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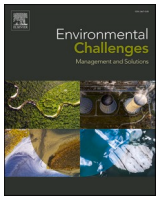

Performance evaluation of calcined eggshell waste (Sorbent) for biogas upgrading: Adsorption isotherms, adsorption kinetics, and fixed bed studies

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ABSTRACT

The use of non-renewable energy resources such as fossil fuels accelerates climate change and environmental degradation necessitating a shift to renewable energy sources. Biogas is a renewable energy resource with great potential. However, its application is limited by the presence of contaminants such as carbon dioxide, which reduces its energy value, and density. Upgrading biogas using locally available materials solves waste management and energy sustainability challenges. In the present study, calcined eggshell waste was employed as an adsorbent for carbon dioxide. The effect of calcination temperature, adsorbent mass and adsorbent particle size was evaluated. The experimental data was fitted to adsorption isotherms, adsorption kinetic models, and breakthrough curves. Eggshells with a particle size of 280 μm, calcined at 850 °C, and mass of 75 g showed the best performance in removing carbon dioxide from biogas. It was noted that data from the experiment fitted Langmuir isotherm with RL 0.00216 while its R^2 was 0.97 and Freundlich $n = 0.6$ while $R^2 = 0.97$. Regarding adsorption kinetics, the intra-particle diffusion model shows good conformity with $k_{id\ of}$ 34, C of 98, and R^2 of 0.977. Breakthrough analysis proved that Yoon Nelson's Model fitted well with the experimental data with an R^2 of 0.989. Thus, calcined eggshell waste is a good sorbent for biogas upgrading that can solve the twin challenges of waste disposal and management and energy sustainability.

1. Introduction

Worldwide, the rise in greenhouse gas emissions is a major concern for policymakers, researchers, and leaders; there is a need to limit the growing impact of climatic change on the environment. Additionally, the global energy demand is expected to rise by about 1.3 % annually until 2040 (Amin et al., 2022). This is attributed to economic growth, population, and advancements in technology leading to dependence on non-renewable energy resources which are major contributors to greenhouse gas emissions, water and air pollution, and, among others (Chuah et al., 2022). Regardless of the harmful environmental impact, the reduction of fossil fuel and fluctuations in oil prices are influencing product end users and industrial sectors. Moreover, the emergence of the COVID-19 pandemic disease remarkably affected the global energy leading to a reduction in global energy demand by 5 % and a reduction in investment of 18 % (Hoang et al., 2021a, 2021b). Meanwhile, the COVID-19 pandemic had a low impact on renewable energy resources like wind energy, biofuels, geothermal, and solar energy. The vision for 2050 on energy outlook is to attain a net-zero emission that necessitates clean and sustainable energy resources like biofuels.

The generation of environmentally friendly, non-conventional energy resources via an anaerobic digestion process is a feasible replacement for non-renewable energy resources that generate greenhouse gasses (Mecha and Kiplagat, 2023). The generation of biogas has rapidly expanded and replaced vehicle fuel, power, and heat. The quantity and quality of biogas generated during microbial digestion rely on the composition of the materials used in the bio-digester. Organic waste is the preferred waste used in biogas generation that recaptures energy and solve the problems of waste management. The constituents of biogas depends on the quality and quantity of feedstock though mainly

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Fig. 1.1. Eggshell preparation for sorption process (a) eggshell (b) uncalcined eggshell (c) lab furnace (d) calcined eggshell.

components methane 55–77 %, and 30–45 % carbon dioxide, though there are some minor impurities of nitrogen, ammonia, hydrogen sulfide, and some trace amount of siloxane compounds (Kiplagat and Mecha, 2023). The concentration and purity of methane are the two key points to be examined concerning energy density and the calorific value of biogas. The existence of carbon dioxide (CO_2) in biogas restricts its usage by reducing its calorific value and energy density, which calls for upgrading techniques.

Recently, various upgrading methods have been used to eliminate CO_2 from biogas such as the physical scrubbing methods, pressure swing technique membrane separation method, and water scrubbing (Dębowski et al., 2021). Nevertheless, most of these approaches have some drawback, as they need high maintenance and operational costs. The usage of locally organic materials for the elimination of CO_2 from biogas has been advantageous in terms of being simple to design, easy to handle, and convenient. Different sorbents have been applied in biogas upgrading including eggshell waste sorbent, activated carbon, and red rock material among others. The bio-methane purified from biogas can be converted into bio-compressed gas for easy distribution through natural gas pipes. It is approximated that bio-compression natural gas will rise from 2% in 2021 to 27% in 2050 (Lóránt and Tardy, 2022; Khan et al., 2021).

Most studies reported in the literature that have used low-cost materials for biogas purification have not undertaken detailed evaluation of the performance of the fixed bed column. In our previous work, we employed calcined eggshell waste for CO_2 removal from biogas in fixed-bed reactor experiments (Mrosso et al., 2023). The study showed that a calcination temperature of 850 °C, adsorbent mass of 75 g, and adsorbent particle size of 280 μm provided the best performance. Based on this, the objective of the current study was to fit the experimental data into existing adsorption kinetics and breakthrough analysis models to extract useful column design parameters. The effect of column bed height, adsorbent mass and biogas flow rate were considered. The breakthrough curves were analyzed using Adams-Bohart, Yoon–Nelson models and Thomas. The novelty of the study lies in the application of this novel adsorbent to remove carbon dioxide from biogas; and extracting useful design parameters from the applied models that can be used for scale-up of the column. This will solve the twin challenges of energy insecurity, and waste disposal.

2. Materials and methods

2.1. Material collection and preparation

Eggshell wastes were collected from Moi University in Eldoret-Kenya and Makumira University's localized cafeteria in Tanzania for four months. They were thoroughly washed and dried in the sun for three days. The feedstocks were ground using a grinder model HK-820 and sieved into particle sizes 280 and 400 μm using sieves. The prepared samples were calcined under three different temperatures 800, 850, and 900 °C to convert the original chemical structure of eggshells ($CaCO_3$) into calcium oxide (lime) Fig. 1.1.

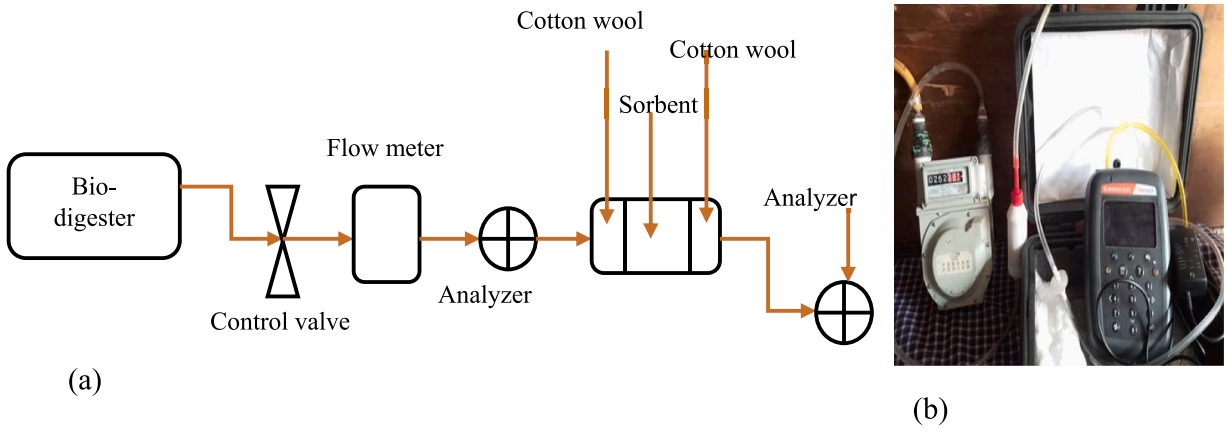


Fig. 2.1. On-site upgrading process: (a) schematic description of experimental set up (b) photograph of the experiment [adapted from (Mrosso et al., 2023)].

2.2. Methods

2.2.1. Performance evaluation of fixed bed column

Adsorption experiments were carried out in a domestic biogas power plant producing biogas from biomass, kitchen waste and human waste in a ratio of 1:1:1. The mixture were mixed with water in a same ratio and the digester was fed twice per day. Co-digestion process enhances methane generation and system stability as it balance the CN ratios. A fixed bed column with 13 cm height and 4 cm width was employed. Cotton wool was packed in a bed column and without the sorbent material biogas was allowed to pass through to verify whether cotton reacted with biogas. It was observed that the biogas had no reaction with cotton wool. Calcined eggshell waste was packed with the additional of non-reactive material to allow the smooth passageway of the gas and both ends of the column were covered with cotton wool and monitored for 15 min. The amount of methane recorded prior to the addition of sorbent was the same at that recorded after the addition of sorbent. Besides, the adsorbent used has preferential adsorption of carbon dioxide hence methane had the least possible reaction with lime material. Fig. 2.1 demostrates the experimental set up used. The results obtained from on-site experiments were justified using adsorption isotherms, adsorption kinetics, and fixed bed adsorption studies/models.

2.2.2. Effect of different process parameters

The adsorption ability of lime derived from calcined eggshell waste was studied using different parameters such as biogas flow rate, mass of sorbents, adsorbent particle size, and sorbent calcination temperatures and the results reported in our previous study (Mrosso et al., 2023). The adsorbent with particle size 280 μm showed an excellent in the removal of CO_2 from biogas due to large surface area to volume ratio. Regarding the effect of biogas flow rate and other parameters, it was observed that mass of 75 g calcined under 850 °C, and a biogas flow rate of 0.03 m^3/h showed a good performance on the removal of impurities such as CO_2. This was attributed to the fact that higher mass provides a larger surface and adsorption sites available for attachment of CO_2 compared to the lower adsorbent masses of had more possibility to be exposed to the adsorption sites for the sorbent rather than small adsorbent masses such as 50 and 25 g. Meanwhile, the low flow rate indicates that the impurity from biogas had more time to contact sorbent material hence high sorption capacity and removal efficiency of 5.0 g/100 g and 82.5 % respectively. Chemisorption was reported as the more dominant process.

2.2.3. Adsorption isotherms

The equilibrium of adsorption was determined by Langmuir, Freundlich, and Jovanvich isotherms, and equilibrium plots were done using OriginPro software. Langmuir adsorption isotherms illustrate monolayer adsorption of the adsorbate onto a homogenous adsorbent surface. Initially, it was developed for gas-to-solid adsorption but it can also used for varieties of adsorbent materials. It is an empirical isotherm that is based on kinetic fundamentals; that is, the surface rates of desorption and adsorption are equal to zero accumulation at an equilibrium point. The parameters of Langmuir isotherm describe the maximum capacity of adsorption and the properties of sorbent material. The Langmuir model postulates that at maximum adsorption, monolayer is formed, and adsorbate molecules do not deposit on already adsorbed molecules of adsorbate, only on the free surface of the adsorbent (Nadimi et al., 2021). The necessary parameters were computed using Eqs. (1), (2), and (3), respectively.

$$q_{max} = \frac{1}{intercept} \tag{1}$$

$$KL = \frac{1}{Slope * q_{max}} \tag{2}$$

$$RL = \frac{1}{1 + K_L C_o} \tag{3}$$

Unlike the Langmuir adsorption isotherm, Freundlich isotherm is an empirical isotherm that can be used for multilayer sorption on heterogeneous adsorption sites. It assumes that the affinities toward the heterogeneous surface and the adsorption heat distribution are non-uniform. It explains the heterogeneous adsorption on a multilayer process where isotherm assumes that the adsorption process occurs on the heterogeneous surface of the adsorbent. The Freundlich parameters can be calculated in Eqs. (4)–(7) which were obtained from the graph of log *qe* vs log *Ce* after regression for analyzing the applicability of the Freundlich adsorption isotherm.

$$qe = K_F {C_e}^{1/n} \tag{4}$$

$$n = \frac{1}{Slope} \tag{5}$$

$$Intercept = \log kf \tag{6}$$

$$Log\ q_{e=}\frac{1}{n} logC_e + logK_f \tag{7}$$

Where 1/n is the surface heterogeneity or adsorption intensity while b is the adsorption capability. when $1/n > 1$ referred as unfavorable adsorption, irreversible at $1/n = 1$. While $0 < 1/n < 1$, adsorption is considered favorable with the chemisorption process.

From the Linearized Freundlich, a graph of log qe vs log Ce provide a straight line with a intercept = ln b and slope = 1/n and where all the parameters can be easily calculated. The linear form is an uncomplicated and simple kind of isotherm, although it can generate propagation errors that have some effects in erroneous predicting Freundlich parameters. Thus, the use of a non-linear Freundlich adsorption isotherm acts as a mitigating measure to solve the problem associated with the linear form of Freundlich adsorption isotherm. It explains adsorption through multilayer and assumes decay in the energy distribution is exponential for adsorbed sites. Nevertheless, it can not work for a large range of data. The determination of R^2 and the comparison between the experimental and the approximated qe are the most used standards to validate the fitting of the adsorption isotherm to the on-sit experimental data.

The Jovanovich model considered the assumptions as in the Langmuir classic isotherm and remains successful in the existence of lateral interplay among the adsorbed molecule species. Nevertheless the probability of mechanical contact between the adsorbate and adsorbent is taken into account in the Jovanovich isotherm model (Al Jaberi et al., 2020). It is appropriate for both mobile and localized adsorptions. The parameter n examine the lateral interaction between the molecules adsorbed. The Jovanovich isotherm reaches the saturation point at a very high pressure. The equation of this isotherm reaches the maximum saturation point when the amount of the sorbate is high, meanwhile at low concentration it is reduced to Henry's law. When making a comparison to the Langmuir adsorption equation, the Jovanovich isotherm equation has a lower approach to saturation (Al-Ghouti and Da'ana, 2020). The linear Jovanovich isotherm equation is written as per Eq. (8), while slope and intercept is as Eqs. (9) and (10) (Mutegoa et al., 2021).

$$In\ q_e = Inq_{max} - K_j C_e \tag{8}$$

$$Kj = Slope \tag{9}$$

$$In\ qmax = Intercept \tag{10}$$

Where q_e (mg/g) is the concentration of impurities adsorbed, q_{max} (mg/g) is the maximum adsorption, K_j (l/g) is the Jovanovich constant, and C_e (mg/L) is the concentration at equilibrium.

Table 1
Linear adsorption kinetic models.

Adsorption kinetics model	Linear form	Equation
Pseudo first-order	$In\left(\frac{C_i}{C_t}\right) = k_1 t$	11
Pseudo second-order	$t/q_t = \frac{1}{kqe^2} + t/qe$	12
Elovich model	$qt = \frac{1}{\propto} In(\propto\beta) + \frac{1}{\propto} Int$	13
Intra-particles diffusion model	$qt = k_{id}t^{0.5} + C$	14

2.2.4. Adsorption kinetics

Four adsorptions kinetic, namely, pseudo-first order, pseudo-second order, intra-particle diffusion model, and Elovich were used to explain the kinetics of biogas purification using the calcined eggshell waste. The equations for the kinetics of adsorption are presented in Table 1 and linear plots were done using originPro. Literature shows that Lagergren introduced the pseudo-first-order (PFO) in the late 19th century (Demirbas et al., 2004). There is a relationship between adsorption rate and the surface of adsorption of the respective material. It is expressed in linear form as shown in Eq. (11).

The Pseudo second order (PSO) was first applied in 1984; it explains the linear relationship between the adsorption rate and surface of adsorption of the material. The model can be written in linear form as per Eq. (12). Tompkins and Aharonic developed the Elovich adsorption model in 1970. It relates the chemisorption essence of adsorption and the interlinkage of biogas molecules with the heterogeneous surface of the sorbent surface Eq. (13). Morris and Weber and developed the intra-particle diffusion in 1963, which is an older model. It describes the controlled mechanism of diffusion and it is can be indicated in linear form as per Eq. (14).

Whereas k_1 is the pseudo-first-order rate constant (min^{-1}), q_t is the capacity of adsorption at a particular time, K_2 is rate constant for pseudo-second-order (g/mg.min K_{id} is intra-particle diffusion rate mg/g.$min^{0.5}$, t is time, C is constant, β is the desorption constant (mg/g) and α is the initial adsorption rate (mg/g.min),

2.2.5. Fixed bed column adsorption studies

Three models were employed in this study Adams-Bohart, Thomas, and Yoon-Nelson models, to describe the dynamic characteristics of the bed in column performance. From each model various parameters which describe the achievement of the adsorption column were derived. The three fixed models were used to fit the data attained from on-site experiments, and they were compared using the coefficient of determination R^2 (Chu, 2020). The nonlinear and linear adsorption models are described in Table 2.

Adams-Bohart model, model predicts the linear relationship between the depth of the bed and the time used for the breakthrough R^2. The linear relationship of this model clarify the tasks of absorber design, analysis and gives a straightforward technique to running trial tests as per Eqs. (11)–(13). The necessary parameters such as k_{AB} and N_o were obtained from the plot In (C_t/C_o) against time as per stated equations; where N_o is maximum adsorption capacity (L/mg min) while k_{AB} is Bohart –Adams constant.

$$Slope = k_{AB} * C_o \tag{11}$$

$$k_{AB} = \frac{Slope}{C_O} \tag{12}$$

$$Intrecept = -k * N_o * \left(\frac{Z}{U_{O)}}\right) \tag{13}$$

In Thomas's model, the model presumes the flow behavior within the bed reactor. In general, it is a popular model used to explain the performance theory of the adsorption mechanism in any fixed column (Chen et al., 2012). The values of q_o and k_{Th} can be obtained from the graph of ln [(Co/C_t)−1] vs time, where k_{Th} is Thomas's constant (mL/min mg), and q_o is the adsorption capacity (mL/min mg). The parameters were obtained using Eqs. (14) and (15).

$$k_{Th} = -\left(\frac{Slope}{C_o}\right) \tag{14}$$

$$q_o = \frac{Intercept}{k_{Th}} \tag{15}$$

Yoon-Nelson, the model is normally expressed in the as per the Eqs. (16).

$$In\left(\frac{C_t}{C_O - C_t}\right) = K_{YN}t - \tau K_{YN} \tag{16}$$

Where τ is the time needed for 50 % breakthrough expressed in (min), and k_{YN} is the Yoon-Nelson rate coefficient (min^{-1}), both parameters k_{YN} and ɼ can be estimated from intercept and the slope of the Yoon-Nelson graphs respectively at various bed height, concentrations, and biogas flow rates as per Eqs. (17) and (18).

$$k_{YN} = Slope \tag{17}$$

$$\tau_{kY} = Intercept \tag{18}$$

3. Results and discussion

3.1. Adsorption equilibrium isotherms

The equilibrium adsorption isotherms were examined via

Table 3
Summarized isotherm parameters for the adsorption of carbon dioxide from biogas during on-site experiments.

Model	Langmuir isotherm				Freundlich isotherm		
Parameters	qmax mg/g)	KL (L/mg)	RL	R^2	kf	n	R^2
CO_2	4.36	15	2.16×10^{-3}	0.97	6.02	0.6	0.97

Model	Jovanovich isotherm		
Parameters	qmax mg/g)	Kj (L/g	R^2
CO_2	2.54	0.003	0.882

Table 2
Fixed bed column models used in the current study.

Models	Nonlinear	Linear	Plot made	Refs.
Adams-Bohart	$T = \left[\frac{N_{oz}}{C_{ov}}\right] - In\frac{\left(\frac{C_o}{C_t} - 1\right)}{C_o k_{AB}}$	$In\left(\frac{C_t}{C_o}\right) = \frac{k_{BA}N_oL}{U} - k_{BA}C_o t$	$In\left(\frac{C_t}{C_o}\right) Vs\ t$	Hanbali et al. (2014)
Thomas	$\frac{C_t}{C_o} = \frac{1}{[1 + exp(k_{Th}\ q_{Th}m)]} - k_{Th}C_o t$	$In\left(\frac{C_t}{C_o} - 1\right) = \left(\frac{k_{Th}q_{Th}m}{Q}\right) - k_{Th}C_o t$	$In\left(\frac{C_o}{C_t}1\right)$ Vs t	Chen et al. (2012)
Yoon-Nelson	$\frac{C_t}{C_o} = \frac{1}{1 + e^{KYN(\tau - T)}}$	$In\left(\frac{C_t}{Co - C_t} = K_{YN}t - \tau K_{YN}\right.$	$In\left(\frac{C_t}{C_o - C_t}\right) Vs\ t$	Chen et al. (2012)

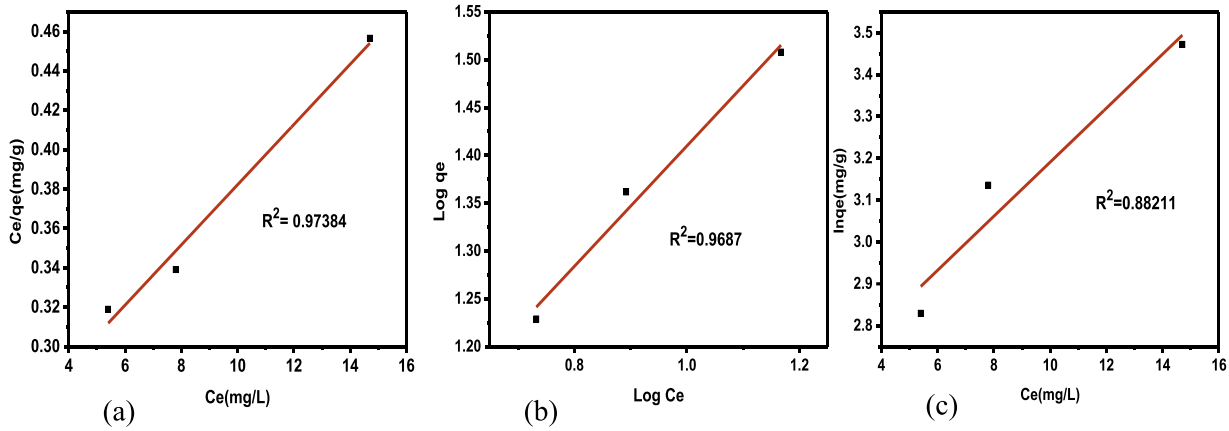


Fig. 3. Adsorption isotherm plots for biogas upgrading (a) Langmuir (b) Freundlich (c) Jovanovich isotherms.

Freundlich, Langmuir, and Jovanovich's isotherms models to investigate the interaction way of behaving between active mesoporous sites of calcined eggshells as surfaces and the carbon dioxide. These isotherm give the relationship between the equilibrium amounts of carbon dioxide adsorbed, and that are in the adsorbent phase.

3.1.1. The Langmuir adsorption isotherm

The parameters for Langmuir isotherm are summarized in Table 3 were calculated using Eqs. (1)-(3) to give the graphs shown in Fig. 3**(a).** The slope and intercept of linearized plot for Langmuir Ce/qe against Ce were applied to acquire the value for RL, KL, R^2 and qm. The usefulness of adsorption was worked out by the separation factor value RL. Scientifically when RL=1 there is a linear adsorption, RL>1 is considered an unfavorable adsorption, favorable adsorption is when 0<RL<1, while RL = 0 is an irreversible (Baskaralingam et al., 2006). Based on the values of R^2 obtained from the carbon dioxide adsorption mechanism in Table 3 it shows that Langmuir isotherms fit well on carbon dioxide removal with an RL value of 0.00216 while its R^2 was 0.97384. This stipulate that the adsorption of CO_2 from biogas fitting Langmuir isotherm.

3.1.2. The Freundlich isotherm

Freundlich adsorption model described the adsorption of CO_2 from biogas for multilayer adsorption processes occurring due to heterogeneous surfaces. This model fails at high pressure, and therefore more studies are needed not only to determine the up taking of biogas impurities but also to determine the suitability of the model in the adsorption process. According to Freundlich isotherm, the surface of adsorbent material has heterogeneous energy levels indicating that can be homogenous and others can be heterogeneous. The homogenous parts behave as Langmuir. The linearized plots for log q_e Vs log C_e shown in Fig. 3**(b)** and Eqs. (5), and (6) were used to identify the value of parameters n and K_f in Table 3 providing awareness of heterogeneity and the degree of adsorption. Using this adsorption isotherm the process is favorable if $0 < 1/n < 1$ or$1 < n < 10$. On the other hand, when $n < 1$ indicates the sorption process is slow while $n = 1$ there is a linear adsorption process. The 1/n value obtained in this study was 0.6 for CO_2 removal with an R^2 of 0.97. The obtained results showed that the uptake of CO_2 fits well with this isotherm as it had a correlation coefficient near 1 and the values for 1/n were in a range of $0 < 1/n < 1$ which is in line with the literature (Chen et al., 2012). It was concluded that the Freundlich isotherm was capable to predict the adsorption of CO_2 from biogas.

3.1.3. The Jovanovich adsorption isotherm

The Jovanovich adsorption isotherm was assessed and the obtained results are outlined in Table 3. A graph of In qe vs Ce Fig. 3**(c)** and equations were applied to find the adsorption isotherm parameters using the experimental statistics. From the results attained through a plot of Jovanovich isotherm the adsorbent capacity is 2.54 mg/g for carbon dioxide removal (Table 3) with a correlation coefficient of 0.88211. The less q_{max} value shows that the adsorbent materials has a weak sorption capacity (Ragadhita and Nandiyanto, 2021). It concluded that the Jovanovich adsorption isotherm was not good to speculate the adsorption of carbon dioxide from biogas.

3.2. Kinetics of adsorption

The kinetics of removal of CO_2 from biogas using calcined eggshell waste was studied in a room environment. The experimental results were fitted into four different kinetic models: pseudo-first order, pseudo-second order, intra-particle diffusion, and Elovich models. Mathematical equations were transfigured into linear forms, from which regressions were obtained from the experimental data. Finally, the value of correlation coefficient R^2 and q_{max} were used to assess the correlation of the data from on-site experiments with the adsorption kinetics model.

3.2.1. Pseudo-first order

The model is rational only when the adsorption kinetics are governed by surface reaction and there is a low concentration of adsorbate or excess adsorbent mass (Vareda, 2023) and suggests occupancy of only one active surface site by the CO_2 (adsorbate) from biogas. The

Table 4
Adsorption kinetics model parameters for the four models on CO_2 removal.

Pseudo-First order			Pseudo-second order			Elovich model		
k_1	R^2	qe(mg/g)	k_2	qe(mg/g)	R^2	α	β	R^2
2.14×10^{-4}	0.893	1.01	3.2E-06	13.64	0.599	0.008	9.1	0.922

Intra-particle			
Parameters	k_{id}	c	R^2
Value	34	98	0.977

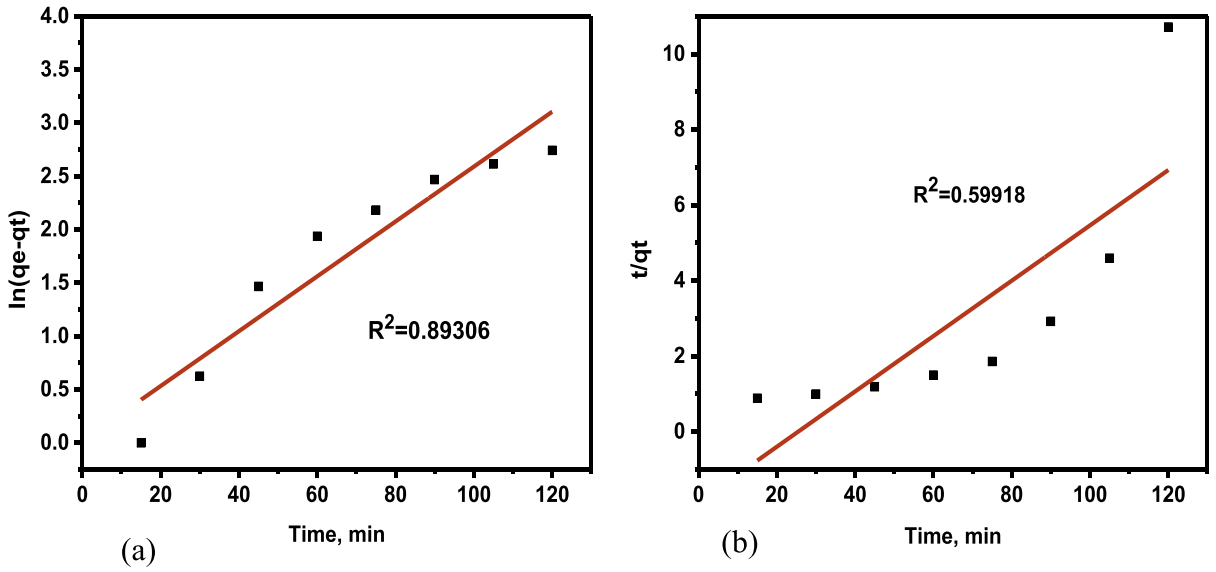


Fig. 4. Adsorption kinetics model for biogas upgrading (a) Pseudo-first (b) Pseudo-second.

first-order adsorption kinetics model is related to the adsorption process being only dependent on the amount of adsorbate, a diffusion-controlled process. Linear Pseudo-first order (PFO) model needs a preliminary knowledge of q_e to estimate the other necessary parameters using an equation. On the other hand, qe can be approximated by deducing the onsite experiment data to $t=\infty$. All these can be possible by making an assumption of an initial value of qe and performing a linear fitting to look for k_1 and a new value of qe. The values of qe, k_1 as well and R obtained using pseudo-first-order kinetics for CO_2 removal from biogas are as indicated in Table 4 and the model can be shown in linear form in Fig. 4**a**. The model explained that there is a direct relationship between the adsorption rate and the surface of adsorption of the sorbent material. The fitness of the model can be obtained when the value of qe (mg/g) calculated approaches the experimental qe (mg/g). The calculated qe for carbon dioxide did not match with the experimental qe, and thus the model did not fit the on-site experimental data.

3.2.2. *Pseudo-second order*

The pseudo-second order can be written in linear form and the necessary parameters can be obtained as indicated in Table 4. The data from the on-site experiment were used to plot Fig. 4**b** and the necessary parameters were deduced from the figure. The adsorption kinetics studies of CO_2 removal from biogas using pseudo-second order were made in batch adsorption systems under room temperature. It can be noticed that the adsorption of CO_2 from biogas increased rapidly in the first 50 min Fig. 4**b.** The adsorption kinetic parameters, obtained from the second-order kinetics equation, are represented in Table 4. The values of the linear plots (R^2) for carbon dioxide uptake using the Pseudo-second order (PSO) were 0.599 for carbon dioxide uptake. The obtained values of R^2, k, and qe show that the pseudo-second-order did not fit the data from the experiment. However, the pseudo-second-order can be more applicable for carbon dioxide removal at a time of less than 50 min (Moussout et al., 2018; Lakhanpal et al., 2021). Generally, the calculated qe and R^2 for carbon dioxide proved that the model did not fit the on-site experimental data.

3.2.3. *Elovich*

The summary of the parameters obtained in this model for carbon dioxide removal is in Table 3 and Fig. 5**a**. The values of the linear regression plots for carbon dioxide uptake using the Elovich model were

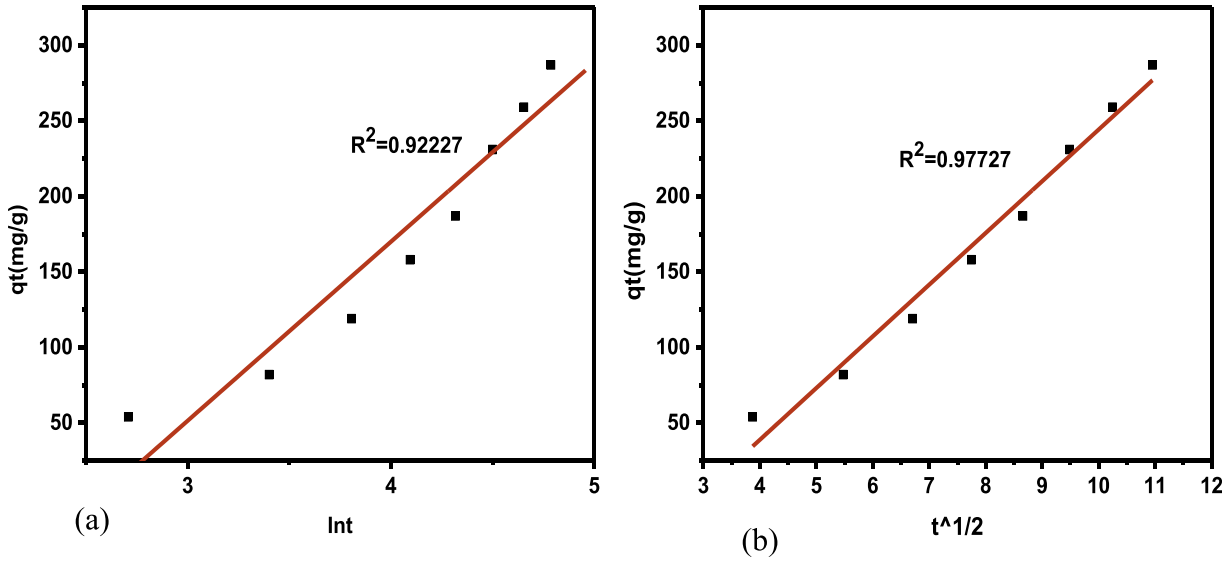


Fig. 5. Adsorption kinetics model for biogas upgrading (a) Elovich (b) Intra-particle diffusion.

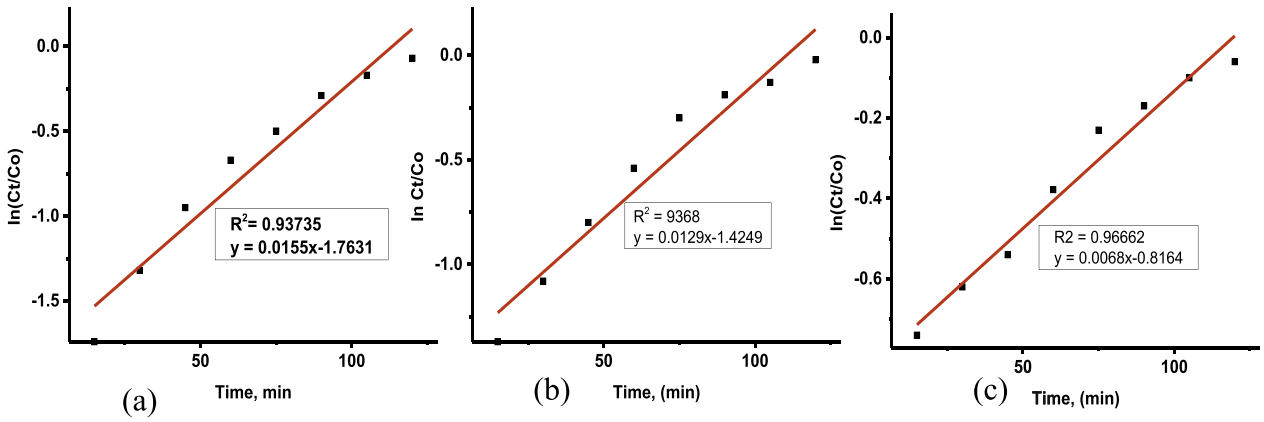


Fig. 6. Adams–Bohart model for the removal of CO_2 from biogas (a) 75 g (b) 50 g and (c) 25 g.

0.92227. The Elovich model pressumes the sites for adsorption rise exponentially with a multilayer adsorption process through the kinetics principles. The model concludes that the rate of adsorption decreases exponentially with the increase in the number of calcined eggshell waste following the mechanism of chemisorption. The kinetics of this model is described by α, β, and R^2 where the necessary parameters can be obtained from the linear plots of both carbon dioxide. It was noted that the obtained value of R^2 for carbon dioxide removal is closer to unity compared to PFO and PSO. This showed that there is a good chemisorption interaction between carbon dioxide with the sorbent material. The values of β and α were obtained from the graph of qt vs Int Fig. 5**a**. The corresponding parameter values are tabulated in Table 4, which indicates that the Elovich kinetics model provides a moderate fit to the on-site data based on the R^2 values of less than 0.95.

It was observed that there is minimal adsorption between the initial adsorption rate of carbon dioxide using the calcinated eggshells (0.008 mg/g min). On the other hand, the desorption rate (β) of carbon dioxide using calcined eggshell waste seems to be higher in CO_2 uptake from biogas. This suggested that the rate of desorption of carbon dioxide using calcined eggshells is higher (Yakub et al., 2020).

3.2.4. Intra-particle diffusion

The Intra-particle diffusion equation demonstrates a linear regression relationship between sorption ability and the square root of time Fig. 5**b.** It shows a graph of qt versus $t^{\wedge 1/2}$ for carbon dioxide adsorption in calcined eggshell waste. The plot propose that the process of adsorption takes place via surface adsorption and intra-particle. The k_{id} and c parameters can be determined from the intercept and the slope of the plot of q_t versus $t^{\wedge 1/2}$. If a linear regression fitting is noticed in the plot of q_t vs $t^{\wedge 1/2}$ and passes via the origin point it is probably to verify that there was a mass transfer process taking place in the adsorption process (Vinhal et al., 2017). The variables derived from the plots are tabulated in Table 4. The values of R^2 for carbon dioxide removal from biogas are closer to unity compared to other models and thus suggested the mechanism for the diffusion of carbon dioxide using calcined eggshell waste. The values of k_{id} obtained and c (mg/g) depict the depth of the boundary and therefore suggest that both sorbents can be applied for the chemisorption process. Thus, the model fits well the on-site experimental data in comparison to other models.

Whereas k_1 is the rate constant for pseudo-first-order, (min^{-1}), q_t is the adsorption capacity at a certain time, k_2 is rate constant for pseudo-second-order (g/mg.min), K_{id} is intra-particle diffusion rate mg/g.$min^{0.5}$, t is time, C is constant parameter, β is the desorption constant (mg/g) and α is the initial adsorption rate (mg/g.min),

3.3. Breakthrough curves modeling

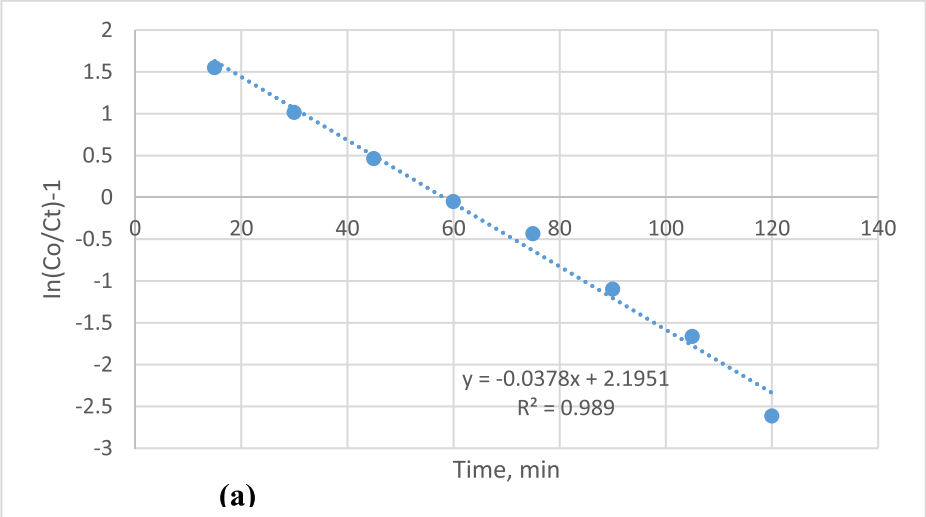
Three models were employed in the present study Adams-Bohart, Thomas, and Yoon-Nelson models, which were developed to explain and possibly to assume the dynamic behavior of the fixed-bed in column. Various variables were obtained from these models, which explains the performance of the fixed-bed adsorption unit. The fixed bed columns are admired as their model equation can be linearized authorizing their unknown variables to be evaluated using linear regression analysis. In the current study, the three fixed models were used to fit the data acquired from on-site experiments, and they were compared using the coefficient of determination R^2 (Chu, 2020).

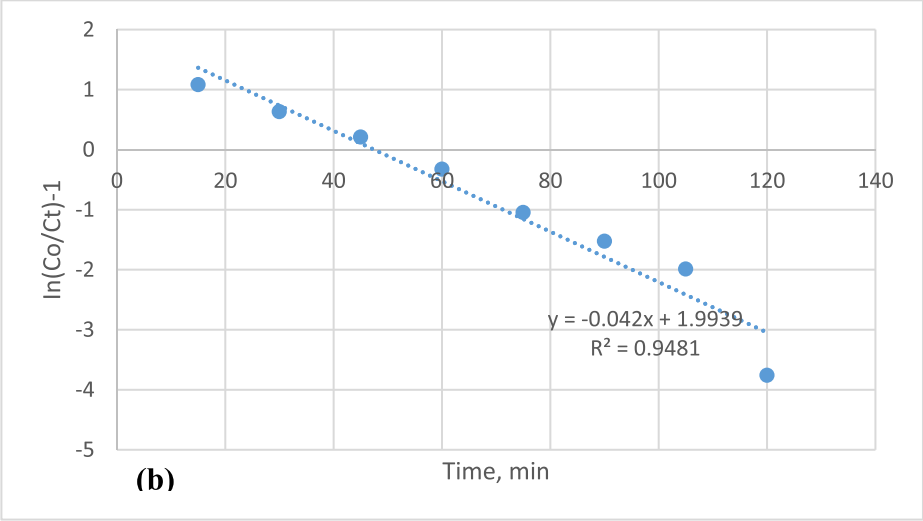
3.3.1. Adams–Bohart model

To prove the adsorption ability of the adsorbent material the continuous fixed column adsorption experiment was conducted at different initial concentrations of the sorbents with different bed heights 75 g (10 cm), 50 g (7 cm), and 25 g (4 cm). Fig. 6**(a-c)** indicate the column adsorption capacity and the breakthrough curves for calcined eggshells for biogas upgrading. The values of K_{AB} (coefficient of mass transfer) and N_o (maximum adsorption capacity) were obtained from the intercept and slope of Adams-Bohart plot at various bed heights, and concentrations as indicated in Table 5. The values of k_{AB} were noticed to increase with the increase in concentration and bed height along with the correlation coefficients (R^2). Generally, it indicates the system kinetics was influenced by external mass transfer (Ahmad and Hameed, 2010) while its value decreased with an increase in bed height for calcined eggshells sorbent which is in line with (Moussout et al., 2018). The Adams–Bohart model gives a comprehensive and simple approach to evaluating and conducting the sorption-column experiment. Nevertheless, its rationality is restricted to the various conditions used

Table 5
Variables of the three models under different conditions using linear regression analysis on biogas upgrading.

Adams–Bohart Model - CO_2 adsorption					Thomas model			Yoon Nelson Model		
Co (%)	Z (cm)	kAB*10–4 (L/mg min)	N_o (mg/L)	R^2	$k_{Th}*10^{-6}$ (mL/ min mg)	qo (mL/min mg)	R^2	$k_{YN}*10^{-2}(min^{-1})$	ɼ (min)	R^2
30.8	4	2.2	28.15	0.9463	9.12	16,257	0.9374	4.2	58	0.9629
30.8	7	4.0	15.00	0.9458	1.36	14,661	0.9368	3.8	47	0.9119
30.8	10	5.0	10.56	0.9714	1.23	11,924	0.9666	2.8	25	0.8722





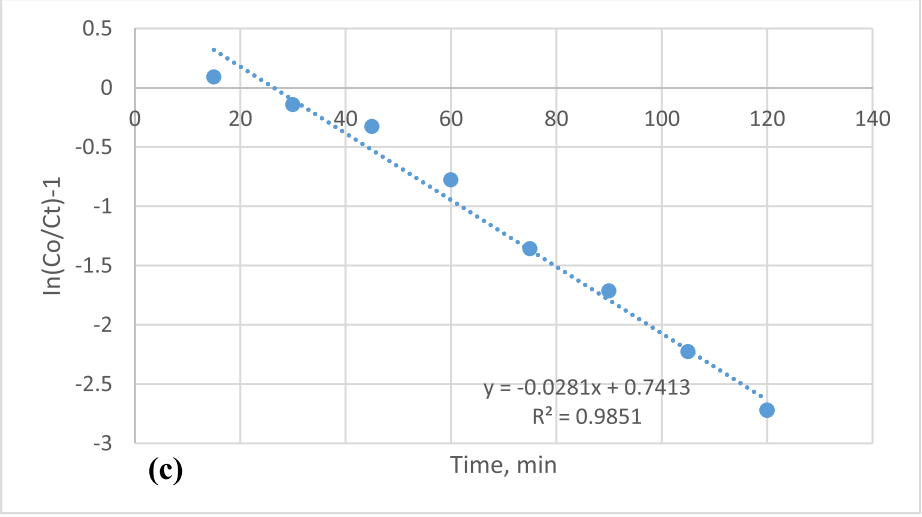
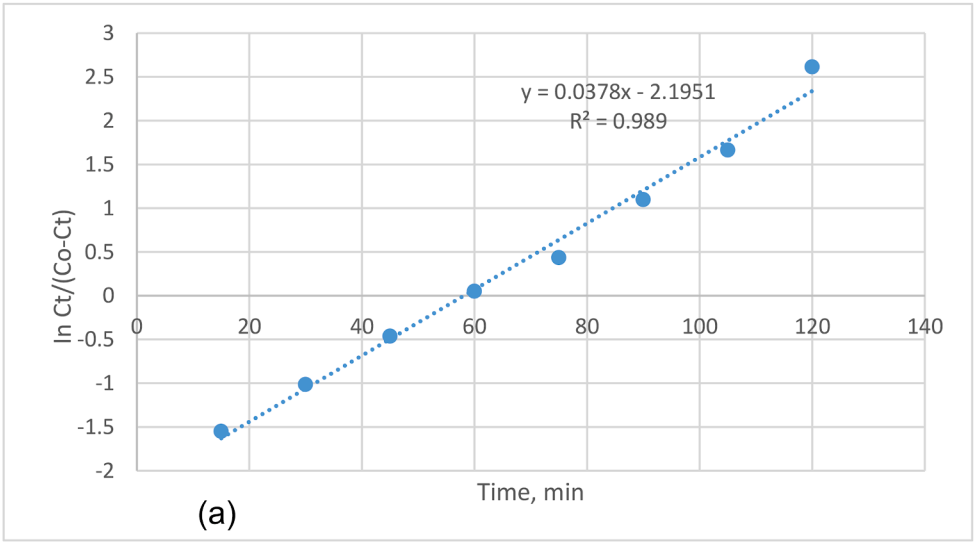
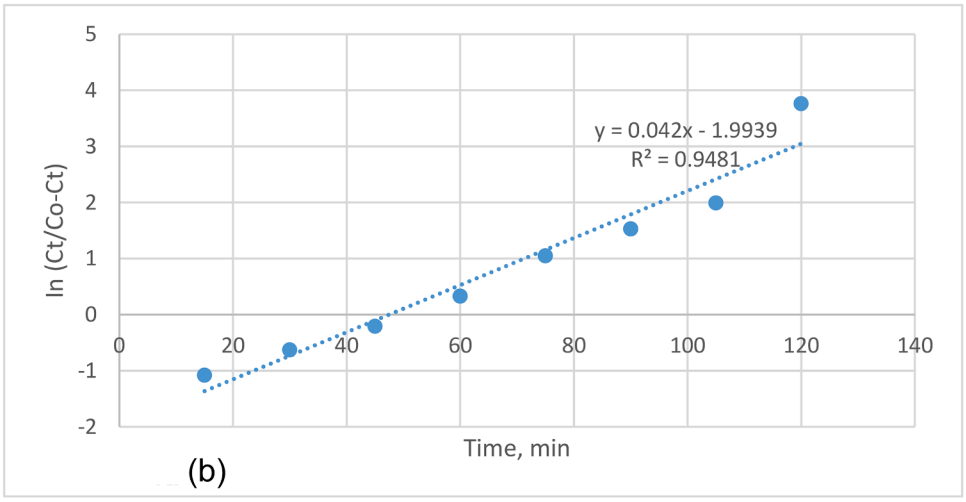


Fig. 7. Biogas upgrading curve at a different height (a) 10, (b) 7, and, (c) 4 cm.





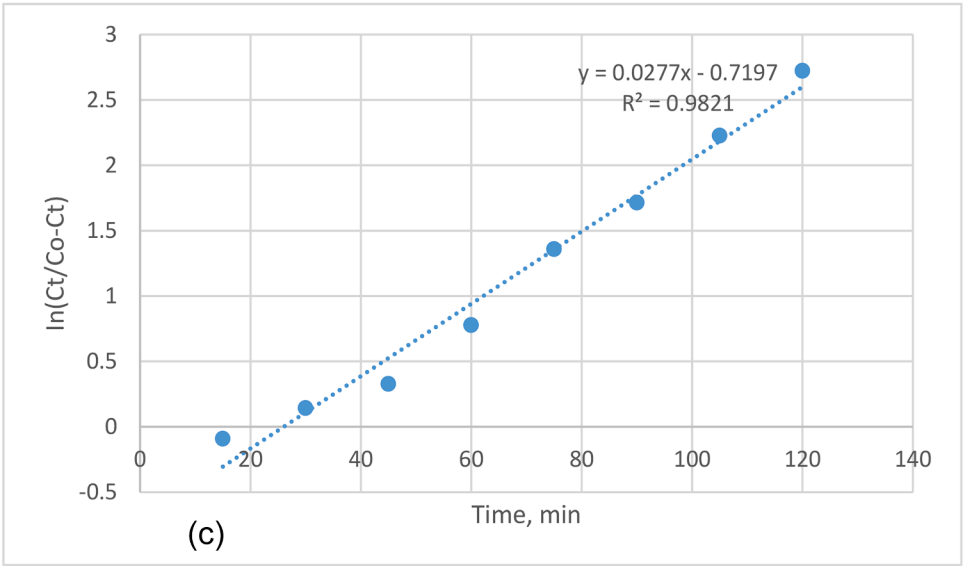


Fig. 8. Biogas upgrading curve at a different height (a) 10, (b) 7, and, (c) 4 cm.

3.3.2. Thomas model

Thomas model was applied in fitting the on-site experiment data, coefficients and relative constants were deduced via linear regression analysis and the obtained results were represented in Table 5 which were obtained using Fig. 7, and was observed that the Thomas mode R^2 ranged from 0.9481- 0.989. From Table 5 it can be noticed that the k_{Th} values decreased with the increase in the bed depth while an increase in flow rate and concentration leads to an increase in both q_o and k_{TH}. Based on the experimental data, as bed height increased from 4 cm (Fig. 7**a**), 7 cm (Fig. 7**b**), and 10 cm (Fig. 7**c**) the values of q_o and k_{TH} decreased, which is supported by literature (Omitola et al., 2022). It was accredited as the kinetics for adsorption due to difference in concentration. Therefore, the higher the bed depth, higher influent concentration, and lower flow rate would increase the adsorption of CO_2 from biogas on the fixed bed adsorption column. The experimental data for carbon dioxide removal were found to be well fitted with the Thomas model with coefficients ranges from 0.95 to 0.98. Thomas model breakthrough graphs for the elimination of CO_2 from biogas at different bed heights.

3.3.3. Yoon Nelson model

The parameters such as ɾ (time required for 50 % carbon dioxide breakthrough) and rate constant (k_{YN}) values were estimated from the graph using the intercept and slope and as shown in Table 5, obtained from Fig. 8**(a-c).** The k_{YN} values were noticed to increase with the decrease in bed height and flow rate while values of τ decrease with the increase in height of the bed and concentration. An increase in τ as the flow rate increases indicates that as the flow rate increases, the rate at which the adsorbent bed is consumed is slower which is advantageous for the sorption process of the material. The value of ɾ represents the time at which 50 % of the adsorbent in the column would reach a breakthrough point, as the value becomes higher, the better the performance of the bed column, similar information was reported by Omitola et al. (2022), Yagub et al. (2014). Yoon- Nelson breakthrough curves for the removal of CO_2 from biogas at various bed heights.

Thus; the influence of adsorbent mass on the elimination of CO_2 from biogas was studied using masses 75, 50, and 25 g, and was conducted and it was found that in the Adam-Bohart model, the increase in amount of calcined eggshells adsorbent leads to the increase of K_{AB} while a decrease in N_o. In the Thomas-Bohart, model increase in mass leads to a decrease in both K_{TH} and q_o. In Yoon Nelson, an increase in the mass of both sorbents leads to the decrease of K_{YN} and ɾ, the parameters for both models were deduced.

3.4. Summary of the main research findings

The important results drawn from the current study show that the onsite experiment for biogas upgrading was successfully fitted into Langmuir isotherm with RL of 2.16×10^{-3}, Freundlich isotherm with intensity of adsorption or surface heterogeneity (n) of 0.6, and Jovanovich isotherm with Jovanovich constant (Kj) of 0.003. The regression coefficient of 0.97 for both Langmuir and Freundlich was obtained using plots drawn from OriginPro while for Jovanovich was 0.882. Thus, Freundlich and Langmuir were the best models that fit into the on-site experimental data. Furthermore, the kinetics of adsorption of carbon dioxide from biogas were studied via pseudo-first order, pseudo-second order, intra-particle diffusion, and Elovich models. The value of k_1 (2.14×10^{-4}), q_e 1.01 mg/g, and R^2 0.893 for the first order kinetics were obtained which suggests that it doesn't fit well to the on-site experimental data as the calculated q_e for carbon dioxide did not match with the experimental q_e, and thus the model didn't fit the on-site experimental data. The second pseudo-order reaction shows that q_e (13.64 mg/g) while R^2 was 0.599 thus the model did not fit as its coefficient regression was less than. On the other hand, Elovich's initial adsorption rate (α) of 0.008 was obtained which indicated the model did not fit the data from the experiment. The Intra-particle diffusion model had a k_{id} of 34 and R^2 of 0.977 thus the model fits well. Breakthrough analysis was done using the Adams–Bohart model, Thomas model, and Yoon Nelson, based on R^2 values from both models it was proved that Yoon Nelson's Model fitted well with the experimental data with an R^2 of 0.989.

Table 6
Comparison of performance of various adsorbents used for CO_2 removal.

Sorbent	Purposes	Isotherms fitted	Kinetics	Refs.
Activated carbon	Adsorption of a two mixture of 12 % CO_2 + 88 % N_2	Langmuir isotherm	–	Nadimi et al. (2021)
Activated carbon	Removal of CO_2 from biogas	Langmuir, Freundlich and Sips	Intra-particle diffusion	Rainone et al. (2021)
Activated carbon	Elimination of CO_2 from biogas	–	pseudo-second order	Abdullahi et al. (2018)
Zeolite CBV 8014	Carbon dioxide removal from biogas	–	pseudo-second order	Abdullahi et al. (2018)
Natural zeolite	Carbon dioxide removal from biogas	Langmuir	pseudo-first order	Sidabutar and Iriany (2018)
Cobalt-Based Metal-Organic Framework	Removal of CO_2 from biogas	Toth	pseudo-first order	Ismail et al. (2023)
Calcined eggshell waste	Carbon dioxide removal from biogas	Langmuir and Freundlich	Intra-particle diffusion	This study

3.5. Comparison of the current study with the literature

The removal of CO_2 from biogas using calcined eggshell waste was compared with other studies in the literature based on the best model and adsorption kinetics that fit well as per Table 6. From the table, it was observed that the nature of the material, chemical behavior, and its physical properties determine the best-fitted model and adsorption kinetics.

3.6. Limitations of the study and future perspective

This study evaluated the performance of calcined eggshell waste which is considered a waste material. However, it is a valuable resource that can be used for biogas purification and contribute to achieving circular economy and environmental safety. There are many types of wastes but only calcined eggshells were employed in the study. In addition, the study applied the adsorbent in the removal of carbon dioxide from raw biogas, biogas has other contaminants. The study was conducted using a laboratory-scale experimental setup and only a limited number of variables could be evaluated. For the practical large-scale application of this adsorbent, there is need for pilot studies and eventually full-scale studies. More rigorous column adsorption studies and models should be applied especially at large scale. Future studies should also evaluate the performance of other related waste materials for comparison.

4. Conclusions

Lime derived from eggshell waste was successfully used in biogas upgrading in a fixed-bed column for the removal of carbon dioxide. The experimental data was modeled using adsorption isotherms, kinetic models, and breakthrough curve models to extract useful design parameters for scale-up. The Langmuir and Freundlich isotherm fitted well with the experimental data with RL of 0.00216, R^2 of 0.974 and $n = 0.6$, and R^2 of 0.97, respectively. The adsorption kinetics indicate that the experimental data best fitted the intra-particle diffusion model with an

R^2 of 0.97. Yoon Nelson's model best fitted the experimental data with an R^2 of 0.989. The extracted design parameters can be readily applied in the design of pilot and large-scale adsorption columns for biogas purification. The calcined eggshell waste is a low-cost sorbent, with excellent upgrading ability and addresses the problem of waste management.

Data availability

Data used to support these findings are available when they are required.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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