

Adsorption of Sulphur in Biogas by Activated Carbon Derived from Mangrove Fruits (*Rhizophora stylosa*) as Solid Residue of Natural Dyes Extraction

Paryanto, Wusana Agung Wibowo, Nandika Aji Saputra, Rosana Budi Setyawati

*Program Studi Sarjana Teknik Kimia, Fakultas Teknik, Universitas Sebelas Maret
Jl. Ir. Sutami No.36 A, Jebres, Surakarta, 57126
E-mail : paryanto.uns@gmail.com*

Abstract

Hydrogen sulfide (H_2S) is considered as an impurity in biogas. H_2S could react to form sulfur dioxide (SO_2) and sulfuric acid (H_2SO_4) during the burning process. The corrosive property of these compounds possibly causes damage to the power plant system. Overcoming this problem, activated carbon impregnated with KOH has been proven to work very well in adsorbing H_2S . On the other hand, mangrove fruits pulp residue from the natural dyes extraction process has not utilized. Mangrove (*Rhizophora stylosa*) fruits contain about 50% fixed carbon which is possibly made as activated carbon. The purposes of this research were to determine the adsorption efficiency of H_2S in biogas using activated carbon derived from mangrove fruits residue and to determine isotherm equilibrium constants for adsorption. The small scale adsorption devices consist of cooler, flow stabilizer, flow regulator, flow meter and column adsorber. At a certain flow rate, biogas was sampled every 10 minutes and then analyzed using a portable H_2S gas analyzer. Temperatures of biogas entered the adsorption column were in the range of 33-34°C. The optimum biogas flow rate was 4 litre per minute (lpm) for 250 grams (16 cm of height) of activated carbon. We found the adsorption efficiency was decreased by time and still reached 79.6% for 50 minutes of contact time. Based on the coefficient of correlation value (R^2) on the isotherm model, The Langmuir model is more suitable for the H_2S adsorption of biogas in this study. We found the Langmuir equilibrium constant k was 0.033 and maximum adsorption capacity $(x/m)_{max}$ was 0.284 mg/mg.

Keywords: Biogas, Activated Carbon, Hydrogen Sulfide, Adsorption, *Rhizophora stylosa*

INTRODUCTION

Activated carbons are versatile adsorbents. Their adsorptive properties are due to their high surface area, a microporous structure, and a high degree of surface reactivity, they are, used, therefore, to purify, decolorize, deodorize, dechlorinate, separate, and concentrate in order to permit recovery and to filter, remove, or modify the harmful constituent from gases and liquid solutions (Ludlow, 2006). The use of activated carbon as an adsorbent in various applications has increased rapidly every year (Nwabanne and Igbokwe, 2011).

Mangroves, especially *Rhizophora stylosa* sp., are widely planted in Indonesian coastal areas

as abrasion retaining plants. Every year, mangrove forests can adsorb 42 million tons of carbon in the air or equivalent to carbon gas emissions from 25 million cars (Ardianto, 2011). By using the advantage of mangrove for carbon-storing, it opens opportunities to be used as raw material for activated carbon. Mangroves fruits can be utilized as natural dyes through water extraction. This extraction process remains wet solid residue that has not maximally utilized. Mangrove fruits contain moisture in air-dried sample (6.48%), volatile matter (41.91%), fixed carbon (48.56%), and ash (3.05%) that possibly converted into activated carbon (Paryanto *et al.*, 2018)

Biogas is one of the energy sources that can be produced from biomass sources such as food

waste, agricultural waste, livestock waste (animal waste), or mud from processing plant waste used as an energy source for electricity generation (Sanches-Percira *et al.*, 2015). However, biogas contains Hydrogen Sulfide (H_2S). This compound becomes one of the impurities in biogas with negative impacts. H_2S can be converted into sulfur dioxide (SO_2) and sulfuric acid (H_2SO_4) during the combustion process. These are undesirable corrosive compound that cause damage the power generation devices (Kennedy *et al.*, 2013). Therefore, biogas purification process is needed before its utilization as fuel, especially for power generation.

Many studies have been carried out about the purification of biogas both physically, physico-chemical, and biological such as water scrubbing. This method was relatively simple and low cost, but the simultaneous adsorption of H_2S and CO_2 into water cause fouling and clogging in piping systems. Therefore, it is better to get rid of H_2S separately (Persson *et al.*, 2006). There was no other method that uses TiO_2 /Zeolite composite as an adsorbent medium followed by photocatalyst. The results was quite promising, and able to adsorb H_2S as much as 72% -87%. Nevertheless, this method is quite complicated to be commercialized (Liu *et al.*, 2015).

Activated carbon, which already has a chemical or physical activation process has been widely used for H_2S adsorption of gas. Activated carbon that has been chemically activated using acid or alkaline solutions, has been shown to work better than carbon with physical or thermal activation (Guo *et al.*, 2007). Carbon that has been activated by the impregnation process using alkaline solutions can adsorb H_2S from the gas with an acid-base reaction process on the carbon surface (Yan *et al.*, 2002). Activated carbon impregnated with KOH liquid has been proven to work very well in adsorbing H_2S gas, which produces small H_2S levels in the adsorbed output stream which is can be used for internal combustion engine (Sitthikhankaew and Predapitakkun, 2011).

The activated carbon must be efficient, which have high capacity and selectivity for H_2S , and can be regenerated (Menezes *et al.*, 2018). It is important to know the real picture H_2S purification effectiveness in biogas and to find the

Freundlich and Langmuir equilibrium constants in order to estimate adsorption retention time (Alwathan *et al.*, 2013).

The purposes of this research were to determine the adsorption efficiency of H_2S purification in biogas with activated carbon originated from mangrove fruits residue, and to determine the Freundlich and Langmuir equilibrium constants for adsorption. This research used activated carbon from mangrove fruits residue by KOH activation resulting from previous research (Paryanto *et al.*, 2019).

RESEARCH METHODS

The material for activated carbon was mangrove (*Rhizophora stylosa*) fruit as a residue of water-based natural dyes extraction. Mangrove was obtained from the coastal area of Cilacap, Central Java. Activated carbon must be formed of pellet because it is good for uses in gas phase adsorption. Activated carbon was produced by pyrolysis of solid residue at a temperature of $400^\circ C$ for 3 hours by using a 0.5 M KOH solution as an activator. This process produced an active area of $18.089 \text{ m}^2/\text{g}$ (Paryanto, Saputro *et al.*, 2019). Biogas which is produced from cow dung digester in Sambu, Boyolali, Central Java, was used in this research.

The series of adsorption types of equipment are shown in Figure 1. This set consists of a single tube cooler with 0.5 inch internal tube diameter and 3 inch internal shell diameter with a 40 cm length (3), a flow stabilizer tank with 19 L in volume (4), and an adsorber column with 3 inches inside diameter and 60 cm length (6). The apparatus was equipped with pressure gauge WIPRO $0-6\text{kg}/\text{cm}^2$ (2), thermometer (1), flow meter WIEBROCK for 1 atm pressure (5), flow regulator (8), gate valve (9), and gas distributor (7). The types of equipment were arranged and placed near a digester in Sambu, Boyolali.

The amount of activated carbon used in each biogas flow rate was 250 grams (about 16 cm of height). Biogas flow rates were varied by 3, 4, 5, 6, and 7 liters per minute (lpm). In every 10 minutes of the adsorption process, biogas was sampled and H_2S content was measured by using portable H_2S Gas Analyzer Detector KXL-802. Beforehand, the inlet biogas was tested before the adsorption process.

RESULTS AND DISCUSSION

Adsorption level of H₂S gas

The efficiency of H₂S adsorption from biogas can be calculated by:

$$Efficiency (\%) = \frac{C_0 - C}{C_0} \times 100\% \quad (1)$$

C₀ is the initial H₂S concentration before entering the adsorber (ppm) and C is the H₂S concentration after passing the adsorbent (ppm). The initial concentration of H₂S was obtained around 348 to 414 ppm. The efficiency of H₂S adsorption at various flow rates and contact times is shown in Figure 2.

Based on Figure 2, the best H₂S adsorption efficiency is obtained at 3 lpm and 4 lpm for 10 minutes of adsorption time. The H₂S adsorption efficiency is reduced by the longer the contact time, it is due to the reduced effective area of activated carbon. After 50 minutes of contact time, the efficiency of H₂S adsorption is still reached 79.6%. This is still quite far compared to using activated carbon with a mixture of zeolites with an efficiency of 98.98% (Harihastuti *et al.*, 2016).

In figure 2 efficiency of 3 lpm at 50 minutes increases compared to at 40 minutes. This is likely due to a significant decrease in the H₂S concentration of the inlet gas. this is the cause calculation errors.

Determination of Equilibrium Constants

The equilibrium concentration (C_e) at various flow rates is obtained graphically by plotting H₂S concentration with time as shown in Figure 3. The equilibrium concentration is assumed as the concentration of H₂S exits the adsorption column that does not change as a function of time.

The Freundlich and Langmuir equilibrium constants can be determined graphically by Eq. 2 and Eq. 3, respectively:

$$\log \frac{x}{m} = \frac{1}{n} \log C_e + \log k \quad (2)$$

In the Freundlich equation (Eq. 2), x/m is the total H₂S adsorbed per gram of adsorbent, m is the mass of adsorbent, C_e is the H₂S concentration at equilibrium condition, k and n are constants. The graph of Freundlich's isotherm model is shown in Figure 4.

$$\frac{C_e}{x/M} = \frac{1}{(x/M)_{max}} C_e + \frac{1}{(x/M)_{max} k} \quad (3)$$

In the Langmuir equation (Eq. 3), x/m is total H₂S adsorbed per gram of adsorbent, m is the mass of adsorbent, k is constant, (x/m)_{max} is the maximum adsorption capacity, and C_e is the H₂S concentration at equilibrium condition (Said, 2018). The graph of Langmuir's isotherm model is shown in Figure 5.

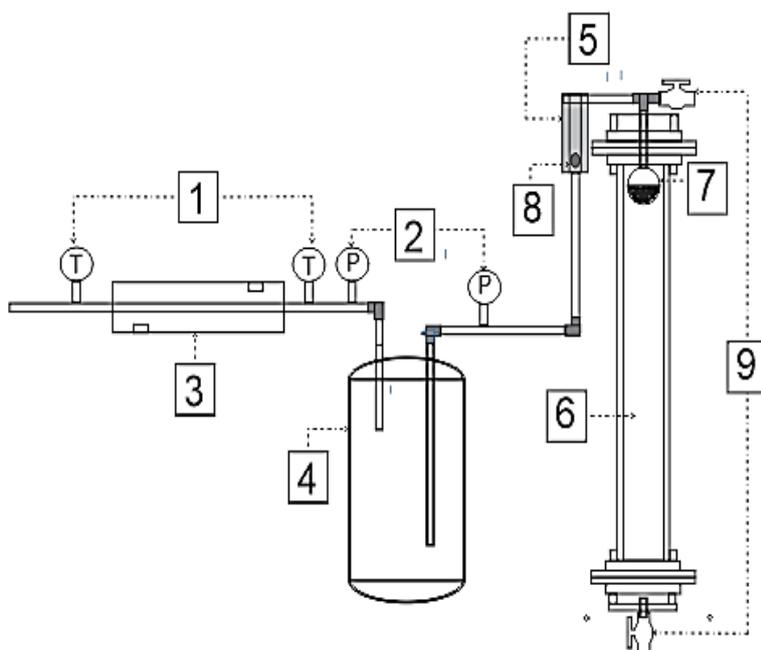


Figure 1. Series of adsorption set

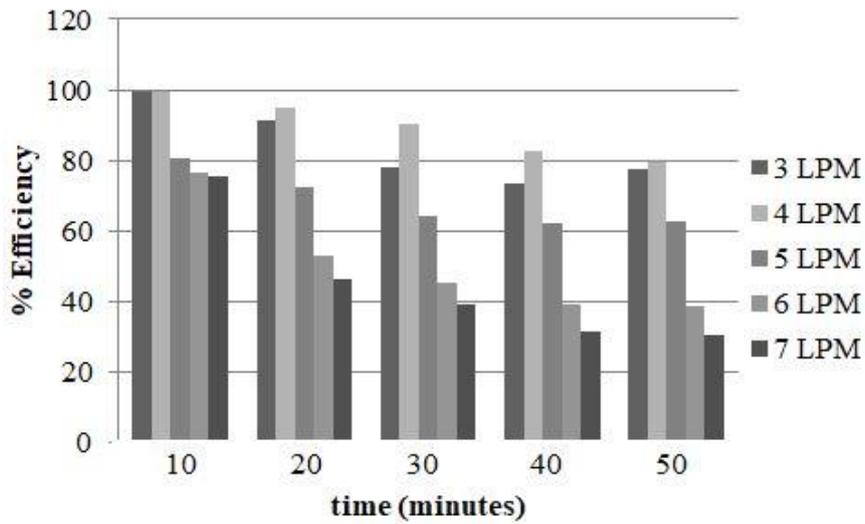


Figure 2. The efficiency of H₂S Adsorption in Various Flow Rates (lpm) and Retention Times (minutes)

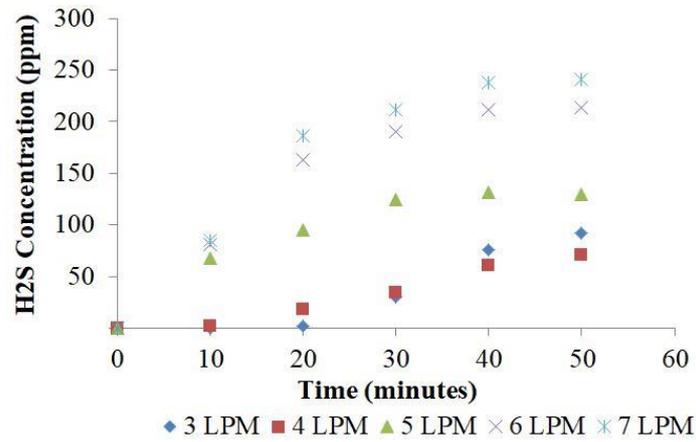


Figure 3. The concentration of H₂S versus time

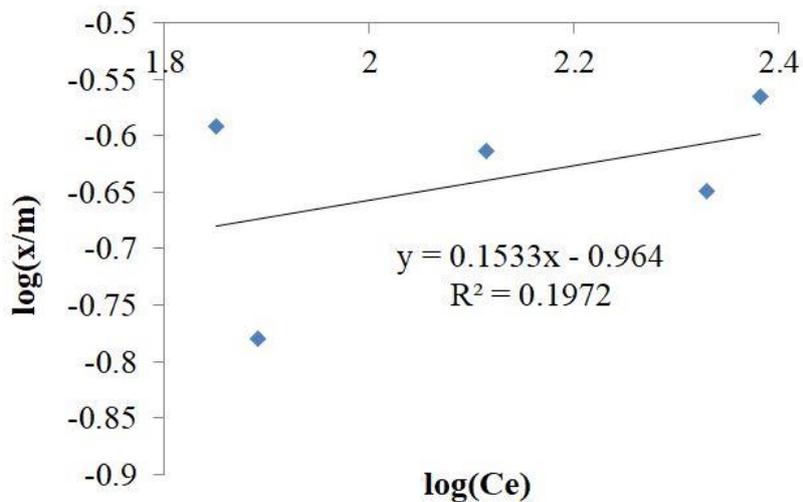


Figure 4. The plot of Freundlich Model

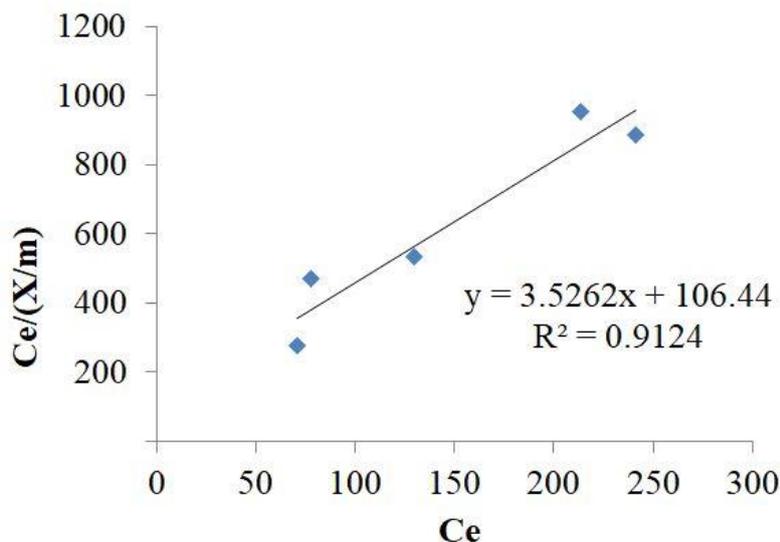


Figure 5. The plot of Langmuir Model

Isotherm model that represents the adsorption process is determined based on coefficient value (R^2) that close to 1 (Gueu *et al.*, 2007). As shown in Figure 4 and Figure 5, it is obtained that the Langmuir isotherm model has a coefficient value (R^2) higher (close to 1) than the Freundlich isotherm model. Therefore, Langmuir model is more suitable for data in this study. Freundlich's isotherm itself is more effective for heavy metals adsorption (Bernasconi *et al.*, 1995). From the calculation, we found that the Langmuir equilibrium constant k was 0.033 and the maximum adsorption capacity $(x/m)_{max}$ was 0.284 mg/mg.

CONCLUSION

Based on the adsorption efficiency, the optimum biogas flow rate for H_2S adsorption by activated carbon used in this study was 4 lpm. At adsorption temperature of 33-34°C, the isotherm Langmuir model was more suitable for H_2S adsorption in biogas. We found that the Langmuir equilibrium constant k was 0.033 and the maximum adsorption capacity $(x/m)_{max}$ was 0.284 mg/mg.

ACKNOWLEDGEMENT

Research team thanks to the Director-General of Research and Development and UNS

LPPM on the basis of research related to PTUPT with contract numbers: 089/SP2H/Lt/ DRPM/2018 and coordinator of the Biogas Unit in Ringinwok, Sambu, Boyolali, Central Java which has given opportunities to conduct a research.

REFERENCES

- Alwathan, A., Mustafa, M. & Thahir, R., 2013, Pengurangan Kadar H_2S dari Biogas Limbah Cair Rumah Sakit dengan Metode Adsorpsi, *Jurnal Konversi UNLAM*, 2,(1):1-6.
- Ardianto, T., 2011, Mangrove sebagai Penangkap Karbon, Pendingin Udara serta Penahan Tsunami, Diambil dari www.survey-pemetaan.com [7 March 2012].
- Bernasconi, G., Gerster, H., Hauser, H., Stauble, H. & Schneiter, E., 1995, Teknologi Kimia Bagian 2, Terjemahan Lienda Handojo. Pradnya Paramita. Jakarta.
- Gueu, S., Yao, B., Adouby, K. & Ado, G., 2007, Kinetics and Thermodynamics Study of Lead Adsorption on to Activated Carbons from Coconut and Seed Hull Of The Palm Tree, *International Journal of Environmental Science & Technology*, 4(1):11-17.
- Guo, J., Luo, Y., Lua, A. C., Chi, R.-a., Chen, Y.-l., Bao, X.-t. & Xiang, S.-x., 2007, Adsorption of Hydrogen Sulphide (H_2S) by Activated Carbons Derived from Oil-Palm Shell, *Carbon*, 45(2):330-336.

- Harihastuti, N., Purwanto, P. & Istadi, I., 2016, Pemurnian Biogas untuk Mencapai Pipeline Quality Gas sebagai Sumber Energi Terbarukan yang Ramah Lingkungan, Programme of Postgraduate.
- Kennedy, N., Zhao, Q.-B., Frear, C. & Chen, S., 2013, The Selective Removal of H₂S over CO₂ from Biogas in a Bubble Column Using Pretreated Digester Effluent, 2013, Kansas City, Missouri, July 21-July 24, 2013, American Society of Agricultural and Biological Engineers.
- Liu, C., Zhang, R., Wei, S., Wang, J., Liu, Y., Li, M. & Liu, R., 2015, Selective Removal of H₂S from Biogas Using a Regenerable Hybrid TiO₂/zeolite Composite, *Fuel*, 157, 183-190.
- Ludlow, D.K., 2006, Activated Carbon Adsorption by Roop Chand Bansal and Meenakshi Goyal (Panjab University, Chandigarh, India). CRC Press (an imprint of Taylor and Francis Group): Boca Raton, FL. 2005. xxii+ 498 pp. \$189.95. ISBN 0-8247-5344-5, ACS Publications.
- Menezes, R. L., Moura, K. O., de Lucena, S. o. M., Azevedo, D. C. & Bastos-Neto, M., 2018, Insights on the Mechanisms of H₂S Retention at Low Concentration on Impregnated Carbons, *Industrial & Engineering Chemistry Research*, 57(6):2248-2257.
- Nwabanne, J. & Igbokwe, P., 2011, Preparation of Activated Carbon from Nipa Palm Nut: Influence of Preparation Conditions, *Research Journal of Chemical Sciences*.
- Paryanto, P., Saputro, M. E. & Nugroho, R. A., 2019. Produksi Karbon Aktif dari Buah Mangrove Menggunakan Aktivator Kalium Hidroksida. *Jurnal Inovasi Teknik Kimia*, 4(1):33-35
- Paryanto, P., Wibowo, W. A., Puspitaningrum, A. L. & Hapsari, R. H., 2018. Karbon Aktif dari Ampas Buah Mangrove Sisa Pembuatan Zat Warna Alami Menggunakan Aktivator H₃PO₄. *Jurnal Inovasi Teknik Kimia*, 3(2):17-22
- Persson, M., Jönsson, O. & Wellinger, A., 2006, Biogas Upgrading to Vehicle Fuel Standards and Grid Injection. IEA Bioenergy task.
- Said, N. I., 2018. Pengolahan Air Minum dengan Karbon Aktif Bubuk Prinsip Dasar Perhitungan, Perencanaan Sistem Pembubuhan dan Kriteria Disain. *Jurnal Air Indonesia*, 3(2):96-110
- Sitthikhankaew, R. & Predapitakkun, S., 2011, R.(Wibulswas) Kiattikomol, S. Pumhiran, S. Assabumrungrat N. Laosiripojana, Comparative Study of Hydrogen Sulfide Adsorption by Using Alkaline Impregnated Activated Carbons for Hot Fuel Gas Purification. *Energy Procedia*. 9:15-24.
- Yan, R., Liang, D.T., Tsen, L. & Tay, J.H., 2002, Kinetics and Mechanisms of H₂S Adsorption by Alkaline Activated Carbon, *Environmental science & technology*, 36(20):4460-4466.