

MICROWAVE ASSISTED K_2CO_3 PALM SHELL ACTIVATED CARBON AS SORBENT FOR CO_2 ADSORPTION APPLICATION

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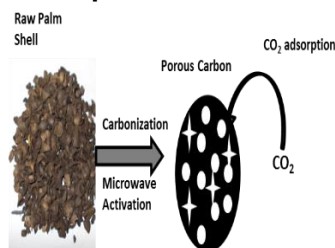
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Graphical abstract



Abstract

Carbon dioxide is believed to be a major greenhouse gas (GHG) that contributes to global warming. In this study, palm shells were used as a precursor to prepare CO_2 activated carbon sorbents via carbonization, chemical impregnation with K_2CO_3 and microwave activation. Adsorption equilibrium data for CO_2 adsorption on the porous carbon were obtained at different temperatures using static volumetric adsorption method. Langmuir, Freundlich, Sips and Toth models were used to correlate the experimental data. The CO_2 adsorption capacity at 303.15, 343.15, 378.15, 443.15 K and 1 bar on the sorbent was 2.71, 1.5, 0.77, 0.69 mmol/g respectively. Sips isotherm was found to have the best fit. The results indicated that the porous carbon sorbent prepared by carbonization and microwave K_2CO_3 assisted activation have good CO_2 uptake. The porous carbons produced are therefore good candidates for CO_2 adsorption applications.

Keywords: Palm shell, microwave, activated carbon, CO_2 adsorption isotherms

Abstrak

Karbon dioksida dipercayai menjadi gas rumah hijau utama yang menyumbang kepada pemanasan global. Dalam kajian ini, tempurung kelapa telah digunakan sebagai pelopor bagi menyediakan penjerap karbon yang diaktifkan oleh CO_2 melalui karbonisasi, pesenyawaan kimia dengan K_2CO_3 dan pengaktifan gelombang mikro. Data keseimbangan penjerapan bagi penjerapan CO_2 ke atas karbon berliang diperolehi pada suhu-suhu yang berbeza menggunakan kaedah penjerapan isipadu statik. Model Langmuir, Freundlich, Sips dan Toth telah digunakan untuk menghubungkan data eksperimen. Kapasiti penjerapan CO_2 pada 303.15, 343.15, 378.15, 443.15 K dan 1 bar ke atas penjerap masing-masing adalah 2.71, 1.5, 0.77, 0.69 mmol/g. Isotherm Sips didapati mempunyai kesesuaian yang terbaik. Keputusan menunjukkan yang penjerap karbon berliang yang disediakan melalui karbonisasi dan gelombang mikro K_2CO_3 dibantu pengaktifan mempunyai pengambilan CO_2 yang baik. Karbon berliang yang dihasilkan adalah penjerap yang bagus untuk aplikasi penjerapan CO_2 .

Kata kunci: Tempurung kelapa sawit, gelombang mikro, karbon diaktifkan, penjerapan isoterma karbon dioksida

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1.0 INTRODUCTION

There is growing concern on carbon dioxide emissions due to global warming issues, CO₂ emission is largely caused by fossil fuel combustion [1, 2]. There are so many ways of reducing CO₂ emissions like improvement in energy efficiency, substitution of low or non-carbon fuels, or by the capture and storage of CO₂ (CCS) [3]. One approach that holds great promise for reducing GHG emissions is carbon capture and sequestration (CCS). But the main challenge remains the cost CO₂ capture and reducing the efficiency penalty that is imposed on the process [3]. For the capture of CO₂, the most popular technology is the absorption process using alkanolamine solvents [4]. The major drawback in using amine solutions are: High energy consumption, degradation and vapourization of solvent and corrosion of process equipment [5]. Adsorption with solid sorbent is considered to be a promising alternative to the amine based process [6] because of its low energy consumption, low cost and high stability over wide range of pressure and temperature [5]. Solids sorbent including zeolites, silica metal-organic frameworks (MOFs), porous carbons, hydrotalcites and organic-inorganic hybrid sorbents have been tested for CO₂ adsorption. However, some sorbents require costly and multi-step fabrication procedures that involve the impregnation or grafting of porous solids. Others require high regeneration temperatures and undergo a substantial loss of adsorption capacity after several cycles [4].

One of the ways of reducing such issues is using thermally stable material and low-cost and abundantly available lignocellulosic material as the precursor for the preparation of activated carbon as CO₂ sorbent. Biomass is abundant in large scale from various sources; it does not compete with the food chain, moreover its cheap and environmental friendly [7]. Converting these wastes into value added product such as activated carbon could solve environmental problems such as accumulation of agricultural waste, air pollution and water pollution [8]. Main products of pyrolysis are bio-oil and bio-char which is in turn used in production of activated carbon. Adsorption performance and specific application of activated carbon is strongly dependent on pore structure, surface area and surface chemistry of the porous carbons [9].

In principle, the preparation of activated carbon from carbonaceous material involves two stages, namely pyrolysis and activation (physical and chemical activation) [10]. In the first stage, the material is pyrolyzed in oxygen free environment at about 600-800°C. This results in the release of volatile matters (VM) and produce chars with rudimentary pore structures [11]. The second stage involve activation where by the chars are heated in an oxidising atmosphere of steam, oxygen or carbon dioxide. The activation process has tremendous effects on the pore structure and adsorption capacity

of the prepared activated carbon (AC). There are two methods of activation: physical and chemical. The physical method takes longer time and usually conducted at higher temperature than the chemical method [12]. In the chemical method, the precursor is impregnated with acids (e.g. H₂SO₄, H₃PO₄, e.t.c.), bases (e.g. NaOH, KOH, K₂CO₃, e.t.c.) or salts (e.g. CaCl₂). Chemical activation involves temperatures lower than that used in physical activation. The carbonization step and activation step could be carried out separately or simultaneously. There are two basic methods of heating in the production of AC: Conventional thermal heating and microwave heating. In conventional thermal methods, external heating are used for the carbonisation and activation of raw material [13]. In microwave heating, energy is readily transformed into heat inside the particles by dipole rotation and ionic conduction. Microwave treatment offers advantage of precise temperature control, lower consumption of inert, shorter period of synthesis and producing basic groups on the sorbent material [9]. In addition, microwave irradiation induces rapid heating and increases chemical reactivity. For the above mention reasons microwave heating is now widely applied in environmental engineering [14].

Many studies have been conducted on production of activated carbon from palm shells [15, 16]. Activated carbon had been used in water treatment and air purification [17, 18]. Some studies were also conducted on CO₂ adsorption on palm shell AC [19, 1, 20]. In this study, CO₂ palm shell AC sorbent was prepared via carbonization and K₂CO₃ microwave assisted activation. CO₂ adsorption on the sorbent at temperatures of 303.15, 343.15, 378.15 and 443.15K was measured using static volumetric method. 303.15 K temperature was considered as ambient temperature while 378.15 K was considered as post combustion temperature. Effect of temperature and pressure on the CO₂ adsorption was studied also. The adsorption experimental data were correlated with 2-parameter Langmuir and Freundlich equations, together with 3-parameter Sips and Toth models. The studies also provide insight on the properties of the microwave palm shell activated carbon together with its CO₂ adsorption properties.

2.0 METHODOLOGY

This section presents the materials and apparatus used in this work. The procedures followed in conducting the experiment were also highlighted in this section.

2.1 Materials and preparation of activation carbon

Palm kernel shells (PKS) were collected from Koperasi Kampung Jawi Johor Bahru Berhad, Malaysia. The material was washed repeatedly with water to remove dirt and impurities from its surface and then oven-dried at 105 °C for 24 h. The dried palm shells

were then crushed (crusher, model RT-20). The ground palm shell samples were sieved in a vibrating sieve shaker (Endecotts EFL MK3). The grinded palm shells (0.85- 1.7 mm) were loaded into stainless steel tubular reactor (28mm i.d. and 300 mm length) which was placed in a well lagged vertical tube furnace. About 50 g of PKS material was placed in the reactor and then heated at a rate of 10 °C/min from room temperature to 700 °C. Continuous flow of 100 cm³/min nitrogen was maintained during the experiment. The heating was held at that temperature for 2 hours before cooled down to room temperature under nitrogen flow. Temperature of the bed was monitored and controlled with furnace temperature controller and K-type thermocouple. The resultant palm kernel shell char (PKC) was then stored in a desiccator.

The char was mixed with impregnating agent (K₂CO₃) in the ratio of 1:1. The impregnation ratio defined as the dry weight of activation agent per weight of char. The mixture of precursor and chemical solution was heated and stirred at 85 °C and 6 r.p.m for 2 h. It was then placed in an oven for 24 hours. About 10g of the dried impregnated char was charged into a high temperature quartz reactor (Figure 1). 200 cm³/min of nitrogen was used for 5 min to purge air and to preheat the system at 100W. The flow was then switch over to CO₂ at flow rate of 200 cm³/min for each gram of the precursor for 6 minutes. Power level was set at 400W from the power controller of the modified microwave oven (Samsung ME0113M model) at irradiation exposure time was set at 6 minutes.

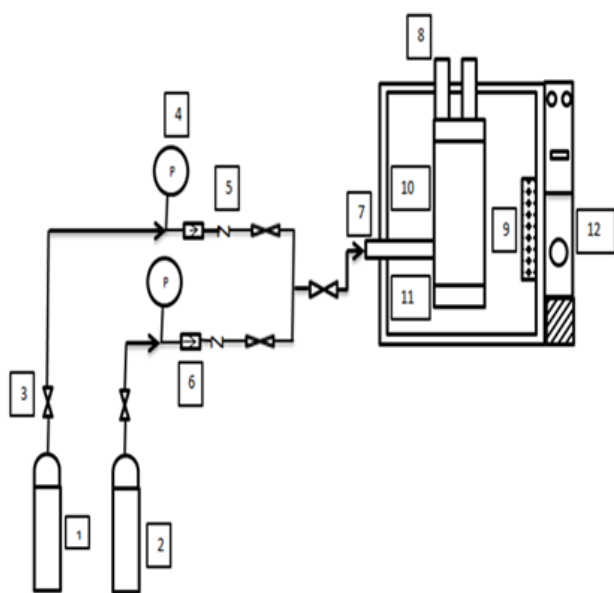


Figure 1 Schematic diagram of microwave heating equipment (1-CO₂ gas cylinder, 2-N₂ gas cylinder 3- Control valve, 4-Pressure gauge, 5-Check valve, 6- Flow controller, 7- Gas inlet, 8-Outlet, 9-Microwave Source, 10-Microwave cavity, 11-Quartz reactor and 12-Microwave control panel

The activation was performed in the high temperature quartz glass reactor fixed in a microwave chamber (Figure 1). The resultant microwave porous carbon was wash thoroughly with hot and warm deionized water. The yield of the char (Y_C) is defined as grams of char per gram precursor (palm shell) utilized for carbonization (equation 1). The yield of the activated porous carbon (Y_{PC}) is defined as grams of activated porous carbon per gram char utilized for activation (Equation 2). It is express as:

$$Y_C = \frac{W_2}{W_1} \quad (1)$$

$$Y_{PC} = \frac{W_3}{W_2} \quad (2)$$

Where W_1 is the mass of the precursor (palm shell), W_2 is the mass of the char and W_3 is the mass of the porous activated carbons produced.

2.2 Characterization Of Samples

The characterization carried out on the raw palm shells, bio-char and microwave activated carbon includes: Scanning electron microscopy (SEM), nitrogen adsorption, proximate analysis and ultimate analysis.

2.2.1 Scanning Electron Microscopy (SEM)

Scanning electron microscope of Karl Zeiss (EVO50 XVPSEM, Germany) was used to analyse the surface morphology of the sample materials. Prior to analysis, samples were dried at 373 K and stored in a desiccator overnight. The samples were then mounted on an aluminium platform for analysis. Each sample was examined morphologically under different magnifications.

2.2.2 Nitrogen Adsorption

Pore structures of the porous carbons were characterized by adsorption of liquid nitrogen at -196°C to obtained adsorption isotherms which was subsequently used to obtain the surface area. This was achieved using volumetric techniques (Micrometrics ASAP 2020). Samples were degassed before generating the isotherms. The surface area was evaluated by Brunauer, Emmett and Teller (BET) assuming an average micropore activated carbon. The surface area was calculated by the BET method from the adsorption data in the relative pressure (P/P_0) range of 0.04 to 0.2.

2.2.3 Proximate Analysis

Proximate analysis with the aid of TGA was used to determine the moisture, volatile matter (VM), fixed carbon (FC), and ash content. The moisture content was obtained at 120 °C while volatile matter (VM) was obtained from the TGA at 700 °C. Ash was determined by getting the residue that remained after heating the sample at 800°C in a furnace to constant weight. The

amount of fixed carbon was obtained as difference of VM, ash and moisture from 100%.

2.2.4 Ultimate Analysis

Ultimate analysis was carried out using PerkinElmer CHNS/O elemental analyzer. Elements covered in the analysis are carbon (C), hydrogen (H), nitrogen (N), sulfur (S) and oxygen obtained as the difference from 100% (O).

2.3 CO₂ Adsorption

The CO₂ adsorption equilibrium data was obtained using static volumetric measurement in a purpose fixed bed adsorption unit. The unit is equipped with digital pressure transducer (Autonics PSA/PSB series). A K-type thermocouple, inserted axially in the middle of the adsorption cell was used to monitor the cell temperature continuously. The temperature was controlled using a thermal insulated electric furnace. Vacuum pump was used in evacuation to regenerate the adsorbent. Connections in the apparatus were made with stainless-steel tubing and proper swagelok fittings. Pressure and temperature measurements in the loading cell and adsorption cell were used to obtain the amount of CO₂ adsorbed. CO₂ adsorption equilibrium data was collected using simple volumetric measurement. The adsorption cell was loaded with 3 g of AC sample during each test. The sample was dried in an oven overnight and then further dried in-situ at 150 °C under nitrogen flow for 1 h, it was cooled down or heated up to the desired adsorption temperature. The CO₂ adsorption was measured at 303.15, 343.15, 378.15 and 443.15K. The adsorption cell was put at the selected temperature using isothermal furnace equipped with a control system while the valves remain closed. The initial pressure of 0 - 4 bars at constant temperature was used in getting the various points of the isotherm curve. The valve between the loading cell and the adsorption cell was open to allow the gas contact the adsorbent in the cell. The equilibrium pressure of the gas was recorded with the aid of digital pressure sensor (Autonics PSA/PSB series). Adsorption equilibrium is a state when the temperature and pressure are constant (aprox. 10 min).

The adsorption capacity was calculated using mass balance equations (Equation 3) in terms of measurable quantities (i.e. T, P) before and after equilibrium state:

$$q = \frac{1}{m} \left[\frac{V_v}{R} \left(\left| \frac{P}{ZT} \right|_i - \left| \frac{P}{ZT} \right|_{eq} \right)_a + \frac{V_l}{R} \left(\left| \frac{P}{ZT} \right|_i - \left| \frac{P}{ZT} \right|_{eq} \right)_l \right] \quad (3)$$

2.4 Adsorption Isotherm Modeling

Equilibrium relationships correlate the amount of gas adsorbed on a solid sorbate with the applied gas pressure (adsorption isotherms). The correlation of experimental data using isotherm equations is essential for adsorption data interpretation, prediction and performance analysis [20]. The experimental equilibrium adsorption data for CO₂ have been tested by using the two-parameter Langmuir and Freundlich isotherm equations together with three-parameter Sips and Toth isotherms.

2.4.1 Freundlich Adsorption Isotherm

Freundlich isotherm is the earliest known relationship describing the non-ideal and reversible adsorption. The empirical model can be applied to multilayer adsorption, with non-uniform distribution of adsorption heat and affinity over the heterogeneous surface [21]. It is derived by assuming that the adsorption sites are distributed exponentially with respect to the heat of adsorption. The Freundlich adsorption isotherm (equation 4) is represented as:

$$q = K_F P^{1/n} \quad (4)$$

K_F and $1/n$ are the Freundlich adsorption constant and a measure of adsorption intensity.

Where, q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mmol/g), P is pressure of the CO₂ in the bulk gas phase (bar), K_F and $1/n$ are the Freundlich adsorption constant and a measure of adsorption intensity, respectively. The magnitude of the exponent n gives an indication of the favourability of adsorption. Whereby, values $n > 1$ represent favourable adsorption condition.

2.4.2 Langmuir Adsorption Isotherm

Langmuir's isotherm assumes monolayer adsorption and that the surface is homogeneous. The adsorption occurs only at finite number of sites that are identical [21]. That the adsorption is reversible; at equilibrium pressure P , the rate of adsorption and desorption from the solid is equal (equation 5).

$$K_{ads}PS(1 - \theta) = K_{desp}S\theta \quad (5)$$

Where S is the number of adsorption sites, K_{ods} and K_{desp} are the adsorption and desorption constants respectively. If $K_L = K_{ads}/K_{desp}$

Langmuir's isotherm model is express as (equation 6):

$$\theta = \frac{q}{q_m} = \frac{K_L P}{1 + K_L P} \quad (6)$$

Therefore $q = \frac{q_m K_L P}{1 + K_L P}$

Where; θ is the occupancy ratio or fractional coverage of the surface, which can be defined as the ratio of the adsorbed mass (q) to the maximum adsorbed mass at monolayer coverage (q_m) [22]. K_L is the Langmuir constant that is dependent on temperature according to the Van't hof relation.

q_m is the saturation limit (mg/g) which is also temperature dependent.

$$K_L = K_{0L} \exp(-\Delta H_{ads}/RT) \quad (7)$$

R is the ideal gas constant, ΔH_{ads} is the adsorption enthalpy and K_{0L} is constant that depend on molecular area (0.22 nm² for CO₂) and molecular weight of the adsorbate.

2.4.3 Toth Adsorption Isotherm

Toth isotherm is a three parameter empirical equation developed to improve the fit of the Langmuir isotherm and to describe heterogeneous adsorption systems with $n \neq 1$ [23]. Toth's model (equation 8) is represented as:

$$\frac{q}{q_m} = \frac{\alpha_T P}{[1 + (\alpha_T P)^n]^{1/n}} \quad (8)$$

Where α_T and n are Toth's constants

P is the adsorbate gas pressure at equilibrium (bar), q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mmol/g), α_T and n are Toth's constants.

2.4.4 Sips Adsorption Isotherm

Sips isotherm is a combination of the Langmuir and Freundlich isotherm type models and expected to describe heterogeneous surfaces much better. At low adsorbate concentrations it reduces to a Freundlich isotherm, while at high adsorbate concentrations it predicts a monolayer adsorption capacity characteristic of the Langmuir isotherm [24]. Sips extended the Freundlich isotherm to include a finite limit at sufficiently high pressures [23].

$$q = \frac{q_m K_{LF} P^{1/n_{LF}}}{1 + K_{LF} P^{1/n_{LF}}} \quad (9)$$

K_{LF} is the Sips (L-F) constant which is temperature dependant, n_{LF} is the parameter that characterize the system heterogeneity.

2.4.5 Model Validity And Fitting

The validity of the models to fit the experimental data was evaluated by the root-mean-square deviation (RMSD) (equation 10) and coefficient of determination (R^2). Parameter estimation was carried out by non-linear analysis of isotherm models for CO₂ adsorption based on input functions of Microsoft Excel spread sheets. It was achieved by minimizing the root mean square deviation (RSMD) using solver add-in of Microsoft Excel. RSMD is a commonly used statistical tool for measuring the predictive power of a model. RSMD standard equation is defined as:

$$RSMD = \left[\frac{1}{n} \sum (q_{exp} - q_p)^2 \right]^{1/2} \quad (10)$$

The coefficient of determination represents the percent of the closeness of experimental data to

the line of best fit/prediction. R^2 is defined by the following expression:

$$R^2 = 1 - \frac{\sum_{n=1}^i (q_{exp} - q_{exp})^2}{\sum_{n=1}^i (q_{exp} - \bar{q}_p)^2} \quad (11)$$

The coefficient of determination is such that $0 < R^2 < 1$, the more the R^2 is close to 1, the better the model fits the data. Where q_{exp} (mmol/g), q_p (mmol/g) and \bar{q}_p (mmol/g) are the experimental, theoretical and average theoretical adsorption capacity. The lower the RMSD value the better the estimated model performs.

3.0 RESULTS AND DISCUSSION

3.1 Characteristics of the Activated Carbon Sorbent

The activated carbon sorbent was characterized based on proximate analysis, ultimate analysis, scanning electron microscopy and nitrogen adsorption.

3.1.1 Proximate Analysis

The proximate analysis involves determination of fixed carbon (FC), moisture, ash and volatiles of the palm shell and the porous carbons produced. The results of the proximate analysis of the palm shell are indicated in Table 1. Low moisture content (5.5%), high percentage of volatile matter (70.0%), average contents of fixed carbon 23% and low ash content (4.28%), were present in the palm kernel shells. The yield and proximate analysis of chars and microwave palm shell activated carbon (MPA) are also given in Table 1. The volatile content of the chars decreased from 23.24 to 13.52, while the fixed carbon content increased from 72.99 to 79.77%.

Table 1 Proximate analysis and yield of PKS, char and activated porous carbon.

Sample	Parameter				
	Moist.	Volatiles	Ash	Fixed Carbon	Yield (%)
PKS	5.50	70.00	4.28	23.00	-
PKC	2.16	23.24	1.61	72.99	35.14
MPA	3.28	13.52	3.43	79.77	63.05

This is due to the release of increasing volatile components with increasing temperature, predominantly forming porous carbon at high pyrolysis temperatures [25]. No much difference in the moisture content of the porous carbons.

3.1.2 Scanning Electron Microscopy (SEM)

Porosity in activated carbon is due to the conversion of cellulose, hemicelluloses and lignin in the plant precursors by the process of dehydration, linkage breaking reactions, the structural ordering process of the residual carbon and polymerization reactions. SEM micrographs of raw palm kernel shell (PKS), palm kernel char (PKC) produced at 700°C, 2 h, and the microwave porous carbons produced by K₂CO₃ microwave assisted activation process (MPA) are depicted in Figure 2. It can be observed that the surface of the raw material was dense containing wooden deposits with no cracks and voids, which is a typical characteristic of lignocellulosic material [26] (Figure 2a). The absence pore network in the PKS accounts for its poor or negligible surface area. More cleared surface with little pores was observed on the char sample. This could be due to volatiles removal producing a fixed carbon mass with only rudimentary pores as shown in Figure 2b.

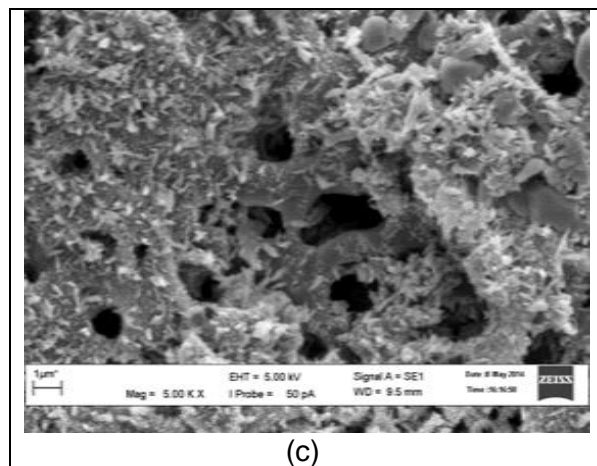
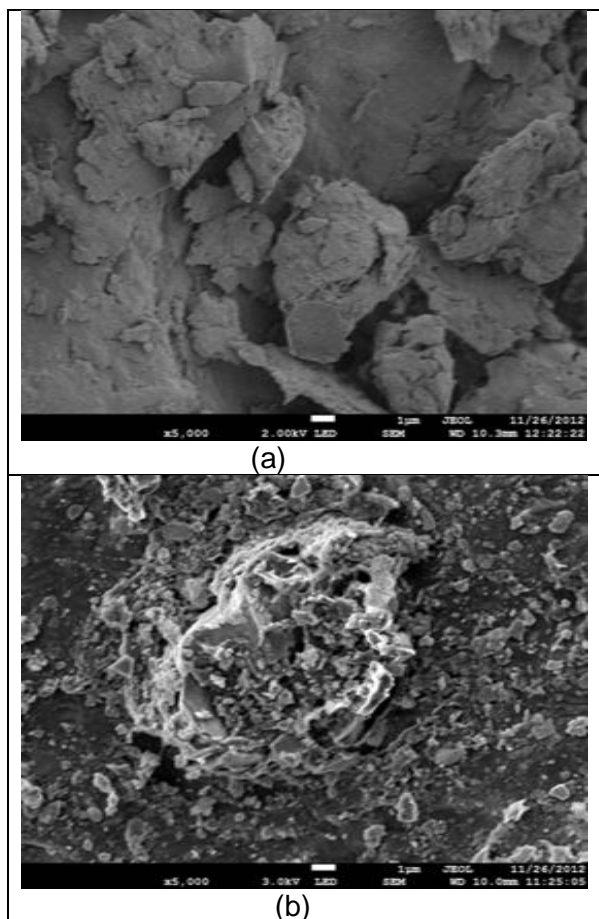


Figure 2 SEM micrographs of (a) raw palm kernel shell (PKS), (b) palm kernel char (PKC) (c) microwave palm shell activated carbon (MPA)

The pores created are restricted or too small to adsorb molecules. Widening of pore diameters and creation of new ones (Figure 2c) is achieved after activation of the samples [27]. For the impregnated and microwave treated samples (i.e. MPA), the activating agent diffused into the texture structure of the lignocellulosic material. On heating the material, Pores are form as a result of chemical reaction between the activating agent and the carbonaceous material, or evaporation and decomposition of the activation agent leaving the space being previously occupied by the activating agent. The small particulate matters on the external surface of activated carbon may be the reliquus activating agent [28].

3.1.3 Ultimate Analysis

The ultimate analysis of palm shell indicated a carbon, hydrogen, nitrogen, and sulfur and oxygen content of 47.77%, 5.98%, 0.90%, 0.03% and 45.31% respectively (Table 2). The low nitrogen and sulphur content from the analysis indicates that PKS is environmental friendly. The carbon content of PKS increased tremendously with concomitant decreased in N, H and O contents after carbonization to form PKC and subsequent activation to form MPA. Similar observations were reported in previous studies [29] about preparation of activated carbon from agro-wastes. This is associated with released of volatiles matter in the material leaving a fixed carbon mass.

Table 2 Ultimate (Elemental) analysis of palm shell (PKS), biochar (PKC) and activated carbon (MPA)

Element/Sample		PKS	PKC	MPA
Ultimate analysis (wt%)	C	47.770	82.600	77.84
	H	5.980	2.840	2.18
	N	0.900	1.179	2.59
	S	0.030	0.050	0.025
	O	45.310	13.330	17.36

There is decreased in the carbon element (C) content in the MPA sample than the char (PKC) (Table 2) which is due loss of carbon in the carbon-CO₂ reaction. The decrease in carbon content of MPA resulted in relative increases in the corresponding nitrogen (N) (1.179 to 2.59 %) and oxygen (O) contents (13.33 to 17.36 %).

3.1.4 Nitrogen Adsorption

Activated carbons with higher micropore volume have much higher capacity to adsorb small molecules, such as VOCs (volatile organic chemicals) and gases. Therefore, activated carbons with high micropore are more suitable for gas storage and separation applications [30]. The textural properties of the activated carbons were analysed by nitrogen adsorption. The BET surface area and porosity results of palm kernel shell derived porous carbons (PCs) are shown in Table 3. There is improvement in both surface area and pore volume after activation of samples. This could be attributed to creation of new pores after activation of the samples [27].

Table 3 Porosity parameters of microwave palm shell porous carbons obtained from nitrogen adsorption.

Sample	S _{BET} (m ² /g)	V _{tot} (cm ³ /g)	V _{micro} (cm ³ /g)	D _{avg} (nm)
PKC	24.5000	0.01517	0.0087	2.4770
MPA	322.536	0.1718	0.1053	2.1306

3.2 CO₂ Adsorption Isotherm Modeling

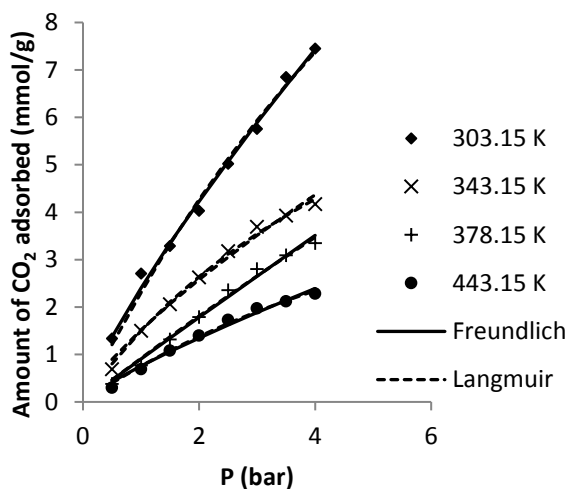
The adsorption isotherm indicates how the adsorbate (CO₂) and adsorbent (porous carbons) interact. Correlation of equilibrium data is vital in design and optimization of sorbent performance. Due to the

inherent bias resulting from linearization, alternative isotherm parameter sets were determined by non-linear regression. The adsorption studies were carried out at different initial pressures between 0 to 4 bar and four different temperatures, i.e. 303.15, 343.15, 378.15 and 443.15K. In this study, 2-parameter Langmuir and Freundlich adsorption isotherms models were applied together with three parameter Sips and Toth models.

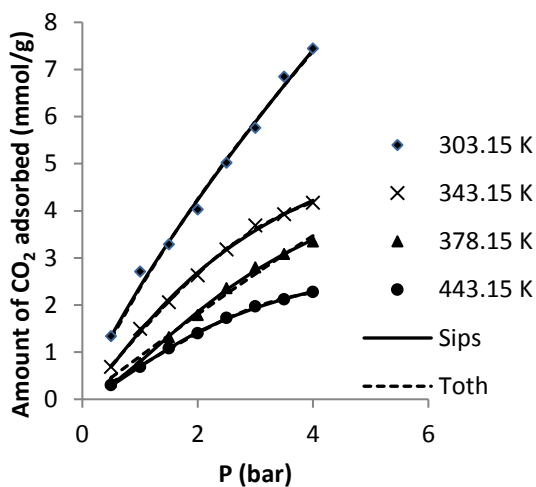
Effect of temperature and pressure on the CO₂ adsorption capacity of MPA was also studied. As depicted in Figure 3, the amount of CO₂ adsorbed increases with an increase in the pressure of the system. This is due to the fact that increasing the pressure increases the van der Waals attraction forces between the sorbate gas and adsorbent. In this study, the highest amount of CO₂ uptake by MPA adsorbent was 7.45 mmol/g at 303.15 K and 4 bar (Figure 3). The CO₂ uptake isotherm profile is of type 1 according to IUPAC classification of isotherms. For typical isotherm type I, initially, there is drastic increase in CO₂ uptake at lower pressure but then slowly increased with increase in pressure.

The plots of the experimental adsorption data and the predicted data from Langmuir and Freundlich isotherm models are shown in Figure 3. The solid lines represent the Sips isotherm and Freundlich isotherm in the three parameter and two parameter models respectively. The broken lines represent the Toth isotherm and Langmuir isotherm in the three parameter and two parameter models respectively. The detailed isotherm parameters are listed in Table 4 for the two and three parameter models respectively. The Langmuir and Freundlich isotherm models were valid and exhibited satisfactory fits to the experimental data for MPA. Both models gave R² > 0.98 (Table 4). Low values of RSMD for the Langmuir and Freundlich models indicated that the models fit well with the experimental data (Table 4).

For MPA sorbent, the Langmuir isotherm performed better at all other temperatures except at 303.15 K, this entails that the adsorption process is multi-layer and then changes to monolayer with increase in temperature. The magnitude of the n (adsorption intensity) from the Freundlich isotherm gives an indication of the favourability of the adsorption. Whereby, values n > 1 represent favourable adsorption condition. The value for n is greater than 1 at all temperatures for MPA. The Freundlich model is used for heterogeneous systems with interaction between the molecules adsorbed. This indicated that Freundlich isotherm describe the adsorption system better at lower temperatures while the Langmuir isotherm is better at higher temperature.



(a)



(b)

Figure 3 Equilibrium isotherm of CO₂ adsorption on MPA at various temperatures correlated with (a) 2-parameter Freundlich and Langmuir models (b) 3-parameter Sips and Toth models

For the three parameter models, both Sips and Toth model fits the CO₂ adsorption data on the PCs well base on R² and RSMD values (Table 4). Sips model gives higher correlation coefficient at all temperatures (i.e 303.15 and 243.15, 378.15 and 443.15K) than the Toth model. Lower RSMD values also suggest that Sips model fits the experimental data better than the Toth model. This is further elucidated by the fact that the Sips model line is in close proximity with the experimental data points (Figure 3b). The adsorption capacity of all the sorbent decreased with increase in temperature (Figure 3); the higher the adsorption temperature, the lower the amount of CO₂ adsorption. This is due to the fact that adsorption is exothermic.

According to the Le Chatelier's principle, the endothermic desorption will be favoured when

temperature increases [31]. Therefore, less amount of CO₂ is adsorbed at higher temperatures.

The affinity constant, *b*, constant is a measure of how strong adsorbate molecules are attracted onto a surface. Hence, it seems obvious that CO₂ is strongly attracted to the surface. In an exothermic process like adsorption, *b* decreases with temperature for all the adsorbates.

Table 4 Sips, Toth, Freundlich and Langmuir Isotherm and fitting parameters for the adsorption of CO₂ on MPA.

Isotherm	T (K)	q _m	b	n	R ²	RSM D
Sips	303.	138.6	0.0	1.1	0.99	0.158
	15	6	2	9	4	
	343.	7.21	0.2	0.8	0.99	0.055
	15	5	0	8		
	378.	5.93	0.1	0.6	0.99	0.050
	15	6	4	8		
	443.	3.45	0.2	0.6	0.99	0.018
	15	5	7	9		
Toth		q _m	b	n		
	303.	185.9	0.0	0.4	0.99	0.172
	15	9	2	6	2	
	343.	5.00	0.2	2.9	0.99	0.047
	15	9	2	8		
	378.	14.80	0.0	1.6	0.99	0.099
	15	6	4	1		
	443.	2.44	0.2	5.1	0.99	0.025
15	9	0	9			
Freundlich		n	K _F		R ²	
	303.	1.23	2.4	-	0.99	0.153
	15	1	4			
	343.	1.31	1.5	-	0.98	0.130
	15	2	8			
	378.	1.02	0.9	-	0.98	0.109
	15	0	9			
	443.	1.21	0.7	-	0.98	0.084
15	6	4				
Langmuir		q _m	K _L			
	303.	27.31	0.0	-	0.99	0.196
	15	9	0			
	343.	11.22	0.1	-	0.99	0.080
	15	5	5			
	378.	43.21	0.0	-	0.99	0.103
	15	2	0			
	443.	7.80	0.1	-	0.99	0.061
15	1	2				

The parameter *n* in the sips equation indicates the heterogeneity of the system. The value of *n* obtained was usually higher at lower temperature (303.15 K) then gradually decreases with increase in temperature. At lower temperature where *n* > 1 (Table 4.), suggest some degree of heterogeneity of the gas/activated carbon system [32]. Pakseresht et al. [33] made similar observation for the decrease in the value of *n* with temperature on adsorption of CO₂ on 5A molecular sieve. The detailed isotherm parameters were listed in Table 4. The *n* parameter from Tóth's model reflects heterogeneity of the sorbent surface. In most of the results obtained for the PCs sorbents *n* is

not one, which indicated the heterogeneity of the surface which is favourable for adsorption [34].

4.0 CONCLUSION

In this study, CO₂ activated carbon was prepared from palm shell via carbonization and microwave assisted K₂CO₃ activation. Results revealed formation of rudimentary pores after carbonization while more cavities and widening of pore network are achieved after activation. MPA recorded 2.71 mmol/g CO₂ uptakes at 303.15 K, 1 bar. The adsorption capacity increases with the decreasing temperature and increases with pressure. Sips model was the best to fit the isotherm data for the adsorption of CO₂ on MPA. The study shows that the microwave palm shell activated carbon is a potential sorbent for CO₂ adsorption applications.

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