DOI: 10.19184/ICL.v1i2.202

The Permeation of High Concentration Hydrogen Sulfide (H_2S) Gas Using PTFE (Polytetrafluoroethylene) and PVDF (Polyvinylidene Fluoride) membranes

Asnawati,[a] Alifah Mustafidah, [a] Diah Ayu Nur Sholehah, [a] Dwi Indarti, [a] Tri Mulyono, [a] Bambang Piluharto, [a] and Yeni Maulidah Muflihah*[a]

Abstract: Hydrogen sulfide (H_2S) is a toxic, corrosive, and flammable gas. The presence of H_2S gas can be reduced by a permeation method using PTFE (Polytetrafluoroethylene) membranes and PVDF (polyvinylidene fluoride) membranes. This H_2S gas passed through the membrane and was then captured by the SAOB (Sulfide Anhydride Oxidant Buffer) in S2- species form. A visible spectrophotometer was applied for the analysis of passed H_2S gas. Using a PTFE membrane, the optimum flow rate was obtained at 14.71 mL/min, with a mass flux of 0.825 kg/m^2.hour, permeability coefficient of 0.696 kg/m^2.hour.bar, and percent removal of H_2S gas was 88.14%. The optimum flow rate for the SAOB was obtained at a rate of 0.30 mL/min with a mass flux of 0.843 kg/m^2.hour and a percent removal of H_2S gas of 89.98%. Based on the results obtained on the PVDF membrane, the mass flux produced in the optimization of H_2S gas is 0.742 kg/cm^2.hour, and the optimization of the SAOB solution is 0.754 kg/cm^2.hour. The resulting permeability coefficient value is 0.741 kg/cm^2.hour. The results indicate that this study can remove H_2S gas at the optimum H_2S gas flow rate of 4.76 mL/minute of 94.89% and the optimum SAOB flow rate of 0.3 mL/minute of 95.66%.

Keywords: Permeation; PTFE (Politetrafluoroethylene); PVDF (polyvinylidene fluoride); Hydrogen sulfide; removal.

INTRODUCTION

H_2S gas is a widely known toxic gas [1]. The potential source of this gas was biogas and natural gas. Biogas is composed of 50-75% CH4, 24-40% CO_2, and ± 2% H_2S, while natural gas consists of several hydrocarbon compounds such as CH_4 (83.029%), N_2 (0.52%), CH_2 (11.48 %), CO_2 (4.97%) and H_2S (0.0008%) [2]. The H_2S gas could potentially damage the pipes and compressor equipment because of its corrosive nature, causing acid rain, damaging the environment, and interfering with human health [3].

One of the studies to eliminate the presence of H_2S gas is using membrane applications. The common membrane for the H_2S gas permeation process is hydrophobic [4], including PVDF (Poly-Vinylidene Difluoride), PTFE (Poly-Tetrafluoroethylene), PP (Polypropylene), and PE (Polyethylene) membranes [5]. Among these membranes (PTFE, PVDF, PP, and PE), PTFE and PVDF membranes have more advantages [6]. Besides these membranes are hydrophobic membranes which are very stable in the gas permeation process; the PTFE membrane is also inert. Hence, in the H_2S gas permeation process, H_2S gas could pass the membrane without any chemical reactions [4].

In this study, we focused on removing H_2S gas using PTFE and PVDF membranes by passing H_2S gas through the membrane. The SAOB solution will then trap the permeate. The permeation of H_2S gas using PTFE and PVDF membranes is carried out using a cross-flow system with SAOB solution as an H_2S gas capture solution. It prevents the change of S^{2-} to HS^- or H_2S [7]. According to [8], the factors potentially affecting gas permeation results using membranes are H_2S gas flow rate, SAOB capture solution flow rate, permeation time, and temperature. In this study, the H_2S gas flow rate and the SAOB flow rate as a trapping solution were studied carefully. These two factors significantly affect the results of H_2S gas permeation; this is because the significant flow rate of H_2S gas is fed through the membrane, and the significant flow rate of the SAOB capture solution will affect the amount of H_2S gas permeate into the membrane [4].

According to [8], the principle of permeation is based on the difference in concentration between the feed and permeate. The mass transfer will occur from a high concentration to a lower concentration. Research by [4] reported that the ratio of the H_2S gas velocity to the optimum SAOB solution velocity was 9:1. It can be assumed that the faster the flow rate of H_2S gas and the slower the flow rate of the SAOB solution, the greater the possibility of permeation. The slow movement of the SAOB solution allowed the SAOB solution to capture more H_2S gas.

METHODS

Chemical

The materials used include 90% FeS (Merck), 37% HCl pa, 99.99% N_2 gas, PTFE (Poly-Tetrafluoroethylene) membrane, commercial PVDF (Polyvinylidene Fluoride) membrane with a pore size of 0.22 µm (Millipore FGLP 29325), NaOH 95% (Merck), ascorbic acid 99% (Merck), Na_2EDTA 99% (Merck), H_2SO_4 97%, KIO_3 (Merck), KI 99.5% (Merck), $FeCl_3$.6H2O 99% (Merck), Na_2S .9H2O 99% (Merck), starch, N, N-Dimethyl-1,4-Phenylen Diammonium Dichloride 99% (Merck) solution, and distilled water.

Instrumentation

UV-Vis spectrophotometer (model 752), filtration cell

[a] Asnawati, A. Mustafidah. DAN. Sholehah, D. Indarti, T. Mulyono, B. Piliharto, YM. Muflihah
Department of Chemistry, Faculty of Mathematics and Natural Sciences, University of Jember.
*e-mail: yeni.maulidah.fmipa@unej.ac.id

(acrylic) dimension 11x11, thickness cm 1 cm, glassware, tubing, mass flow controller SEC-4400 (STEC), power supply ± 15 Volt and ± 24 Volt (S-120- 24), LabJack (UE9-Pro), Volt meter, pH meter (EUTECH), cuvette (GB-T26791), LabView program and peristaltic pump.

Production of H_2S gas

Five grams of FeS were put in a closed bottle connected to a pipe, and added with 50 mL of 15% HCl. The resulting gas is then flowed into the permeation cell using a tube controlled by mass flow control.

Design and operation of permeation systems.

The H_2S gas used resulted from the reaction between FeS and HCl. H_2S gas is controlled by mass flow control streamed into the permeation cell with a membrane in the middle. The upper part of the membrane was passed by H_2S gas. This gas crosses through the membrane into the SAOB solution, which flows at the bottom of the membrane. The SAOB solution flows with the help of a peristaltic pump into the permeation cell as a solution trapping H_2S gas that escapes from the membrane. Pretreatment first by flowing N_2 gas into the hose to expel other gases. The flow rate of H_2S gas was varied. Both through the membrane (PTFE and PVDF) and those that did not pass through the membrane (as the initial gas). The permeate obtained was collected as much as 10 mL. The experiment was carried out with three repetitions. Likewise, the water rate of SAOB (Sulfide Anhydride Oxidant Buffer) is varied at the optimum H_2S gas flow rate.

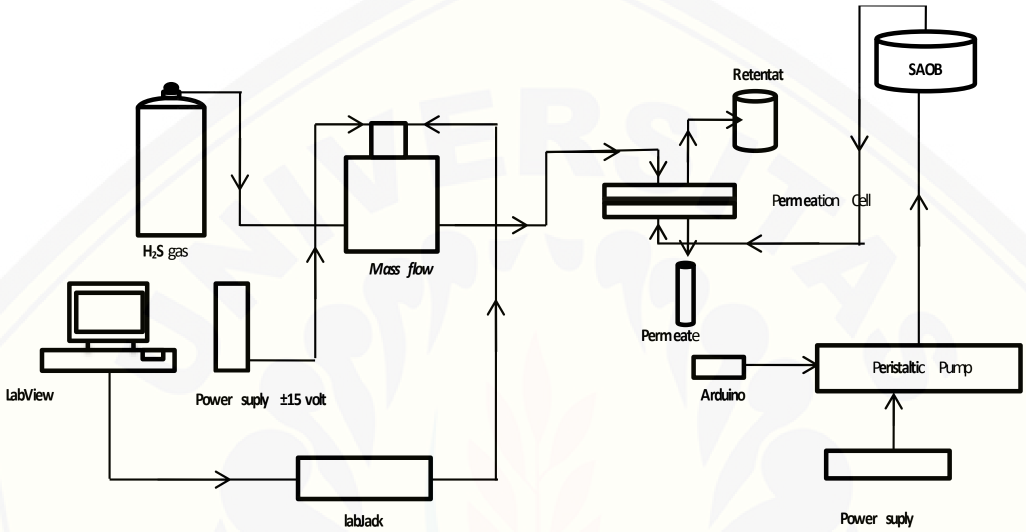

Figure 1. Design of permeation system

The Analysis H_2S gas

The permeate obtained from the permeation results was diluted and taken as much as 10 mL, then added with 0.5 mL of sulfuric acid-amine reagent solution and three drops of $FeCl_3$ methylene blue complex then its absorbance was measured with a visible spectrophotometer at the maximum wavelength. The concentration of H_2S gas is determined from the calculation of the linear equation obtained from the calibration curve. Flux analysis and permeability coefficient

Flux analysis and permeability coefficient were carried out to determine the performance of the membrane in H_2S gas permeation using a PTFE membrane. This analysis is carried out by calculating the amount of flux. The permeability coefficient is obtained from the slope resulting from plotting between flux and pressure.

Percent analysis of H_2S gas removal

The percentage of H_2S removal is used to determine the percentage of the amount of H_2S gas that can be removed by calculating the H_2S gas that passes through the membrane. Percent analysis of H_2S removal was carried out by comparing the mass of H_2S gas in the permeate with the mass of the initial H_2S gas multiplied by 100%. The mass of H_2S gas in the permeate was obtained from H_2S gas that passed through the membrane, which was captured by the SAOB solution, while the initial mass of H_2S gas was obtained from H_2S gas, which was captured directly by the SAOB solution without passing through the membrane. Permeation removal percentage can be calculated using equation 1.

$$\%\ removal: \left[\frac{Mass\ of\ H_2S\ permeate}{Mass\ of\ H_2S\ originate}\right]\ x\ 100\%$$

Mass of H_2S gas originate = mass of H_2S gas without passing through the membrane

Massa of permeate H_2S = mass of gas H_2S passing through the membrane

RESULT AND DISCUSSION

PTFE and PVDF membranes are types of non-polar porous membranes. The flow patterns of gas permeation in porous membranes include the Knudsen flow pattern, a pattern of gas flow through tiny pores that causes collisions between the pore walls and gas particles resulting in laminar flow [8]. Polar H_2S gas particles pass through/rub with non-polar PTFE and PVDF membranes which are very beneficial because the nature of the two is repulsive. There will be no interaction so that the permeation process can take place.

Permeating H_2S gas with PTFE and PVDF membranes uses a cross-flow system with SAOB solution for capturing H_2S gas [4]. The H_2S gas permeation process occurs in a permeation cell made of acrylic media with the membrane positioned in the middle (Figure 2). The H_2S gas that has passed through the membrane is called the permeate, which the SAOB solution will then capture.

Initial concentration of H_2S gas

The H_2S gas source used in this study came from the reaction of FeS with an HCl solution. The reaction equation that occurs can e seen in the following reaction:

$$FeS_{(s)} + 2HCl_{(l)} \rightarrow FeCl_{2\,(aq)} + H_2S_{(g)}$$

The reaction occurs quickly without the need for heating to produce H_2S gas. A pungent smell, like the smell of rotten eggs, can detect the presence of H_2S gas produced. The smell of rotten eggs is one of the physical properties of H_2S gas. The initial concentration of H_2S gas was obtained from H_2S gas, which was captured directly by the SAOB solution without passing through the membrane.

Optimum Flow rate for H_2S gas and SAOB solution

H_2S gas permeation was carried out by varying the flow rate of H_2S gas and the SAOB solution. Based on the results obtained in Figure 3a shows that at various gas flow rates, the optimum permeation results were obtained at a gas rate of 14.71 mL/minute with a permeate absorbance of 0.709. This is possible because, at a rate of 14.71 mL/min, the resulting pressure is the optimum pressure to allow gas to pass through the membrane so that the H_2S gas particles that enter the membrane's pores move stably and laminar flow occurs.

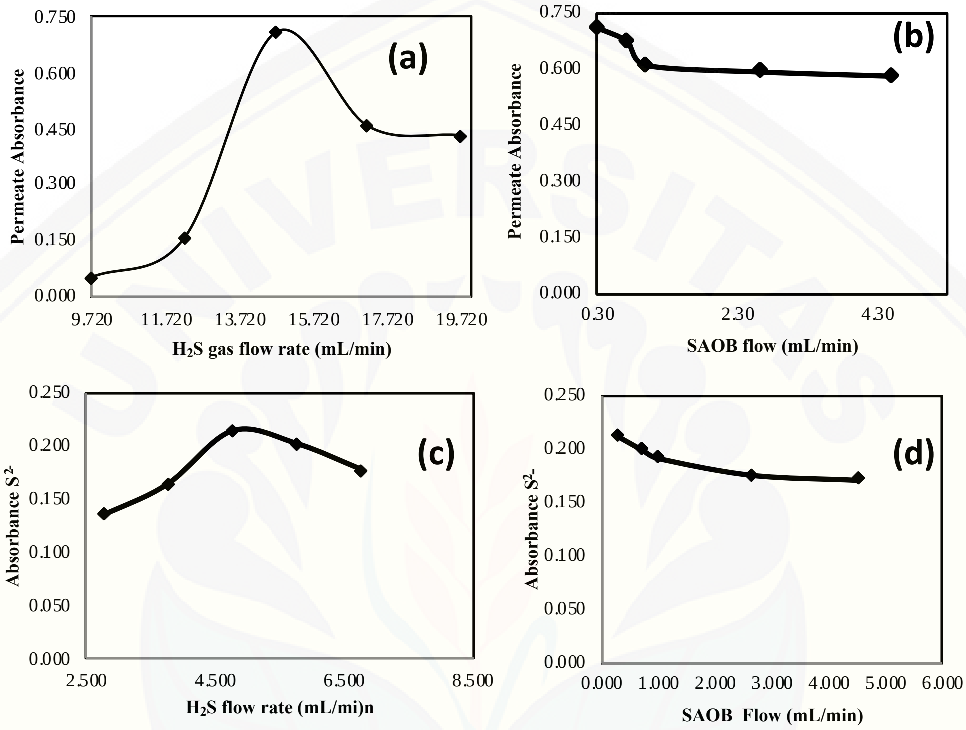

Figure 2. The flow rate effect of on the permeation (a) H_2S gas using PTFE membrane, (b) SAOB using PTFE membrane, (c) H_2S gas using PVDF membrane and (d) SAOB using PVDF membrane

The optimum permeation for varying SAOB rates lies in the SAOB rate of 0.30 mL/min with a permeate absorbance of 0.710 (Figure 2b). This is possible because, at a lower speed, it will be more accessible and more optimal for the SAOB solution to capture the H_2S gas that passes through the membrane. Variations in the flow rate of H_2S gas used in permeation using PVDF membranes were 2.77 mL/minute, 3.76 mL/minute, 4.76 mL/minute, 5.76 mL/minute, and 6.77 mL/minute with the flow rate of the SAOB capture solution being kept constant at 0.3 mL/ minutes shown in Figure 2c. The variation in SAOB flow rate is 0.3 mL/minute, 0.72 mL/minute, 0.98 mL/minute, 2.63 mL/minute, and 4.5 mL/minute. The optimization results can be seen in Figure 2d.

The results show that the optimum optimization of H_2S gas permeation is at the speed of H_2S gas 4.76 mL/minute with the SAOB solution speed of 0.3 mL/minute. These results indicate that stable H_2S gas passes through the membrane at an H_2S gas velocity of 4.76 mL/minute. At the lowest SAOB solution speed of 0.3 mL/minute, the SAOB solution flows slower in acrylic media so that more H_2S gas is captured.

Flux and permeability coefficient

Membrane performance can be determined from the value of the flux and the permeability coefficient. Flux is the amount of gas that can pass through the membrane per unit area per unit of time. Based on the results obtained, it shows that at variations in gas rates, the optimum flux is obtained at a gas rate of 14.71 mL/minute with a flux of 0.825 kg/m^2 hours, and at a variation of SAOB flow rate, the optimum flux value lies at a SAOB rate of 0.30 mL/minute with a flux of 0.843 kg/m^2hour. The increase in flux is possible because the more significant the gas flow rate, the more gas will enter the membrane's pores, which causes the resulting flux to also increase [9]. The decrease in flux is possible because, at that speed, the pressure generated is large enough, making it difficult for H_2S gas to enter the pores of the membrane so that it will come out as a retentate resulting in a decrease in the resulting flux. The decrease in flux is also possible due to the interaction between the H_2S gas and the PTFE membrane, which causes the membrane pores to close.

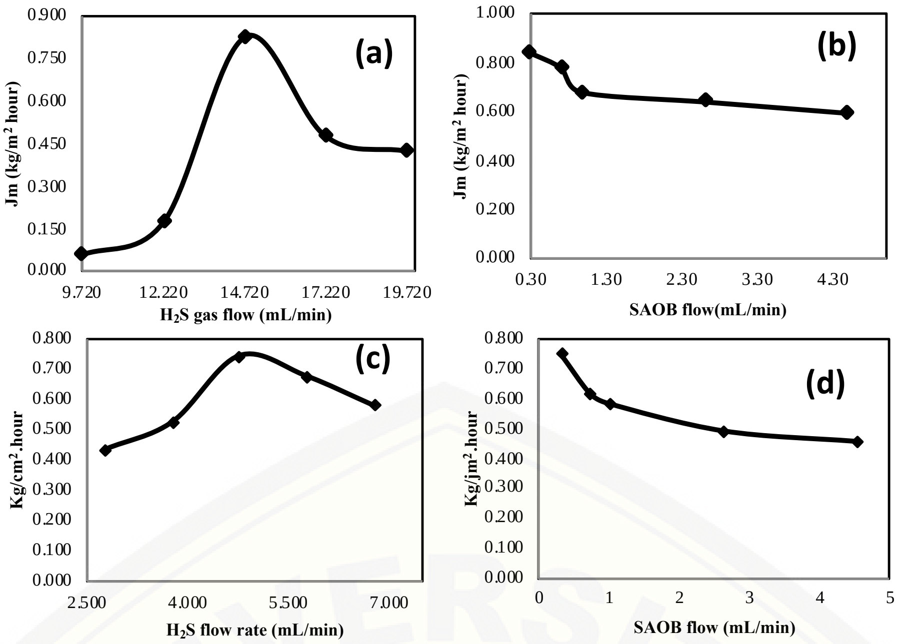

Figure 3. The effect of flow rate on the resulting flux. (a) H_2S gas on PTFE (b) SAOB on PTFE (c) H_2S gas on PVDF and (d) SAOB on PVDF

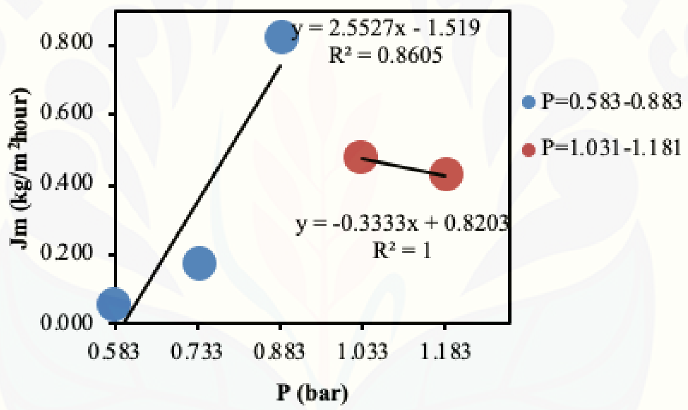

Figure 4. The effect of H_2S gas flow on the permeability coefficient of PTFE membrane

Figure 3 The effect of flow rate on the resulting flux. (a) H_2S gas on PTFE (b) SAOB on PTFE (c) H_2S gas on PVDF and (d) SAOB on PVDF

The resulting flux showed that the performance of the PVDF membrane was the optimum at the H_2S gas rate of 4.76 mL/minute and the SAOB solution rate of 0.3 mL/minute. The flux value for H_2S gas optimization was 0.742 kg/cm^2.hour and for SAOB solution optimization was 0.754 kg/cm2.hour. Figure 4 The effect of H_2S gas flow on the permeability coefficient of PTFE membrane

The permeability coefficient is the ability of the membrane to be able to pass gases. The permeability coefficient is obtained based on the slope resulting from plotting between flux and pressure [8]. Based on the trend in Figure 4, it shows that there was an increase in flux at a pressure of 0.583-0.883 bar, but after that, the flux decreased starting from a pressure of 1.031-1.181 bar. Based on this trend, the resulting slope does not have good linearity. Therefore, the pressure range is divided into two curves, resulting in two permeability coefficients in the pressure range of 0.583-1.181 bar.

Table 1. Permeability coefficient at pressure 0.583-1.181 bar

pressure (bar)	J_m (kg/m^2.hour)	Lp (kg/m^2.hour.bar)
0.583	0.058	
0.734	0.177	2.552
0.883	0.825	
1.031	0.477	-0.295
1.181	0.427	

The emerging trend shows that there was an increase in flux until a peak was formed at a pressure of 0.883 bar, but then the flux decreased until a pressure of 1.181 bar. The increase in flux indicates that at a pressure of 0.583-0.883 bar, the pressure makes it easier for H_2S gas to pass through the membrane, as indicated by the immense permeability coefficient value (Table 1). The permeability coefficient obtained is the average of three repetitions. According to [10], the greater the value of the permeability coefficient of a membrane, the easier it will be for the solute to pass through the membrane resulting in high flux. The permeability coefficient on each membrane has a different value. The PES/NMP membrane has a permeability coefficient of 35.77 L/m2.hour.bar, and the PES/DMF membrane has a permeability coefficient of 15.36 L/m2.hour.bar [10].

The results of the permeability coefficient using the PVDF membrane can be seen in Figure 5.

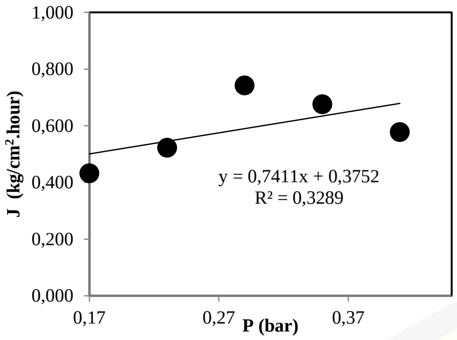

Figure 5. The effect of H_2S gas pressure on the flux at pressure 0.17-019 bar

A pressure of 0.17-0.29 bar produces a positive permeability coefficient, while a pressure of 0.35-0.41 bar produces a negative permeability coefficient. A tremendous pressure to use is 0.17–0.29 bar because the resulting slope is linear. Based on (Figure 5) shows that the resulting flux increased to a speed of 4.76 mL/minute and decreased to a speed of 6.77 mL/minute. The increasing flux indicates that the pressure obtained at a speed of 2.77-4.76 mL/minute causes H_2S gas to pass through the membrane more easily. This is indicated by the positive permeability coefficient value, which equals 2.583 kg/cm2.hour.bar. The resulting permeability coefficient is the average of three repetitions. The flux results decreased at 5.76 mL/minute and 6.77 mL/minute, indicating that the resulting pressure caused H_2S gas to be quite tricky to pass through the membrane. This can be seen from the negative value of the permeability coefficient, namely -1.627 kg/cm^2.hour.bar. A negative permeability coefficient value indicates that H_2S gas permeation is not optimal.

Removal of H_2S gas

The percentage of H2S gas removal is the percentage of H_2S gas that can pass through the membrane. The PTFE membrane could pass H2S gas optimally at a gas speed of 15 mL/minute with a percentage of H2S removal of 88.14% (Figure 6). The percentage of H2S removal using a PTFE membrane obtained showed higher results than the percentage of H2S removal using a ceramic membrane containing 25% ZnO. Ceramic membranes with a 25% ZnO content could only pass 87.57% H2S gas [3]. The optimum percentage of H2S removal at the SAOB flow rate variation was 89.98% at a SAOB solution rate of 0.3 mL/minute (Figure 6)

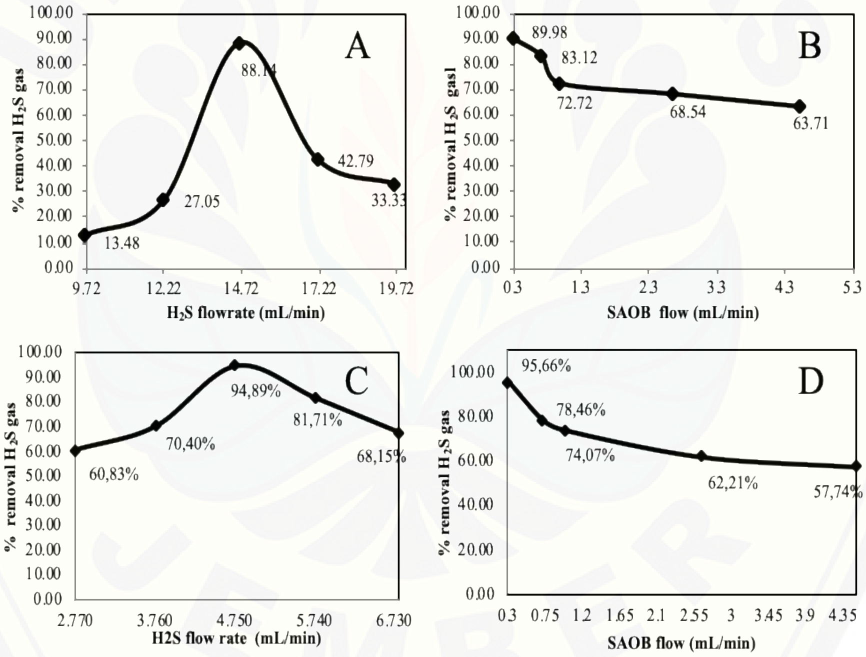

Figure 4. The effect of the rate (a) H_2S on PTFE (b) SOAB on PTFE (c) H_2S on PVDF (d) SOAB on PVDF

The optimum result for varying the speed of the H_2S gas using the PVDF membrane is at a speed of 4.76 mL/minute of 94.89%, and the optimum result for the variation of the speed of the SAOB solution is 95.66%.

CONCLUSION

The H_2S gas flow rate affected the permeation process using PTFE and PVDF membranes. The greater the speed of H_2S gas, the gas permeation tends to increase with the magnitude of the optimum H_2S gas removal percentage of 88.14% at an H_2S gas solution rate of 15 mL/minute (PTFE) and 94.89 % at a rate of 4.76 mL/min (PVDF). The influence of the flow rate of the SAOB trapping solution on the results of H_2S gas permeation using PTFE membranes, namely, the lower the speed of the SAOB solution, the captured H_2S gas will increase with the magnitude of the optimum H_2S gas removal percentage of 89.98% (PTFE) and 95.66% (PVDF) at solution velocity SAOB of 0.3 mL/min.

REFERENCES

[1] A. W. Bande, Analisis Penanganan Konsentrasi Hidrogen Sulfida Dalam Minyak Bumi Lapangan Tiaka Kabupaten

Morowali Utara Provinsi Sulawesi Tengah, *J. Geomine*, vol. 4, no. 2, 2016.

[2] F. E. Rahayu and Sunaryo, Itm-04: Analisis Reduksi Gas H 2 S Untuk Meningkatkan Kualitas Biogas Berbahan Baku Sampah Organik Buah- Buahan, *Pros. Semin. Nas. Fis.*, vol. 3, pp. 287-288, 2014

[3] F. Asip and T. Okta, Adsorbsi H 2 S Pada Gas Alam Menggunakan Membran Keramik Dengan Metode Titrasi Iodometri, *J. Tek. Kim.*, vol. 19, no. 4, pp. 22–28, 2013

[4] [R. Redondo, V. C. MacHado, M. Baeza, J. Lafuente, and D. Gabriel, On-line monitoring of gas-phase bioreactors for biogas treatment: Hydrogen sulfide and sulfide analysis by automated flow systems, *Anal. Bioanal. Chem.*, vol. 391, no. 3, pp. 789-798, 2008.

[5] A. W. M. Yani, Purwoko and Departemen, Penghilangan Gas H2S Dengan Teknik Biofilter Menggunakan Bahan Pengisi Kompos Dan Arang Aktif," *Tek. Ind. Pertan.*, vol. 19, no. 3, pp. 138-144, 2011

[6] M. Baeza, J. Alonso, and J. Bartrolí, Residual aqueous ozone determination by gas diffusion reverse flow injection analysis, *Anal. Bioanal. Chem.*, vol. 382, no. 2, pp. 388-395, 2005.

[7] [ASTM E 96, "Standard Test Methods for Water Vapor Transmission of Materials, E 96/E 96M - 05," *ASTM Int.*, vol. I, no. October, pp. 1-8, 1995.

[8] M. Mulder, Basic Principles of Membran Technology, 2nd edition, Dordrecht: Kluwer Academic Publisher, 1996.

[9] K. L. Wang and E. L. Cussler, Baffled membrane modules made with hollow fiber fabric, *J. Memb. Sci.*, vol. 85, no. 3, pp. 265-278, 1993.

[10] S. Mulyati, F. Razi, and Z. Zuhra, Karakteristik Membran Asimetris Polietersufone (PES) dengan Pelarut Dimetil Formamide dan N-Metil-2-Pyrolidone, *Biopropal Ind.*, vol. 8, no. 1, pp. 55–62, 2017.