

Kinetic Equilibrium and Isotherm Modeling Adsorbed Methane Assessment on Synthesized PEEK-Porous Sorbent Carbon of Sustainable Coconut Shell Kernel

Noor Shawal Nasri^{a,*}, Hayatu Umar Sidik^c, Muhammad Abbas Ahmad Zaini^b, Norhana M. Rashid^a, Zulkifli Abdul Majid^a, Shreeshivadasan Chelliapan^d, Thanikasalam Kumar^a, Husna Mohd Zain^a, Rahmat Mohsin^a, Nabilah Zaini^e

^aSustainable Waste-To-Wealth Program, UTM-MPRC Institute for Oil and Gas, Resource Sustainability Research Alliance, Universiti Teknologi Malaysia, UTM Johor Bahru, Johor, Malaysia

^bDepartment of Chemical Engineering, School of Chemical and Energy Engineering, Universiti Teknologi Malaysia, UTM Skudai, Johor, Malaysia

^cDepartment of Chemical Engineering Technology, School of Engineering Technology, Federal Polytechnic P.M.B Mubi, Adamawa State, Nigeria

^dDepartment of Engineering, UTM Razak School of Engineering and Advanced Technology, Universiti Teknologi Malaysia, 54100 Kuala Lumpur, Malaysia

^eSHIZEN Conversion and Separation Technology, Department of Chemical Process Engineering, Malaysia-Japan International Institute of Technology (MJIIT), Universiti Teknologi Malaysia, 54100 Kuala Lumpur, Malaysia
 noorshaw@utm.my

It is important to understand methane (CH₄) adsorption onto available biomass surfaces quantitatively for its storage as Adsorbed Natural Gas (ANG). Coconut shell being among the abundant agro-waste in Malaysia has chosen with polyetheretherketone (PEEK) as a precursor for preparation of hybrid activated carbon via microwave induced potassium hydroxide activation for methane storage. M33P15 Porous carbon prepared at 300 Microwave power with 3 min irradiation and 15 wt% amount of PEEK and M33P0 was prepared under the same condition as M33P15 but without addition of PEEK. The porous carbons were used for CH₄ adsorption as the interactions between carbon and methane is based the pore diffusion and partly film diffusion. The ideal CH₄ adsorption capacities of the activated carbons were conducted using volumetric adsorption equipment at pressures (5-30 bar). The obtained experimental data at initial pH of 8.0 and 9.0 were correlated using linear regression analysis with common adsorption kinetic (Pseudo-first order, Pseudo-second order, Elovich) and isotherm models (Freundlich, Langmuir, Sip, and Toth). The pseudo-second-order kinetics describe the best fitness with a correlation coefficient of 0.9998 for sample M33P15. For adsorption isotherms, Sip model shows better fitness for sample M33P15 with the regression coefficient (R²) 0.9800 and with lowest RSMD value (0.1438) than other models. The findings revealed the potential of kinetic and isotherm models in methane adsorption applications.

1. Introduction

Natural gas used in industries, for transportation vehicles, and for households (Martins et al., 2015). For industries application, where there is no pipelines system, it sometimes has to be transported to the location using transportation systems (vehicles). For it to be transported, it has to be stored in heavy tanks with pressure ranges between 200-250 bars at room temperature (Nasri et al., 2017). Compression and liquefaction methods were earlier adapted to increase the fuel density to meet up with several applications: however, they were found to be attributed to high-pressure applications and the high cost of processing. To overcome these deficits, the gas should be stored by adsorption onto the surface of porous carbon at relatively lower pressure (35 – 40 bar) to that of compression and at a lower cost to both (Liu et al., 2014).

Therefore, there is need to develop an adsorbent from local and inexpensive available materials such as agricultural waste. Better adsorbent adsorption properties are greatly influenced by the parent material and the method employed in the production (Saleh and Danmaliki, 2016). It had reported that PEEK porous carbon has good properties for high compressive strength and gas storage applications (Thomas et al., 2010). This is due to the excellent textural properties of the PEEK porous carbon namely high porosity and better mechanical property (Hayatu et al., 2017).

The objectives of this paper are to determine the adsorbent characteristics, adsorption performance, isotherms and kinetics of a coconut shell based activated carbon (non-hybrid) and coconut shell-PEEK based activated carbon (hybrid), and to assess the effect of PEEK toward the adsorption of methane on the surface of the activated carbon impregnated with potassium hydroxide. The novelty of this work is towards adsorbent preparation and adsorption models evaluation. Mylläri et al. (2012) opined that most studies on PEEK focus on thermal stability since it is one of the highest temperature (260 °C) resistance among all plastics. The use of PEEK in adsorption application has not received sufficient research attention.

2. Experimental

2.1 Sorbent synthesis and adsorption

Two precursors with different structural properties were selected to suit the purpose of this research. Raw coconut shell obtained from Johor State in Malaysia was washed, sun-dried and dehydrated at 105 °C for 24 h using the oven. It was carbonized using the furnace at 720 ± 20 °C under nitrogen flow for 2 h to obtain char and the system was allowed to cool before removing sample. The carbon particles ground and sieved to 0.841-0.425 mm. The PEEK also carbonized at 850 ± 20 °C for 45 min under a nitrogen flow and sieved to same size particle with coconut shells char. The char denoted as CPBC-15 was prepared by blending 15 wt % of PEEK with 85 wt% coconut shell char of the total amount of the char. The blended chars then treated with KOH at a ratio of 1: 1.5 and then activated using the microwave, the activated carbon denoted as a hybrid (M33P15). While the char denoted as CPBC-0 was prepared from coconut shell only. The CPBC was treated with KOH at a ratio of 1:1.5 and then activated using microwave, the porous carbon denoted as non-hybrid (M33P0). The CH₄ adsorption achieved at ambient temperature and initial pressures of 5, 7.5, 11, 17, 25 and 30 bar using the static volumetric unit setup. The setup comprises of load cell and adsorption cell. The height of load cell found to be 14 cm and 5.5 cm, while the inner diameters were 2 cm and 1 cm. The inner height and the diameter of the adsorption cell are 2 cm and 2.5 cm.

The detailed methodology of impregnation, microwave activation, and adsorption was given elsewhere (Sidik et al., 2017). The porous carbons were characterized for its specific surface area and bulk density.

2.2 Adsorption kinetic and isotherm models

The kinetic models were selected for this research based on their simplicity applicability in describing the solid-gas interaction and rate of adsorption behavior. The fitting of the experimental kinetics data was achieved using linear regression by plotting $\ln(q_e - q_t)$ (mmol/g) vs. t (min) for pseudo-first order, t/q_t vs. t for pseudo-second order and q (mmol/g) vs t (min) for Elovich. Where q_e and q_t are the adsorbed amount of gas (mmol/g) at equilibrium and at time t (min), k_1 (1/min) and k_2 (g/mmol min) are the adsorption rates constants of pseudo-first-order and pseudo-second-order. Value of k_1 was determined from the slope of the linear plots of $\ln(q_e - q_t)$ (mmol/g) vs. t (min), while k_2 (g/mmol min) from the intercept and the slope of plot t/q_t vs. t . The kinetics experimental results were analyzed to predict the constants of adsorption using the three kinetic models that were selected to correlate with the experimental data, based on their suitability towards solid-gas adsorption characteristics namely: pseudo-1st order (Saleh, 2015), pseudo-2nd order, and Elovich model are shown in Eq(1), Eq(2) and Eq(3).

$$\ln(q_e - q_t) = \ln q_e - kt \quad (1)$$

$$\left(\frac{t}{q_t}\right) = \frac{1}{(k_2 q_e^2)} + \frac{1}{q_e} t \quad (2)$$

$$q_t = \frac{1}{b} \ln(ab) + \frac{1}{b} \ln t \quad (3)$$

2.3 Adsorption isotherm modeling

Adsorption isotherms are models used for identification of how adsorbent and adsorbate interact to give a clear understanding of their behavior. Langmuir isotherm predicts the monolayer at the homogeneous surface (Saleh and Al-Absi, 2017), while Freundlich is for a heterogeneous surface which describes non-ideal and reversible

adsorption (Hamza et al., 2015). Toth isotherm is a modified Langmuir equation with the aim of reducing the error between predicted and experimental values. The model is used in describing heterogeneous adsorption of both low and high adsorbate concentration. Sip is also a modified model that combines the applications of both Langmuir and Freundlich for use on heterogeneous surfaces. The Langmuir, Freundlich, Toth and Sips models were shown in Eq(4), Eq(5), Eq(6) and Eq(7).

$$q = q_m \frac{k_1 p}{1 + k_1 p} \quad (4)$$

$$q_e = k_f p^n \quad (5)$$

$$q = \frac{q_m k_{if} p^{n_{if}}}{1 + k_{if} p^{n_{if}}} \quad (6)$$

$$q = \frac{q_m b p}{[1 + (b p)^n]^{\frac{1}{n}}} \quad (7)$$

q_e is equilibrium sorption capacity (mg/g), q is the sorption capacity with respect to time (mg/g), t is adsorption time (mins), k_1 and k_2 is pseudo-first order rate constant (min^{-1}) and pseudo-second order rate constant ($\text{g mg}^{-1} \text{min}^{-1}$), a (mg/g h) is the initial sorption rate and b (g/mg) is the extent of surface coverage and activation energy for chemisorption. K_F and $1/n$ are Freundlich constants which measure CH_4 adsorption intensity, P is the bulk pressure of CH_4 in the gas phase, q is the amount of CH_4 adsorbed (mg/g), q_m is saturation limit (mg/g) K_L is Langmuir constant, k_{if} and n_{if} are Sip constants, n and b are Toth constants.

2.4 Validity and fitting of the models

Root Square Means Deviation (RSMD) and coefficient of determination (R^2) values obtained using the Eq(8) and Eq(9) were used to validate the experimental data, as well as its fitness.

$$RMSD = \left[\frac{1}{n} \sum (q_{\text{exp}} - q_p)^2 \right]^{\frac{1}{2}} \quad (8)$$

$$R^2 = 1 - \frac{\sum_{n-1} (q_{\text{exp}} - q_p)^2}{\sum_{n-1} (q_{\text{exp}} - \bar{q}_p)^2} \quad (9)$$

q_{exp} (mmol/g) and q_p (mmol/g) are experimental and theoretical adsorption capacities

3. Results and discussion

3.1 CH_4 adsorption

The adsorption study was obtained with respect to time at isotherms of ambient temperature and pressures starting from 5 to 30 bar (Figure 1). It was observed that the adsorption equilibrium increase with an increase in initial pressure from 5 - 30 bar. Increase in working pressure of the system lead to the increase in the methane adsorption uptake. As stated by Fatemi et al. (2011) that increase in working pressure would increase the Van der Waal force of attraction between the adsorbent and adsorbate. The lowest amount of CH_4 uptake at pressures 5, 7.5, 11, 17, 25 and 30 bar depicted on the non-hybrid sample is 2.05, 3.04, 4.30, 6.81, 7.05 and 8.59 mmol/g, while the highest uptake was depicted hybrid as 2.35, 3.06, 4.80, 7.15, 7.51 and 9.18 mmol/g. This might be due to the high surface area displayed in nitrogen adsorption analysis and higher bulk density of PEEK (Thomas et al., 2010). However, the adsorption capacities displayed by the two samples show no significant difference, despite the possession of higher specific surface area by sample M33P15. This might be due to the higher pH value (9.0) displayed by sample M33P15. The specific surface area and bulk density for the porous carbons were $267 \text{ m}^2/\text{g}$ 0.345 g/cm^3 for M33P0 and $479 \text{ m}^2/\text{g}$ and 0.413 g/cm^3 for M33P15. For methane storage adsorbent, the higher the adsorbent bulk density the more its storage factor (Zhang et al., 2010).

3.2 CH₄ adsorption isotherm

CH₄ adsorption isotherms belong to type 1 as the amount of adsorption increase with time then reached equilibrium point (Xing et al., 2015). The CH₄ adsorption isotherm shows how the interaction between CH₄ and the synthesized adsorbents occur. Two parameters isotherm models (Langmuir and Freundlich) together with the three model parameters (Sips and Toth) applied for this study. Figure 2a depicted the plots for the experimental data with predicted from the two and three parameters adsorption isotherms on the porous carbon M33P15, while figure 2b depicted for porous carbon M33P0. In general, the suitability of the four isotherm models predicting the interaction behavior of CH₄ adsorption on the porous carbons synthesized is in order of Freundlich < Langmuir < Toth < Sips with the corresponding plots as shown in Figures 2a and 2b. This shows that Sips and Toth isotherm models give an accurate description of the interaction between CH₄ and the porous carbon synthesized which was primarily designed to describe gas-solid adsorption (Danmaliki and Saleh, 2016). The details of the model parameters for two and three parameters are given in Table 1. It can be seen that the regression fitting (R^2) for all the adsorption isotherms ranges from 0.96 to 0.98, which reflect the goodness of the data fitting. However, three parameter models fitted better to the experimental values than two parameter models. A similar observation made by Delver et al. (2012) indicates that Sips model fit CH₄ adsorption satisfactorily on Multi-Walled Carbon Nanotubes. The values of adsorption intensity (n) for the three models for both samples were greater than 1, indicating favorable adsorption (Saleh, 2016).

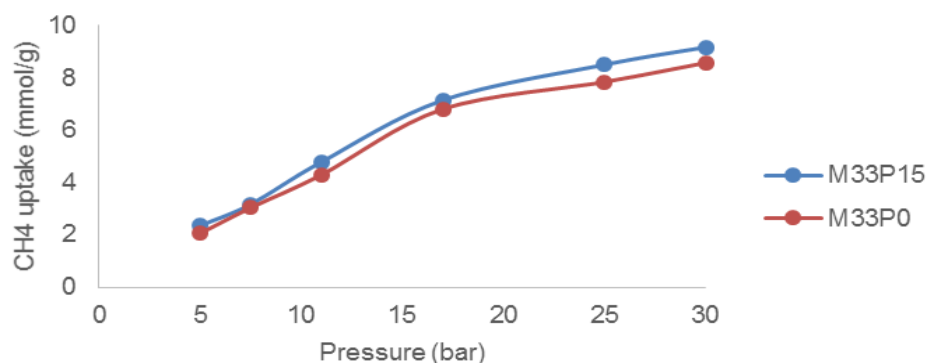


Figure 1: CH₄ experimental adsorption capacity on porous carbons, hybrid and non-hybrid

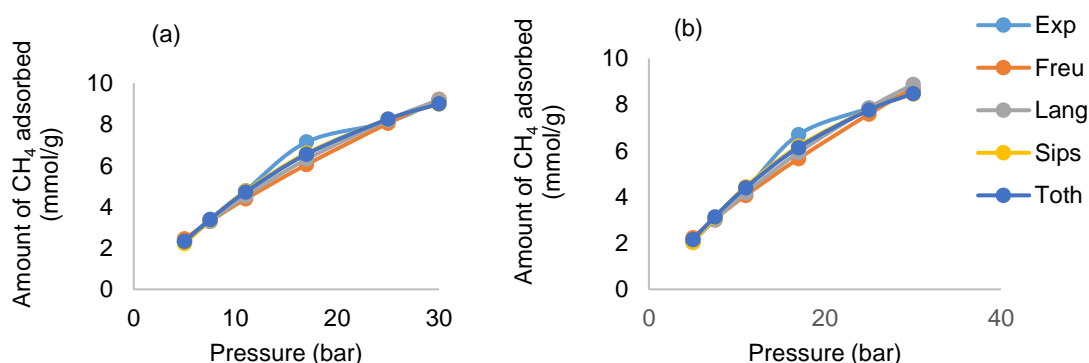


Figure 2: CH₄ adsorption isotherm models plots on porous carbon (a) M33P15 and (b) M33P0

3.3 Adsorption kinetics

The experimental data obtained were fitted to pseudo-first order, pseudo-second order and Elovich kinetic models to evaluate the correlation of CH₄ adsorption between the hybrid and non-hybrid activated carbon. The kinetics data of the methane adsorption on the hybrid and non-hybrid activated carbons are given in Table 2. There is an indication that the values obtained using second order model are more correlated to experimental values. Both of the samples indicate a decrease in K_1 and K_2 values with increase in adsorption pressure.

Despite it was not maintained the similar pattern in all the pressures but in general, it decreases with increase in pressure. The decrease in K_2 indicates high repulsion between CH_4 molecules, which enhance wall collision that leads to decrease in diffusivity (Longanathan et al., 2014). Considering the R^2 values of the models at all the adsorption pressure, the suitability of the three models predicting the kinetic behavior of CH_4 adsorption on the porous carbon synthesized is in order of Elovich < Pseudo-first order < pseudo-second order kinetics with the corresponding values as shown in Table 2. It can be concluded from this results that pseudo-second order kinetics model gives a more accurate description of CH_4 on the porous carbon synthesized.

Table 1: Freundlich, Langmuir, Sips and Toth isotherm fitting parameters for CH_4 on M33P15 and M33P0 porous carbons

Sample	Isotherm	n	KF	q_m	K_L	b	R^2	RSMD
M33P15	Freundlich	1.4934	0.9214	-	-	-	0.9660	0.1872
M33P0	Freundlich	1.4712	0.8388	-	-	-	0.9647	0.1817
M33P15	Langmuir	-	0.0298	19.0469	0.0298	-	0.9769	0.1543
M33P0	Langmuir	-	0.0284	18.3919	0.0284	-	0.9754	0.1515
M33P15	Sips	0.7665	-	13.3601	-	0.0242	0.9799	0.1439
M33P0	Sips	0.7531	-	12.5190	-	0.0228	0.9789	0.1405
M33P15	Toth	1.8055	-	12.2893	-	0.0389	0.9789	0.1473
M33P0	Toth	1.8381	-	11.6111	-	0.0381	0.9776	0.1447

Table 2: Kinetic parameters for adsorption of CH_4 on hybrid and non-hybrid activated carbon

Sample	Pressure(bar)	1 st order		2 nd order		Elovich
		$K_1(\text{min}^{-1})$	R^2	K_2	R^2	R^2
M33P15	5	0.0281	0.9104	0.0581	0.9936	0.7730
	7.5	0.0379	0.7177	0.0770	0.9971	0.7590
	11	0.0355	0.9632	0.0422	0.9990	0.9490
	17	0.0285	0.9883	0.0117	0.9937	0.7080
	25	0.0286	0.9850	0.0093	0.9917	0.7887
M33P0	30	0.0216	0.9531	0.0055	0.9917	0.9910
	5	0.0386	0.8594	0.0589	0.9929	0.9170
	7.5	0.0256	0.9066	0.0774	0.9971	0.9560
	11	0.0283	0.9383	0.0176	0.9857	0.9600
	17	0.0233	0.9595	0.0102	0.9911	0.8770
	25	0.0288	0.9795	0.0113	0.9998	0.9998
	30	0.0246	0.9861	0.0063	0.9927	0.9013

4. Conclusions

The adsorption capacity, adsorption isotherm and kinetic behavior of the synthesized porous carbons in CH_4 adsorption at ambient temperature and pressure range between 5-30 bar were investigated. Porous carbon (M33P15) attained higher adsorption capacity than porous carbon (M33P0). The adsorption isotherm models adopted for this study are Freundlich, Langmuir, Sips, and Toth. While the kinetic models are: Pseudo-1st order, Pseudo-2nd order, and Elovich. The adsorption isotherm and kinetic model that fitted best for this experiment are Toth and Sips models and Pseudo-2nd order kinetic. This was concluded based on their high value of R^2 and low values of RSMD.

Acknowledgments

The authors appreciate and thank the financial support and contribution provided by the Ministry of Higher Education Malaysia and Universiti Teknologi Malaysia through the Research University Grant Q.J130000.2546.13H94 and Q.J130000.2509.10H89. Special appreciation to the Sustainable Waste-To-Wealth Program of UTM-MPRC Institute for Oil and Gas, Universiti Teknologi Malaysia to provide technical support and its technical service grant Q.J090401.23C9.01D08.

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