Promising Adsorption of Sulfidic Acid Gases Using Wet Banana Plant Adsorbent (Musa spp.)

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Highlights:
- Banana plant waste can be used as gas adsorbent.
- The leaves of the banana plant are the most effective in removing pollutants.
- Removal of gaseous pollutants occurs in less than 15 minutes.

Abstract. Bananas have the highest production rate among fruits in Indonesia, which leads to the generation of a significant amount of banana fruit solid waste. In this study, we assessed the potential use of banana waste to remove hydrogen sulfide (H₂S) gas. In particular, the purpose of this study was to analyze the efficiency of banana waste as an adsorbent for H₂S gas. We tested the stems, leaves, and peels of banana plants as H₂S gas adsorbents with varying contact times. To obtain a microscopic view of the adsorbents before and after the experiment, we conducted measurements using scanning electron microscopy with dispersive X-ray spectroscopy. The banana leaves, stems, and peels were found to have H₂S gas absorption efficiency values of 76.52%, 51.83%, and 6.44%, respectively. Based on the experiment, the leaves of the banana plant appear to be the best adsorbents, with an adsorption capacity of 1.67 mg/g. The results also revealed that there was a change in the fiber and stomata appearance of the banana leaves after the adsorption process. Overall, this research indicates that banana leaves have the potential to be used as effective H₂S adsorbents.

Keywords: adsorption; air pollution; gas; odor; plant.

1 Introduction

In 2018, bananas were ranked as the largest contributor to fruit production in Indonesia, with a total production figure of 7.26 million tons, which is above the production figures for mangoes, oranges, pineapples, and durian [1]. Banana production has since increased by 1.42% (101,698 tons) and still ranks first among the fruit production contributors. East Java is the largest banana-producing province, with a total production of 2.06 million tons annually,
accounting for 28.36% of the total national banana production. However, the export of bananas is not as high as that of other fruits, such as salak, mangoes, and mangosteen. The high banana fruit production leads to high production of waste, including skins (peels) and stems. Many researchers have experimented with waste from banana plants, for example, as innovative food ingredient, alternative energy resource, or an essential material in water and waste treatment. Researchers have also used banana peels as antidepressant candy [2] or as an ingredient for milk drinks [3]. The banana plant can also be used as an environmentally friendly alternative for long-lasting battery cells [4], as a raw material for producing bioethanol, or as a complementary material to increase biogas production [5].

Hydrogen sulfide (H\textsubscript{2}S) can have adverse effects on human health, especially if one is exposed to H\textsubscript{2}S through the air. The lungs quickly absorb the gas [6], meaning the respiratory system is the body system that is most sensitive to H\textsubscript{2}S exposure [7]. H\textsubscript{2}S at a concentration of 500 ppm can cause pulmonary edema and even death. It is included in the asphyxiant group because its main effect is to paralyze the respiratory center, meaning death can be caused due to a stoppage in breathing.

Adsorption methods can be widely applied to recover specific air quality from air pollutants if highly selective adsorbents are used. Further, the use of low-cost, sustainable, selective, and eco-friendly adsorbents could be an effective advanced technique to recover air quality. Contemporary researchers are showing great interest in developing new adsorbent materials with excellent properties, diverse compositions, and high selectivity. Our literature survey showed that over the past few decades, a variety of low-cost alternative adsorbents have been proposed, including coconut shells [8], Acacia mangium wood [9], rice husk [10], pomegranate shell [11], bamboo [12], banana waste [13], oil palm waste [12], and date stones [14]. A banana plant can produce fruit once in its lifetime, meaning after fruit harvesting the whole plant is discarded as waste. If this huge amount of waste can be transformed into useful material, it would be of great help to banana growers/farmers. Otherwise, dumping this waste into water or leaving it under humid conditions leads to methane and carbon monoxide gas formation, while burning it can produce large quantities of carbon dioxide gas.

Many studies have been conducted on the use of banana plants (Musa spp.) as bio-adsorbents, which were found to be mainly applicable to liquid waste. Banana peels can be used for the removal of heavy metals from wastewater, as demonstrated by Anwar [15], Vilardi [16], Nada [17], Ali [18], and Ali Ashraf [19]. Bananas are also effective at removing organic substances (especially dyes) from wastewater, as shown by Stavrinou [20], Danish [13], and Munagapati [21]. Furthermore, the use of bananas as adsorbents of waste gas was demonstrated by
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Shen [22] for volatile benzene and toluene. In Indonesia, several studies have revealed the role banana peels can play in removing polluting gases, such as those from motorized vehicles [23]. Sumiyati [24] have listed potential uses of banana plants for removing gaseous pollutants, including sulfidic acid gas. However, no research has been conducted yet to assess banana plants as bio-adsorbents to remove odors from polluting gases, such as H$_2$S. This study aimed to investigate the feasibility of using banana plants (without conversion into activated carbon) as an adsorbent of H$_2$S gases. The research was conducted in two stages: assessing the adsorbent type (fresh leaves, stems, and banana peels) in removing H$_2$S and examining the best adsorbent to remove H$_2$S. The results are expected to be applicable on a larger scale, for example for eliminating odors in the waste industry, determining buffer zones in landfills (as many buffer zones in Indonesia’s landfills are covered with banana plants), possibly removing the smells of livestock and agriculture, and purifying biogas from H$_2$S contaminants.

2 Materials and Method

2.1 Materials Preparation

The banana plant components used in this study are depicted in Figure 1. Fresh banana leaves, banana fruit, and banana stems were cleaned with a damp cloth and allowed to dry for approximately 15 minutes. Then, they were cut with the following details: the banana leaves were chopped to a size of 10 mm x 1 mm, the banana stems were chopped to a size of 2 mm x 2 mm, and the banana peels were chopped to a size of 2 mm x 2 mm. After being chopped, the adsorbent was weighed and put into an adsorbent tube until full. Based on this criterion, the adsorbent mass we got from the banana leaves, banana stems, banana peel was 15 g, 27 g, 32 g respectively. The difference in mass of the adsorbent used was influenced by the density of each adsorbent.

(a) Leaves
(b) Stems
(c) Peels

Figure 1 Materials from banana components used in this study.
2.2 H₂S Gas Preparation and Measurement

A schematic diagram of the experimental setup is shown in Figure 2. In this experiment, we used a standard Erlenmeyer flask (Pyrex) as well as a plug, tubing, air sampler/impinger (AGS), analytical balance (Mettler Toledo ME 204), and UV–Vis spectrophotometer (Thermoscientific Genesys 10S). The procedure for creating the H₂S gas used here was modified from Prasetyo [25]. First, 0.18 g of FeS (Pudak Sci) and 4.5 mL of 1-M HCl (Merck) were reacted. The gas formed was then left to stand for 1 h to ensure a complete reaction and was then transferred from the air sampler/impinger to an adsorbent tube and finally to the adsorbent solution ZnSO₄ (Merck). H₂S gas withdrawal was carried out with a constant flow rate of 0.5 L/min for five variations of contact time (15, 17, 20, 22, and 25 min). In this experiment, measurements were conducted under room temperature, i.e., 25 °C.

The general mechanism of H₂S gas removal has been reviewed elsewhere [26]. For the measurement of H₂S levels via the methylene blue method using a spectrophotometer we referred to Indonesian National Standard (SNI) 19-7117.7-2005 [27]. A solution containing 50 mL of the measurement sample was removed from the device experiment chain and rinsed using distilled water. The sample was then diluted to 100 mL with distilled water. Additionally, 50 mL of absorbent solution was prepared and then diluted with distilled water to a volume of 100 mL (blank).

A 20-mL sample solution was piped into a measurement tube. 2 mL of para- amino dimethyl aniline and 1 mL of FeCl₃ were added to each tube, and the samples were homogenized. Next, each tube was diluted with distilled water to a volume of 25 mL, homogenized again, and left to stand for 30 min. The absorbance of the measurement sample solution was measured at a wavelength of 670 nm, and the concentration of H₂S gas was calculated using a calibration curve.
2.3 Calibration Curve and Adsorption Capacity

The adsorption capacity is defined as the amount of H$_2$S absorbed per unit weight of the adsorbent. The Freundlich and Langmuir adsorption isotherms (mg/g) were used as models. The Freundlich equation is as follows:

\[ \log q = \log K + \frac{1}{n} \log C. \]

where:  
- \( q \) = concentration of adsorbed adsorbate,  
- \( C \) = concentration of adsorbate at equilibrium (mg/L),  
- \( K \) = equilibrium constant,  
- \( N \) = empirical constant depending on the nature of the substance.

The Langmuir equation is as follows:

\[ \frac{1}{q} = \frac{1}{(q_m KC)} + \frac{1}{q_m}. \]

In these equations, \( q \) = concentration of adsorbed adsorbate, \( q_m \) = maximum capacity of adsorbent (mg), \( K \) = equilibrium constant, \( C \) = concentration of adsorbate at equilibrium (mg/L).

Based on the above equations, a linear adsorption isotherm curve was generated, from which the values of the regression coefficient, slope, intercept, and adsorption capacity could later be drawn. The solution concentration of absorbed H$_2$S was then measured using the methylene blue method with a UV-Vis spectrophotometer. We then used a calibration curve, which had been made in advance, to determine the absorbed H$_2$S concentration.

The calibration curve consisted of five variations of the H$_2$S working solution (0, 5, 10, 15, and 20 mL). The absorbance and concentration results were plotted on a graph to obtain a linear equation in the form of \( y = ax + b \). This equation was then used to calculate the amount of measured H$_2$S. The results of the calibration curve are shown in Figure 3. The linear equation obtained was \( y = 0.375x + 0.076 \), with a slope of 0.375 and an intercept of 0.076.

![Figure 3 Linear equation of the H$_2$S calibration curve.](image)
3 Result and Discussion

3.1 Measurement Results of H$_2$S Gas Concentration

The research was carried out in triplicate to obtain a better estimated concentration value. Table 1 shows the concentration of H$_2$S (mg/L) with variation of adsorbent type and contact time.

In this study, the concentrations were normalized with control treatment (no adsorbent). We assumed there would be no adsorption in the control treatment, except negligible gas adsorption in the adsorption device (tubing, adsorbent tube).

<table>
<thead>
<tr>
<th>Adsorbent Type</th>
<th>Contact Time (min)</th>
<th>15</th>
<th>17</th>
<th>20</th>
<th>22</th>
<th>25</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leaf</td>
<td></td>
<td>1.951±0.513</td>
<td>2.344±0.307</td>
<td>3.304±0.135</td>
<td>3.884±0.135</td>
<td>9.131±0.106</td>
</tr>
<tr>
<td>Stem</td>
<td></td>
<td>4.003±0.042</td>
<td>6.444±0.2197</td>
<td>5.88±0.0286</td>
<td>8.680±0.125</td>
<td>9.901±0.200</td>
</tr>
<tr>
<td>Peel</td>
<td></td>
<td>8.236±0.3088</td>
<td>8.374±0.2779</td>
<td>9.060±0.0286</td>
<td>9.357±0.063</td>
<td>10.157±0.104</td>
</tr>
<tr>
<td>No adsorbent</td>
<td></td>
<td>8.309±0.1478</td>
<td>8.847±0.0619</td>
<td>4.19±0.0860</td>
<td>9.938±0.1800</td>
<td>10.780±0.112</td>
</tr>
</tbody>
</table>

It was found that the concentration of H$_2$S without adsorbent increased with contact time, with the lowest concentration being 8.3 mg/L and the highest concentration 10.78 mg/L. The difference in concentration among the five contact times was quite significant (one-way ANOVA at p < 0.05), as the contact time interval given was relatively short (around 2 to 3 min). Several different physical characteristics were noted when measurements were made with and without the adsorbents. At the time of measurement, there was a change in the absorbent solution’s color; the longer the contact time, the cloudier the absorbent solution became. During the measurement without adsorbent, an odorless white fog appeared, while when an adsorbent was used no fog appeared. The zinc sulfide compound caused a change in color and moisture. These results came from the reaction between H$_2$S and the adsorbent solution (ZnSO$_4$). According to Moreira [28], the longer the contact time, the greater the adsorbent solution’s ability to absorb the adsorbate. This is due to the long contact time between the adsorbent and the adsorbate, allowing additional bonds to form until the equilibrium point is reached. However, when the contact time between the adsorbent and the adsorbate is too long, the adsorbent saturates and the adsorbate is released.

3.2 Bananas Adsorbent Characteristics

Observation of the adsorbent’s characteristics before and after the measurements was carried out to support the research results. Before the measurements, the banana leaves were bright green and looked fresh. After the measurements were
made, the most noticeable difference was in the leaves, which appeared paler and some of the pieces had turned brown (Figure 4).

![Banana adsorbents before (a) and after (b) the adsorption process.](image)

**Figure 4** Banana adsorbents before (a) and after (b) the adsorption process.

Figure 5 shows the differences in the banana leaf adsorbent with and without H$_2$S. Before contact with H$_2$S, many leaf fibers can be seen crossing the leaf epidermal cells and the stomata are still visible. After the H$_2$S had passed through them, the leaf fibers were no longer visible. Thickened leaf epidermal cells could be seen, so that their striations became visible. The stomata were damaged, as marked by the presence of elements attached to them. From the scanning electron microscopy (SEM) observation results it can be concluded that the H$_2$S that had passed through the banana leaf adsorbent caused it to deteriorate.

Several other studies based on SEM analysis about the role of stomata in capturing air pollutants have proved this. For example, 500x magnification SEM showed that fine particles smaller than 0.1 µm were able to penetrate leaf tissue through stomata [29]. Song, *et al.* [30] found the fine particles for up to 2 µm (1000x magnification SEM). In addition, Zha, *et al.* [31], using 1000x magnification SEM, found that capturing air contaminants, i.e. particles and PAH, could be facilitated by grooves surrounding the stomata.
Based on the calculation results obtained using the Freundlich and Langmuir isotherms (Table 2), it was found that the banana leaves had a consistently large adsorption capacity, whereas the banana peels had a small capacity. In particular, the banana leaf adsorption capacity reached 16 to 22 times that of the banana peels. However, differences could be seen among the results of the different adsorbent types when using the two isotherm models. When the Freundlich isotherm was used, the results regarding the adsorption of leaves and stems were almost the same, but when the Langmuir isotherm was used, the values of the adsorption of leaves were more than twice those of the banana stems. Based on
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these results it can be concluded that banana leaves have the greatest potential for use as H$_2$S adsorbents.

Table 2  Average H$_2$S concentration (mg/L) after contact with an adsorbent.

<table>
<thead>
<tr>
<th>Adsorbent Type</th>
<th>Freundlich Isotherm</th>
<th>Langmuir Isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R Capacity (mg/g)</td>
<td>R Capacity (mg/g)</td>
</tr>
<tr>
<td>Leaf</td>
<td>0.94</td>
<td>1.6750</td>
</tr>
<tr>
<td>Stem</td>
<td>0.92</td>
<td>1.6761</td>
</tr>
<tr>
<td>Peel</td>
<td>0.58</td>
<td>0.1063</td>
</tr>
</tbody>
</table>

According to Viena [23], banana plants are usually used as adsorbents to reduce pollutant gases and can reach an adsorption capacity of up to 952 mg/g. However, in such a case, the bananas are usually prepared in the form of activated carbon. The analysis results of the efficiency of each obtained adsorbent are shown in Figure 6.

![Figure 6](image-url)  
**Figure 6**  Removal efficiency for H$_2$S adsorption.

The banana leaf adsorbent had the highest efficiency at a contact time of 15 min, with a value of 76.52%. However, as the contact time increased, the absorption efficiency of the H$_2$S gas concentration decreased slowly.

The efficiency value decreased quite drastically for a contact time of 20 min, from 73.51% to 22.45%, and finally, the lowest efficiency was reached at a contact time of 25 min (15.30%). The highest absorption efficiency of H$_2$S in the banana stem adsorbent reached 51.83% at a contact time of 15 min, while the lowest
efficiency of 11.87% was observed at a contact time of 25 min. The least significant decrease in efficiency occurred between contact times of 15 and 17 min, with a difference of 26.93%. This result indicates that the saturation time of the banana stem adsorbent in absorbing gas was 15 min and that when the contact time for \( \text{H}_2\text{S} \) absorption increased past this point, the efficiency decreased. The efficiency level of the absorption of \( \text{H}_2\text{S} \) gas for the banana peel adsorbent fluctuated significantly. The highest efficiency of 6.44% was observed at a contact time of 25 min, while the lowest efficiency of 0.89% was observed at a contact time of 15 min. The fluctuations in the data were caused by the unstable condition of the adsorbent. One of the factors in this is the wet nature of the banana skin, which also has mucus on its surface.

The \( \text{H}_2\text{S} \) absorption efficiency values from the three adsorbents contrasted significantly with one another. The banana peels had a relatively small and fluctuating efficiency of \( \text{H}_2\text{S} \) absorption (<6%). From the fluctuating efficiency results it can be concluded that banana peels are not an optimum adsorbent media. Banana stems had their highest \( \text{H}_2\text{S} \) absorption efficiency (51.8%) at 15 min of contact time and their lowest efficiency (11.87%) at 25 min of contact time. The banana stems thus showed a significant decrease in absorption efficiency when compared with the banana peels. According to Rodriguez [32], banana stems have fiber consisting of 60% to 65% cellulose, 6% to 8% hemicellulose, 5% to 10% lignin, and 10% to 15% water. Hemicellulose is highly useful and can be applied as an adsorbent to remove oil, heavy metals, and pollutants [33].

The adsorption efficiency is also influenced by the length of contact time in the adsorption process. Based on the research results it can be seen that the best adsorption efficiency was obtained at 15 min. This is because the adsorption process reached an optimum state at this time. After 15 min of contact time, the adsorption efficiency decreased due to the lengthy contact time between the adsorbent and the adsorbate, which caused the adsorbent to saturate and the adsorbate to be released. At the same time, the adsorbent works inefficiently before the optimum conditions are reached. Based on the three adsorbent types and the five contact times used in this study it can be concluded that banana leaves are the best adsorbents and have an optimum contact time of 15 min. The fiber in banana leaves has a higher density than that in banana stems and peels. Moreover, banana leaves have more stomata when compared to branches and peels. Stomata are an important pathway for air pollutant uptake in plants [34]. Thus, having more stomata means having greater potential to absorb gaseous pollutants. The ability of stomata to absorb gas was also investigated in Wei, et al. [35], where sulfuric acid gas could be captured molecularly by the stomata in addition to being captured in the stem and bark. This was confirmed by Tiessen [36], who found that stomata facilitate the exchange of gaseous pollutants. This also explains why pollutants are found in the stomata [37]. The rate of gas exchange
permeability depends on the degree of stomatal opening at 4 to 10 nm [38]. Due to the deposition of pollutants in the stomata, there is a reduction in the average stomata pore area [39].

The absorption capacity increases as the surface area of the absorbent increases. For example, Hoang, et al. [40] revealed that the uptake of air pollutants in polyurethane rice straw was about 3 to 4 times higher than that of artificial pure polyurethane due to the higher surface area. Huang, et al. [41] found that molecularly imprinted polymers (MIPs), which have a higher surface area than other adsorbents, gave the best results in capturing gaseous pollutants. Various banana plants in Indonesia have a higher number of stomata on the abaxial surface. Auliya, et al. [42] reported that some banana plant leaves can have 21-42 stomata/field of view based on SEM analysis.

Based on the results of electron-dispersive X-ray spectroscopy (EDX) without H$_2$S (shown in Table 3 and Figure 7), the fresh banana leaves were found to possess several constituent elements, including C, O, N, K, Mg, Cl, and Si. In fresh banana leaves, the lowest weight percentage value belonged to Si, which had a percentage atomic weight of 0.07, and the highest percentage value belonged to C, which had a percentage atomic weight of 65.47. In the results of EDX with H$_2$S, all the same elements were found. However, there was also an additional element, S, which has a percentage atomic weight of 0.24. The presence of S confirms that H$_2$S was adsorbed into the banana leaves. Further research is needed to analyze contact times under 15 min. In future work, adsorbent cutting should also be homogenized so that the adsorption capacity is evenly distributed.

<table>
<thead>
<tr>
<th>Element</th>
<th>Without H$_2$S</th>
<th>With H$_2$S</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>65.47%</td>
<td>67.68%</td>
</tr>
<tr>
<td>O</td>
<td>28.53%</td>
<td>17.54%</td>
</tr>
<tr>
<td>N</td>
<td>4.64%</td>
<td>5.92%</td>
</tr>
<tr>
<td>K</td>
<td>0.71%</td>
<td>3.66%</td>
</tr>
<tr>
<td>Mg</td>
<td>0.42%</td>
<td>0.14%</td>
</tr>
<tr>
<td>Cl</td>
<td>0.16%</td>
<td>4.75%</td>
</tr>
<tr>
<td>Si</td>
<td>0.07%</td>
<td>0.21%</td>
</tr>
<tr>
<td>S</td>
<td>—</td>
<td>0.24%</td>
</tr>
</tbody>
</table>

Table 3  Average H$_2$S concentration (mg/L) after contact with an adsorbent.
4 Conclusion

Based on the experiment in this study, three banana components, i.e. leaves, stems, and banana peels, had H$_2$S gas absorption efficiency values of 76.52%, 51.83%, and 6.44%, respectively. Banana leaves having the highest absorption efficiency may be caused by the presence of stomata in the leaves, which is supported by changes in the appearance of fibers and stomata in banana leaves after the adsorption process. This study showed that banana leaves have good potential to be used as adsorbent of H$_2$S gas.

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