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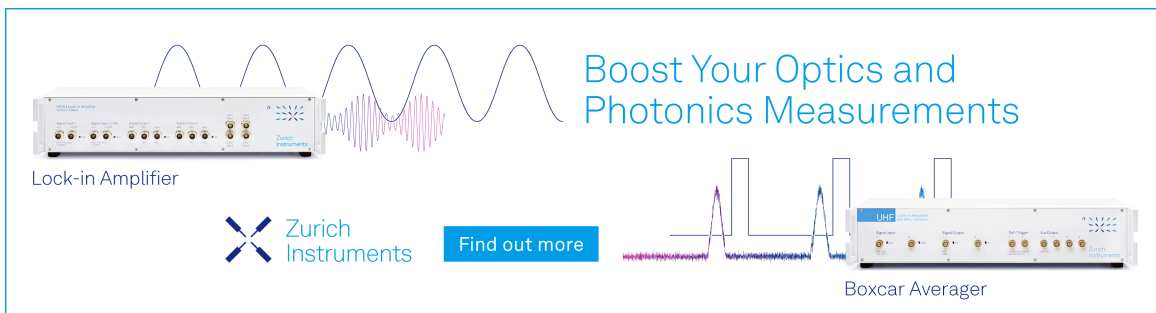
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Biogas Purification by Using Zeolite Packing Columns

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Abstract. Biogas is a product of anaerobic digestion, which consists of a mixture of methane (CH_4), carbon dioxide (CO_2), and some impurities such as hydrogen sulfide (H_2S) and water. The contaminants, especially H_2S, can cause metal corrosion, reduce the biogas calorific value, and are toxic to humans and the environment. The purpose of this study is to use natural materials such as zeolite to purify biogas, especially H_2S removal. The specific surface area can be increased by physical or chemical activation, which helps increase adsorption capacity. It was found that zeolite with calcination has a high affinity for H_2S. The bed height in the packed bed reactor and biogas flow rate have affected the efficiency of H_2S removal. The highest adsorption capacity and removal efficiencies are obtained with the calcined zeolite with 20-30 mesh and 10 cm of packing column height with the saturated zeolite; the time is 160 minutes.

INTRODUCTION

Fossil fuels increase pollution, which leads to acid rain and climate change. Moreover, it cannot be renewed. In Indonesia, crude oil resource is expected to last up to 13 years [1]. So, there is a need for renewable energy to overcome this problem.

Biogas is an environmentally friendly renewable product from the anaerobic degradation of organic materials. Conventionally, biogas is commonly produced from various biomass feedstocks such as animal, agricultural, and organic waste [1]. Biogas is a renewable energy source composed primarily of methane (CH4), carbon dioxide (CO2), sulfide acid (H2S), and water, with their respective compositions outlined in Table 1. One of the key advantages of biogas lies in its status as an environmentally friendly energy alternative. The production of biogas is a relatively straightforward process that holds the potential to address and mitigate environmental pollution resulting from the accumulation of untreated organic waste.The primary constituents of biogas, methane and carbon dioxide, are crucial contributors to its energy-generating properties. Methane, in particular, is a potent greenhouse gas, and capturing it for energy production helps reduce its release into the atmosphere, thereby mitigating its impact on climate change.

The process of biogas production involves the anaerobic digestion of organic materials, such as agricultural residues, animal manure, and organic municipal waste. During anaerobic digestion, microorganisms break down these organic materials in the absence of oxygen, leading to the production of biogas. This process not only yields a valuable source of renewable energy but also helps in the effective disposal of organic waste, preventing the release of harmful pollutants into the environment. Biogas has an energy content of 500-700 BTU/ft^3 [2].

The calorific energy of biogas depends on the concentration of CH_4, while all gases other than CH_4 contained in biogas are considered contaminants. Lower Caloric Value (LCV) of biogas with a methane content of 60-65% is 20-25 MJ/m^3 of biogas [3]. Therefore, the higher the CO2 or other impurity gas content, the lower the LCV of biogas [3]. As a comparison, natural gas (LNG), a mixture of methane, propane, and butane, has a calorific value of 35.6 MJ/m^3 [4].

TABLE 1. Component of Various Biogas

Biogas	CH$_4$ (%)	CO$_2$ (%)	N$_2$ (%)	O$_2$ (%)	H$_2$S (ppm)	Ref
Landfills	45-62	24-40	1-17	1-1.26	15-427	[5,6,7]
Sewage digester	58-65	33-40	1-8	<1	0-24	[5,8 9]
Organic waste digester	60-70	30-40	1	1-5	10-180	[5]

This research focuses on H$_2$S removal from biogas since it can cause corrosion and change the catalysts. At a concentration of 100-200 ppm, H$_2$S may cause blurred vision and death following exposure up to 1-8 hours, and at up to a concentration of 50 ppm, it can be toxic to bacteria in the environment. Therefore, to reduce the effect of H$_2$S, it must be removed by adsorption to less than <0.5 ppm [10].

From the results of previous research, there are various methods for biogas purification. For example, water scrubbing requires high energy for its operation [11], biofiltration requires supervision because it is very vulnerable to operating conditions for the proliferation of bacteria [12], and adsorption with and adsorbents specific [13]. Adsorption methods have often been used in the air separation industry, natural gas enhancement, hydrocarbon separation for petrochemicals, and wastewater purification [14]. Among the adsorption technologies, adsorption columns are often used for ease of maintenance and relatively economical costs compared to other separation methods [14]. Along with H$_2$S, zeolite can remove water, CO$_2$, and other impurities.

METHOD

Materials

Natural zeolite with an average particle size of 5-16 mesh and 20-30 mesh was supplied by CV. ADY WATER, Bandung, Indonesia, and biogas were supplied by PIAT (Pusat Invovasi Agroteknologi) Universitas Gadjah Mada Yogyakarta. H$_2$S content is measured before and after the biogas purification process using a BH-90A portable single gas detector from BOSEAN.

Method

Calcination And Characterization Of Zeolite

The method decreased moisture content in zeolite channels by activating only by calcination at 400°C for two hours with a furnace. After calcination, moisture content data is used to find out the water vapor content in zeolite channels, using equations as follows, with Wo being the mass of zeolite before calcination and W1 being the mass of zeolite after calcination. [15] :

$$Burn - off = \frac{Wo - W1}{Wo} x\ 100\% \tag{1}$$

Characterization is made of a particular specific surface area, and pore volume was measured by using N$_2$ (nitrogen) adsorption analysis (Quantachrome, NOVA 2000) with BET (Brunauer-Emmet-Teller) Characterization. In this analysis, the Quenched Solid Density Functional Theory (QSDFT) method calculates pore size distribution in porous materials.

Adsorption Studies In A Packed-Bed Reactor

Adsorption studies were conducted at a temperature of 25°C and a pressure of 1 atm. The experiments utilized a packed-bed column with an internal diameter of 7 cm and a height of 40 cm, as seen in Figure 1. The zeolite light fluctuations inside the bed measure 5, 10, and 15 cm. The biogas stream, characterized by an average hydrogen sulfide (H$_2$S) content of 400 parts per million (ppm), was introduced into the packed bed

reactor from the upper inlet. It then traversed through the zeolite materials within the reactor before exiting out the lower outlet of the packed bed reactor.

The concentrations of H_2S at the top and bottom of the packed bed reactor were measured at various time intervals. The measurement of H_2S removal efficiency was conducted by measuring the amounts of H_2S at both the intake and output using a BH-90A portable single gas detector. The breakthrough curves of hydrogen sulfide (H_2S) adsorption within the packed-bed reactor were determined by graphing the ratio of the outlet concentration of H_2S to the beginning concentration of H_2S in biogas (C/Co) against the operational period. In this experimental study, the flow rate of biogas was maintained at a constant value of one to two liters per minute.
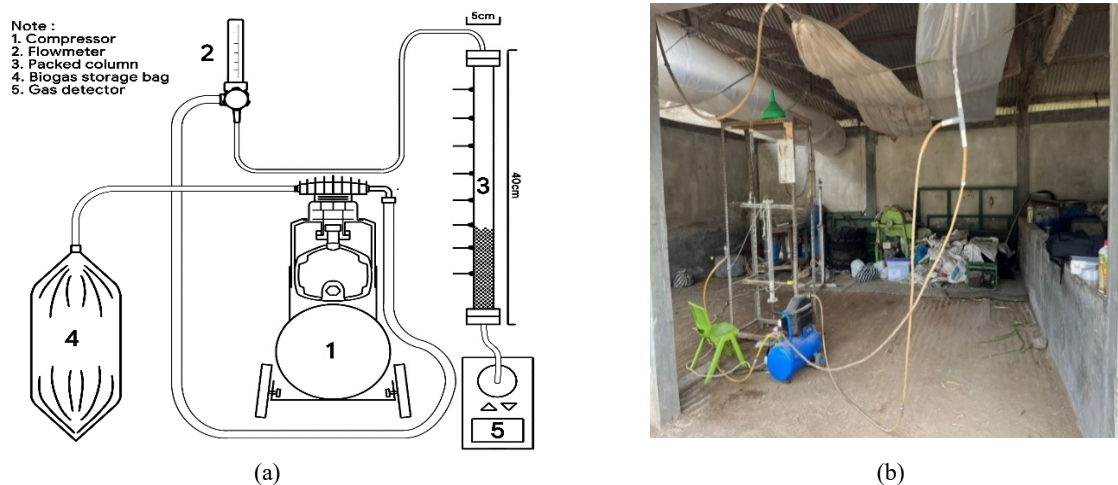
FIGURE 1. (a) Experimental Diagram, (b) Real Picture of Experiment Setting

RESULTS AND DISCUSSION

Zeolite Moisture Content

The moisture content of zeolite is determined between the mass of zeolite uncalcined and calcined because a mass reduction happened, as shown in Table 2. Indicates the evaporation of water vapor in the zeolite channel due to calcination and can expand the specific surface area of the zeolite. In this study, we obtained an average moisture content of 9% with three different calcination periods for the same zeolite.

TABLE 2. Zeolite Moisture Content Data

Period	Wo (gr)	Wi (gr)	Moisture Content (%)
1	1168	1072	8.22%
2	958	871,8	9%
3	930	839,6	9.72%

Porosity of Zeolite

The samples that were subjected to analysis include uncalcined zeolites, as well as calcined zeolites in the presence of hydrogen sulfide (H_2S). The zeolites were prepared in both uncalcined and calcined forms, with a bed height of 10 cm. The biogas flow rate used during the experiments was maintained at 2 L/minute. According to the data presented in Table 3, the specific surface area of uncalcined zeolite is measured to be 40.871 m2/g, whereas for zeolite that has undergone calcination, the specific surface area is determined to be 52.668 m2/g. These values fall within the range reported in the literature. According to the results presented in Table 3, the specific surface area of uncalcined zeolite is measured to be 40.871 m2/g, whereas for zeolite

that has undergone the calcination process, the specific surface area is determined to be 52.668 m2/g. These values fall within the range of detailed surface area data reported in the literature. The uncalcined zeolite exhibits a volume of 0.097 cm3/g, while the calcined zeolite displays a volume of 0.099 cm3/g. Additionally, the calcined zeolite possesses a mean pore diameter ranging from 17 to 20 Å. This particular pore is classified as belonging to the mesoporous category. According to the literature, the pore size of uncalcined zeolite is determined to be 7.4 Å based on the arrangement of tetrahedra consisting of silicon and aluminum atoms [16]. In theory, it has been determined that the kinetic diameter of H_2S is approximately 3.6 Å [17]. It is anticipated that zeolite possesses pores that are bigger than the diameter of H_2S particles, enabling the adsorption of H_2S within the zeolite channels. The adsorption of hydrogen sulfide (H_2S) occurs within the pores of a small diameter, specifically less than 10Å [18], as observed in the literature. Therefore, the porous zeolite structure appears suitable for the adsorption hydrogen sulfide (H_2S).

The porosity of zeolite, when exposed to H_2S in the channel, exhibited a reduced peak and a modest shift towards smaller diameters in both the uncalcined Z and calcined Z + H_2S samples. The presence of the adsorbate in both uncalcined Z and calcined Z + H_2S pores is responsible for the observed state. In this particular scenario, the process of zeolite regeneration involves subjecting the material to calcination at temperatures below 120°C while simultaneously applying a vacuum of around 10^5 torr. The aforementioned procedure is capable of effectively eliminating hydrogen sulfide (H_2S) from the system. Additionally, it is emphasized that the deposition of elemental sulfur onto the walls of the pores is a desirable outcome. The observations exhibit similarities and suggest that sulfur can decrease the micropore volume and the pore diameter.

TABLE 3. Data Analysis Surface Area and Porosity

Sample	Spesific surface area m^2/g	Pore volume (cm^3/g)	Mean pore diameter (Å)
Uncalcined zeolite	40.871	0.097	19.662
Zeolite calcination	52.668	0.099	18.083
Uncalcined Z+ H$_2$S	31.427	0.077	17.954
Calcined Z+ H$_2$S	33.691	0.083	18.026

Effect Of Bed Height On Packed-Bed Reactor Experiment

The effect of the bed is higher, the adsorption efficiency, and the longer it will take to achieve saturation in the zeolite. Viewed in Fig.2 with a biogas flow rate of 2L/minute, a height of 5 cm for a C/Co ratio from 0 to 1 takes 120 minutes, a height of 10 cm to achieve saturation takes 150, and a height of 15 cm takes 250 minutes. Increasing the zeolite mass will increase the total surface area and the number of empty sites on the zeolite and provide a longer contact time between the adsorbent and the adsorbate, thereby increasing the amount of H_2S adsorbed.

The addition of empty channels in the zeolite will adsorb a lot of H_2S, and a biogas speed of 2L/minute is considered sufficient and slow to give time for the adsorption process. Especially for calcined zeolite, heating will provide more channel space because it is clean from impurities and water vapor, so it takes a long time to be saturated. But when viewing a bed height of 10 cm using zeolite that has been calcined better than a bed height of 15 cm, it can be seen in Fig.2 (c). So, the height of 10 cm will be used to compare biogas speed.
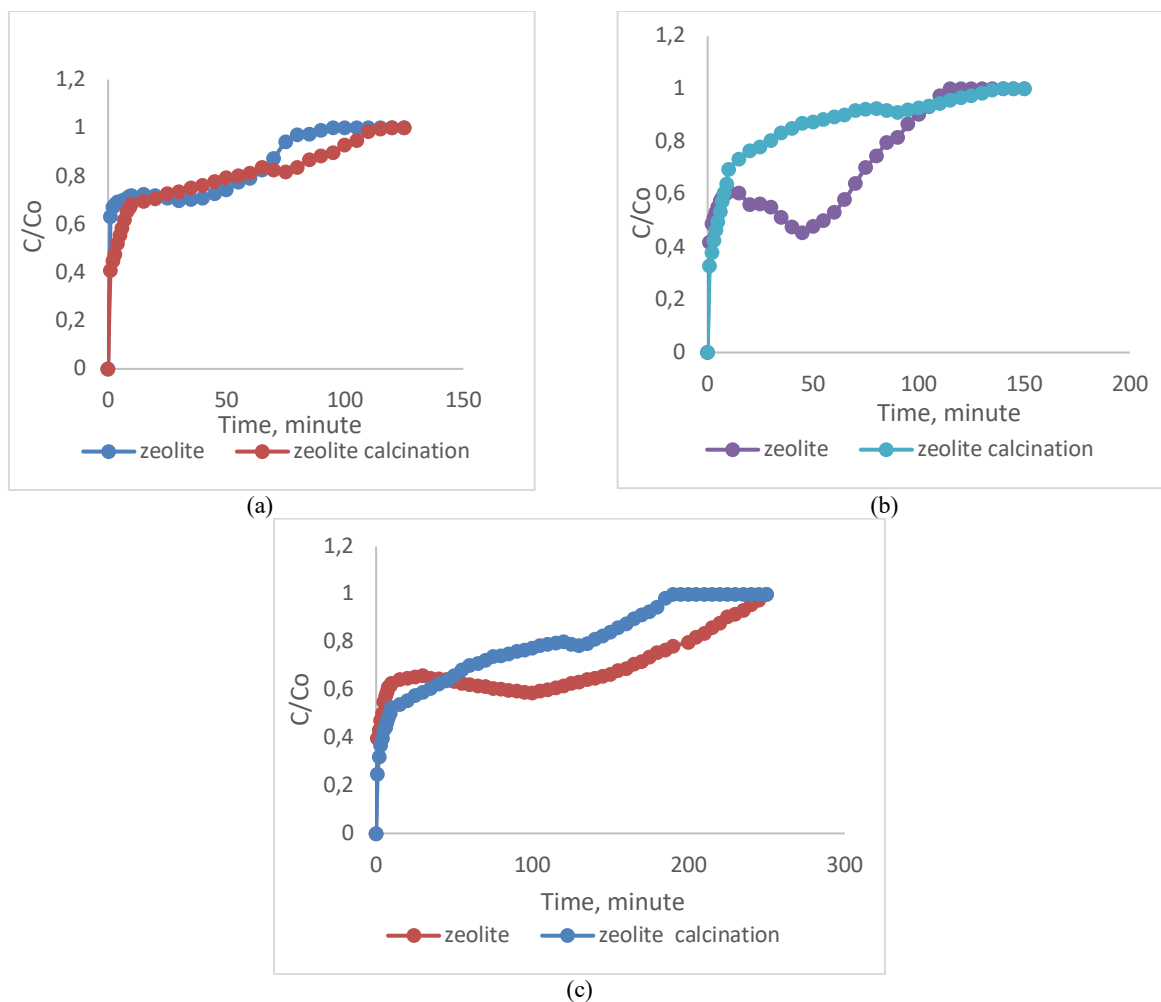
(a)

(b)

(c)

FIGURE 2. (a) graphic H_2S for height bed 5 cm, (b) graphic H_2S for height bed 10 cm, and (c) graphic H_2S for height bed 15 cm

Effect Of Flow rate of Stream Biogas and Size Zeolite

As a further comparison, it's shown in Fig 3 that lowering the speed of the biogas flow to 1L/minute and for a bed height of 10 cm will provide an even longer contact time between the adsorbent and the adsorbent. Thereby increasing the efficiency of the adsorption process, which can decrease the concentration of H_2S. For this case, it takes up to 135 minutes for the C/Co ratio to be worth one or reach saturated condition.

The last comparison is to compare the particle size of the zeolite, with a biogas flow of 1L / minute and a bed height of 10 cm, it was found that the smaller the particle size, the greater the specific surface area of the zeolite, to increase the efficiency of biogas adsorption. Especially in zeolite that has been calcined at 20-30 mesh, it takes 160 minutes for the C/Co ratio to be worth 1. In addition to the surface area factor, it also affects the diffusion process. Film diffusion is a rate control at low concentrations, and diffusion in zeolite particles controls the rate at high concentrations. Since H_2S gas is low concentration, the controlled diffusion of the increased film should be proportional to the surface area, which should also increase.

Further research so that this research can develop from a lab scale to a semi-industrial scale requires focusing on several aspects as follows: (i) Determining the performance of adsorption columns for biogas with various compositions (i.e. H_2S, CO_2, water vapor, CH_4, and impurities such as siloxane), (ii) Understanding the mechanism of adsorption, such as the interaction between adsorbate and surface phenomena of adsorbent,

(iii) Improve performance to be able to adsorb biogas with a large capacity according to the semi-industrial scale.
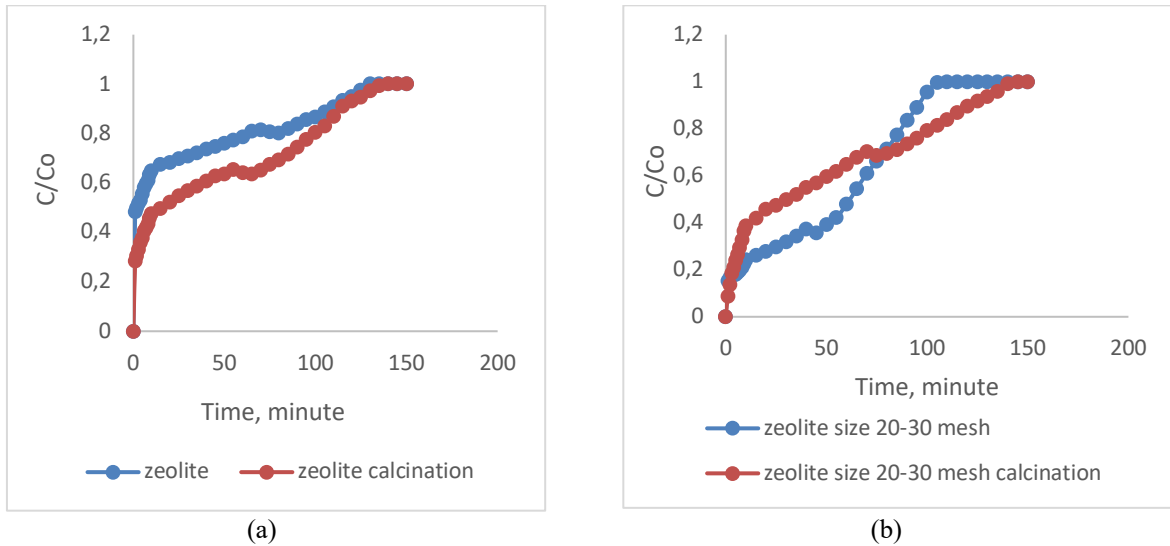

FIGURE 3. (a) Graphic H_2S for the biogas Flow rate of 1L/minute, (b) Graphic H_2S for different sizes of zeolites.

CONCLUSION

The results of this study show that zeolites could be a promising adsorbent, especially effective for purifying biogas from H_2S. The average yield of zeolites value around 9% of moisture content contains water in channel zeolites. Adsorbent type, reactor bed height, adsorbent size, and biogas flow rate significantly affect the efficiency of H_2S removal. The highest adsorption capacity and removal efficiencies are obtained with the zeolite's calcination process on 20-30 mesh, due to its large specific surface area and channels that are clean from water vapor because it has passed the calcination process.

Increasing the bed height increases the adsorption capacity of H_2S because it will add resistance to the reactor bed so that there is a long time for H_2S to be adsorbed inside the zeolite channel. According to the case study conducted in Palestine, the higher the bed, the maximum adsorped H_2S in raw biogas [19]. It also applies with a difference in flow rate from biogas, providing a long contact time for adsorbent with biogas. The lower flow rate of raw biogas will give a long contact time, and H_2S can interact with the adsorbent surface to make the attraction more potent [20] [21]. Based on the obtained data, using zeolite with the calcination process for purifying biogas is recommended. These results of the research are seen as very beneficial from an economic point of view because zeolite has lost costs and can be regenerated by calcination to evaporate contaminants in the zeolite channel [22]. However, there will be a decrease in the performance of zeolite.

ACKNOWLEDGMENTS

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REFERENCES

1. S. Liu, G. Yang, J. Fu, and G. Zhang, Environ. Sci. Pollut. Res. **25**, 35154 (2018).
2. C. Polprasert, *Organic Waste Recycling, Water. Intell. Online* (2015).
3. Nicolas Abatzoglou and Steve Bolvin*., A review of biogas purification processes,* (Biofuels, Bioproducts and Biorefining, Canada, 2012), pp. 246–256.
4. F.W. Hutber, Stat. **33**, 1 (1984).
5. S. Rasi, A. Veijanen, and J. Rintala, Energy **32**, 1375 (2007).
6. A. Jaffrin, N. Bentounes, A.M. Joan, and S. Makhlouf, Biosyst. Eng. **86**, 113 (2003).
7. H.C. Shin, J.W. Park, K. Park, and H.C. Song, Environ. Pollut. **119**, 227 (2002).
8. R.J. Spiegel and J.L. Preston, Waste Manag. **23**, 709 (2003).
9. R.J. Spiegel and J.L. Preston, J. Power Sources **86**, 283 (2000).
10. Airgas, *Safety Data Sheet for Hydrogen Sulfide* (an Air Liquide Company, USA, 2017), pp. 1–12.
11. C.-C. Lien, J.-L. Lin, and C.-H. Ting, J. Agric. Chem. Environ. **03**, 1 (2014).
12. N. Abdehagh, M. Taghinejad Namini, S.M. Heydarian, B. Bonakdarpour, and D. Zare, Iran. J. Environ. Heal. Sci. Eng. **8**, 245 (2011).
13. Fredric Bauer, Chritian Hulteberg, Tobias Persson and Daniel Tamm*., Biogas upgrading – Review of commercial technologies* (Swedish Gas Technology Centre (SGC), Swedish, 2013), pp. 230-234.
14. A. Alonso-Vicario, J.R. Ochoa-Gómez, S. Gil-Río, O. Gómez-Jiménez-Aberasturi, C.A. Ramírez-López, J. Torrecilla-Soria, and A. Domínguez, Microporous Mesoporous Mater. **134**, 100 (2010).
15. City, L. and Verduijn, J. P. U.S. Patent No. 6,039,864, (21 March 2000).
16. Z. Bacsik, O. Cheung, P. Vasiliev, and N. Hedin, Appl. Energy **162**, 613 (2016).
17. Tien, C., *INTRODUCTION TO ADSORPTION Basics, Analysis, and Applications*, *Introduction to Adsorption* (Elsevier Ltd, Netherlands, 2019), pp 1-2.
18. M. Abdirakhimov, M.H. Al-Rashed, and J. Wójcik, Energies **15**, (2022).
19. H. Sawalha, M. Maghalseh, J. Qutaina, K. Junaidi, and E.R. Rene, Bioengineered **11**, 607 (2020).
20. G. Molino, M. Gandiglio, S. Fiorilli, A. Lanzini, D. Drago, and D. Papurello, Molecules **27**, (2022).
21. R.A.S. Lestari, W.B. Sediawan, S. Syamsiah, Sarto, and J.A. Teixeira, J. Environ. Chem. Eng. **4**, 2370 (2016).
22. S.K. Wahono, J. Stalin, J. Addai-Mensah, W. Skinner, A. Vinu, and K. Vasilev, Microporous Mesoporous Mater. **294**, 109871 (2020).

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