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Comparative studies on the kinetics of biogas purification using activated Carbon and Zeolite

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Abstract. The study focus on CO_2 adsorption using activated carbon and zeolite for the purification of the produced biogas and developed kinetic study for the AC and zeolite CBV 8014 adsorption. Furthermore, model equations were developed for the upgraded biogas purity as a function of adsorption time and adsorbent dosage to predict biogas purity. The adsorbents and kinetic study was evaluated using a cylindrical glass column. The biogas produced from chicken droppings and cow dung were characterized and found to contains CH_4 gas (53.26%), CO_2 (33.44%) and other gases in small quantity. The highest purity of 84.34% and 91.01% was obtained for AC and zeolite CBV 8014 respectively at 20 min adsorption time and the model equations developed well represent the experimental data. The adsorption capacity of the adsorbents was evaluated using a cylindrical glass column and was found to be in the order of zeolite CBV 8014 (91.01%) > AC (84.34%) at 0 – 20 min adsorption time with adsorption increasing over time. The kinetic study of the biogas purification shows that the CO_2 adsorption onto AC and zeolite CBV 8014 obeys the pseudo-second-order model, due to its regression coefficient (R^2) value closer to unity. The equilibrium and kinetic study of CO_2 adsorption onto AC and zeolite CBV 8014 shows that the magnitude of activation energy for both adsorbent are lesser than 40 kJ/mol, indicating the occurrence of physisorption mechanism. The intra-particle diffusion model also indicates that intra-particle diffusion is not the sole rate-limiting step in the adsorption process for both adsorbent (AC and zeolite CBV 804). The zeolite CBV 8014 has higher CO_2 adsorption capacity than AC.

Keywords: *Activated Carbon, Adsorption, Biogas, Carbon dioxide, Zeolite CBV 8014.*

1. INTRODUCTION
Globally, energy is known to be an integral part of any developed economic and society. It has been a fundamental factor in poverty alleviation of any society [1]. The availability and access to energy ingredient of national development and in improving the standard of living of any nation. However, global energy demand has continued to rise, while availability and access to energy are dwindling. The dependence on petroleum based fossil fuel and petroleum products as the only chief source of energy

has led to global climatic changes, environmental degradation and pollution, increase in sea level as a result of the melting of the ice caps resulting from temperature increase. This problems therefore, lead to environmental and health problems. Petroleum based fossil fuel, though finite, it damages the ecosystem in many and diverse ways, acid rain, destruction of the ozone layer, and exerting greater influences upon biogeochemical cycles [2]. These has led credence to the need to turn energy systems towards sustainability.

Africa as a content with very weak law against environmental pollution is facing greater environmental challenges such as; flooding, air and water pollution caused by degradation of the ecosystem due to pollution from petroleum fossil fuel. Reference [3] argued that less than 10% of the total population of 21 sub-Saharan African countries have access to electricity. Thus, the need for alternative renewable sources of energy from renewable and sustainable locally available resources cannot be over emphasized. In developing countries like Nigeria, lack of access to adequate energy has remained a major hindrance to improving key indicators of human development [4]. Currently over 60% of the population in Nigeria depends almost entirely on wood as sources of energy for cooking, heating and agro-processing activities. Furthermore, electricity which is a major requirement for modern economies is not readily available and or better still unreliable and in short supply. Thus, there is an urgent need to sources alternative renewable forms of energy before the petroleum based oil supplies run dry. Hence, in the midterm 2008 – 2015 and long term, 2016 – 2025, Nigeria envisions an energy transition from crude oil to renewable energy [5]. However, an alternative source of energy must be technically feasible, economically competitive, environmentally acceptable and readily available and accessible. One key and possible alternative to petroleum based fuel is the use of biofuel resources.

Biofuel resources are key renewable energy sources and relatively distributed. The production of biofuels has become a global agenda. Biofuel includes, biogas, bioethanol and biodiesel. Biogas is can be produce from many different environments to include sewage sludge, landfills and during anaerobic degradation of biomass material [6]. Biogas comprises mainly of CH_4 (methane: 45 – 75% vol.), CO_2 (carbon dioxide: 25-55% vol.), and other compounds in trace amount to include H_2S (hydrogen sulfide: a couple of thousand parts per million), H_2O and other trace gas compounds (N_2, CO, O_2 etc.) [7]. Methane is a potent greenhouse gas if emitted into the atmosphere, however it also represent a valuable renewable source of energy, with the potential to reduce Green House Gas (GHG) emissions when it is collected and substituted for petroleum based fuels.

In Nigeria, biogas utilization is on the low side despite huge reserves of biogas feedstock within the country. For example, animal and agricultural waste and residues generated in Nigeria stood at a million tons per day [2]. This implies that from animal and agricultural waste alone, Nigeria can generate over 4.75×10^9 MJ per annum indicating that that a large proportion of Nigeria's energy need can be sourced from biogas. In order to upgrade raw biogas to a high purity of over 95% methane to ensure environmentally friendly energy source and reduce emission of large GHG (CO_2), CO_2 generated from the gas need to be captured. Amine based and physical adsorption are the most commonly used for CO_2 capture.

Studies have shown that amine based adsorbents of CO_2 are associated with several problems to includes; high regeneration energy requirement, corrosive tendency and degradation of amines [9]. Selecting a suitable separation process is determined by adsorption and diffusion activity which characterizes most activated carbon (AC) materials also limits their applications [10]. However, many studies have documented successful use of AC and zeolite for CO_2 capture. Reference [10] reported the comparative studies of CO_2 capture using acid and base modified activated carbon from sugarcane bagasse and observed that acid and base modified sugarcane bagasse AC produced have enhanced capacity for CO_2 adsorption. Several studies on the use of AC for CO_2 adsorption have shown that AC are with a highly developed porous structure with good adsorption properties. Therefore, the relative abundance, low cost, minimal sensitivity to moisture and high thermal stability make AC to have distinctive characteristics and also placed it in a vantage position as an exceptionally viable and cheap adsorbent for CO_2 capture.

Biogas is said to comprise of methane (45-75% by volume CH_4), carbon dioxide (25-55% vol. CO_2) and trace quantities of hydrogen sulfide (H_2S), ammonia (NH_3), volatile organic compounds (VOCs), siloxanes, carbon monoxide (CO), oxygen (O_2), and water (H_2O) [8]. The concentration of CO_2 in the atmosphere was projected to increase from pre-industrial concentration of 270 ppm to a high concentration of 407 ppm as of mid-2017 [11]. There is therefore the need to prevent the release of large quantities of CO_2 into the atmosphere. CO_2 emissions to the atmosphere can be effectively reduced through several methods which include extraction and sequestration from GH gases emission with chemical solvents and physical adsorption method commonly used methods of GHG emission. This necessitate the need to investigate and optimized the purification (CO_2 capture) of biogas produced from animal waste. The aim of this research work is to investigate the production of biogas and kinetic study of CO_2 capture from biogas produced from animal waste.

2. METHODOLOGY

2.1. *Materials*
The materials and major equipment used in the course of the research are Cow dung and Chicken Droppings obtained from FUT Minna and Minna respectively in Niger State. The Activated Carbon was obtained from Kaduna Polytechnic and Zeolite CBV 8014 from Chemical Engineering Department, FUT Minna. Analytical grade ammonium hydroxide and distilled water were obtained from Chemical Engineering Laboratory, Kaduna Polytechnic and Chemical Engineering Laboratory, FUT Minna.

2.2. *Sample Collection*
Cow dung was collected from the Federal University of Technology Farm, Gidan Kwano, Minna, Niger State while chicken droppings were collected from the poultry farm in Minna. The cow dung and chicken droppings collected were weighed according to the calculated ratio and mixed together to ensure homogeneity of the substrate.

2.3. *Substrate Preparation and Biogas Production*
The experiments were carried using an improvise batch laboratory scale bio-digester (10 liters sea way gallon). The digesters was closed with a cork and a puncture hole was bored at the top of the cork. A rubber tube of 10 mm in diameter was inserted through the hole and then sealed with gum which made the digester air tight completely (anaerobic).

The feed stocks used in this experiment are the prepared cow dung and chicken droppings above. From the experiment carried out by [12] shows that at 20% (1:4) and 25% (1:3) concentration of cow dung and chicken dropping respectively gives the highest biogas yield at ambient temperature. Therefore, 1kg (1000 g) of chicken dropping were mixed together with 4 liters (4000 mL) of distilled water to give a ratio of 1:4 and substrate concentration of 20%. Also 1 kg (1000 g) of cow dung with 3 liters (3000 mL) of water which give a ratio of 1:3 and substrate concentration of 25% was also prepared and mixed together. The mixing of both biomass were thoroughly carried out to ensure homogeneity and the substrate were charged into the 10 liters batch type digester. The digester was connected to 16 rim tire tube to collect the biogas generated for about 22 days. The anaerobic digestion take place at ambient temperature of 27 – 32 ^{o}C.

2.4. *Test for the Presence of Methane in Biogas Produced*
The presence of methane was tested by lighting flame on a Bunsen burner connected to the biogas reservoir. The gas that came out from the reservoir burns with blue flame which indicate the presence of methane (CH_4).

2.5. *Carbon (IV) Oxide Adsorption*
The glass adsorption column used for this study was fabricated in SEDI, Minna. The adsorption of CO_2 was carried out in the fabricated glass column while activated carbon (AC) and Zeolite CBV

8014 were used as adsorbents. The adsorption column was held firmly tight to a designed stand and biogas delivery pipe was connected from biogas storage (tire tube) to the top of the adsorption column that contains the adsorbent. Then the purified biogas pass through the delivery tube to the blood bag (purified biogas storage) for analysis. In order to optimize the CO_2 capture, adsorbent dosage and contact time were varied from 1g – 4g and 0 – 20 min respectively.

   1 g AC of particle size 0.8 – 1 mm was poured into the adsorption column and firmly corked. The apparatus was connected to the tire tube containing the biogas produced, then the biogas flow rate control valve was opened and the gas was released in to the adsorption column at the rate of about 60 mL/min and held at atmospheric pressure and ambient temperature, over the time intervals of 2.5, 5, 7.5, 10, 15 and 20 min. The treated biogas was then collected in the treated biogas collector (blood bag). The weights of the AC samples were measured with an electronic weighing balance at every time intervals to note the difference in weight of the AC samples until a constant weight was reached, which indicates its maximum adsorption capacity. The same procedure was repeated for the other AC samples of 2g, 3g and 4g. After the completion of the AC sample, the same procedure was also repeated using Zeolite CBV 8014 as adsorbent for 1 – 4 g Zeolite sample and time intervals of 2.5, 5, 7.5, 10, 15 and 20 min. Prior to usage, the zeolite was activated with ammonium hydroxide (NH_4OH) in an oven at a temperature of 550 ^{o}C for 2 hrs. The overall experiment for each adsorbent sample comprise of 16 runs each obtained from a full factorial experimental design. The amount of CO_2 adsorbed from each experimental run were calculated from equation 1 given by [12].

$$\text{Amount of CO2 Adsorbed} = \frac{Q_t(mg) - Q_o(mg)}{Q_o} \tag{1}$$

where Q_o = initial weight of adsorbent before adsorption, Q_t = final weight of adsorbent after adsorption at time, t

2.6. Adsorption Kinetics

Adsorption kinetics studies gives the capacity of the adsorbent and the equilibrium relationships between adsorbent and adsorbate described by adsorption isotherms which are usually the ratio between the quantity adsorbed and the remaining in solution at fixed temperature at equilibrium [13]. A sorption isotherm (also adsorption isotherm) describes the equilibrium of the sorption of a material at a surface (more general at a surface boundary) at constant temperature. It represents the amount of material bound at the surface (the sorbate) as a function of the material present in the gas phase and/or in the solution. The adsorption kinetics for AC and zeolite CBV 8014 were further studied using the model discuss below.

2.6.1. Lagergren's pseudo-first-order and pseudo-second order models.
Lagergren's pseudo-first-order and pseudo-second order models were used to test the kinetic behavior of the two adsorbent and the conformity of the experimental work and kinetic model were analyzed by the regression coefficient (R^2) values. The linearized form of the Lagergren pseudo-first-order model is generally expressed by equation 2 given by [14].

$$\log(q_e - q_t) = \log q_e - \frac{k_1(t)}{2.0303} \tag{2}$$

where qe and qt = the amount of CO_2 adsorbed in mg/g at equilibrium and at time t, respectively, k1 = the rate constant of pseudo-first-order model (min-1).
According to [14], the pseudo-second-order model and initial rate of adsorption, h (mg/g.min) is given by equation 3.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e{}^2} + \frac{1(t)}{q_t} = \frac{t}{q_t} = \frac{1}{h} + \frac{1(t)}{q_t} \tag{3}$$

$$\text{where} \qquad\qquad\qquad h = k_2 q e^2 \tag{4}$$

According to [14], applying the pseudo-second-order kinetic model in the adsorption process result in the plot of 1/qt against time (t) which gives a straight line with 1/qe and 1/h as the slope and y-intercept respectively.

2.6.2. Activation energy. According to [14], the Arrhenius equation shown in equation 5 below can be used to estimate the activation energy of the adsorption process.

$$\ln k = -\frac{E_a}{RT} + \ln k_o \qquad (5)$$

where k = the pseudo-second-order kinetic model rate constant (g/mg.min), E_a = the activation energy of the adsorption process (J/mol), R = the gas constant (8.314 J/mol.K), T = the adsorption temperature in Kelvin, k_o = the temperature independent factor (g/mg.min).

2.6.3. Intra-particle diffusion model. Ho *et al*. [15] gives the intra-particle diffusion model as expressed by equation 6.

$$q_t = k_{id} t^{1/2} + C_i \qquad (6)$$

where qt = the amount of CO2 adsorbed at any time t (mg/g), kid = the intra-particle rate constant (mg/g.min1/2), t = the contact time (min1/2). According to [14], the adsorption process obeys the intra-particle diffusion model if a straight linear plot that passes through the origin is observed.

3. RESULTS AND DISCUSSION
3.1. Biogas Production
Table 1 present the composition of the biogas produced from chicken droppings and cow dung substrate (unpurified). The CH_4 present in the raw biogas is observed to be 53.26%, which is in conformity with the compositions of raw biogas reported by [14] for a commercial biogas plant. From Table 1, the values obtained for all component were in conformity with the standard value except for H_2 and O_2 which are higher than the standard value. The slightly higher value of H_2S as observe from Table 1 may partially be attributed to the sulfur in the substrate. In pure biogas, O_2 and H_2S content should be negligible as possible.

Table 1: Compositions of produced biogas (unpurified).

Component	Value (%)	Standard Value
Methane (CH_4)	53.26	45 – 70
Carbon (IV) Oxide (CO_2)	33.44	25 – 55
Carbon monoxide (CO)	1.26	0 – 2
Hydrogen (H_2)	3.53	0 – 2.5
Oxygen (O_2)	8.04	0 – 3
Hydrogen Sulphide (H_2S) (ppm)	4700	10 – 20000

3.2. Biogas Production
Raw biogas produced from digestion is roughly 33.44% CO_2 and other gases (CO, O_2, H_2 and H_2S), it is not high quality enough to be used as fuel gas for machinery. The corrosive nature of H2S alone is enough to destroy the internals of the machinery. Also, the need to upgrade raw biogas to a high purity of over 95% methane to ensure environmentally friendly energy source and reduce emission of large GHG generated from the gas necessitate the purification of raw biogas gas. The composition of CH_4 is taken to imply the biogas purity.

   It was observed that the biogas purity increases slightly from 53.26% – 55.96 % for an adsorption time of 0 – 20 min using 1g of AC adsorbent while biogas purity increases from 53.26% – 61.15% for an adsorption time of 0 – 20 min using 2g of AC adsorbent. For the same adsorption time, the biogas purity increases from 53.26% – 68.39% using 3g of AC adsorbent, however, highest purity of 84.34% was observed at 20 min adsorption time using 4g of AC adsorbent. This indicate that purity of CH4 gas increases with time and adsorbent dosage with 4g AC adsorbent at 20 min having the highest

purity of 84.34% using AC. This implies that more impurity gases (CO_2, CO, O_2 H_2 and H_2S) are remove with more adsorbent dosage due to availability of more adsorption site [16].

It was also observed that at adsorption time of 0 – 20 min, the purity of the biogas produced increases from 53.26% – 56.75% using 1g CBV 8014 zeolite while the biogas purity increases from 53.26% – 61.61 % at 0 – 20 min adsorption time using 2g CBV 8014 zeolite adsorbent. At the same adsorption time, biogas purity increases from 53.26% – 72.42% using 3g of CBV 8014 zeolite adsorbent while biogas purity of 91.01% was observed at adsorption time of 20 min using 4g of CBV 8014 zeolite adsorbent. This indicate that the biogas purity increases with time and increase in CBV 8014 zeolite dosage [16]. For 1 g – 2 g of both AC and CBV 8014 zeolite it was observed that there was no significant different in the biogas purity at adsorption time of 0 – 20 min. This further indicates that there is significant removal of more impurity gases (CO_2, CO, O_2, H_2 and H_2S) from 3 g – 4 g CBV 8014 zeolite dosage compare to highest of 61.61 % and 61.15% CH_4 for 1 g – 2 g CBV 8014 zeolite and AC dosage respectively. Comparing the two adsorbent (AC and zeolite CBV 8014), it was observed that the purification of raw biogas using zeolite CBV 8014 adsorbent gave a better purity compared to AC adsorbent as the adsorption time increases from 0 – 20 min. Thus indicating that the longer the contact time, the higher the removal efficiency of the adsorbents.

3.3. *Statistical Analysis*

A second-order model is useful in approximating a portion of the true response with parabolic curvature. A second-order model includes all the terms in the first-order model, plus all quadratic terms like $\beta_{11} x_1^2$ and all cross product terms like $\beta_{13} x_{1i} x_{3j}$. It is usually expressed as equation 7;

$$\sum_{j=1}^{q} \beta_j x_j + \sum_{j=1}^{q} \beta_{jj} x_j^2 + \sum \sum_{i<j} \beta_{ij} x_i x_j + \varepsilon \qquad (7)$$

Minitab 17 was used to carry out a factorial design analysis for the purity of the upgraded gas. Appropriate second order polynomial equation was used to represent the relationship between the input parameters (Adsorption time and Adsorbent dosage) and the output response (upgraded biogas purity in term of CH_4 composition). Analysis of regression, prediction equation, factorial plots (interactive and main effect) was carried out. The model to represent the relationship between the input parameter and the corresponding response output parameter for both AC and zeolite CBV 8014 was obtained using the experimental data for regression coefficients of a second order polynomial equation. The significance of the regression coefficients was tested using a t-test, VIF and the p-values were used to test the significance of the effect of each variables in the polynomial equation. The result shows that the individual term and the interaction between the terms as well as the quadratic term are very significance ($p<0.05$) [17]. The responses generated were inputted into the Minitab software to generate results presented in Table 2 to Table 3.

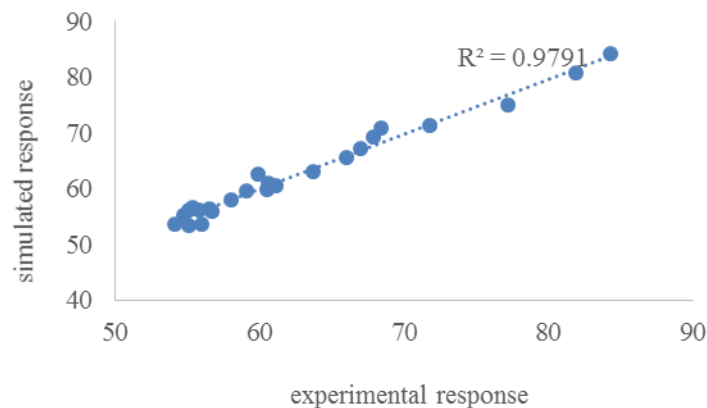**Table 2**: Model Coefficient for biogas upgrading using AC

Term	Coefficient Estimate	T-Value	P-Value	VIF
Constant	56.15	25.57	0.000	
A	0.521	2.09	0.041	26.04
B	-6.24	-4.05	0.001	35.07
A^2	-0.04111	-4.26	0.000	21.04
B^2	1.648	5.67	0.000	32.25
AB	0.4095	9.37	0.000	8.82

From Table 2, the model equation describing the response from the interaction of time and adsorbent dosage during biogas purification using A.C was generated and the model equation for biogas purity using AC in term of actual factor is given in equation 7.

$$\text{Response} = 56.15 + 0.521A - 6.24B - 0.04111A^2 + 1.648B^2 + 0.4095AB \qquad (8)$$

where A = Adsorption Time (min), B = Adsorbent Dosage (g)

The regression coefficient of the model equation for biogas purity using AC and zeolite CBV 8014 are shown in Table 2 and 3 from the table it can be observed that for biogas purity (CH_4) the R-sq, R-sq(adj) and R-sq(pred) are 97.91%, 97.33% and 94.86% respectively for AC, which implies that about 97.91% of the variable in the response (biogas purity) could be capture and explained by the model equation. It also indicate the high significance of the model. The R-sq(pred) value of 94.86% shows reasonable conformity with the R-sq(adj) value of 97.33% which implies a good agreement between the observed and predicted value [18]. It can be observed from Figure 1 the responses from both experimental and simulated results correlate very well with $R^2 = 0.9791$. Suggesting that the model equation generated can be used to predict purification efficiency of the AC when used to purify biogas.

Figure 1: The plot of the experimental responses against simulated responses for activated carbon.

Table 3: Model Coefficient for biogas purity using zeolite CBV 8014

| Term	Coefficient Estimate	T-Value	P-Value	VIF
Constant	55.67	15.11	0.000	
A	1.086	2.60	0.018	26.04
B	-8.62	-3.34	0.004	35.07
A^2	-0.0697	-4.31	0.000	21.04
B^2	2.428	4.98	0.000	32.25
AB	0.4781	6.52	0.000	8.82

The model equation for upgraded biogas purity using zeolite CBV 8014in term of actual factor is given in equation 7.

$$\text{Response (Purity)} = 55.67 + 1.086A - 8.62B - 0.0697A^2 + 2.428B^2 + 0.4781AB \qquad (9)$$

where A = Adsorption Time (min), B = Adsorbent Dosage (g)

For biogas purity using zeolite CBV 8014, the R-sq, R-sq(adj) and R-sq(pred) are 96.67%, 95.74% and 91.86% respectively. This implies that about 95.74% of the variable in the response (biogas purity) could be capture and explained by the model and also indicate the high significance of the model. The R-sq(pred) value of 91.86% shows reasonable conformity with the R-sq(adj) value of 95.74%. This implies a good agreement between the observed and predicted value [18]. However, the R-sq, R-sq(adj) and R-sq(pred) for AC are higher than those of zeolite CBV 8014 which implies that the obtained experimental data for AC are highly correlated than those of zeolite CBV 8014. Figure 2 show that model equation generated for the purification of biogas using zeolite CBV 8014 can be used to predict purity of the biogas as the prediction gave a correlation coefficient (R^2) = 0.9667.
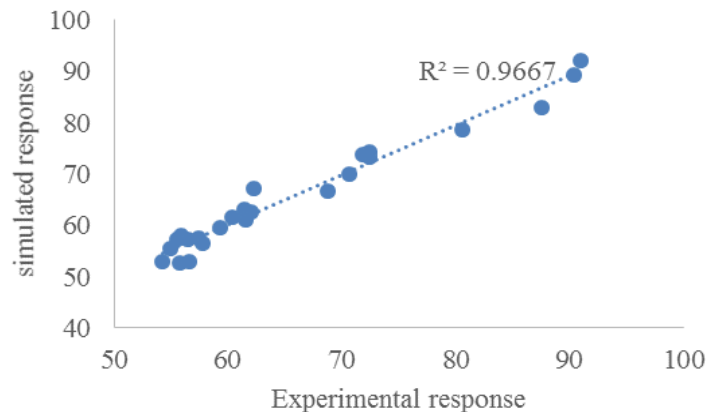
Figure 2: The plot of the experimental responses against simulated responses of Zeolite.

| (a) | (b) |
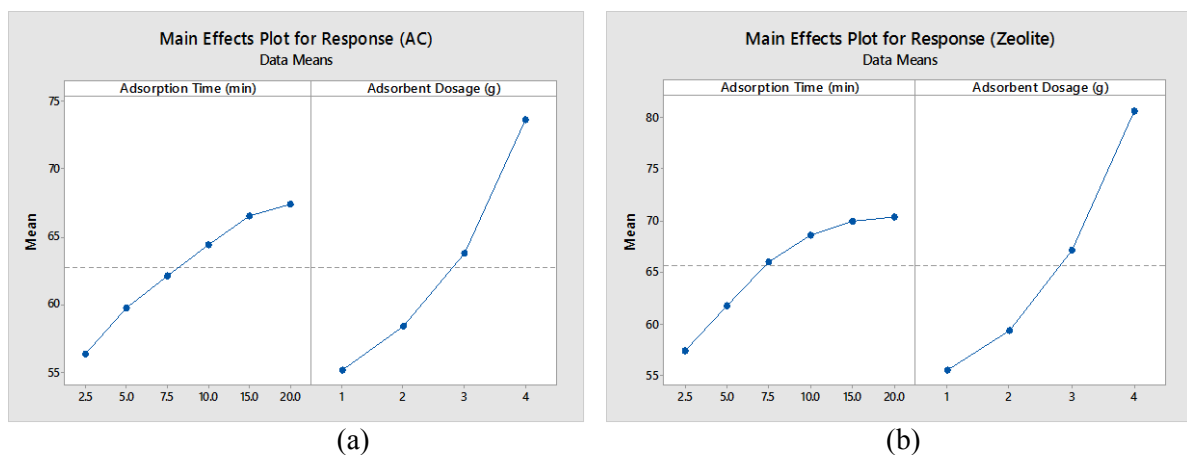
**Figure 3**: Main effect plot for biogas purity using (a) AC and (b) zeolite CBV 8014.

Figure 3 (a) and (b) are the main effect plot for the biogas purity. The main effect plot is used to examine the difference between level mean for one or more factors. It is believed that there is a main effect when different levels of a factor affect the response in different manner (Montgomery, 2004). From Figure 3 (a) and (b) it can be observed that the mean responses increases slightly from $15 - 20$ min for both AC and zeolite CBV 8014, which implies that further increase in time will not have significant on the mean response which is in conformity with the findings of [10] who shows that impurity adsorption flattens as time increase beyond 20 min which could be due to the adsorbent reaching its maximum adsorption capacity. For the adsorbent dosage, it has the highest effect on purity. The mean response increases almost linearly with increase in adsorbent dosage from $2 - 4$ g which could be attributed to availability of more adsorption site [10].

From Table 2 and 3, it can be seen that the linear, quadratic and interaction term of the model equation for biogas purity using AC and zeolite CBV 8014 have significant effect ($p<0.05$). Also the VIF values is an indication of the correlation of the predictors. The VIFs are not close to 1, but higher which indicates that the predictors are correlated. The VIFs are high because of the interaction terms which are correlated with main effect terms because they include the main effects terms. This also indicates that the biogas purity model developed in equation 8 and 9 well represent the experimental data.

Residual plot was also use to analyze the observed and predicted responses. Residual plot present the differences between the observed and predicted or fitted values. From Figure 3 and 4, it can be seen that the point in the residual plot are randomly dispersed around the horizontal axis, this implies that a linear regression is appropriate for the data which indicate a good fit for linear model [12].

The normal probability plot is used to assess whether or not a data set is approximately normally distributed. If a model is good, its residual should be normal and close to the straight line plot with no large deviation from the line. From Figure 4 (a) and (b), it can be seen that the residual of the plot for both AC and zeolite CBV 8014 are normal and closer to the straight line plot, indicating a good model. Figure 4 (a) and (b) shows that the values are following a predicted values which indicate that the model are correct.

Histogram gives a rough sense of the density of numerical data. The histogram of residuals is used to determine whether the data are skewed or whether outliers exist in the data. From Figure 4 (a) and (b), it can be observe that the histogram of residuals suggests that the residuals are normally distributed.

(a)   (b)
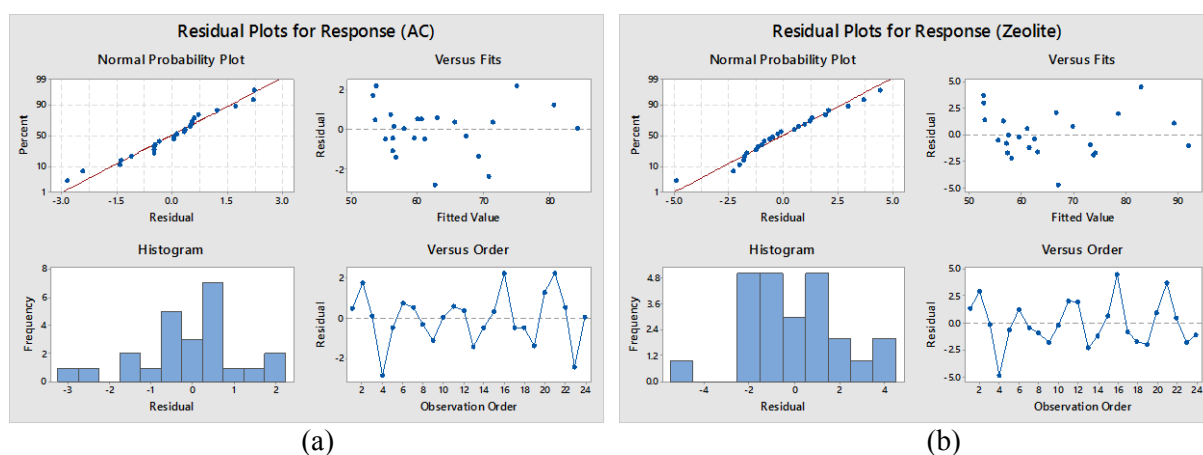
Figure 4: Four-in-One Residual plot using (a) AC Adsorbent and (b) zeolite CBV 8014 Adsorbent

Residuals versus fits plot are used to verify the assumption that the residuals have a constant variance. Residual versus fits plot is a scatter plot with residual on the y-axis and fit on the x-axis. The data for the biogas purity (Figure 4 a and b) shows that the errors are randomly scattered about zero which shows that the residual are fitted and unbiased. The findings of this studies are in agreement with the null hypothesis that the residuals have a constant variance.

3.4. *Physiochemical Properties of Adsorbent Sample*

Microporous materials have become important in the separation or capture of gases such as CO_2, CO, O_2, N_2, H_2, H_2S etc. The surface area and pore size of any adsorbent is a fundamental property to effectiveness of adsorbent materials [16]. Activated carbon and zeolite over the years have become an important adsorbent materials that have been used for several purposes. The adsorbent used for the CO_2 and other gas adsorption are zeolite CBV 8014 and KOH treated activated carbon (AC). It was found that AC prepared by KOH activation is highly micro porous when compared to that produced from $ZnCl_2$ or H_3PO_4 activation or other form of activation [19]. Besides, KOH also enhances the specific surface area and the formation of –OH functional groups on the carbon surface [20]. The –OH functional group makes the produced AC to be more susceptible to chemical reaction with KOH, which consequently leads to the formation of a higher degree of mesopores and micropores. Table 4 present the surface area and pore volume of the AC and CBV 8014 zeolite used for the kinetic studies of the gas adsorption. From Table 4, it was noted that the KOH-activated carbons used possess microporosity with a surface area of 784 m^2/g which implies high adsorption capacity. The AC used has low bulk density of 0.42 g/cm^3 as observed from Table 4. However, it has been reported that low density AC enhances adsorption in gas and liquid phase systems [21].

Table 4: Physiochemical properties of adsorbents

Parameter	AC Sample	Zeolite CBV 8014
Appearance	Black	White
pH	8.4	-
Density, g/cm^3	0.42	0.64
Surface area, $m^2/g/$	784	700
Pore volume, g/cm^3 / Pore diameter (Å)	0.93 (6.72 Å)	7.0

The zeolite CBV 8014 use in the study was activated using NH_4OH at a temperature of 550 °C in an oven for 2 hr. The surface structure of zeolites are usually heterogeneous which means that it consists of a finite number of different kinds of adsorption sites and the heterogeneity of the surface of zeolites led to its consideration for use in CO_2 capture and adsorption of other gases [22]. The properties of the zeolite CBV 8014 used are presented in Table 4. From Table 4, the pore diameter of the zeolite CBV 8014 is 7.10 Å, this implies that the pore diameter of the zeolite CBV 8014 is sufficient for the CO_2 (3.614 Å) to enter into the zeolites CBV 8014 channels. From the properties of the AC and zeolite CBV 8014 presented in Table 4, it can be observed that the CO_2 adsorption capacity of AC is lower than that of zeolite CBV 8014. This is due to the fact that zeolite CBV 8014 has a highly developed porous structure with good adsorption properties and high affinity for CO_2 adsorption than AC. [23]. From literature (Table 2.2) the pore sizes of the various gases are available which are all smaller than that of AC (6.72 Å) and CBV 8014 (7.0 Å) adsorbent which is an indication that the adsorbent have sufficient pore size to adsorbed the impurity gases (CO_2, CO, O_2, H_2 and H_2S) present in the biogas with 2.89 Å – 3.623 Å (Table 2.2).

3.5. *Carbon Dioxide Adsorption Capacity*

Figure 5 and 6 illustrates the adsorption profiles at different adsorbent dosage (1 g – 4 g) for both the AC and CBV 8014 zeolite respectively. From Figure 5 and 6, it can be observed that as time increases from 0 – 20 min, the adsorption of CO_2 and other gases increases for both adsorbent up to a time of 10 min. A sharp and linear increase was noticed at 0 – 10 min for all adsorbent dosage which then tends to flattens as the time increases from 10 – 20 min. This is in conformity with the report of [10] that CO_2 adsorption increases sharp at 5 – 22 min using AC.
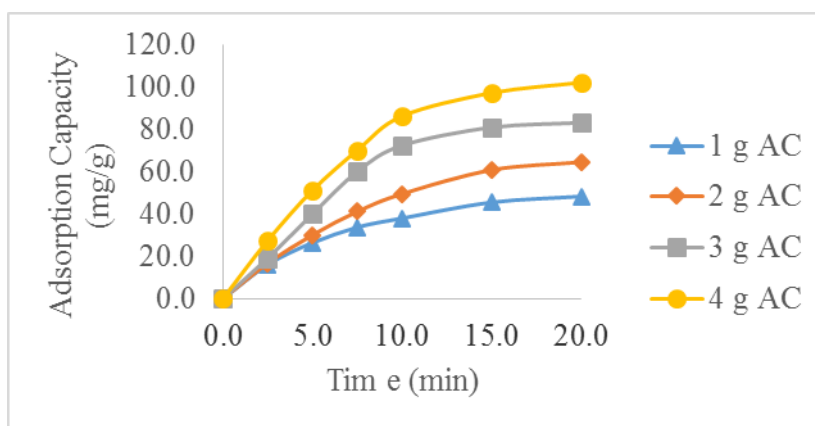
Figure 5: CO_2 adsorption capacity vs time at various AC dosage

The rate of CO_2 adsorption gradually decreased from 10 – 20 min, this might be due to the adsorbents approaching its saturation or maximum adsorption capacity. However, the rapid adsorption rate observed between 0 – 10 min while slow adsorption rate was observed from 10 – 20 min which could be attributed to the high sorbent surface area (Table 4) which is accountable for interaction with the CO_2 and other trace molecules. Over time, the adsorption rate is observed to be on the decreased due to reduction of active sites that may slow down the adsorption process from taking place. In

addition, [10] suggest that the rapid adsorption at the beginning of the process is due to external surface of the adsorbent, and is followed by slower internal diffusion process.
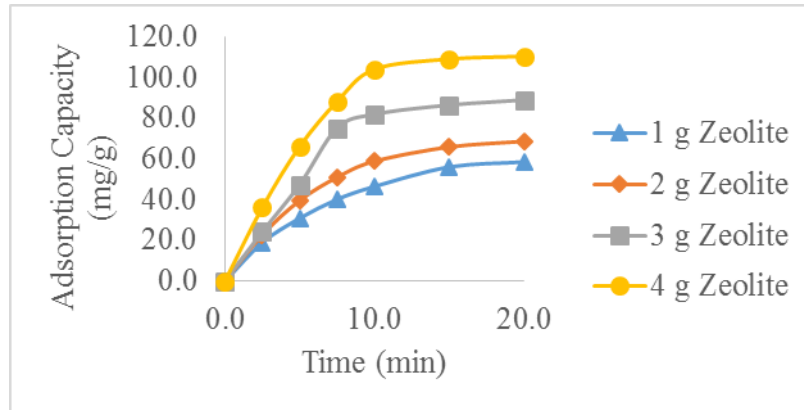
Figure 6: CO_2 adsorption capacity vs time at various zeolite CBV 8014 dosage.

From Figure 5 and 6, it can also be observed that adsorption of CO_2 was in the order zeolite CBV 8014 > AC, which implies that at all dosage, CBV 8014 zeolite has the best adsorption capacity than the AC investigated. This high adsorption capacity observed from CBV 8014 zeolite could be attributed to its high surface area due to the facts that the pore diameter of the CBV 8014 zeolite is 7.0 Å compared to 2.89 Å – 3.623 Å (Table 2.2) for the impurity gases (CO_2, CO, O_2 H_2 and H_2S) present in the biogas, which makes it sufficient for the CO_2 to enter into the zeolites and AC channels. Therefore, from Figure 5 and 6, it can be observed that the rate of adsorption in CBV 8014 zeolite are higher than in AC.

3.6. *Adsorption Kinetic Study*
Adsorption kinetic analysis establishes an adsorption uptake rate and examine the residence time for the adsorption process to be completed. It is also a baseline on determining the adsorption dynamics as well as its performance in real application. Lagergren pseudo first-order model and pseudo-second-order model was examine in this study. The conformity of the experimental work and kinetic model were analyzed by the R2 values. Furthermore, Arrhenius equation was use to estimate the activation energy of the adsorption process and also to determine if the adsorption process obeys the intra-particle diffusion model.

3.6.1. Lagergren pseudo first-order model. Lagergren pseudo-first-order model was used to test the adsorption kinetics of the system using Equation 2 to evaluate the adsorption dynamics. A straight line plot of log (qe-qt) versus time (t) at various adsorbent height of 3.35 cm – 13 cm (1g – 4 g) for both AC and zeolite CBV 8014 was made, and the parameters were tabulated in Table 5. It was observed that the pseudo-first-order kinetic model for both AC and zeolite fit well with the experimental data, with R^2 value found to be within the range of 0.913 to 0.9935 for AC and 0.868 – 0.9704 for zeolite. This implies that AC well obeyed the pseudo-first-order model when compared to zeolite.

Table 5: Lagergren's pseudo-first-order model kinetic parameters

Adsorbent	Parameter	1 g	2 g	3 g	4 g
AC	K1 (min^{-1})	0.030	0.049	0.085	0.189
	R^2	0.913	0.962	0.936	0.994
Zeolite	K1	0.036	0.047	0.082	0.218
	R^2	0.927	0.899	0.868	0.970

The first order adsorption rate constants K1 for both adsorbent are presented in Table 5. From Table 5, the can be observed that the first order adsorption rate constants K for zeolite CBV 8014 are higher than those of the AC. However, first order adsorption rate constants K for both AC and zeolite compared favorably with K values of 0.097, 0.1252 and 0.1140 reported for CO_2 adsorption using based modified activated carbon, acid modified activated carbon and unmodified activated carbon respectively by [10].

3.6.2. Lagergren's pseudo-second-order model. Lagergren pseudo-second-order model was also used to study the adsorption kinetics of the system using Equation 3 to further evaluate the adsorption dynamics. A straight line plot of 1/qt against time (t) was made at various adsorbent height of 3.35 cm – 13 cm (1g – 4 g) for both of the AC and zeolite CBV 8014, and the kinetic parameters obtained were tabulated in Table 6. It was observed that the pseudo-second-order kinetic model for AC at 1 g (3.25 cm bed height), 2 g (6.5 cm bed height) and 4 g (13 cm bed height) only fit well with the experimental data, with R^2 value found to be within the range of 0.8668 to 0.9982. Likewise for zeolite, it was observed that the pseudo-second-order kinetic model at 1g, 2 g, 3 g and 4g adsorbent dosage fit well with the experimental data, with R^2 value of 0.9017 – 9951.

Table 6: Lagergren's pseudo-second-order model kinetic parameters

Adsorbent	Parameter	1 g	2 g	3 g	4 g
AC	K2 (min^{-1})	0.002	0.0007	0.0005	0.0006
	R^2	0.998	0.9827	0.8668	0.9621
Zeolite	K2	0.002	0.0015	0.0009	0.0010
	R^2	0.995	0.9882	0.9017	0.9621

The second order adsorption rate constants K2 for both adsorbent are presented in Table 6. It can be observed from Table 6, that the second order adsorption rate constants K for zeolite CBV 8014 are higher than those of the AC. However, second order adsorption rate constants K for both AC and zeolite compared favorably with K values of 0.0105, 0.0052 and 0.0042 for an adsorption time of 0 – 25 min reported for CO_2 adsorption using based modified activated carbon, acid modified activated carbon and unmodified activated carbon respectively by [10]. The study revealed that the pseudo second order kinetics model for AC and zeolite well fitted the CO_2 adsorption kinetics data than pseudo first order kinetics model. This is because pseudo-first-order model R^2 value for both AC and zeolite CBV 8014 is within the range of 0.95 – 0.998 while pseudo-second-order model R^2 value for both AC and zeolite is 0.8668 – 0.9982.

3.6.3. Activation energy. In adsorption process, the magnitude of the activation energy (Ea) is very significant, as it provides information on the adsorption mechanism. The value of activation energy for physical adsorption is usually in the range of 5 – 40 kJ/mol. However, chemisorption process involves formation of strong bonding between the adsorbate (CO_2) and adsorbent with activation energy in the range of 40 – 800 kJ/mol [24]. Arrhenius equation that is shown in equation 5 is applied to determine the activation energy of the adsorption process. Table 7 shows the activation energy (Ea) for AC and zeolite CBV 8014 adsorbent used in the study for CO_2 adsorption.

Table 7: Activation energy for CO_2 adsorption in AC and zeolite

Adsorbent	Parameter	1 g	2 g	3 g	4 g
AC	Ea (kJ/mol)	14.37	17.12	19.23	17.84
Zeolite	Ea kJ/mol)	15.71	16.18	18.30	17.14

From Table 7, it can be observed that the activation energy value for the study fall within the range of 5 – 40 kJ/mol for physical adsorption [24]. The lower activation energy found in this work implies that the CO_2 adsorption onto both AC and zeolite CBV 8014 is a diffusion-controlled process (phisiosorption) rather than a chemically-controlled process (chemisorption). The results obtained in this study were slightly higher than 5.77, 13.02 and 13.55 kJ/mol reported for based modified activated carbon, acid modified activated carbon and unmodified activated carbon respectively [10] but compare favorably with 17.51 and 14.27 kJ/mol reported for optimized and commercially available activated carbons respectively [13].

3.6.4. Intra-particle diffusion model. The intra-particle diffusion model rate processes are generally presented in respect to square root of time. In contrast to Lagergren pseudo-first-order and pseudo-second-order model, intra-particle diffusion model provides an insight of the mechanism in adsorption process. Adsorption consists of few steps involving the transport of adsorbate from the bulk phase to the surface of solid sorbent, and is followed by the molecules diffusion into the interior of the pores. Intra-particle diffusion, normally is a rate-limiting step in many of adsorption processes described as a slow process. A plot of qt against the square root of time gives the intra-particle rate constant.

Table 8: Intra-particle diffusion rate constant for CO_2 adsorption in AC and zeolite.

Adsorbent	Parameter	1 g	2 g	3 g	4 g
AC	k_{id} (mg/g.min$^{1/2}$)	11.203	17.048	22.68	26.35
Zeolite	k_{id} (mg/g.min$^{1/2}$)	14.072	18.892	26.914	25.677

From Table 8, it can be observed that the intra-particle diffusion rate constant for the adsorption of CO_2 in zeolite are higher at all dosage than those of AC. This implies that the rate of intra-particle diffusion in zeolite is higher than that of AC.

4. CONCLUSION

The biogas produced contains high CH_4 gas (53.26%), CO_2 (33.44%) and other gases in small quantity. The study shows the practicality of both AC and zeolite CBV 8014 to be used as adsorbent for CO_2 capture in industrial applications. The pore diameter of the CBV 8014 zeolite (10 Å) enable it to be most effective in CO_2 adsorption compared to AC.

Comparability in the CO_2 adsorptions capacity indicates the practicality of the AC and zeolite CBV 8014 to be used in industrial applications. The adsorption capacity of the adsorbents was found to be in the order zeolite CBV 8014 > AC at 0 – 20 min and 1-4g adsorbent. The kinetic study shows that the CO_2 adsorption into AC and zeolite CBV 8014 obeys the pseudo-second-order model, due to its R2 value closer to unity. The kinetic study of CO_2 adsorption onto AC and zeolite CBV 8014 shows that the magnitude of activation energy for both adsorbent are less than 40 kJ/mol, indicating the occurrence of physiosorption mechanism. The intra-particle diffusion model study indicates that intra-particle diffusion is the sole rate-limiting step in the adsorption process for both adsorbent (AC and zeolite CBV 8014). In addition, lower activation energy found in this work confirm that the CO_2 adsorption onto AC and zeolite CBV 8014 is a diffusion-controlled process, rather than the chemically-controlled.

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