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Description of Carbon Dioxide Adsorption and Desorption onto Malaysian Coals under Subcritical Condition

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Abstract

Coal bed seams have been considered as promising sequestration reservoirs for CO₂ disposal to mitigate the green house gas emissions. The CO₂ adsorption and desorption attributes of CO₂ on dry Malaysian coals (Sarawak, volatile bituminous) were performed using a sorptomat apparatus (ASAP 2010, Micromeritics, USA) and BELSORP-mini II machine (BEL Japan, Inc.) at 273 K, 298 K and pressure up to 1 bar. The CO₂ adsorption was favourable at low temperature and dry coal conditions. However, S3 and S4 coals have the highest adsorption capacity by 0.71 and 0.73 mmol/g respectively. According to IUPAC classification of adsorption isotherms, CO₂ adsorption isotherm of all coal samples follow type I which most probably describe the adsorption limited to a few molecular layers (micropores). The results of adsorption and desorption isotherm demonstrate a positive hysteresis in all coal samples. The S1 coal and S2 coal have the highest hysteresis between adsorption and desorption isotherm compared to S3 coal and S4 coal. According to hysteresis classifications, the hysteresis during CO₂ adsorption and desorption process for all coal samples follows type H₃ which describes micropores and mesopores. The evaluation of the equilibrium adsorption data were fitted using by Langmuir, Freundlich, Redlich-Peterson, Koble-Corrigan, Toth and Sips models. Toth model provided the best fit for all adsorption experimental data that predicting all coals having heterogeneous surface properties.

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Keywords: CO₂ adsorption and desorption; coal; hysteresis; isother medols.

1. Introduction

The excessive emission of carbon dioxide (CO₂) into the atmosphere is broadly agreed as one of the major causes of global warming and air pollution. The most successful disposal techniques of the captured carbon dioxide

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are geologic storage sites such as depleted oil and gas reservoirs, deep saline aquifers and deep unminable coal bed seams. Geosequestration of carbon dioxide (CO₂) in coal bed seams is reported as a promising CO₂ disposal option with or without methane displacement process. However, CO₂ sequestration into coal bed seams is combination between physical and chemical adsorption with other trapping processes, mostly due to the heterogeneous morphology of coal texture [1] and extreme coal bed seam conditions.

The storing mechanism of CO₂ in coal bed seams mostly relies on the adsorption characteristics of the morphology and the porous coal structures [2, 3]. According to White et al which reported that 95-98% CO₂ stored by adsorption mechanism in the coal matrix depends on the gas in the coal bed seam and there are other storing mechanisms such as gas stored within the coal matrix composition, free gas and gas stored as a solute in the water porous [4].

Thus, it is essential to comprehend the CO₂ adsorption onto Malaysian coals during sequestration process and the CO₂ desorption mechanism from coal by depressurization process. However, the deviation occurs between adsorption and desorption isotherm of gases on porous materials is called hysteresis. Hysteresis indicates that coal desorbs less gas than the sorption volume in the adsorption isotherm at the same pressure. The hysteresis level is independent of the coal physical properties (density, diffusivity, viscosity, surface texture, and gas phase) [2] and operating condition (pressure and temperature). CO₂ sorption hysteresis process is a favourable for the long-range preserve of CO₂ sequestration [5]. Currently, numerous research studies of CO₂ sorption on various coal specimens have been conducted not just only for practical evaluation of coal bed gas capacity but also to comprehend the fundamental mechanisms of the gas adsorption and desorption isotherms on coal. To understand the interactions of CO₂ with coal, it is necessary to conduct experiment on CO₂ adsorption and desorption isotherm on Malaysian coal from low to high temperatures and pressures.

In this study, the CO₂ adsorption/desorption on dry Malaysian coal measured under subcritical conditions. The CO₂ adsorption isotherm conducted at 273 K, 298 K and pressure up to 1 bar. Meanwhile, desorption was performed by depressurizing CO₂ from 1 bar. The results from two different temperatures were compared to each other. Finally, the adsorption isotherm models were utilized to fit the equilibrium adsorption data.

2. Experimental

2.1. Adsorbent

The coal samples were obtained from Merit-Pila coal mine Lower (S1), and Upper (S2) zones and Mukah-Balingian coal mine from Area1 (S3) and Area4 (S4) coordinates, Sarawak, Malaysia. The majority of coals in Sarawak are sub-bituminous coals. Before adsorption measurements on dry coal, the samples were desiccated for more than 12 hr in a vacuum oven (pressure ~ 10kPa) at 378K (105 °C).

2.2. Instruments and Experimental Procedures

Experimental studies of sorption were firstly performed with the use of Sorptomat instrument, ASAP 2010 (Micrometrics, USA) to study CO₂ adsorption and desorption of S1, S2, S3 and S4 coals. CO₂ (99.99%) adsorption conducted at 273 K (0°C) at 760 mmHg (1 bar). At each target pressures, the gas is stored inside the manifold (reservoir) before release onto sample. The pressure was monitor before/after the stored gas in the manifold is release onto sample. When adsorption occurs, the pressure starts decline. By using the gas law the volume of adsorbed is determined by determined the changes in pressures while the temperature is held constant. The volume adsorbed is finally calculated after minus the void volume inside the sample tubes.

For carbon dioxide gas (CO₂), degas was performed to clean the surface of the coal samples prior to analysis. The samples were subjected to constant nitrogen purging while heating the samples to remove any sorbed species from the sample. For the temperature profile of degas, the first hour the temperature was heated up to 90°C to remove the moistures for 60 minutes (1 hr). This is followed by raising the temperature up to 150°C at 10°C/min for 480 minutes (8 hrs) to remove any sorbed species from the samples. Eventually, the samples were subjected to CO₂ gas adsorption using the bath temperature of 0°C by controlled water circulating bath. A target pressure is gradually increased for up to about 800 mmHg and each target pressure points, the amount of CO₂ adsorbed was

determined. For desorption, the sample tube pressure is slowly decrease by vacuum and the volume of CO₂ gas is determined for each pressure points.

Secondly, BELSORP-mini II instrument (BEL Japan, Inc.) was utilized to measure CO₂ adsorption and desorption isotherm on granular coal sample at 298.15K (25 °C) and pressure 101.3 kPa (1 bar) using volumetric technique. Before starting the experiment, the two coal sample cells attached to pretreatment system with vacuuming at 105 °C for at least two hours to remove the remains of moisture in the coal samples. After that setting the weight of coal samples in data acquisition in the system and then start connecting the coal sample cells into port 1 & 3 and port one for blank cell then coal samples cells subjected to pure CO₂.

The experiment begins with measurement of dead volume and adsorption-desorption isotherm measurement at pressure up to 101.3 kPa (1 bar) with using the bath temperature of 298.15 K (25°C) controlled by water circulating bath. In order to measure the adsorption amount of CO₂ on coal, the amount of measuring system has to be measured accurately at means of state equation of gas. Thus, the gas adsorption amount is measured from the change of gas pressure inside the measuring system by the equation of state. A target pressure is gradually increased up to 101.3kPa (1 bar) and each target pressure points, the amount of CO₂ gas is determined. For desorption, the sample tube pressure is slowly decrease by vacuum and the volume of CO₂ gas is determined for each pressure points.

3. Results and Discussion

The amounts of adsorbed CO₂ on all S1, S2, S3 and S4 coals at temperature 273 K and 298 K were increased with pressure. The experimental amounts of adsorbed CO₂ on S1, S2, S3 and S4 coals at 273 K and 298 K are shown in Fig 1. However, the shapes of the isotherms were different in S1 and S2. The amount of adsorbed CO₂ on S1 coal sample at 298K is higher than the amount adsorbed CO₂ at 273 K. This is due to the heterogeneity of S1 coal and it has low specific surface area (0.1824 m²/g) and the adsorbed amount reached 0.40994 mmol/g. The amount of adsorbed CO₂ on S2 coal showed an asymptotic trend. The S3 coal sample has the highest amount of adsorbed CO₂ adsorbed by 0.7389 mmol/g as shown in Fig. 2.

According to IUPAC classification, the shape isotherms of all CO₂ adsorption on all coal samples follow type I representing the monolayer formation of molecules (micropore). However, the CO₂ adsorption curve of S1 and sample S2 show steadily increase in CO₂ adsorption capacity meanwhile the isotherms of S3 and S4 describe a rapid increase in CO₂ adsorption capacity over a low pressure range (<0.4 bar). The experimental isotherms of all CO₂ adsorption of all coal samples demonstrate that their concavities are variable.

The concavities provide a confirmation of the affinity of CO₂ adsorption onto coal. The S1 and S2 adsorption isotherms have shape, explaining the slow affinity to CO₂. Meanwhile S3 and S4 isotherms show the highest concavity. The influence of hysteresis indicates that the sorbent/sorbate system is in a metastable state and at pressure decrease the gas is not readily released to the extent corresponding to the value of thermodynamic equilibrium.

Generally, desorption isotherms lie above the adsorption isotherms [6]. Thus, the adsorbed CO₂ amount from the desorption isotherm was higher than that of the adsorption isotherm in the gas phase [2]. Desorption isotherm at 273 K and 298 K was obtained from depressurization conditions after finishing the adsorption experiment. As shown in Fig. 1 the CO₂ adsorption and the desorption curves of S1, S2, S3 and S4 for the individual revealed various degree of hysteresis. The results of CO₂ adsorption and desorption isotherm of all coal samples describe a positive hysteresis between adsorption and desorption isotherm.

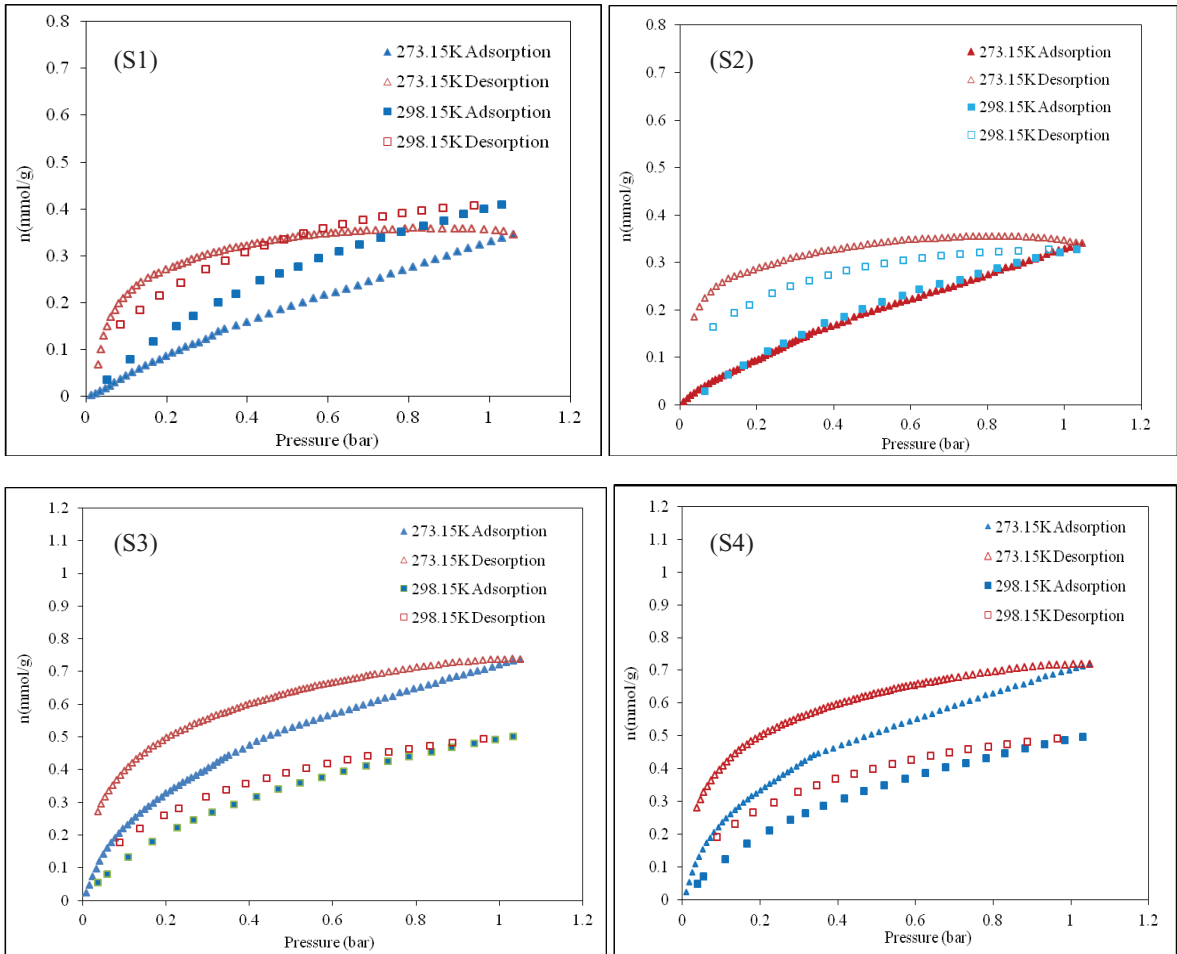


Fig. 1. All adsorption and desorption of CO₂ on S1, S2, S3 and S4 coals at 273.15 K and 298 K respectively.

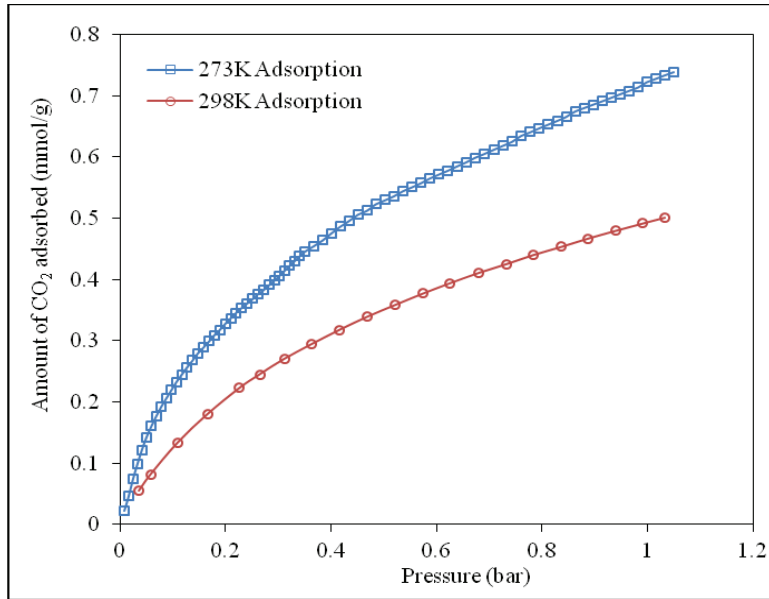


Fig. 2. The amount of adsorbed CO₂ on S3 coal at 273K, 298K and up to 1 bar.

4. Adsorption Isotherms

The theoretical adsorption isotherm models provide significant description of adsorption behaviour. Those models describe how the adsorbate interacts with the adsorbent and offers explanation for the nature and mechanism. They describe how the adsorbate interacts with the adsorbent and offers explanation for the nature and mechanism of gas adsorption onto the adsorbent. Equilibrium isotherm data attained from two and three parameters models provide significant information on adsorption mechanisms and surface properties and affinity of adsorbent [7]. Thus, it is essential to test the suitable correlation of the experimental equilibrium curves to optimize the conditions for designing adsorption systems. In this study, Langmuir, Freundlich, Redlich-Peterson, Koble-Corrigan, Toth and Sips models were applied to explore the adsorption behaviour.

4.1. Langmuir model

Langmuir isotherm proposed by Ivan Langmuir [8] and it is built on rational assumption that adsorption occurs at specific homogenous sites within the adsorbent surface. It explains that the adsorbent has a finite capacity for the adsorbent (i.e. at equilibrium; a saturation point is obtained which no further adsorption can occur. The equation below shows the Langmuir model is represented to fit the adsorbed amount (n_{ads}) is given by [9]:

$$n_e = \frac{n_m b p_e}{1 + b p_e} \quad (1)$$

Where n_e is the number of adsorbed amount of gas (mmol/g), p_e is gas pressure (bar), n_m is the theoretical maximum adsorption capacity (mmol/g) and b is the Langmuir isotherm constant.

4.2. Freundlich model

The Freundlich isotherm is another theoretical model widely applied in interpreting equilibrium adsorption curves. The model simulates to adsorption on heterogeneous surface with interaction between adsorbed molecules. It assumes that adsorption energy exponentially decreases on the completion of the sorptional centres in the adsorbent [9, 10].

The Freundlich equation is given as:

$$n_e = K_F p_e^{1/n} \quad (2)$$

Where n_e is the CO₂ adsorbed amount per unit mass of adsorbent at equilibrium (mmol/g), p_e is the equilibrium pressure (bar), K_F is the Freundlich adsorption constant related to the adsorption capacity of the adsorbent (mmol/g) and n is a dimensionless constant, that can be utilized to elucidate the extent of adsorption and the adsorption intensity.

4.3. Redlich-Peterson

Redlich-Peterson isotherm is a hybrid and it is attributing both Langmuir and Freundlich models that incorporate three parameters into an empirical equation. The model has a linear dependence on pressure in numerator and an exponential function in the denominator to represent adsorption equilibria over a wide pressure range, that can be applied either in homogeneous or heterogeneous systems due to its versatility. However, it approaches Freundlich at high pressure and it is in accordance with the low pressure limit of the ideal Langmuir condition. The Redlich-Peterson model can be presented as follows [11]:

$$n_e = \left(\frac{K_R p_e}{1 + A_T p_e^S} \right) \quad (3)$$

4.4. Koble-Corrigan model

Koble-Corrigan model [12] incorporated both Langmuir and Freundlich models for representing the equilibrium adsorption data. The isotherm constants, A, B and n are evaluated from the linear plot using a trial and error optimization. The Koble-Corrigan model could be shown as follows:

$$n_e = \left(\frac{A p_e^n}{1 + B p_e^n} \right) \quad (4)$$

4.5. Toth model

Toth model is an empirical equation developed to enhance Langmuir isotherm fittings and practical in describing heterogeneous adsorption system that satisfying both low and high pressure. The Toth model can be shown as follows [13]:

$$n_e = \left(\frac{K_T p_e}{(a_T + p_e)^{1/t}} \right) \quad (5)$$

4.6. Sips model

Sips isotherm a incorporated form of Langmuir and Freundlich expressions deduced for predicting the heterogeneous adsorption systems and circumventing the limitation of the sing adsorbate concentration associated with Freundlich model. The Sips isotherm can be shown as follows [14]:

$$n_e = \left(\frac{n_m b p_e^{1/n}}{1 + b p_e^{1/n}} \right) \tag{6}$$

The equation of coefficient of determination “R²” was applied to estimate the unknown isotherm parameters and to examine the best-fitting isotherm models to the experimental equilibrium data. The value of coefficient of determination “R²” is maximized between the experimental data and model by permitting the values of different parameters for the model to change according to the optimization procedure. The coefficient equation of determination “R²” is represented equation [15].

$$R^2 = \frac{\sum (n_{mod} - \bar{n}_e)}{\sum \left((n_{mod} - \bar{n}_e)^2 + (n_{mod} - n_e)^2 \right)} \tag{7}$$

Where n_{mod} is the equilibrium capacity obtained from the isotherm model, n_e is the equilibrium capacity obtained from experiment and \bar{n}_e is the average of n_e . Two and three parameter models have been investigated to describe the CO₂ adsorption on coal. Equation of these two and three parameter models are shown in Table 2. Correlation coefficients and constants of the isotherm models were given in Table 1. (two parameters) and Table 2. (three parameters). As can be seen from Table 1 and Table 2 and Fig 3., experimental results with the best fit Toth isotherm model.

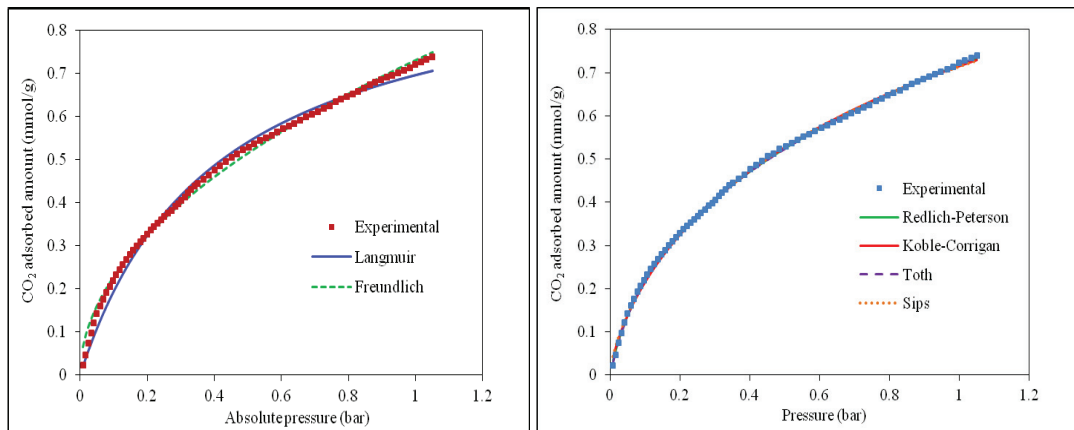


Fig. 3. Experimental and predicted isotherms obtained from two and three parameter isotherm models.

Table 1. Two parameter model constants and correlation coefficients.

Isotherm models	Constants	R ² (Linear)
Langmuir	n_m (mmol/g)	0.9791
	K_L (bar ⁻¹)	2.4770
Freundlich	K_f (mmol/g)	0.9988
	$1/n$	0.9993

Table 2. Three parameter isotherm models parameters values obtained by non-linear analysis.

Isotherm Models	Constants		R ² (Non-linear)
Redlich-Peterson	K_{RP}	5.0989	0.9995
	$a_{RP}(\text{bar}^{-1})$	6.0976	
	g	0.6617	
Koble-Corrigan	A	1.2746	0.9990
	$B(\text{bar}^{-1})$	0.7811	
	n	0.7099	
Toth	$K_T(\text{mmol/g})$	0.7434	0.9999
	$a_{RP}(\text{bar}^{-1})$	0.0571	
	$1/t$	0.5872	
Sips	$b(\text{bar}^{-1})$	0.7795	0.9998
	n_m	1.6302	
	$1/n_s$	0.7057	

5. Conclusions

Four coal samples from different locations were tested for CO₂ adsorption/desorption at temperature of 273 K, 298 K and pressure up to 1 bar. The S3 has the highest adsorption capacity by 0.73 mmol/g. According to IUPAC classification of adsorption isotherms, CO₂ adsorption isotherm of all coal samples follow type I which most probably describe the adsorption limited to a few molecular layers (micropores). The results of adsorption and desorption isotherm demonstrate that there is hysteresis between adsorption and desorption isotherms for all coal samples. The coal samples, S1 and S2 have the highest hysteresis level compared to coal samples S3 and S4 which show a positive hysteresis between their adsorption and desorption isotherms. According to hysteresis classifications, the hysteresis during CO₂ adsorption and desorption process for all coal samples type H₃ which describes the shape of pores which slites. Toth model presented the best fit with experimental data by predicting that material exhibits heterogeneous surface properties.

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