

Enhancing biomethane quality via the activation of natural zeolite from Lombok Island

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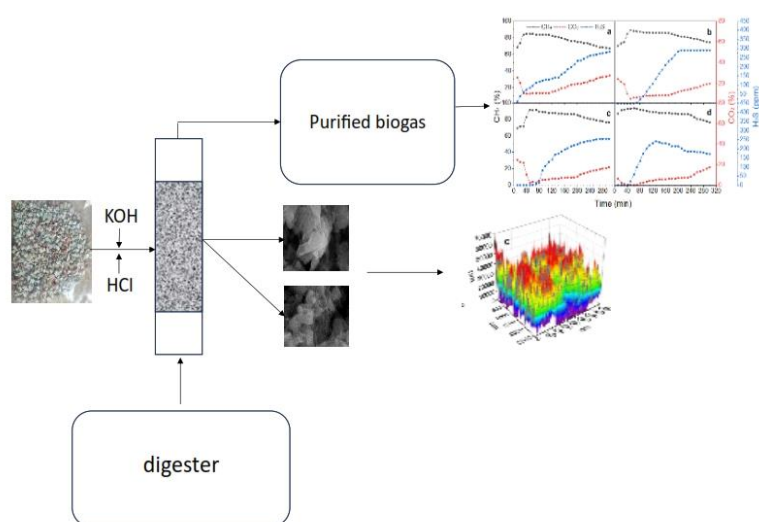
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GRAPHICAL ABSTRACT



ABSTRACT

This study presents the results of the biogas purification test using the fixed-bed column method. As an adsorbent, natural zeolite from the Lombok island Indonesia was used. Zeolite is used for the purpose of purifying biogas produced from the anaerobic digestion (AD) process. To enhance the adsorption capacity, the zeolite underwent activation using distinct strong base and acid solutions—potassium hydroxide (KOH) and hydrochloric acid (HCl)—with concentrations of 10%, 15%, and 20%, individually. The experiment was carried out until the adsorbent reached saturation, at which point the methane (CH₄) concentration began to decline. It was revealed that the typical Lombok zeolite showed good performance in increasing the concentration of CH₄ in biogas. Furthermore, zeolites work better when activated with strong base solutions and at high concentrations. This is

indicated by the achievement of higher CH₄ concentrations and a longer saturation time. The results from analyzing zeolite features and pore characteristics indicate that acidic and base compounds yield distinct outcomes in terms of the surface structure of zeolite pores.

Keywords: biogas purification, Lombok zeolite, KOH, HCl

1. Introduction

In the face of diminishing fossil fuel supplies and volatile prices, biogas has emerged as one of the viable fuel sources. The AD method is used to produce biogas, and it is considered as a simple technological process that has been around for a long time. Furthermore, the raw material for biogas production is readily available and inexpensive, as it can be in the form of food leftovers or even livestock manure. However, biogas produced from the fermentation process is not optimal when used directly for various purposes, especially in the combustion process. This is because biogas contains impurities like CO₂ and H₂S which adversely affect the combustion process. CO₂, a non-combustible gas, can dilute the combustible gases like methane, making combustion less efficient and requiring more energy to burn. On the other hand, H₂S, which is toxic and corrosive, can react with water vapor during combustion to create sulfuric acid, leading to equipment damage, safety hazards and the production of harmful SO₂ air pollutants (Peluso *et al.* 2019, Wang *et al.* 2019). Considering that biogas is currently widely used in various applications such as electricity generation, cooking and heating, transportation and agriculture, it is essential to purify it properly.

Pressure swing adsorption (PSA), cryogenic distillation, membrane separation, chemical or physical absorption, adsorption on a solid object, and water scrubbing are all kinds of purification technologies that are widely used today (Mishra *et al.* 2021, Mulu *et al.* 2021). Moreover, activated charcoal and zeolite are two popular materials utilized in the processes. Both materials are considered to have benefits in terms of highly selective adsorption capability and a huge surface area (Jiang *et al.* 2018).

Moreover, clinoptilolite zeolite is an attractive material to employ in the biogas purification process. This is due to the fact that zeolite is an inexpensive and easily accessible material found

throughout virtually all parts of Indonesia. Given Indonesia's location in the ring of fire, natural zeolites are abundantly available. However, it's important to note that each region has its own distinct characteristics. The varied zeolite compositions in each location are determined by hydrothermal environment parameters such as pressure, temperature, and water content (Li *et al.* 2021).

Zeolites are crystalline microporous aluminosilicates with a framework of SiO_4 and AlO_4 tetrahedra connected in varied regular patterns by oxygen atom sharing. This creates porous structures with crossing channels including cages that are populated by extra-framework, loosely bound, alkaline, or alkaline earth cations, which balance the negative surface charge of the AlO_4 tetrahedra. These materials' broad inner surfaces and resultant adsorption capabilities, together with cation exchange and molecular sieving capabilities, provide them with unique and important applications in a wide range of industrial processes (Wang *et al.* 2019).

Natural zeolite has been extensively used in the adsorption process, and it has been demonstrated that natural zeolite has such a long saturation period and a high adsorption ability (Elboughdiri 2020). The findings of the study into the usage of natural zeolite show that it is an excellent material for increasing biogas quality. The ability of natural zeolite to separate CH_4 from CO_2 and H_2S was found to be twice as good as that of synthetic zeolite in adsorption process. Natural zeolite can also be regenerated and is stable through multiple adsorption cycles. In addition, the low price and abundant availability also encourage the widespread use of natural zeolite (Alonso-Vicario *et al.* 2010).

To enhance its adsorption capacity, natural zeolite requires prior activation. Depending on the targeted substance for adsorption, natural zeolite can be activated using acidic or basic compounds (Ba Mohammed *et al.* 2019). Activation processes using acidic and alkaline solutions are both useful for cleaning zeolite from contaminants and impurities that may interfere with its adsorption ability. Activating zeolite with these chemical compounds also promotes increased chemical

interactions and reactions between zeolite and compounds in biogas, thereby strengthening zeolite's ability to trap unwanted compounds in biogas (Verboekend *et al.* 2013).

Furthermore, activating zeolite using an acidic solution such as HCl will increase the surface area of zeolite and simultaneously create more active sites, making it more effective in absorbing unwanted compounds in biogas (Ifa *et al.* 2022). Similarly, when zeolite is activated with a basic compound such as KOH, it will enhance zeolite's ability to neutralize acidic compounds in biogas such as CO₂ and H₂S. In addition, basic activators can create more active adsorption sites and alter the pore structure of zeolite, thus increasing the pore capacity, which in turn enhances zeolite's ability to trap unwanted compounds (Yuan *et al.* 2022). As a result, it is expected that the concentrations of these two compounds will decrease. However, the effectiveness of natural zeolite or adsorption is hindered by its undefined chemical composition. This composition varies among natural zeolites, primarily due to differences in their origin regions (Davaranah *et al.* 2020).

Zeolites have been investigated as biogas purification adsorbents in order to achieve pure methane. Many studies have looked into the efficacy of zeolites like 13X, 5A, and clinoptilolite in removing impurities from biogas, resulting in methane purities of up to 99%. A recent pilot-scale investigation discovered that a zeolite-based adsorbent reached above 98% methane purity (Pang *et al.* 2020). The research aims to understand more about the potential of natural zeolite (clinoptilolite) to adsorb undesirable compounds from biogas. So far, no research has been performed to evaluate the characteristics of natural zeolite from Lombok in terms of its potential to adsorb undesirable chemicals in biogas. This study was considered relevant because the island of Lombok is one of Indonesia's most important cattle-producing areas. Due to the quantity of raw materials, developing biogas with a large number of cows has outstanding potential. Several tests will be conducted to achieve the goal of varying the quantities of acid and base solutions in the natural zeolite activation process. Changes in the surface morphology of the zeolite following activation with various acid and base compounds are also observed. The results are intended to understand of the role of acid and base solutions on the changes experienced by natural zeolite, allowing for the identification of

the optimal solution and concentration for getting maximum biomethane concentration. Furthermore, the simplicity of the adsorption method, combined with its ability to yield optimal results, makes it a viable option for numerous breeders in Indonesia, thus justifying its selection over the other biogas purification techniques mentioned earlier.

2. Materials and methods

2.1. Materials

The natural zeolite utilized originates from Lombok Island, Indonesia. The zeolite was crushed to the required size, and then, through the use of a test sieve, the desired size was achieved. The zeolite employed in this investigation has a mesh size of 10.

2.2. Activation Process

Two different chemicals, KOH and HCl, were utilized to activate the zeolite. The focus of the research would be how acid and base compounds impregnated in the zeolite activation process affected the ability to adsorb CO₂ and H₂S in biogas. Zeolite was immersed in a solution of KOH and HCl separately with an impregnation ratio of 1:2. The KOH and HCl concentrations used were 10, 15, and 20%, respectively. Moreover, each soaking process is conducted over multiple hours to ensure thorough mixing and uniform distribution of the solution on the zeolite. Following filtration and cleansing with demineralized water until the pH reached neutrality, any residual contaminants, acid, and alkaline solutions were eliminated from the zeolite. To ensure complete dehydration, the zeolite was dried in a desiccator. Subsequently, physical activation of the zeolite was achieved by heating it for three hours at 300°C in a furnace.

2.3. Biogas Production

For biogas production, cow manure from smallholder farms is introduced into a dedicated research digester with a 3 m³ capacity. To expedite the biogas generation process, 200 ml of effective microorganism (EM-4) was added to the digester (Tira *et al.* 2019). With the aid of EM-4, biogas can be produced in as little as three days after the start of the anaerobic process. The digester is supplied with a 1:1 ratio of water to cow dung, and the resulting biogas is stored in a biogas

storage unit until needed. A manometer is installed in the line between the digester and the biogas storage unit to monitor the production of biogas, and the storage unit has the capacity to hold up to 4 m³ of biogas. Drain valves are installed in the channel to ensure that the biogas reservoir is always full. Additionally, another biogas storage unit is prepared to hold the purified biogas. The research plan is depicted in Figure 1.

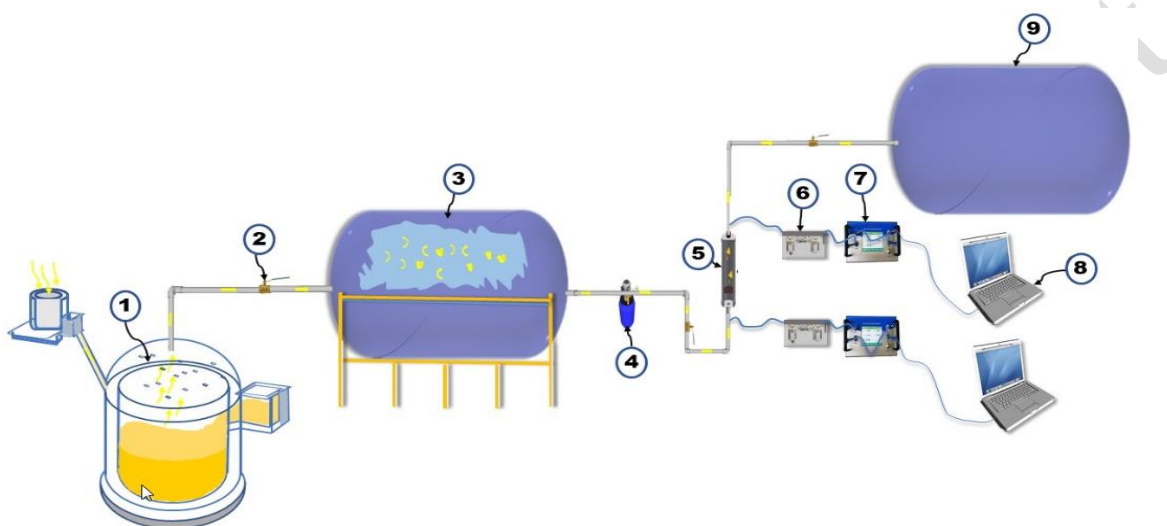


Figure 1. Schematic diagram of experimental setup. 1-digester; 2-ball valve; 3-biogas reservoir; 4-vacuum pump; 5-fixed bed column; 6-pre-treatment device; 7-portable biogas analyzer; 8-laptop; 9-purified biogas reservoir

2.4. Biogas Purification Process

The activated zeolite was placed in a fixed-bed column before beginning the purification process. 200 grams of activated zeolite were placed in an adsorption column with a diameter to height ratio of 1:16. The first test was performed on KOH-activated zeolite, followed by an HCl-activated zeolite test. The two are then compared, and the results are discussed in the next section.

A vacuum pump is used to deliver the biogas to the fixed-bed column, ensuring that the biogas flows smoothly and at a constant rate. A ball flowmeter dedicated to biogas was used to measure the biogas flow rate of 1 L/min. A portable infrared biogas analyzer TY-6300P was used to measure the concentrations of CH₄, CO₂, and H₂S. The technical parameters of the equipment are showed in Table 1.

Table 1. Technical parameters of the biogas analyzer

Technical parameters	CH ₄	CO ₂	H ₂ S
Measurement indicators	0-100%	0-50%	0-9999 ppm
Resolution	0.01%	0.01%	1 ppm
Measurement accuracy	±2% FS	±2% FS	±3% FS
Repeatability error		≤1% FS	
Stability	Zero drift ≤1%FS/7d	Range drift ≤1%FS/7d	
Intake air flow		0.7~1. L/min	
Intake pressure		0~150 kPa	

In order to ensure the accuracy of the measurements, two trapping units were employed to eliminate any micro-particles or dirt that may have been present in the biogas. Data collection was performed continuously throughout each 5-hour test at 10-minute intervals.

The initial measurement of biogas composition was performed on fermented biogas, yielding concentrations of 61.54% CH₄, 33.32% CO₂, and 290 ppm H₂S. Subsequent testing was then conducted on both activated and unactivated zeolite samples to evaluate their suitability for biogas upgrading. The tests were repeated three times to ensure accuracy. Prior to testing each activated zeolite sample, the fixed-bed column was thoroughly cleaned to eliminate any remaining particles or adsorbents. Throughout the test, the pressure within the fixed-bed column was maintained at the ambient pressure, and the biogas that passed through the adsorbent was collected and stored in a prepared biogas container.

Following the completion of biogas concentration data collection, a small sample of zeolite was extracted for SEM and EDX testing. This experiment was conducted to gain further insight into the adsorption mechanism involved in biogas purification.

3. Results and Discussion

Improving the CH₄ concentration begins with the purification of biogas using an unactivated zeolite. This phase was conducted to confirm if the scrubbing operation with activated zeolite resulted in a difference in CH₄ concentration. The observations obtained are an increase in the concentration of biomethane compared to that produced by fermentation alone. The increase in the

biomethane concentration was caused by the trapping of CO₂ and H₂S in the zeolite pores, thereby increasing the percentage of CH₄.

The result shows that the level of concentration obtained is not considerable. Likewise, the duration to maintain the CH₄ value at the maximum number is not too long. According to the results, the concentration of CH₄ reduced after the 40th minute (Figure 2a). This indicates that the zeolite has reached its tolerance limit for CO₂ and H₂S molecules. This is most likely due to impurity cations and some water vapour is still trapped in the pores of the unactivated zeolite. In order to improve the results achieved, biogas was passed through the activated zeolite with two different types of chemicals, namely base compounds, KOH, and acidic compounds, HCl.

3.1. Biogas Purification using KOH-activated zeolite

There was a noticeable difference when biogas was purified utilizing a KOH-activated zeolite adsorption approach. As shown in Figure 2b, c, and d, respectively, the concentration of CH₄ increased sharply, whereas CO₂ and H₂S levels declined significantly. At the KOH concentration utilized, all variables evaluated showed an increase in CH₄ and a decrease in CO₂ and H₂S. Similarly, activated zeolite can maintain this rising trend for an extended period. Under the unactivated zeolite, the relatively high concentration of CH₄ can only be maintained for about 1 hour during the purification process, whereas with activated zeolite, the duration is at least doubled. Moreover, at operating conditions containing 20% KOH, high CH₄ concentrations can be sustained for an extended period.

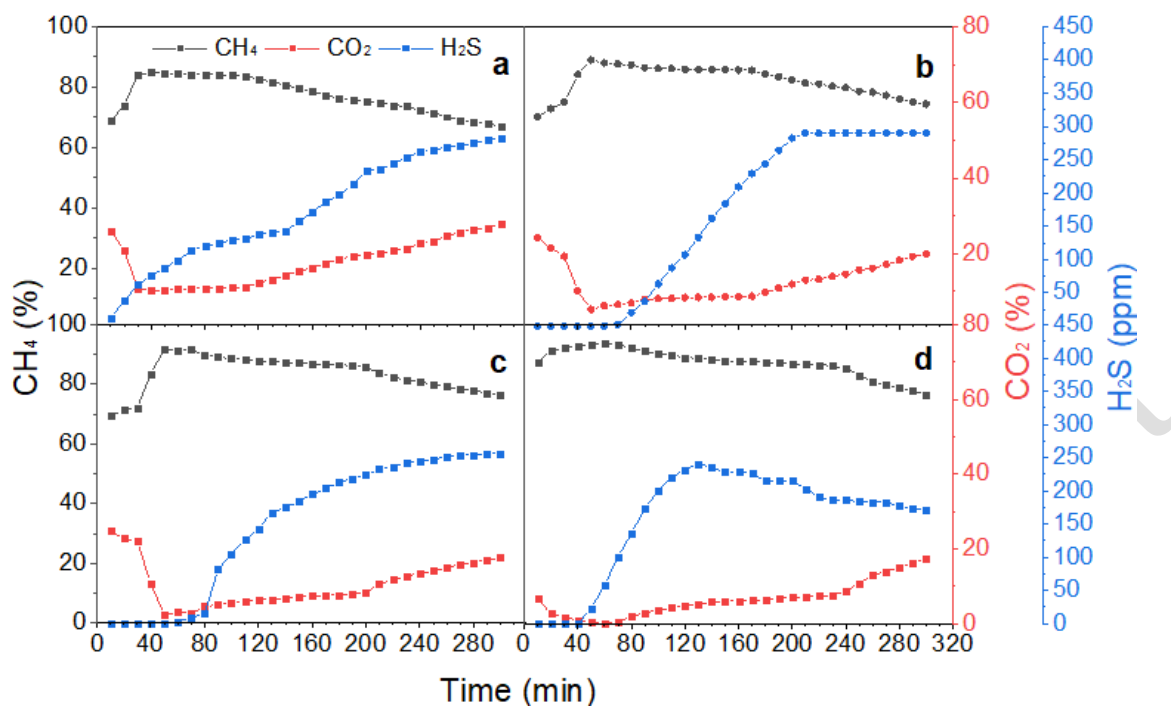


Figure 2. Concentration of biogas components under; a. unactivated zeolite; b. 10% KOH-activated zeolite; c. 15% KOH-activated zeolite; d. 20% KOH-activated zeolite

CO₂ levels increased for several hours after the purification process was started on treatment with activated zeolite, but at a lower rate than purification with unactivated zeolite. Even the value becomes much lower when the purification process is carried out with 20% KOH. Similarly, the concentration of H₂S can be reduced in the early minutes, while it slightly increases a few moments later. As shown in Figure 3, the results reveal that activating the zeolite with 20% KOH produced the most remarkable results.

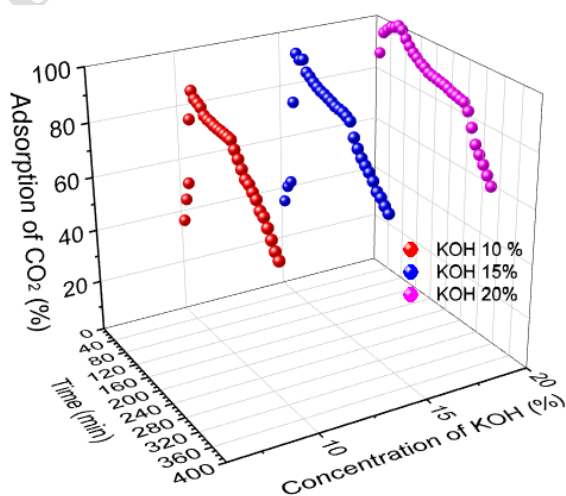


Figure 3. Adsorption of CO₂ with 10, 15, and 20% KOH-activated zeolite

Physical activation of zeolite by heating impacts opening the pores of the zeolite molecular size. The more open and widening the pores will make it easier for CO₂ and H₂S to be trapped. Furthermore, after 3 hours of heating, many impurity compounds initially present in the zeolite were released and separated from the pore structure of the zeolite. In addition, heating natural zeolite to 300°C causes the water in the pores to evaporate, separating molecules based on molecular size and increasing the adsorption ability of zeolite (Sujan *et al.* 2018).

On the other hand, chemical activation with KOH plays a role in rearranging the atoms in the zeolite. It reduces the silica content and impurity cations in the zeolite by causing desilication and de-ionization of zeolite, which increases the surface area of the zeolite (Meng *et al.* 2018). The reduced silica content due to the reaction between base compounds (KOH) and silica forms silicate compounds, causing a decrease in silica content (4⁺) which is then replaced by alumina compounds (3⁺). This impacts on the zeolite surface, which becomes more negative (Wang *et al.* 2012). The more negative the zeolite leads to the adsorption of the more significant CO₂ and H₂S molecules (Verdoliva *et al.* 2019).

The CO₂ gas adsorption rate measures the adsorbent's ability to absorb CO₂ gas in biogas. Adsorption ability is the relationship between the efficacy of CO₂ gas adsorption by the adsorbent and the desired goals. In this case, the expected CO₂ adsorption rate is 100 percent. The following formula can be used to quantify the number of CO₂ absorbed (Pirola *et al.* 2015):

$$Adsorption = \frac{(y_1 - y_2)}{y_1} \times 100\% \quad (1)$$

Where:

Y₁ = CO₂/CH₄ molarity ratio before purification

Y₂ = CO₂/CH₄ molarity ratio after purification

As demonstrated in Figure 3, the best results were obtained in biogas purification with a 20% KOH-activated zeolite. This was confirmed by observing the weakening of the adsorption ability of 10 and 15% KOH-activated zeolite. The trend shows a steep pattern compared to 20% KOH. CO₂

adsorption in biogas using natural zeolite is caused by the polarity of CO₂ molecules, where the O₂ atom has a negative charge, which enables it to transfer electrons to positively charged cations on the surface of the zeolite, such as Li⁺, Na⁺, K⁺, Ca²⁺, Sr²⁺, Ba²⁺, Cu²⁺, Zn²⁺, and Mg²⁺ (Barelli *et al.* 2018). Similarly, activation with KOH causes the concentration of impurity cations to decrease, which are subsequently replaced by K⁺ cations, increasing the quantity of K⁺ cations in the zeolite. This occurs because there is a cation exchange between the zeolite and the activator solution during base compound activation (Khalilzadeh *et al.* 2019). By replacing particular cations in the zeolite with K⁺ cations, the zeolite will become a homoionic compound with uniform pore size, and its ability and selectivity will be improved (Kumar *et al.* 2020). According to the results, the higher the KOH concentration, the more K⁺ cations are exchanged with impurity compounds in the zeolite. As the K⁺ cations in the zeolite increase, the ability to absorb CO₂ will improve.

As illustrated in Figure 3, activation with a strong base (KOH) causes the silica group to be eliminated, leaving the zeolite more hydrophilic and increasing the affinity of polar molecules (Susanti and Widiastuti 2019). This encourages the ability to adsorb H₂S will be better because H₂S is a polar compound. Thus, the higher the KOH concentration in the zeolite activation process, the better the zeolite's ability to absorb H₂S. Therefore, the recorded concentration decreases further after passing through the adsorbent. Even though all of the different KOH concentration variables revealed an increase in H₂S, particularly after the 40th minute, the H₂S increased by 20%, and KOH proved to be more moderate than the other two concentrations.

3.2. *Biogas purification using HCl-activated zeolite*

Activated natural zeolite with HCl also increased CH₄ concentration while simultaneously lowering CO₂ and H₂S levels, as depicted in Figure 4. The ability to adsorb CO₂ and H₂S improves after activating the zeolite with a higher concentration of HCl. This study found that activation with 20% HCl gave the best results compared to the other two variations. As can be seen, the CH₄ concentration could be maintained at least until the 220th minute. Similarly, the CO₂ concentration can be kept low until the 220th minute, which is longer and lower than other variations.

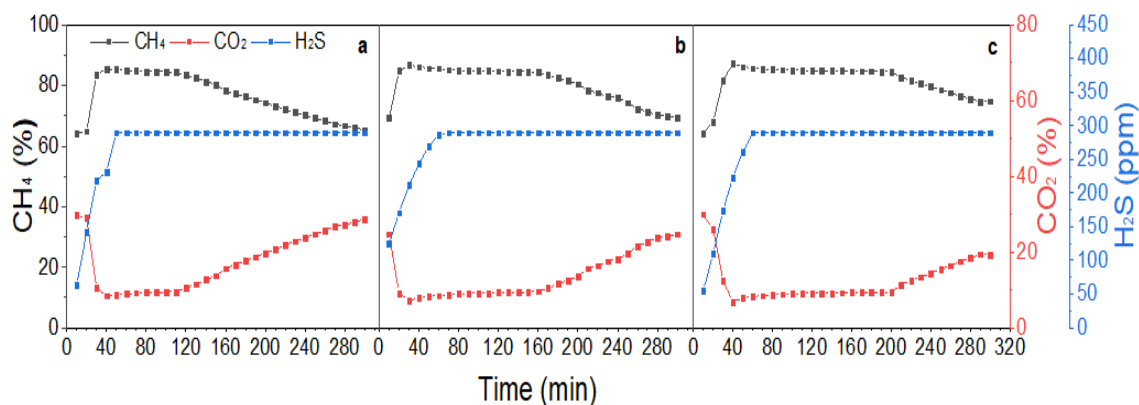


Figure 4. Concentration of biogas components under; a. 10% HCl-activated zeolite; b. 15% HCl-activated zeolite; c. 20% HCl-activated zeolite

The adsorbent performance began to deteriorate after the 220th minute. The drop in CH₄ levels observed following purification reached its highest point due to the formation of a film layer on the zeolite's surface, which led the zeolite to become saturated and its adsorption ability to decline gradually.

Figure 5 shows that the ability to adsorb CO₂ from natural zeolite activated by HCl at 10, 15, and 20% can only reduce CO₂ levels by a small amount at the initial stage before steadily increasing again. After attaining the maximum level of adsorption, the ability to adsorb decreases. From all variations, 20% HCl-activated zeolite performs the best.

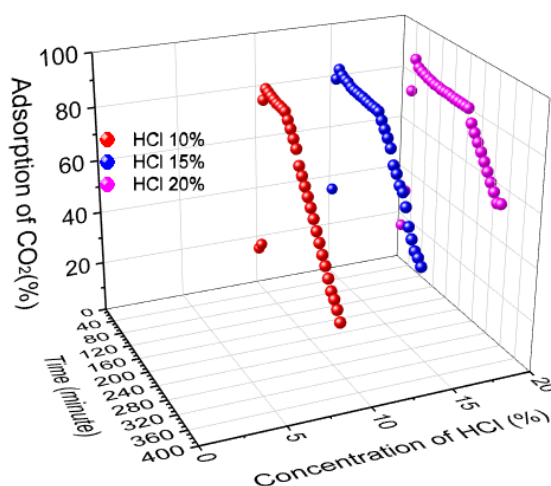


Figure 5. Adsorption of CO₂ with 10, 15, and 20% HCl-activated zeolite

Natural zeolite's adsorption capability was improved by physical and chemical activation.

Physical activation at 300°C for 3 hours causes the zeolite to lose water, segregate molecules of

substances based on molecular size, and increase pore surface area. On the other hand, chemical activation with HCl results in removing the Al group in the zeolite framework. This occurs because the H^+ ion that comes from the decomposition of HCl in the water medium will be attacked by oxygen atoms bonded to Si and Al. Furthermore, the bond dissociation energy of Al-O is lower than that of Si-O, which is 116 kcal/mol and 190 kcal/mol, respectively (Park *et al.* 2019). As a result, the Al-O bond will break down more easily, forming silanol molecules.

Cl^- , which has a strong electronegativity, will be more likely to attach to Al, which has a high valence and lower electronegativity than Si (Sharma *et al.* 2020). Reduced Al content in zeolites makes them more hydrophobic, which means they have a lower affinity for polar molecules like H_2S . HCl activation, which extends the pore surface of the zeolite, affects the fall of mineral salts such as Ca^{2+} , K^+ , Mg^{2+} , and Na^+ (Muscarella *et al.* 2021). Compared to the unactivated natural zeolite, the increased surface area of the pores enhanced natural zeolite's ability to adsorb CO_2 . However, compared to KOH-activated natural zeolite, the results obtained are still lower. This is possible due to the loss of mineral salts, which causes the surface of the zeolite to become less negatively charged, thereby reducing the ability to absorb CO_2 (Mirzokhid *et al.* 2022).

3.3. Molarity ratio

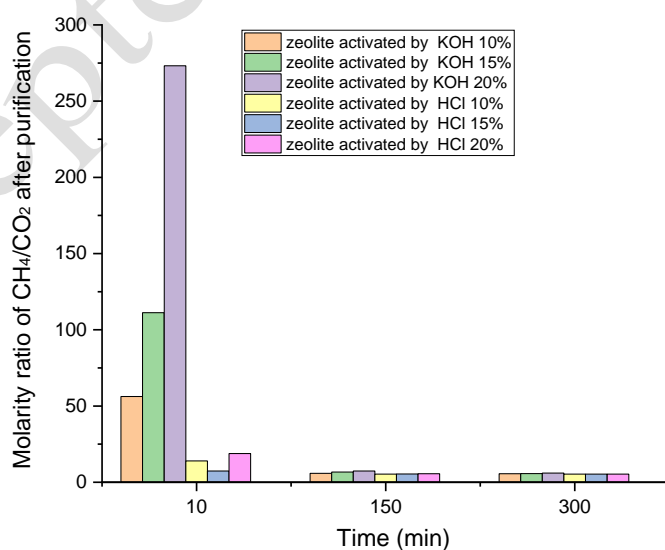


Figure 6. Molarity ratio of CH_4/CO_2 after purification

Figure 6 shows the molarity ratio of CH_4/CO_2 in biogas after purification. The molarity ratio is essential for obtaining a more complete and clearer picture of the effectiveness of zeolite adsorption on unwanted substances in biogas. The graph shows that purification using zeolite activated with 20% KOH had the highest CH_4/CO_2 molarity ratio compared to the other variations. The higher the concentration of the alkaline activator, the more effective the adsorption process. This study shows that the alkaline activator is far more effective at adsorbing CO_2 than CH_4 , as it outperforms acidic activators. This could be because the alkaline solution interacts more strongly with CO_2 , making it easier to adsorb than CH_4 . Activation with alkaline solutions improves bonding strength and provides adsorption sites which are better suited for CO_2 than CH_4 . The chemical environment created by the alkaline solution might influence the interaction of the adsorbent and gases in biogas, affecting the adsorption selectivity for CO_2 and CH_4 (Derbe *et al.* 2021). However, the advantage of the alkaline solution only lasts for the initial minutes. Its efficacy will gradually decline, similar to that of acidic solutions.

3.4. The test results of SEM and EDX

Several samples were taken to carry out the zeolite analysis using SEM and EDX. The samples were unactivated natural zeolite, 20% KOH-activated natural zeolite, and 20% HCl-activated natural zeolite. The results of the SEM and EDX tests can be seen in Figure 7.

Figure 7a shows the results of analyzing unactivated natural zeolite. It suggests that the morphological surface of natural zeolite has many contaminants sticking to it. This substantially impacts the zeolite's capacity to adsorb CO_2 and H_2S molecules, resulting in the pores becoming blocked and the zeolite's affinity decreasing. Furthermore, the ratio of Si/Al zeolite, where the natural zeolite employed has a Si/Al ratio of 5, as shown in Table 2, has an ineffective impact on the ability to separate CH_4 from impurities compounds in biogas.

Furthermore, the morphological structure of the zeolite shows significant alterations in crystal shape and size when compared to the unactivated surface, as illustrated in Figure 7b. The activated zeolite's pores appear cleaner and have a larger surface area, with the formation of smaller, more

numerous pores, and a more regular crystal distribution. These alterations are likely due to the effect of alkaline compounds, which induce a more homogeneous and controlled reaction during activation (Biel *et al.* 2020). Consequently, the activated zeolite develops a stronger and more stable surface structure, impacting its adsorption selectivity towards specific molecules, particularly CO₂ and H₂S. This transformation is a result of the activation process, particularly chemical activation, which eliminates contaminant cations in the zeolite by restructuring its atoms (Khan *et al.* 2019). The EDX result in Figure 7b and Table 3 shows that the zeolite compound's composition changes as the Si/Al ratio decreases from 5 to 4. In this case, activation with KOH causes the zeolite's silica concentration to decrease. As the Si/Al ratio decreases, the zeolite becomes more hydrophilic, the attraction to polar molecules increases and cation exchange becomes easier (Bacariza *et al.* 2018). After activation with KOH, the accumulation of cations such as Na⁺, Mg²⁺, Ca²⁺, Fe²⁺, and K⁺ was observed. This occurs due to cation exchange between the KOH solution and the zeolite. As these cations accumulate, the adsorption ability improves as the zeolite surface becomes more negatively charged. It was also revealed that the ability to adsorb H₂S compounds improved as the FeO level of the zeolite rose. This occurs when FeO compounds react with H₂S to form FeS and H₂O, which reduces H₂S levels in biogas.

The surface morphology of 20% HCl-activated natural zeolite is shown in Figure 7c. It can be seen that the pores of the zeolite are cleaner when compared to the unactivated natural zeolite. This is because chemical activation with HCl can remove mineral salts, allowing the zeolite's surface to become wider (Wang *et al.* 2019). Furthermore, the pore or crack structure formed appears larger compared to the base compound activator. This occurs because acidic compounds like HCl erode the zeolite structure and create empty spaces by damaging metal cation bonds (Zhang *et al.* 2020). The larger pore structure leads to higher adsorption of non-polar compounds. However, due to the corrosive and strong acidic influence of substances like HCl, the stability of zeolite can be compromised, affecting its long-term durability and capabilities.

In addition, the results of the EDX test (Table 4) demonstrate that the concentrations of Na⁺, Mg²⁺, Ca²⁺, and K⁺ cations have significantly decreased. The concentration of Na⁺, Mg²⁺, Ca²⁺, and K⁺, Fe²⁺ drops when the concentration of HCl increases.

Table 2. Elements and compound compositions of unactivated zeolite

Element	Mass%	Mol%	Compound	Mass%
C	11.19	40.34	C	11.19
O	43.56			
Na	1.21	1.14	Na ₂ O	1.63
Mg	0.32	0.56	MgO	0.52
Al	6.72	5.39	Al ₂ O ₃	12.69
Si	30.76	47.41	SiO ₂	65.81
K	1.41	0.78	K ₂ O	1.69
Ca	2.05	2.22	CaO	2.87
Fe	2.79	2.16	FeO	3.58
Total	100.00	100.00		100.00

Table 3. Elements and compound compositions of 20% KOH-activated zeolite

Element	Mass%	Mol%	Compound	Mass%
C	14.98	49.37	C	14.98
O	38.17			
Na	0.48	0.41	Na ₂ O	0.64
Mg	0.51	0.83	MgO	0.84
Al	6.13	4.50	Al ₂ O ₃	11.58
Si	24.72	34.85	SiO ₂	52.88
K	7.43	3.76	K ₂ O	8.95
Ca	3.20	3.16	CaO	4.48
Fe	4.39	3.11	FeO	5.64
Total	100.00	100.00		100.00

Table 4. Elements and compound compositions of 20% HCl-activated zeolite

Element	Mass%	Mol%	Compound	Mass%
C	15.53	49.68	C	15.53
O	41.80			
Na	0.73	0.61	Na ₂ O	0.99
Mg	0.26	0.41	MgO	0.43
Al	6.71	4.78	Al ₂ O ₃	12.69
Si	29.89	40.91	SiO ₂	63.95
Cl	0.35	0.38	Cl	0.35
K	1.53	0.75	K ₂ O	1.84
Ca	1.02	0.98	CaO	1.43
Fe	2.17	1.49	FeO	2.79
Total	100.00	100.00		100.00

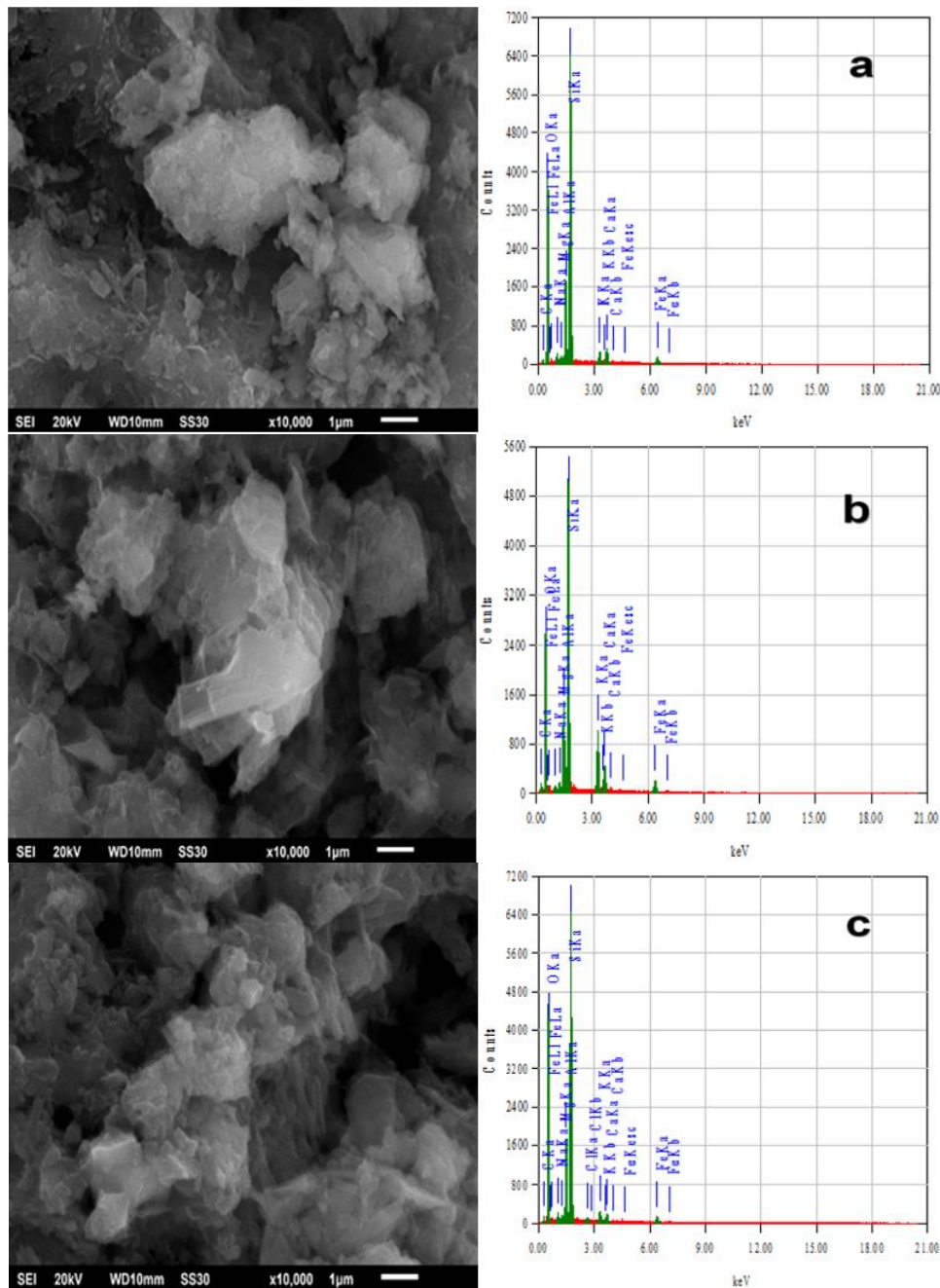


Figure 7. SEM images and EDX result of a unactivated zeolite; b 20% KOH-activated zeolite; c 20% HCl-activated zeolite

3.5. Distribution of pore diameter and porosity of zeolite

From Figure 8, it is apparent that the particle pore diameters vary among samples. In the 20% KOH-activated zeolite, smaller pores dominate, while in the 20% HCl-activated zeolite, pore sizes are more uniform, ranging between 0.5-1.5 μm . Unactivated zeolite exhibits an even distribution of large and small pore sizes, although the latter are slightly dominant. The uniformity in pore size of the 20% HCl-activated zeolite is attributed to the detachment of mineral salts such as Fe^{3+} , Mg^{2+} ,

and Ca^{2+} from the zeolite surface during activation, causing the pores to open (Muscarella *et al.* 2021). These results indicate that activation increases the volume of open pores in the adsorbent, resulting in a significant increase in surface area, which effectively binds impurities in biogas.

The pore size and its distribution in activated zeolite significantly affect its ability to absorb CO_2 , H_2S or CH_4 in biogas. Smaller pore sizes are better suited for adsorbing small molecules like CO_2 and H_2S due to the stronger interactions between gas molecules and zeolite surface in confined spaces. Smaller pores provide more sites for adsorption, resulting in higher adsorption capacity. On the other hand, the larger pore sizes are more effective for adsorbing larger molecules like CH_4 as they provide more accessible sites and better diffusion pathways for gas molecules to reach adsorption sites, leading to faster adsorption kinetics. However, this study showed that 20% KOH-activated zeolite performed better adsorption capacity, suggesting that the adsorption process is not only influenced by pore size but also by surface site conditions of zeolite due to different compound activation. Moreover, uniform distribution of micropores and mesopores provides better adsorption results than pores dominated by only micropores.

Figure 9 shows the three-dimensional surface of the adsorbent. The image was then analyzed to get the percentage of pore volume owned for each variation. It can be seen that the zeolite activated using 20% HCl had the most significant percentage of porosity compared to 20% KOH-activated zeolite and unactivated zeolite, namely 74%, 71% and 68%, respectively. However, when observing the adsorption ability of zeolite, 20% KOH-activated zeolite has a better adsorption ability than 20% HCl-activated zeolite. Pore depth is an important factor that affects adsorption capacity in addition to porosity. It determines the length of channels or cavities in zeolite structures, and its impact on gas adsorption capacity is complex, influenced by various factors such as gas molecule size, shape, interactions with the zeolite surface temperature, and pressure. Activated zeolites with KOH and HCl have larger pore depths compared to unactivated zeolite, providing more surface area for gas adsorption, but it may also affect gas molecule accessibility to the zeolite surface. In this study, the 20% KOH-activated zeolite showed the best adsorption performance.

Therefore, pore depth is a crucial factor in designing and optimizing activated zeolites for gas adsorption.

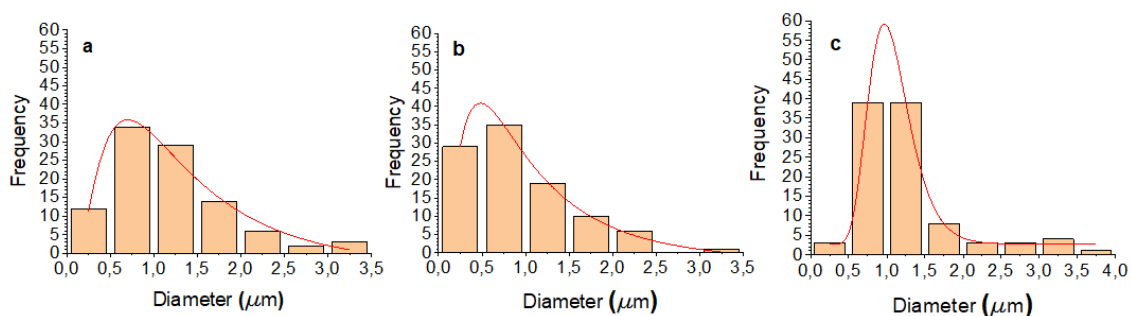


Figure 8. Pores diameter distribution of a unactivated natural zeolite; b 20% KOH-activated zeolite; c 20% HCl-activated zeolite

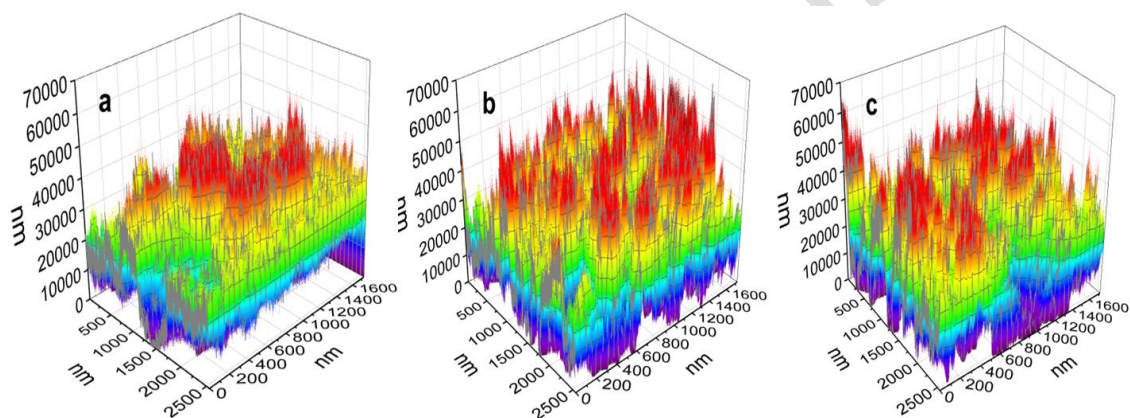


Figure 9. 3D surface morphology of a. unactivated natural zeolite; b. 20% KOH-activated zeolite; c. 20% HCl-activated

4. Conclusion

The chemical compounds used in the activation process impact the adsorption properties of natural zeolite obtained on the island of Lombok. Furthermore, heating zeolite to 300°C significantly improves CO₂ and H₂S adsorption. The zeolite's ability to adsorb CO₂ increased by 80% after chemically and physically activated. Biogas quality can also be improved simultaneously, as indicated by CH₄ concentrations exceeding 99%. The higher the concentration of alkaline solution employed in the impregnation method, the better the CH₄ yield. The highest achievement was attained by zeolite, which was activated by base compounds (KOH). Meanwhile, using acidic

compounds, it was only able to increase CH₄ concentrations by 37.1%, compared to 56.4% using alkaline compounds. The surface morphology test revealed that the KOH and HCl solutions had the same impact in triggering a cleaner surface and greater pore size than when not activated. However, adding an alkaline solution to the zeolite results in more cations, which is inversely proportionate to adding an acid solution, which results in a reduction of cations. As cation concentrations in the zeolite are increased, the capacity to attract CO₂ and H₂S improve.

Acknowledgements

The authors thank the University of Mataram for providing grants for this research through the PNBP (non-tax revenue) research grant scheme 2022.

References

- Alonso-Vicario A., Ochoa-Gómez J.R., Gil-Río S., Gómez-Jiménez-Aberasturi O., Ramírez-López C.A., Torrecilla-Soria J. and Domínguez A. (2010). Purification and upgrading of biogas by pressure swing adsorption on synthetic and natural zeolites. *Microporous and Mesoporous Materials*, **134**, 100–107.
- Ba Mohammed B., Yamni K., Tijani N., Alrashdi A.A., Zouihri H., Dehmani Y., Chung I.M., Kim S.H. and Lgaz H. (2019). Adsorptive removal of phenol using faujasite-type Y zeolite: Adsorption isotherms, kinetics and grand canonical Monte Carlo simulation studies. *Journal of Molecular Liquids*, **296**, 111997.
- Bacariza M.C., Graça I., Lopes J.M. and Henriques C. (2018). Enhanced activity of CO₂ hydrogenation to CH₄ over Ni based zeolites through the optimization of the Si/Al ratio. *Microporous and Mesoporous Materials*, **267**, 9–19.
- Barelli L., Bidini G., Micoli L., Sisani E. and Turco M. (2018). 13X Ex-Cu zeolite performance characterization towards H₂S removal for biogas use in molten carbonate fuel cells. *Energy*,

160, 44–53.

- Biel O., Ro`zek P., Florek P., Mozgawa W. and Król M. (2020). Alkaline activation of kaolin group minerals. *Crystals*, **10**(268), 1-10.
- Davarpanah E., Armandi M., Hern S., Fino D., Arletti R. and Bensaid S. (2020). CO₂ capture on natural zeolite clinoptilolite: Effect of temperature and role of the adsorption sites. *Journal of Environmental Management*, **275**, 111229.
- Derbe T., Temesgen S. and Bitew M. (2021). A short review on synthesis, characterization, and applications of zeolites. *Advances in Materials Science and Engineering*, **2021**, 1-17.
- Elboughdiri N. (2020). The use of natural zeolite to remove heavy metals Cu (II), Pb (II) and Cd (II), from industrial wastewater. *Cogent Engineering*, **7**, 1782623.
- Ifa L., Syarif T., Sartia S., Juliani J., Nurdjannah N. and Kusuma H.S. (2022). Techno-economics of coconut coir bioadsorbent utilization on free fatty acid level reduction in crude palm oil. *Heliyon*, **8**, e09146.
- Jiang Y., Ling J., Xiao P., He Y., Zhao Q., Chu Z., Liu Y., Li Z. and Webley P.A. (2018). Simultaneous biogas purification and CO₂ capture by vacuum swing adsorption using zeolite NaUSY. *Chemical Engineering Journal*, **334**, 2593–2602.
- Khalilzadeh M.A., Sadeghifar H. and Venditti R. (2019). Natural clinoptilolite/koh: an efficient heterogeneous catalyst for carboxymethylation of hemicellulose. *Industrial and Engineering Chemistry Research*, **58**, 11680–11688.
- Khan W., Jia X., Wu Z. and Choi J. (2019). Incorporating hierarchy into conventional zeolites for catalytic biomass conversions : A review. *Catalysts*, **9**, 127.
- Kumar S., Srivastava R. and Koh J. (2020). Utilization of zeolites as CO₂ capturing agents: Advances and future perspectives. *Journal of CO2 Utilization*, **41**, 101251.
- Li Y., Xia G., Wu Q., Chen W., Lin W., Zhang Z., Chen Y., Chen T., Siddique K.H.M. and Chi D. (2021). Zeolite increases grain yield and potassium balance in paddy fields. *Geoderma*, **405**, 115397.

- Meng Y., Zhao B., Zhang H., Liu X. and Cao J. (2018). Synthesis of zeolite W from potassic rocks activated by KOH sub-molten salt method. *Crystal Research & Technology*, **1700216**, 1–10.
- Mirzokhid A., Mohsen H.A. and Janusz W. (2022). Recent attempts on the removal of H₂S from various gas mixtures using zeolites and waste-based adsorbents. *Energies*, **15**, 5391.
- Mishra A., Kumar M., Bolan N.S., Kapley A., Kumar R. and Singh L. (2021). Multidimensional approaches of biogas production and up-gradation: opportunities and challenges. *Bioresource Technology*, **338**, 125514.
- Mulu E., M'Arimi M.M. and Ramkat R.C. (2021). A review of recent developments in application of low cost natural materials in purification and upgrade of biogas. *Renewable and Sustainable Energy Reviews*, **145**, 111081.
- Muscarella S.M., Badalucco L., Cano B., Laudicina V.A. and Mannina G. (2021). Ammonium adsorption, desorption and recovery by acid and alkaline treated zeolite. *Bioresource Technology*, **341**, 125812.
- Pang T., Yang X., Yuan C., Elzatahry A.A., Alghamdi A., He X., Cheng X. and Deng Y. (2019). Recent advance in synthesis and application of heteroatom zeolites. *Chinese Chemical Letters*, **32**, 328-338.
- Park H., Terhorst S.K., Bera R.K. and Ryoo R. (2019). Template dissolution with NaOH–HCl in synthesis of zeolite-templated carbons: effects on oxygen functionalization and electrical energy storage characteristics. *Carbon*, **155**, 570–579.
- Peluso A., Gargiulo N., Aprea P., Pepe F. and Caputo D. (2019). Nanoporous Materials as H₂S adsorbents for biogas purification: a review. *Separation and Purification Reviews*, **48**, 78–89.
- Pirola C., Galli F., Bianchi C.L. and Manenti F. (2015). Biogas to biomethane upgrading by water absorption column at low pressure and temperature. *Technology*, **03**, 99–103.
- Sharma R., Segato T., Delplancke M., Terryn H. and Baron G.V. (2020). Hydrogen chloride removal from hydrogen gas by adsorption on hydrated ion-exchanged zeolites. *Chemical Engineering Journal*, **381**, 122512.

- Sujan A.R., Koh D.Y., Zhu G., Babu V.P., Stephenson N., Rosinski A., Du H., Luo Y., Koros W.J. and Lively R.P. (2018). High-temperature activation of zeolite-loaded fiber sorbents. *Industrial and Engineering Chemistry Research*, **57**, 11757–11766.
- Susanti I. and Widiastuti N. (2019). Activation of zeolite-Y templated carbon with KOH to enhance the CO₂ adsorption capacity. *Malaysian Journal of Fundamental and Applied Sciences*, **15**, 249–253.
- Tira H.S., Padang Y.A. and Supriadi. (2019). Effect of acidity level of substrate by lime water and acetic acid addition on biogas production. *AIP Conference Proceedings*, **2114**, 060006.
- Verboekend D., Keller T.C., Milina M., Hauert R. and Perez-Ramírez J. (2013). Hierarchy brings function: mesoporous clinoptilolite and L zeolite catalysts synthesized by tandem acid–base treatments. *Chemistry of Materials*, **25**, 1947–1959.
- Verdoliva V., Saviano M. and De Luca S. (2019). Zeolites as acid/basic solid catalysts: recent synthetic developments. *Catalysts*, **9**, 248.
- Wang C., Leng S., Guo H., Cao L. and Huang J. (2019). Acid and alkali treatments for regulation of hydrophilicity/hydrophobicity of natural zeolite. *Applied Surface Science*, **478**, 319–326.
- Wang G., Zhang Z. and Hao Z. (2019). Recent advances in technologies for the removal of volatile methylsiloxanes: A case in biogas purification process. *Critical Reviews in Environmental Science and Technology*, **49**, 2257–2313.
- Wang S., He Y., Jiao W., Wang J. and Fan, W. (2019). Recent experimental and theoretical studies on Al siting/acid site distribution in zeolite framework. *Current Opinion in Chemical Engineering*, **23**, 146–154.
- Wang X., Ozdemir O., Hampton M.A., Nguyen A.V. and Do D.D. (2012). The effect of zeolite treatment by acids on sodium adsorption ratio of coal seam gas water. *Water Research*, **46**, 5247–5254.
- Xu Z., Yue Y., Bao X., Xie Z. and Zhu H. (2019). Propane dehydrogenation over Pt clusters localized at the Sn single-site in zeolite framework. *ACS Catalysis*, **10**, 818–828.

Yuan M., Liu T., Shi Q. and Dong J. (2022). Understanding the KOH activation mechanism of zeolitic imidazolate framework-derived porous carbon and their corresponding furfural/acetic acid adsorption separation performance. *Chemical Engineering Journal*, **428**, 132016.

Zhang B., Guo H., Deng L., Fan W., Yu T. and Wang Q. (2020). Undehydrated kaolinite as materials for the preparation of geopolymer through phosphoric acid-activation. *Applied Clay Science*, **199**, 105887.

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