Utilization of *Mendong* Plants Activated Charcoal as H$_2$S and NO$_2$ Gas Adsorbent: Preliminary Study

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**ABSTRACT**

The study of adsorption H$_2$S and NO$_2$ gases by utilizing *Mendong* plants as activated charcoal. In this study, activated charcoal were prepared from *Mendong* plant (*Frimbistylis globulosa*), using modified tools and activated by maceration using ZnCl$_2$ with concentrations of 2.5; 5; 7.5; and 10% (w/v) for 24 hours to determine the efficiency of H$_2$S adsorption. The concentration of H$_2$S and NO$_2$ adsorption was analyzed using UV-Vis spectrophotometry. Determinations of H$_2$S gas carried out using the blue methylene’s method for 1 hour and showed the highest effectiveness of *Mendong* activated charcoal at 2.5 % ZnCl$_2$ w/v with 80% of H$_2$S removal. Further, the *Mendong* activated carbon with a concentration of 2.5% ZnCl$_2$ w/v was used for NO$_2$ adsorption. The adsorption of NO$_2$ gas was conducted for 1 hour using Griess Saltzman’s method. The result showed that the highest concentration of adsorbed NO$_2$ ($C_o$) is at in HNO$_3$ concentration was 1.5 M (0.057 µg/mL). The percentage of NO$_2$ efficiency adsorbed was at 28%. The result of the characterization by FTIR showed that the *Mendong* plant ZnCl$_2$ activated charcoal has hydroxyl group and aromatic ring of cellulose, hemicellulose and lignin.

**Keywords:** *Mendong*, adsorbent, exhaust gas, H$_2$S, and NO$_2$.

**INTRODUCTION**

According to PP No. 41 of 1999, air pollution is the entry of substances, energy and/or other components into ambient air directly or indirectly due to human activities so that air cannot function well [1]. Pollutants can be gases, liquids and solid particles. Air pollutants in the form of gases are CO$_2$, NO$_2$, SO$_2$, CO, H$_2$S or solid objects such as ash. Hazardous substances are usually derived from the results of human business, such as industrial waste, vehicle fumes and natural activities. This dangerous condition occurs when the levels of air pollutant compounds are above the threshold tolerated by WHO as presented in Table 1 [2]. Meanwhile, road traffic is one of the main sources of NO$_2$ outdoors [3].

Jakarta as the capital city of Indonesia with a population in 2018 reaching 10.4 million people [4] now ranks second as the city with the worst Ambient Air Quality Index after Krasnoyarsk, Russia and before Dubai, United Arab Emirates and Shanghai, China [5], which has an impact on the health of living things around them. In addition, based on the Air Pollution Standard Index by the Ministry of Environment and Forestry, it is noted that the ISPU NO$_2$ value of Tangerang City is 85 of the medium categories. Judging from the air quality criteria based on KEPMEN LH Num: KEP-45/MENLH/10/1997, the air quality of Tangerang City does not have an effect on human or animal health but affects sensitive plants and the aesthetics [6].
Table 1. Quality Standard of Pollutant in Ambient Air

| Parameters | Quality Standard (µg/m$^3$) | Measurement Time |
|------------|-----------------------------|------------------|
| NO$_2$     | 200                         | 1 hour           |
|            | 40                          | 1 year           |
| SO$_2$     | 500                         | 10 minutes       |
|            | 20                          | 24 hours         |
| O$_3$      | 100                         | 8 hours          |
| PM$_{2.5}$ | 25                          | 24 hours         |
|            | 10                          | 1 year           |
| PM$_{10}$  | 50                          | 24 hours         |
|            | 20                          | 1 year           |

Source: WHO, 2005

The characteristics of hydrogen sulfide gas (H$_2$S) are it has odor like a rotten egg, is poisonous, colorless, and flammable. A large amount of H$_2$S can cause health problems and air pollution that disturbs the environment. According to the Minister of the Environment Decree Number 50 of 1996 concerning the odor level standard, the maximum concentration of H$_2$S is 0.02 ppm (0.028 mg/m$^3$) [7]. States humans can normally smell H$_2$S at a concentration of 0.0005-0.3 ppm and at a concentration of 500 ppm, H$_2$S can cause death with respiratory arrest [8]. Studies on H$_2$S have been carried out resulting that it has an effect on public health such as coughing, headaches, asthma, and sleeplessness [9]. Other studies conducted show that there are excess H$_2$S levels or exceeding the threshold in a rubber industry and landfills (TPA) [10].

Meanwhile, studies on NO$_2$ gas emissions in the air have begun to be carried out in Indonesia [11, 12]. Meanwhile, the tolerance of NO and NO$_x$ gas emissions in motor vehicles is 0.25 ppm. NO$_2$ is a poisonous gas which has a pungent odor to the nose and can be seen clearly from its brownish color. The NO$_2$ gas is produced from the combustion of motor vehicle fuel at high temperatures, industry and fossil fuel power plants. Stoker and Seager (1972) in Fardiaz (1992) prove that at a concentration of 1.0 ppm, it will cause spots on leaves. With a higher concentration (≥ 3.5 ppm), the gas can cause necrosis or damage to leaves [13]. Several efforts have been done to reduce levels of exhaust emissions in the air [14-19].

The adsorption method is a proven method that shows an increase in gas storage and distribution efficiency with an excess of high surface area and fast adsorption kinetics. In the adsorption method, the adsorbent will work better if given an activation treatment both chemically and physically. The chemical activator used in this study was ZnCl$_2$ [14]. Mendong (Fimbristylis globulosa) or also known as purun tikus is one type of grass that lives in marshes and belongs to the Cyperaceae family with the Fimbristylis genus. In general, this plant is often used as the material for woven mats or furniture. This makes Mendong farming spread in several regions in Indonesia. The morphology of the Mendong plant is that it has shiny green stems, short rhizomes, fibrous roots and is grooved like rice. Mendong fiber contains 72.14% of cellulose, 20.2% of hemicellulose, 3.44% of lignin, 4.2-5.2 of moisture content and 4.2% of other materials [20,21]. Until now, Mendong also used as phytoremediation plant, microcrystalline cellulose and polymer composite [22]. With a high enough cellulose content, it indicates that mendong will be an effective adsorbent.
EXPERIMENT

Chemicals and Instrumentation

The materials used are dry Mendong plants, Cu powder (CU4l), ZnCl₂ crystals (Merck), 68% analysis of HNO₃ (Merck), NEDA (Merck), sulfanilic acid crystal, pro analysis glacial acetic acid (Merck), acetone (Merck), NaNO₂ solid (Merck), Na₂S₂O₃ (Merck), FeCl₃ powder (Merck), H₂SO₄ solution (Merck), p-aminodimethylaniline, FeS powder (Merck), HCl solution (Merck) and distilled water. The adsorption results are then analyzed using UV-Vis spectrophotometry (Shimadzu 1601) and the sample is characterized by Shimadzu FTIR.

Reaction Procedure

Material Preparation

Dried Mendong plant that had been cut for 2-4 cm then burned into charcoals for 1 hour. Then, the charcoal was blended until smooth and sieved using a 100-mesh sieve. Furthermore, it was activated using maceration method for 24 hours by soaking the charcoal powder with a concentration of ZnCl₂ activators of 2.5, 5, 7.5, and 10% in room temperature. Then, the residue was sieved until neutral and dried in an oven at 105°C for 1 hour. After that, it forms into 3-mm pellet and dried in an oven at 175°C for 1 hour. It called AMA 2.5, 5, 7.5 and 10%.

Hydrogen sulfide (H₂S) gas adsorption

H₂S gas source is obtained from a reaction between 30% HCl solution and FeCl₃ powder. The concentration of H₂S in solution determined by Blue methylene’s method and analysis using UV-Vis Spectrophotometer based on SNI-19-7117.7-2005 [23]. In this section, a preliminary study has conducted a variation of activator concentration Mendong-charcoal as an adsorbent and H₂S as an adsorbate to determine the most effective adsorbent. Schematic diagram of adsorption H₂S gas as shown in Figure 1. 10 mL H₂S adsorbent solution was filled into each of the 6 impingers bottles. They will adsorb H₂S that is not trapped by AMA. H₂S gas formation was done in a glasstronic by reacting FeS powder with 30% HCl solution at 57°C. It flows impinge box through PVC pipe that contains 30 g AMA. The gas flow is controlled by a vacuum pump with a flow rate of 1.0 L/min for 1 hour [23]. H₂S in the Adsorbent solution is reacted with 1 mL FeCl₃ and 2 mL p-aminodimethylaniline solutions and stayed for 30 minutes. This reaction will produce a light blue color then measured immediately using UV-Vis spectrophotometer at λ_max = 670 nm.

Figure 1. Schematic figure of testing tools for H₂S adsorption using Blue Methylene method [23]
Nitrogen Dioxide (NO\textsubscript{2}) gas Adsorption

The concentration of NO\textsubscript{2} in solution was determined by Griess Saltzman method with analysis using UV-Vis Spectrophotometer based on SNI-19-7119.2-2005 [24], NO\textsubscript{2} gas source from a reaction between 0.005 g Cu powder with HNO\textsubscript{3} solution. In this section, a preliminary study conducted with variation initial concentration of NO\textsubscript{2} as adsorbate that obtained from variation concentration of HNO\textsubscript{3} used i.e. 0.5, 1, and 1.5 Molar. Afterward, NO\textsubscript{2} gas flow from glasstronic into impinger box which contains Griess Saltzman solution through 30 g Mendong-activated charcoal (AMA 2.5%). Griess Saltzman solutions dissolve NO\textsubscript{2} gases that are not trapped by AMA 2.5%. The gas flow is controlled by a vacuum pump with a flow rate of 0.4L/min for 1 hour [24]. NO\textsubscript{2} in the adsorbent solution reacts to produce pink-colored after 15 minutes. It happened because of the azo dye compound. After that, concentration measurements were made directly using a UV-Vis spectrophotometer at $\lambda_{\text{max}}$ = 550 nm. Schematic diagram of adsorption NO\textsubscript{2} gas as shown in Figure 2.

![Figure 2. Schematic figure of testing tools for NO\textsubscript{2} adsorption using Griess Saltzman method][24]

In each adsorption process, there are 2 sets of tools were used simultaneously at one-time test with 1 variation.

**Determination of Adsorbed H\textsubscript{2}S and NO\textsubscript{2} gas ($C_t$)**

The absorbency of the solution was measured by UV-Vis spectrophotometer to determine the amount of gas adsorbed by AMA. In case the calculation of H\textsubscript{2}S and NO\textsubscript{2} gases adsorbed is the same. Calibration curves were made based on SNI-19-7117.7-2005 for H\textsubscript{2}S and SNI-19-7119.2-2005 for NO\textsubscript{2}. The adsorbed gas concentration ($C_t$) is calculated from the difference of the initial gas concentration ($C_o$) minus final gas concentration ($C_e$).

$$C_t = C_o - C_e$$

For the adsorption capacity, determined by

$$q = \frac{C_t}{w} \times \text{Vol solution}$$

And for the adsorbent level, it calculated by

$$\%C_t = \frac{C_t}{C_o} \times 100\%$$

**RESULT AND DISCUSSION**

**H\textsubscript{2}S Gas Testing**

Mendong-charcoal was prepared by chemical methods with ZnCl\textsubscript{2}. Zinc Chloride is one of the commonly used as a chemical agent for the activation of various precursor. Activation
lignocellulose precursor with ZnCl$_2$ causes degradation of cellulosic material, on carbonization and dehydration. Therefore, it produces charring and aromatic carbon and prorous structure [14]. H$_2$S adsorption process using a series of testing tools at laboratory scale. It refers to SNI-19-7117.7-2005. After contacting process, the Adsorbent solution that contain of H$_2$S leftovers, was added with 1 mL FeCl$_3$ and 2 mL p-aminodimethylaniline and left alone for 30 minutes. The reaction that occurs is shown in Figure 3. Then it was tested using UV-Vis Spectrophotometer at $\lambda_{max}$ = 670 nm and the result is shown in Table 2.

![Figure 3. Reaction of H$_2$S Gas with FeCl$_3$ and p-aminodimethylaniline](image)

From the test results, a blue solution is obtained, which indicates the existence of H$_2$S gas leftovers as shown in Figure 4.

![Figure 4. Test Result Solution](image)

In this study, testing was carried out 3 times with the results as shown in Table 2.

| ZnCl$_2$ Variation | C$_o$ (µg/mL) | C$_e$ (µg/mL) | C$_t$ (µg/mL) | W (g) | q (µg/g) | H$_2$S adsorbed (%) |
|--------------------|--------------|--------------|--------------|-------|----------|-------------------|
| Without Activator  | 2.3380       | 0.8027       | 1.5353       | 30    | 51.1760  | 65.67             |
| 2.5%               | 2.3380       | 0.4547       | 1.8832       | 30    | 62.7737  | 80.55             |
| 5%                 | 2.3380       | 0.5277       | 1.8102       | 30    | 60.3406  | 77.43             |
| 7.5%               | 2.3380       | 0.7212       | 1.6168       | 30    | 53.8929  | 69.15             |
| 10%                | 2.3380       | 0.6725       | 1.6655       | 30    | 55.5150  | 71.24             |

Based on the Table 2, Mendong- activated charcoals with 2.5% ZnCl$_2$ as an activator has higher Adsorption and efficiency, amounting to 62.7737 µg/g and absorbed level is 80.55%. The adsorption capacity of Mendong-charcoal without activator; using ZnCl$_2$ 2.5%; 5%; 7.5%; and 10% are 51.1760; 62.7737; 60.3406; 53.8929; and 55.5150 µg/g. It shown there is a peak increase in capacity adsorption at 2.5% ZnCl$_2$ then decreased. This refers to the theory that the Adsorption of the substance will be constant after reaching a certain concentration because the concentration of the substance will meet the empty active site on activated carbon and after that it will reach a saturation point, so the constant Adsorption occurs [25,26,27]. The
adsorption capacity shows how much adsorbate can be absorbed or accumulated on the surface of the adsorbent. Adsorption parameters affect the amount of adsorption capacity of an adsorbent.

Therefore, the Mendong-activated charcoal adsorbent of ZnCl₂ has optimum Adsorption at 2.5% of activator concentration variation. Then, the characterization by FTIR to find out the functional groups in the adsorbent is shown in Figure 5.

![FTIR result](image)

**Figure 5. FTIR result**

IR spectra has an Adsorption peak with a wavenumber of 3386 cm⁻¹ it is referred an O-H group stretching from hemicellulose and lignin [21]. The peak at wavenumber 2899 cm⁻¹ there is H-C-H group from aliphatic stretching. Then at the adsorption peak at wavenumber 1597 cm⁻¹, there is a C=C bond. The adsorption peak at wavenumber 1604 cm⁻¹ is assigned the skeletal vibration of aromatic rings of lignin [21]. The bands ranging wavenumber from 1163-1027 cm⁻¹ indicate the asymmetric bridge oxygen and C-O stretching of cellulose and hemicellulose [21]. Then, the Adsorption also appears at the wavenumber of 468 cm⁻¹ which indicates there is a Zn-O group. This is in accordance with the study conducted by [28] who have Zn-O groups in activated carbon at wavenumber from 370-500 cm⁻¹. Zn-O groups indicating the existence of Zn²⁺ cations that functions to absorb substances at activated carbon sites. In this study, it is evident that the Adsorption of Mendong-charcoals without activation with activated plant charcoal with concentrations of 2.5%, 5%, 7.5%; and 10% experiences a shift, although little. This indicates that the adsorbent of the plant charcoal is activated with ZnCl₂.

**NO₂ Gas Testing**

NO₂ adsorption process using a series of testing tools at laboratory scale. NO₂ gas testing only used adsorbents that had been activated with ZnCl₂ of 2.5% w/v as a good activator on H₂S adsorption. The process of testing the NO₂ gas was carried out with 2 sets running simultaneously, where set 1 is without adsorbents as a control and set 2 contains AMA 2.5% ZnCl₂. The source of NO₂ gas comes from the reaction between HNO₃ solution and Cu powder.
4HNO₃(aq) + Cu (s) → Cu(NO₃)₂(s) + 2NO₂(g) + 2 H₂O (l)

After contacting process, the Adsorbent solution that contain of NO₂ leftovers will be change the colors from clear into pink solution. The testing resulted in a pink solution which is a result of the Azo Dye compound "diazobenzene sulfonic acid" which is formed between the cations of diazonium and the NED compound [26], it shown in Figure 6.

![Figure 6. Results of Contact with NO₂ Gas](image)

If less NO₂ gas is left, the color of the solution will fade. Then, it was tested using UV-Vis Spectrophotometer at λₘₐₓ = 550 nm. In this study, the test was carried out twice for each variation and showed the results as in Table 3.

| [HNO₃] | C₀ NO₂ (μg/ml) | C₂ NO₂ (μg/ml) | C₇ NO₂ (μg/ml) | w (g) | q NO₂ (μg/g) | NO₂ absorbed (%) |
|--------|----------------|----------------|----------------|-------|--------------|------------------|
| 0.5M   | 0.206          | 0.173          | 0.033          | 30    | 1.099        | 15               |
| 1.0M   | 0.195          | 0.156          | 0.039          | 30    | 1.297        | 19               |
| 1.5M   | 0.200          | 0.168          | 0.057          | 30    | 1.915        | 28               |

Based on the Table 3, we can conclude that the highest adsorption capacity of AMA 2.5% ZnCl₂ occurs when the HNO₃ concentration of 1.5M is 1.915 μg/g as well as the largest percent efficiency, namely at the concentration of HNO₃ 1.5M of 28%. According to the theory, the greater the concentration of HNO₃, more NO₂ gas molecules are formed because the number of molecules in the solution is directly proportional to the concentration. Meanwhile the results of the experiments tend to be the same. This is possible because the concentration used has a small range, which is 0.5M.

The experimental data show that AMA 2.5% ZnCl₂ has not experienced the saturation point or the active side of the adsorbent has not been covered by the adsorbate as a whole indicated by no decrease in adsorption capacity after a drastic increase. It is also seen from the samples used with 3 variations of HNO₃ concentrations that cannot show a trend of AMA 2.5% ZnCl₂ to NO₂ gas. AMA 2.5% ZnCl₂ is still more likely to have the potential for an increase in the adsorption capacity and efficiency percentage of the adsorbent if the concentration of HNO₃ is increased. When viewed from the concentration of NO₂ gas that is absorbed, the adsorbed concentration is classified as small but still experiences a decrease although a little. These results indicate that AMA 2.5% ZnCl₂ can be used as an adsorbent to adsorb NO₂ gas, but it needs to be reviewed.
CONCLUSION

Excess NO₂ and H₂S gas levels in the environment are very dangerous for human health. One way to reduce NO₂ and H₂S gas levels is by Adsorption of NO₂ gas using adsorption method with AMA of 2.5% ZnCl₂ and the effectiveness of 28% for 30 g AMA 2.5% ZnCl₂. In addition, the optimum Adsorption of H₂S gas can be done using 30 grams of Mendong-activated charcoals with 2.5% of ZnCl₂ and an efficiency of 80.55%. This study needs to be examined further to obtain optimal results.

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