651. The PSO model was based on the assumption that adsorption occurs irreversibly or chemically. The solute and adsorbent form a strong bond during this chemical adsorption process, which involves electron transfer (William Kajumba et al., 2019).

CONCLUSIONS

Based on the results of the characterization, it is possible to conclude that the adsorbent produced by pyrolysis of cocoa shells meets the
requirements for water content, ash content, and iodine absorption specified in SNI 06-3730-1995 for technical activated charcoal. Analyses of FTIR, SEM, and XRD data also revealed that activated charcoal derived from the pyrolysis of cocoa shells could be used as adsorbents. Results of mercury ion utilization show that the adsorbent produced by pyrolysis of cocoa shells can absorb mercury ions with a capacity of 0.106 mg/gram after 90 minutes of contact. In this study, the adsorption of mercury ions with the adsorbent followed pseudo-second-order models with an R2 value of 0.9929.

Acknowledgments

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