

Utilization of *Mendong* Plants Activated Charcoal as H₂S and NO₂ Gas Adsorbent: Preliminary Study

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Received 20 January 2020; Accepted 05 March 2021

ABSTRACT

The study of adsorption H₂S and NO₂ 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 ZnCl₂ with concentrations of 2.5; 5; 7.5; and 10% (w/v) for 24 hours to determine the efficiency of H₂S adsorption. The concentration of H₂S and NO₂ adsorption was analyzed using UV-Vis spectrophotometry. Determinations of H₂S gas carried out using the blue methylene's method for 1 hour and showed the highest effectiveness of *Mendong* activated charcoal at 2.5 % ZnCl₂ w/v with 80% of H₂S removal. Further, the *Mendong* activated carbon with a concentration of 2.5% ZnCl₂ w/v was used for NO₂ adsorption. The adsorption of NO₂ gas was conducted for 1 hour using Griess Saltzman's method. The result showed that the highest concentration of adsorbed NO₂ (C₀) is at in HNO₃ concentration was 1.5 M (0.057 µg/mL). The percentage of NO₂ efficiency adsorbed was at 28%. The result of the characterization by FTIR showed that the *Mendong* plant ZnCl₂ activated charcoal has hydroxyl group and aromatic ring of cellulose, hemicellulose and lignin.

Keywords: *Mendong*, adsorbent, exhaust gas, H₂S, and NO₂.

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 CO₂, NO₂, SO₂, CO, H₂S 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 NO₂ 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 NO₂ 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 ($\mu\text{g}/\text{m}^3$)	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 (H₂S) are it has odor like a rotten egg, is poisonous, colorless, and flammable. A large amount of H₂S 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 H₂S is 0.02 ppm (0.028 mg/m³) [7]. States humans can normally smell H₂S at a concentration of 0.0005-0.3 ppm and at a concentration of 500 ppm, H₂S can cause death with respiratory arrest [8]. Studies on H₂S 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 H₂S levels or exceeding the threshold in a rubber industry and landfills (TPA) [10].

Meanwhile, studies on NO₂ 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. NO₂ is a poisonous gas which has a pungent odor to the nose and can be seen clearly from its brownish color. The NO₂ 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 ZnCl₂ [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 (CU4I), ZnCl₂ crystals (Merck), 68% analysis of HNO₃ (Merck), NEDA (Merck), sulfanylic 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 $\lambda_{max} = 670$ nm.

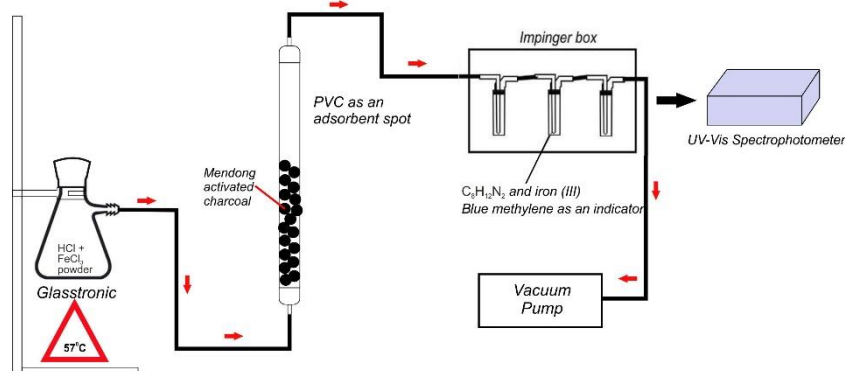


Figure 1. Schematic figure of testing tools for H₂S adsorption using Blue Methylene method [23]

Nitrogen Dioxide (NO₂) gas Adsorption

The concentration of NO₂ in solution was determined by Griess Saltzman method with analysis using UV-Vis Spectrophotometer based on SNI-19-7119.2-2005 [24]. NO₂ gas source from a reaction between 0.005 g Cu powder with HNO₃ solution. In this section, is a preliminary study conducted with variation initial concentration of NO₂ as adsorbate that obtained from variation concentration of HNO₃ used i.e. 0.5, 1, and 1.5 Molar. Afterward, NO₂ 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 NO₂ 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]. NO₂ 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 λ_{max} = 550 nm. Schematic diagram of adsorption NO₂ gas as shown in Figure 2.

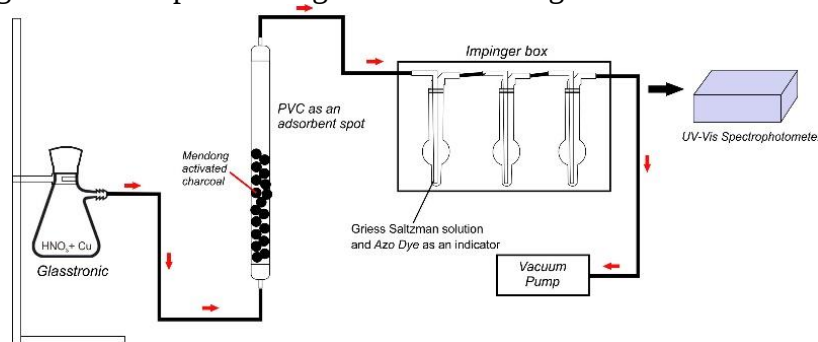


Figure 2. Schematic figure of testing tools for NO₂ adsorption using Griess Saltzman method [24]

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

Determination of Adsorbed H₂S and NO₂ 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 H₂S and NO₂ gases adsorbed is the same. Calibration curves were made based on SNI-19-7117.7-2005 for H₂S and SNI-19-7119.2-2005 for NO₂. 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

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

And for the adsorbent level, it calculated by

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

RESULT AND DISCUSSION

H₂S Gas Testing

Mendong-charcoal was prepared by chemical methods with ZnCl₂. 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 porous structure [14]. H_2S 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_2S 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 $\lambda_{\text{max}} = 670 \text{ nm}$ and the result is shown in Table 2.

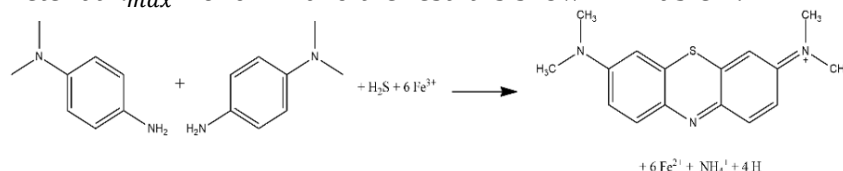


Figure 3. Reaction of H_2S Gas with FeCl_3 and p-aminodimethylaniline

From the test results, a blue solution is obtained, which indicates the existence of H_2S gas leftovers as shown in Figure 4.



Figure 4. Test Result Solution

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

Table 2. Data Tabulation of Adsorption Capacity and Efficiency

ZnCl ₂ Variation	C ₀ (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 ZnCl_2 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.

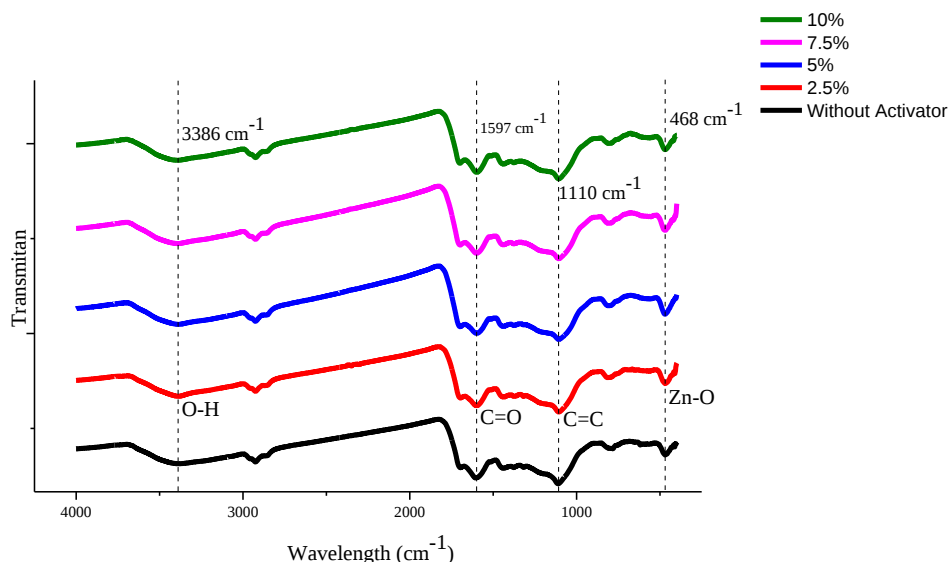


Figure 5. FTIR result

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 $1163\text{--}1027 \text{ cm}^{-1}$ 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 $370\text{--}500 \text{ cm}^{-1}$. Zn-O groups indicating the existence of Zn^{2+} 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 ZnCl_2 .

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 ZnCl_2 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% ZnCl_2 . The source of NO₂ gas comes from the reaction between HNO₃ solution and Cu powder.



After contacting process, the Adsorbent solution that contain of NO_2 leftovers will 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.

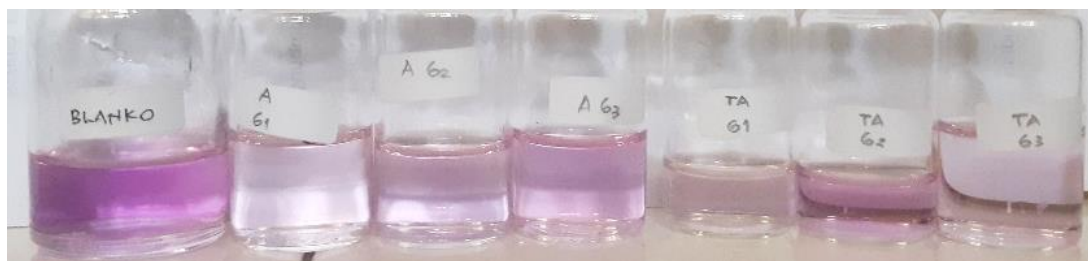


Figure 6. Results of Contact with NO_2 Gas

If less NO_2 gas is left, the color of the solution will fade. Then, it was tested using UV-Vis Spectrophotometer at $\lambda_{\text{max}} = 550 \text{ nm}$. In this study, the test was carried out twice for each variation and showed the results as in Table 3.

Table 3. Data Tabulation of Adsorption Capacity and Efficiency

[HNO_3]	$C_o \text{ NO}_2$ ($\mu\text{g/ml}$)	$C_e \text{ NO}_2$ ($\mu\text{g/ml}$)	$C_t \text{ NO}_2$ ($\mu\text{g/ml}$)	w (g)	q NO_2 ($\mu\text{g/g}$)	NO_2 absorbed (%)
0.5M	0.206	0.173	0.033	30	1.099	15
1.0M	0.195	0.156	0.039		1.297	19
1.5M	0.200	0.168	0.057		1.915	28

Based on the Table 3, we can conclude that the highest adsorption capacity of AMA 2.5% ZnCl_2 occurs when the HNO_3 concentration of 1.5M is 1.915 $\mu\text{g/g}$ as well as the largest percent efficiency, namely at the concentration of HNO_3 1.5M of 28%. According to the theory, the greater the concentration of HNO_3 , more NO_2 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% ZnCl_2 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 HNO_3 concentrations that cannot show a trend of AMA 2.5% ZnCl_2 to NO_2 gas. AMA 2.5% ZnCl_2 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 HNO_3 is increased. When viewed from the concentration of NO_2 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% ZnCl_2 can be used as an adsorbent to adsorb NO_2 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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