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Carbon dioxide removal from biogas through sorption processes using natural and activated zeolite adsorbents

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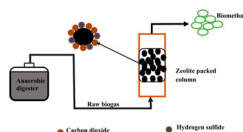
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ABSTRACT

Natural zeolite is among the low-cost materials that can be used to remove contaminants in biogas. The cleaning of biogas increases its energy density and reduces possible negative effects. The current study aimed to upgrade biogas using natural zeolites. The activation of natural zeolite was done using sodium hydroxide. The adsorbent samples were characterised using an XRF machine, while the biogas samples were analysed using Shimadzu gas chromatography and a portable digital gas detector. The effect of zeolite-to-water ratio on the carbonation process was investigated. In addition, the effects of biogas flow rate, adsorbent dose and contact time on the dry adsorption process were studied. The maximum CO₂ uptake of zeolite was 4.8 and 0.2 mmol/g by dry adsorption and wet carbonation process, respectively. The results indicate that surface adsorption favoured by a low Si₂O₃/Al₂O₃ ratio was more prominent than carbonation that requires high basic oxides. The results showed that an increase in the dose of activated clay from 2.5 to 35 g increased the removal efficiency of CO₂ from 11.2% to 79.8%, while the CO₂ uptake decreased from 4.8 to 2.5 mmol/g. Furthermore, the experimental data fitted best to pseudo-first-order kinetics and the Bohart-Adams model for the breakthrough curve.

KEYWORDS

Activated zeolite; breakthrough curves; carbon dioxide capture; natural adsorbents; biogas upgrade



1. Introduction

The primary energy supply worldwide belongs to non-renewable sources, which include coal, natural gas and oil [1]. These energy sources have negative environmental effects such as global warming caused by carbon dioxide emissions. In addition, they are exhaustible and, therefore, are becoming more costly [1]. Biogas is one of the renewable energy sources that are currently used as alternative to fossil fuels. It is produced through anaerobic digestion from a wide range of organic substrates. In the recent past, biogas has found wide applications such as running diesel engines and refrigeration [2]. Methane, which accounts for 50–75% of biogas, is the energy source in biogas. The rest are contaminants of which carbon dioxide contains 20–40% [3]. Other contaminants include trace components such as hydrogen sulphide, water, oxygen, ammonia and siloxanes. They cause corrosion and fouling of application appliances. Furthermore, hydrogen sulphide is harmful to

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the environment and can affect human health [4]. The high content of carbon dioxide has also been found to increase brake-specific fuel consumption (BSFC), which decreases the temperatures and leads to incomplete combustion. In addition, it may cause ignition delay and reduce the laminar flame speed [5]. Moreover, it reduces the specific calorific value of biogas and has a high contribution to global warming. Therefore, biogas should be upgraded and purified by removing carbon dioxide and other contaminants to increase its energy density and promote its safe application.

Biogas can be upgraded using modern technologies such as pressure swing adsorption, water scrubbing, physical scrubbing and membrane separation [6]. These methods are very effective in biogas upgrades but require high initial investments. A comparison of different modern biogas upgrade technologies reported that the initial investment was in the range of 10,00,000–20,00,000€/year for 1000 m³ plant size, while the maintenance cost was in the range of 15,000–25,000€/year [7]. Another study observed that the specific power consumption of the water scrubber for the upgrade was 0.2 KWh/Nm³ raw biogas in a large-scale unit of 2000 Nm³/h size. However, the value was projected to increase to 0.3 KWh/Nm³ for small-scale units of 400 Nm³/h size. These results indicate that the application of modern technologies of biogas upgrade in small-scale digesters is not cost-effective. The upgrade of biogas can also be done using natural adsorbents such as wood ash, clay, fly ash, natural zeolite and activated carbon [8]. Natural adsorbents have a low adsorption capacity for biogas contaminants. However, this capacity can be improved through physical and chemical activation. Recent studies have reported the potential of applying natural and modified adsorbents in biogas upgrades in small-scale digester units where carbon dioxide uptake of 4.5 mmol/g-dry ash was observed [9]. The current study focussed on developing a cheap substrate from natural zeolite for biogas upgrade that is suitable for small biogas plants.

Natural zeolites occur in different forms, such as mordenite, clinoptilolite, chabazite, phillipsite and others. They contain inorganic and organic impurities that cover the pores of zeolite so that its adsorption ability is reduced. However, it can be improved by physical and chemical activation. Furthermore, artificial zeolites are commercially synthesised for applications such as adsorbent [10]. Some of the synthetic zeolites that are used as adsorbents include zeolites 5A and 13X, which are very effective in carbon dioxide uptake but are very expensive. Modified zeolite can be prepared from clay minerals, fly ash, sludge and waste porcelain under hydrothermal activation to enhance its adsorption capacity. This activation can help to clean the pore surface and increase its surface activity. Physical activation is done using around 300–400 °C [11]. Chemical activation can be done using either acids or bases, which remove impurities such as oxides, free silica and alumina, thereby, cleaning the surface of the pores [11].

A previous study used various concentrations of KCl to activate natural zeolite [12]. It was observed that the adsorption capacity of carbon dioxide was in the range of 0.76–2.07 mmol/g. In addition, other published results have reported a carbon dioxide uptake using natural and artificial zeolites which were in the range of 0.2–4 mmol CO₂/g-adsorbent [13–15]. However, there is no comparative study of biogas upgrades using natural zeolite and modified zeolite that is activated with sodium hydroxide. In addition, there is no detailed information on the comparison of the dry adsorption and wet carbonation processes in biogas upgrade. This study examined the upgrading of biogas using natural and modified zeolite through the dry adsorption and carbonation processes for proposing an affordable method of biogas upgrade.

2. Methodology

2.1. Materials and methods

The samples of clinoptilolites zeolite were collected from the Hawassa zeolite area which was sourced from Nationalities Regional State, Ethiopia. The sample site is located 280 km the south of the capital city of Ethiopia, Addis Ababa. Natural and activated zeolites were characterised by Bruker XRF (model S1 titan from China). Raw and upgraded biogas components, including

CH₄, CO₂ and H₂S, were quantified using a portable gas detector (model ATO-SKY2000 series portable gas detector from China) and Shimadzu gas chromatography (GC) from Japan. In addition, biogas was collected using MBT41-1liters gas bags from China that had PTFE valves. The GC had an FID detector that was used to determine the methane content of biogas. The experiment was carried out in triplicate under the same condition to minimise the error. Furthermore, the consistency of the data was analysed using the error bar in MS Excel.

2.2. Activation of zeolite

The modification of zeolite was done to increase its adsorption capacity [16,17]. The natural zeolite samples that had been collected were of gravel size. Their size was first reduced to using mortar and pestle before milling to powder. The adsorbents then underwent particle size separation using a sieving mechanical shaker. The target size fraction was less than 400 µm which was used for the investigations. Zeolite samples, each 200 g was soaked for 24 h in deionised water and then air-dried. To each dried sample, 200 ml of 10% of sodium hydroxide solution was added. Continuous stirring was then done at 70 °C for 2 h. The mixture was left to stand for 24 h after which washing was done [16]. The mixture had its pH continuously monitored during the washing process. The process of washing was stopped when the pH value of 7. Finally, the activated zeolite powder was dried for one hour at 110 °C in an electric oven.

2.3. Upgrade of biogas

The purification of biogas was carried out using natural materials through both carbonation reaction and dry adsorption processes [17]. The effects of the adsorbent dose, the contact time and the biogas flow rate on the dry adsorption process were investigated. The adsorbent dose varied from 2.5 to 35 g, while the biogas flow rate varied from 45 to 250 ml/min. The effect of contact time was studied at adsorbent masses 5, 20 and 35 g. In addition, the effect of the adsorbent to biogas volume ratio was studied by keeping the volume of biogas constant and varying the mass of activated zeolite as follows: 5, 10, 15, 20, 25, 30 and 35 g.

The effect of the slurry ratio (natural zeolite to water) was done by adding 100 ml water to 100 g zeolite to get a 1:1 ratio. Similarly, other ratios (1:1, 1:2, 1:3, 1:4 and 1:5) were obtained for the investigations of carbonation experiments. The effect of temperature on the carbonation process was done at an optimum slurry ratio by varying the slurry temperatures between 18 °C and 80 °C.

2.4. The adsorption kinetics

The process of adsorption can be studied using both linear and nonlinear methods. The linear process unlike the nonlinear one can be done even without evaluation software. However, the process is laborious due to the parameters. The software that was used to study the kinetics of biogas removal using natural zeolite was CAVS for the evaluation of adsorption. The adsorption of CO₂ onto the activated zeolite was modelled using Elovich, intra-particle diffusion model, pseudo-first and pseudo-second-order kinetic models. The mathematical expressions for Elovich (1), intra-particle diffusion model (2), pseudo-first-order (3), pseudo-second-order (4) in nonlinear forms are given below [17,18].

$$q_t = \frac{1}{\beta}(1 + \alpha\beta t) \quad (1)$$

$$q_t = k_{id}t^{0.5} + C \quad (2)$$

$$q_t = q_1(1 - e^{-K_1 t}) \quad (3)$$

$$q_t = \frac{k_2 q_2^2 t}{1 + k_2 q_2 t} \quad (4)$$

whereas q_0 , q_t , q_1 , q_2 are the adsorption capacity at equilibrium, the adsorption capacity at a particular time, the adsorption capacity at the equilibrium of first order (mg/g), adsorbent capacity at the equilibrium of second order (mg/g), respectively. The constants k_1 and k_2 are the pseudo-first-order rate constant (min^{-1}) and pseudo-second-order rate constant (g/mg min) respectively, α is the initial adsorption rate (mg/g.min), k_{id} is the intra-particle diffusion rate $\text{mg/g min}^{0.5}$, β is the desorption constant (mg/g), t is the time and C is a constant.

2.5. Breakthrough curves for fixed bed adsorption

One of the applications of breakthrough curves is in adsorptive separation processes where they are used to evaluate the breakthrough profile and the performance of the fixed bed columns. Various mathematical models are used to study the breakthrough profiles. Some of the models commonly applied for this purpose include Yan, Thomas, Yoon–Nelson and Bohart–Adams equations.

Bohart-Adams model evaluates by relating the concentration and time. The initial portion of the adsorption is dominated by external mass transfer and is described by the model [19].

One of the best models to describe breakthrough curves is the Yan model which is an empirical equation. The model can overcome the weakness in the Thomas model. It can make predictions at initial concentrations. Similarly, the Yan model can predict the adsorption capacity of the initial portion of the breakthrough curve [20]. It is expressed in linear and nonlinear forms shown in Equation (5).

$$\frac{C_t}{C_o} = 1 - \frac{1}{1 + \left(\frac{Q^2 t}{K_y q_y m}\right) K_y C_o / Q} \quad (5)$$

Q is the feed flow rate (ml/min), m is the adsorbent mass (g), K_y is the kinetic rate constant for the Yan model (L/mg min) and q_y is the maximum adsorption capacity (mg/g) of adsorbent by the Yan model.

The Yoon–Nelson model makes the assumption that the probability of adsorbate breakthrough on the adsorbent and the probability of desorption of adsorbate is proportional to the decrease in adsorption [21]. The equation is expressed in the linear and nonlinear form presented in Equation (6).

$$\frac{C_t}{C_o - C_t} = \exp(K_{YN} t - K_{YN} \tau) \quad (6)$$

τ is the time (mins) required for reducing 50% of the initial adsorbate and K_{YN} is the Yoon–Nelson model constant (min^{-1}).

3. Result and discussion

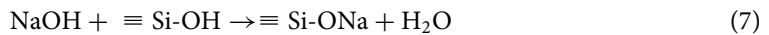
3.1. Characterisation of the chemical components of zeolite

The capture of CO_2 from biogas through dry adsorption processes at low pressures is dependent on the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio [17,22]. However, for the carbonation process, the elimination of CO_2 from biogas is mainly dependent on the contents of CaO and other basic oxides in the sorption material. This implies that the characterisation of adsorbent can help predict its ability for CO_2 uptake. Table 1 gives the summary of the chemical composition of natural and activated zeolite analysed in this study.

Table 1. Chemical composition of natural and activated zeolite.

Chemical composition	Natural zeolite (% mass)	Activated zeolite (% mass)
SiO ₂	81.20	82.63
Al ₂ O ₃	8.56	9.08
K ₂ O	2.18	1.96
CaO	1.47	1.61
SiO ₂ /Al ₂ O ₃	16.10	15.40

The results confirm that the main components of zeolites are silica and alumina, along with trace components such as potassium oxide, calcium oxide and iron. The molar Si₂O/Al₂O₃ ratio before activation for natural zeolite was 16.1. However, after activation with 10% of sodium hydroxide, the ratio decreased to 15.4. This suggests that the CO₂ adsorption capacity of activated zeolite could be higher than that of natural zeolite. A previous study that investigated the effects of SiO₂/Al₂O₃ ratio on ZSM-5 zeolite performance reported a higher adsorption capacity of CO₂ for a ratio of 50, compared to that of 30 at 10.5 atms [22]. However, the opposite was observed at lower pressures (0–9 atms), where the ratio of 30 produced higher adsorption capacity compared to that of 50 [22]. In the current study, the slight decrease of the SiO₂/Al₂O₃ ratio after activation at low pressure is favourable for CO₂ uptake. The contaminants in natural zeolites block the adsorption pores of the adsorbent which decreases its adsorption capacity. The removal of these impurities by activation increases the adsorption capacity of the adsorbent. Another mechanism through which the chemical activation of zeolite can improve its adsorption capacity is by replacing hydrogen with sodium ions in the complex structure of the zeolite, as illustrated in Equation (7) [11].



The activated zeolite showed high adsorption capacity compared to natural zeolite probably due to the above factors including lower SiO₂/Al₂O₃, removal of pore contaminants and replacement of hydrogen with sodium ion in the adsorbent complex structure discussed above. Furthermore, the activation increases the pore volume and enhances the uniformity of the pores which is good for high adsorption capacity. Previous studies that analysed the specific surface area of natural and activated zeolite using Brunauer-Emmett-Teller (BET) observed that activation of adsorbent increases the surface area which favours high adsorbate uptake [23].

3.2. Dry adsorption process

3.2.1. The effect of flow rate

The biogas flow rate of 45 ml/min was found to produce the highest CO₂ uptake at 4.84 mmol/g for zeolite. The uptake compares with the results from the studies by [24], which observed 4.75 mmol/g uptake capacity using zeolite 13X from palm oil mill fly ash. The minimum biogas flow rate that could be practically applied without dampening the flow by small particles was 45 ml/min. The use of longer bed height is recommended for investigations with low biogas flow rates. Figure 1 shows the effects of biogas flow rate on the adsorption capacity. Suratman et al. reported that the optimum adsorption capacity was achieved at 50 ml/min, which is compared with the current results [25].

3.2.2. The effect of the adsorbent dose

The quantity of adsorbent mass used affects the adsorption capacity when the volume of gas is fixed. The activated zeolite varied from 2.5 to 35 g while the biogas was fixed at 5 litres. The effect of the dose of activated zeolite on adsorption is illustrated in Figure 2. An increase in the activated zeolite from 2.5 to 35 g increased the removal efficiency of CO₂ from 11.2% to 79.82% while the CO₂ uptake decreased from 4.84 to 2.49 mmol/g. The increase in the adsorbent mass increases the surface area and the number of active sites increases the removal efficiency. On the contrary, the uptake

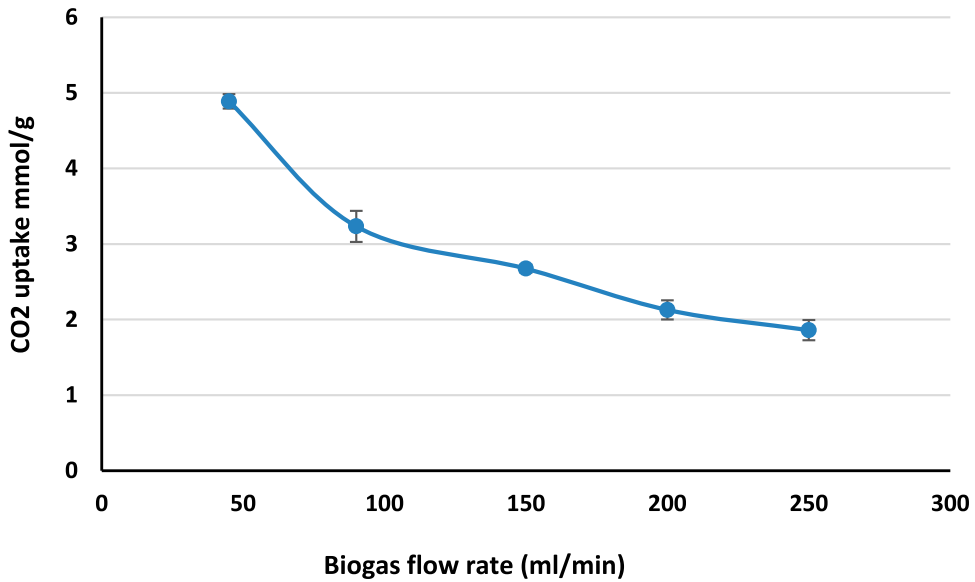


Figure 1. The effect of biogas flow rate on the adsorption capacity.

capacity of CO₂ of the adsorbent reduces with an increase in the mass used. Similar results were reported by [26], who observed that an increase in the adsorbent dose from 3 to 5 g decreased the adsorption capacity from 23.05 to 21.51 mg CO₂/g sorbent. The reduction in adsorption capacity with an increase in adsorbent mass could be caused by the high number of free adsorption sites that remain unused due to low chances of interactions between the adsorbates and the adsorbent. In addition, this could be caused by the overlap of active sites of adsorbent ; therefore, a lot of active sites remained unsaturated during the adsorption of carbon dioxide. Furthermore, this result is in agreement with that from other documented studies where 0.2 g dose of chitosan adsorbent

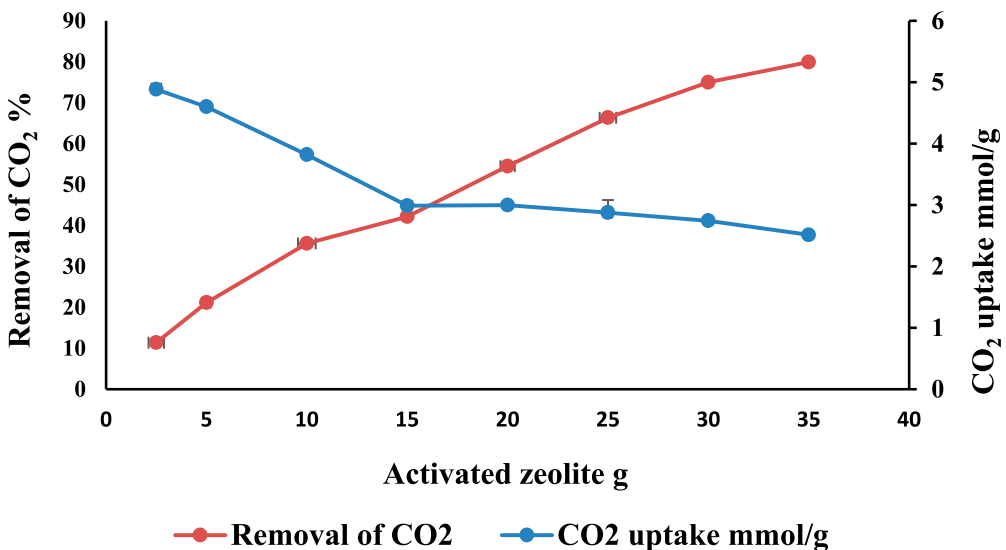


Figure 2. The effect of the adsorbent dose on CO₂ removal.

produced more than 90% iron contaminants from water compared to 70% removal using 0.1 g dosage [27].

3.2.3. The effect of contact time

The effect of contact time on the uptake of CO₂ by zeolite was investigated at different adsorbent masses of 5, 20 and 35 g. The uptake of CO₂ increased gradually until it reached the maximum or the equilibrium point, which was obtained after 15, 30 and 50 min for 5, 20 and 35 g, respectively. Further increase in the contact time after optimum time either maintains the maximum value or causes a slight decrease in the adsorption capacity due to the desorption of adsorbate particles. The effect of contact time on the adsorption capacity of CO₂ is shown in Figure 3. A separate study by Gorzin observed that the increase in the contact time increased the adsorption capacity of CO₂ and then reduced gradually till the equilibrium conditions [28]. In addition, the adsorption time was found to increase with the adsorbent dose, which is confirmed by the findings in this study.

3.2.4. Studies on adsorption kinetics

Kinetic models are used to study the adsorption uptake for time at constant pressure and temperature. Therefore, they are used to analyse the adsorption capacity of activated zeolite for time. The experimental data on CO₂ adsorption were modelled using four kinetic models: pseudo-first-order, pseudo-second-order, Elovich and intra-particle diffusion nonlinear kinetic models. The kinetics parameters of adsorption of CO₂ using activated zeolites for the models which gave the best correlations are summarised in Table 2.

The fitness of the models was analysed using R^2 and the error parameters. The best model should have the highest value of nonlinear regression R^2 . In addition, the model should have the lowest value of the RMSE, SQE and X^2 . The RMSE expresses the total magnitude of the error while the SQE expresses the fitnesses of the model to the experimental data. Moreover, X^2 describes the closeness of the experimental data to the predicted model. The results for multi-parameter evaluation of experimental data for CO₂ uptake using zeolite indicated that it fitted best to the pseudo-first-order

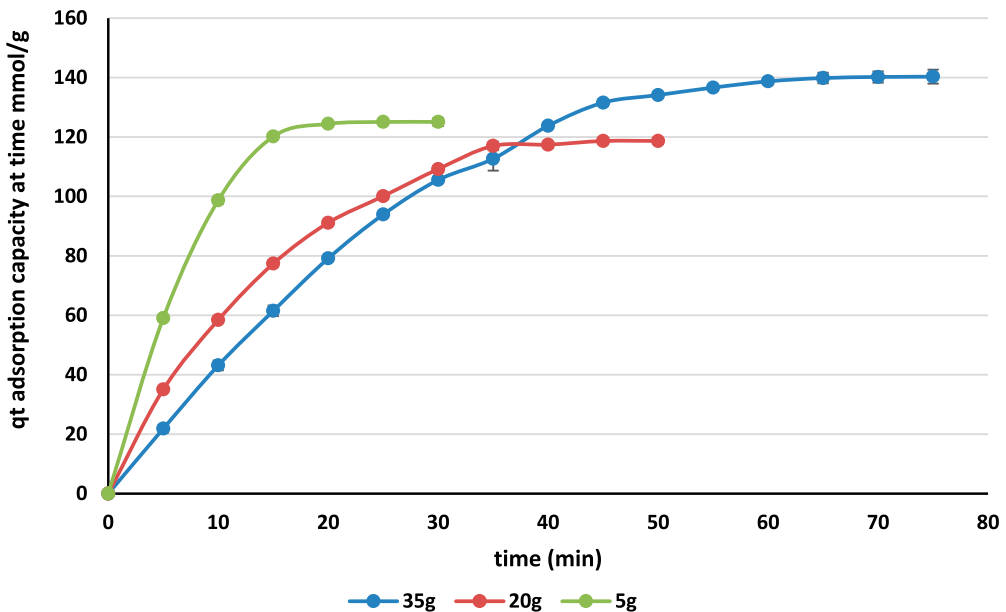


Figure 3. The effect of the contact time at different masses.

Table 2. The kinetic parameters of adsorption of carbon dioxide using activated zeolite.

Kinetic models	Parameters	Kinetic parameters
Pseudo-first-order	R^2	0.992
	SQE	218.9
	RMSE	3.69
	X^2	–
Pseudo-second-order	R^2	0.985
	SQE	469.5
	RMSE	5.42
	X^2	2.88
Elovich	R^2	0.975
	SQE	768.47
	RMSE	6.93
	X^2	5.79
Intra-particle diffusion	R^2	0.95
	SQE	1463.7
	RMSE	9.56
	X^2	13.47

equation. Pseudo-first-order has the highest R^2 (99.29) and lowest RMSE (3.699), SQE (218.87) and X^2 (0) among all kinetic models. The adherence to this model indicates that adsorption capacity is directly related to adsorption time. The adsorption rate depends on the nature of the adsorbate. Figure 4 presents the kinetic plots of carbon dioxide adsorption for pseudo-first-order, pseudo-second-order, Elovich and intra-particle diffusion models.

3.2.5. Breakthrough curves of fixed bed adsorption

Breakthrough curves analyse the adsorption behaviours of adsorbent. They are very important in characterisation of the activated zeolite. A breakthrough curve is a plot that indicates the concentration at the outlet of a fixed bed adsorber with time. In addition, breakthrough curves give the performance of the adsorption bed in both laboratory and industrial applications that inform the regeneration time of the adsorbent. The data of adsorption of CO_2 using activated zeolite were modelled on breakthrough curves using Bohart-Adams, Yan and Yoon & Nelson models. The breakthrough curves were evaluated by considering the R^2 and error parameters as described earlier. The breakthrough curves describe the concentration of effluent from the fixed bed and relate the same with the time of flow. The parameters for the breakthrough curves, which gave the best correlations, are summarised in Table 3.

The evaluation of experimental data indicated that Bohart-Adams described best the experimental data. The model had the highest R^2 (99.1) and lowest SQE (0.010219), RMSE (0.028037) and X^2 (0.016755) values, which indicate that the data fitted well to the model. This shows the importance

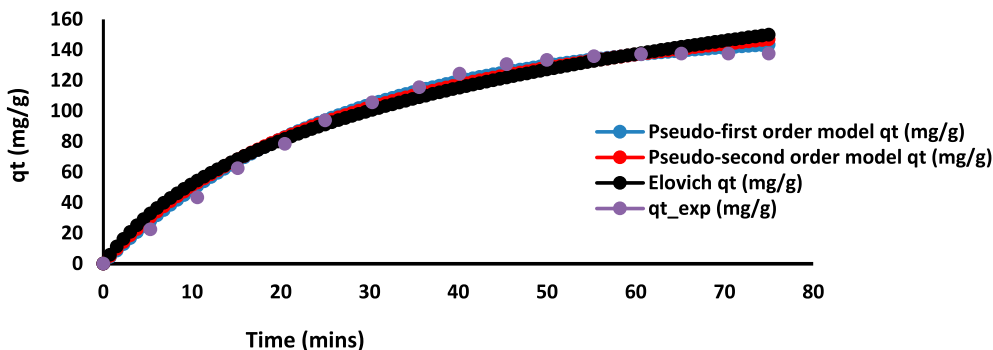
**Figure 4.** The kinetic plots of carbon dioxide removal by adsorption using activated zeolite.

Table 3. The summary of the parameters for breakthrough curves of carbon dioxide adsorption using activated zeolite.

Fixed bed models	Breakthrough parameters	Parameter values
Bohart-Adams	R^2	0.99
	SQE	0.01
	RMSE	0.028
	χ^2	0.017
Yan	R^2	0.95
	SQE	0.05
	RMSE	0.06
	χ^2	0.63
Yoon and Nelson	R^2	0.99
	SQE	0.01
	RMSE	0.028
	χ^2	0.017

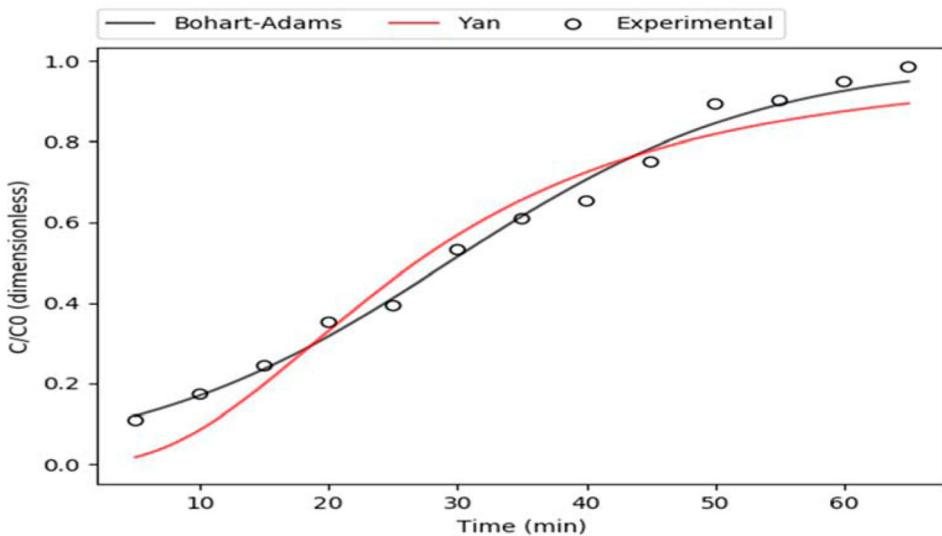
of using multi-parameter criteria in the evaluation of adsorption performance. Figure 5 illustrates the breakthrough curves for the adsorption of carbon dioxide using dry activated zeolite.

The diagrammatic plot indicates that the effluent from the fixed bed after 45 min was 80% of the influent concentration. The breakthrough curve can be used to approximate the breakthrough point of the column. It is the time when the column is just fully saturated with the adsorbates. Adsorptive processes with long breakthrough points are more cost-effective because their bed requires less frequent replacements. The breakthrough point is directly related to the adsorption capacity of the adsorbent in the bed and the volume of the bed which is related to the mass of the adsorbent.

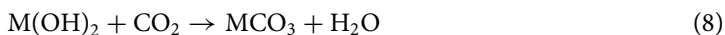
3.3. Wet carbonation process

3.3.1. The effect of zeolite to water ratio on the carbonation processes

Biogas upgrade using a wet carbonation process may entail both adsorption and absorption processes, which is also known as the sorption process [29]. The absorption process entails wet carbonation reactions and is dependent on the adsorbents' oxide content. The presence of high content of alkaline oxides in the adsorbent favours high adsorption capacity in the wet carbonation process. The oxides react with carbon dioxide as shown in Equations (7) and (8) to produce carbonates,

**Figure 5.** Breakthrough curves of carbon dioxide uptake with 30 g adsorbent mass.

hence the name carbonation process.



In previous studies, wood ash slurry was found to produce high adsorption capacity in the wet carbonation process due to the high content of CaO and pH value [29]. The current study shows that zeolite has low oxide content and pH value. Therefore, the carbonation process has little contribution to the zeolite sorption capacity of carbon dioxide in the biogas. Furthermore, previous studies with wood ash indicated that the uptake is dependent on the amount of water present in the adsorbent slurry [17,29]. Therefore, it was necessary to study how water in zeolite affects the uptake of biogas by the adsorbent. Figure 6 shows the results for the effects of different ratios of zeolite and water mixtures on the capacity of biogas purification. The water-zeolite ratio of 1:1 was observed to produce the highest biogas purification capacity. This is probably due to strong polar bonds with the exchangeable cation caused by the presence of water on the zeolite surface. The presence of higher water contents reduces the heterogeneity and strength of the electric field, which decreases the adsorption capacity [30].

The results of this study indicate a decrease in methane enhancement in biogas with an increase in water added to zeolite. This indicates that the purification of biogas using zeolite slurry is mainly by the surface adsorption process. This is supported by the fact that it has a microporous crystalline aluminosilicate structure for surface adsorption. Therefore, wet carbonation is not a suitable method for biogas upgrade applications using natural zeolite in a slurry form.

The treatment of biogas with zeolite slurry at temperatures 25°C, 35°C, 55°C and 65 °C increased methane contents by 20.2%, 17.3%, 12.57% and 4.57%, respectively. The highest performance of the slurry was a 20.2% methane increase at an uptake rate of 0.19 mmol/g adsorbent. The removal of CO₂ through the carbonation process by zeolite forms carbonates that are very stable monodentate on the surface of the zeolite. However, due to the interaction with CO₂ the aluminium oxygen bond and the stable monodentate carbonate species rupture the surface of zeolite [30]. Therefore, the uptake capacity of CO₂ is very low because the pores are blocked by the surface cations. They also reduce the electric field strength and the heterogeneity of the adsorbent.

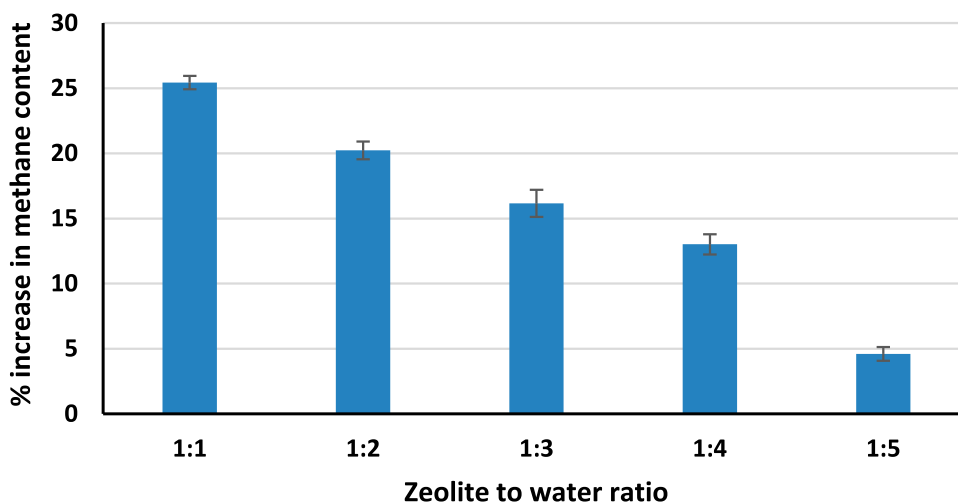


Figure 6. The effects of different ratios of zeolite to water mixture on the capacity of biogas purification.

3.4. The potential of zeolite in CO₂ uptake through dry adsorption and wet carbonation processes

The potential of applying natural or modified zeolite in the upgrade of biogas is mainly determined by its capacity for carbon dioxide uptake. The results from the current study indicate that the maximum CO₂ adsorption capacity of the dry process using natural zeolite was 0.77 mmol/g while that of the carbonation process was 0.19 mmol/g. Furthermore, in the dry adsorption process, the carbon dioxide uptake capacity was found to be improved by activation with 10% NaOH. This suggests that natural zeolite is a more feasible candidate for biogas upgrade through the dry adsorption process.

The high initial pH of the slurry is crucial for high carbon dioxide removal through the wet carbonation process. The pH value of natural zeolite slurry was approximately 8.5. The reduction in the slurry pH during the sorption process from 8.5 to 5.8 indicates that some carbonation reactions were taking place. However, the low pH value of zeolite could be responsible for the low adsorption capacity in the wet carbonation process. This is supported by documented literature that indicates that the high alkalinity of slurry favours the adsorption of CO₂ through the wet carbonation process [17,31]. In addition, the presence of basic oxides is crucial for high carbon dioxide uptake through the wet carbonation process. Documented studies by other researchers using fly ash [32] observed that high content of CaO favoured high carbon dioxide capture in the wet carbonation process. However, the current study found low content of basic oxides in natural zeolite such as CaO (1.5%) which indicates that carbonation reactions play a minor role in carbon dioxide uptake. The main components of zeolites were found to be alumina and silica compounds that favour surface adsorption. The results confirm that CO₂ uptake using zeolite is mainly through the dry adsorption process. Therefore, the dry adsorption process is more feasible for biogas upgrades.

4. Conclusion

Natural and activated zeolite can be used for the purification of biogas through dry adsorption and carbonation processes. The chemical composition of natural zeolite showed that it has high contents of alumina and silica compounds, but low contents of basic oxides. The silica-to-alumina ratio was 16, which suggests that the adsorption capacity of dry zeolite is dominated by physical adsorption compared to carbonation reactions. The dry adsorption process was found to be affected by the biogas flow rate, adsorbent dose and contact time. Furthermore, the purification capacity of biogas using zeolite increased with a decrease in the biogas flow rate. The maximum CO₂ adsorption capacity of natural zeolite and zeolite activated with 10% NaOH was 0.77 and 4.8 mmol/g, respectively which were found at 45 ml/min biogas flow rate. This indicates that natural zeolite should be activated to enhance its biogas purification capacity. Furthermore, the results show that an increase in the adsorbent dose decreases the uptake capacity of the adsorbent. The evaluation of the kinetics and breakthrough curves for experimental data on carbon dioxide adsorption indicated that it fitted best in pseudo-first-order kinetics and Bohart Adam breakthrough curve model, respectively.

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Disclosure statement

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