



## Addition of Water in Calcium Based Adsorbent for CO<sub>2</sub> Adsorption: Experimental and Isotherm Modelling Studies

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In this work, a combined process of adsorption and gas hydrate formation is proposed as an alternative approach for the separation of carbon dioxide (CO<sub>2</sub>) content from gas stream. The objective of this research is to study adsorption isotherms of the CO<sub>2</sub> gas onto the synthesized calcium oxide (CaO) via a static volumetric method at 2 °C at a different amount of water ratio ( $R_w$ ). A large increment of CO<sub>2</sub> adsorption was observed on the wetted sample due to formation of CO<sub>2</sub> hydrates, particularly at high pressure. The highest adsorption capacity was obtained at  $R_w$  of 0.67. The experimental data of CO<sub>2</sub> adsorption isotherms for  $R_w = 0$  and  $R_w = 0.67$  are further analyzed by five isotherm models which are Langmuir, Freundlich, Redlich-Peterson (R-P), Toth and Sips. The Freundlich model satisfactorily describes the CO<sub>2</sub> adsorption onto the dried sample, whilst the R-P model is best fitted for the wetted sample.

### 1. Introduction

Carbon capture and sequestration (CCS) is a promising technology to capture, utilize and sequestration of carbon dioxide (CO<sub>2</sub>) from large stationary sources. There are various techniques that can be employed to capture CO<sub>2</sub> such as amine scrubbing, physisorption, chemisorption and chemical bonding through mineralization. Nevertheless, these methods are currently performed in a small scale and scaling-up may accelerate the total cost. Moreover, it is reported that almost 70 to 80 % of the CCS' cost lies on the CO<sub>2</sub> capturing phase (Blomen et al., 2009). Therefore, an improvement to the existing CO<sub>2</sub> capture process and development of alternative technology is significant in reducing the total cost for the CO<sub>2</sub> capture (Blomen et al., 2009). Accordingly, a gas hydrate system which has high selectivity towards the CO<sub>2</sub> gas instead of other pollutants is proposed in this study. The CO<sub>2</sub> hydrate then will be dissociated to produce a pure stream of CO<sub>2</sub>. This CO<sub>2</sub> hydrate is considered as a green technology since it does not have any impact towards the environment and at the same time, the process consumes less energy consumption (Partoon et al., 2015). However, the major challenges in this technology are related to the slower rate of the hydrate formation as well as low adsorption capacity (Yang et al., 2013). Therefore, capturing CO<sub>2</sub> from gas stream through hydrate formation within the pore structure is recommended, as an option to overcome the limitation of the present technology. The porous structures are preferred because it can accelerate the hydrate formation, owing to increase in local CO<sub>2</sub> super-saturation sites that may reduce the total time for the hydrate formation. Besides, the porous materials that have a large internal porosity will allow high water molecules inside them and accordingly, provide a greater contact area between the sorbed water molecules and gas molecules, which results in more hydrate formation for the gas storage (Kang et al., 2008). While studying the adsorption process, a thorough analysis on the adsorption isotherm is important as it describes the adsorption behaviour with respect to various pressures and under a constant temperature (Gimbert et al., 2008). Furthermore, the equilibrium coefficient from the adsorption isotherm may predict the adsorption's mechanism, expression of the surface property and capacity of the adsorbent, as well as effective modelling of the adsorption system (Foo and Hameed, 2010). Besides, the derived information from the appropriate adsorption isotherm can be used to design the column adsorption system. Therefore, the main objective of this study is to measure the

adsorption equilibrium of the CO<sub>2</sub> on the synthesized calcium oxides (CaO), and to correlate the adsorption equilibrium data with various isotherm models, specifically the Langmuir, Freundlich, Redlich-Peterson (R-P), Toth, and Sips model.

## 2. Experimental

### 2.1 Material preparation and characterization

The synthesized CaO prepared from waste cockle shell had been used in this study. The detailed synthesis and the properties of this CaO sample can be found elsewhere (Azmi et al., 2014). The surface area of the synthesized CaO is 8.79 m<sup>2</sup>/g, while its pore volume is 1.72 x 10<sup>-2</sup> cm<sup>3</sup>/g, which was determined from nitrogen adsorption data at 77 K (- 196 °C, and by using a Brunauer-Emmett-Teller equation.

### 2.2 Measurement of carbon dioxide adsorption

The CO<sub>2</sub> adsorption isotherms were measured by using a static High Pressure Volumetric Analyzer from the Particulate System. Prior to the CO<sub>2</sub> adsorption, about 300 - 400 mg samples were placed inside a 2 cm<sup>3</sup> sample chamber and inserted into a furnace for degassing process. The samples were evacuated at 200 °C under a vacuum condition overnight, to remove any impurities retained inside the sample. Once the degassing process completed, the sample chamber was moved to an analysis port for CO<sub>2</sub> adsorption measurement. The adsorption was started by dosing CO<sub>2</sub> into the system, and valve between the loading and sample cell was opened to allow gas contact with the samples. The final equilibrium pressure ( $P_s$ ) and quantity of the gas adsorbed was recorded when the sample reached equilibrium with CO<sub>2</sub>. This process was repeated at a given pressure interval until maximum pre-selected pressure was attained. Once the experimental run completed, weight of the sample was recalculated. Each of the equilibrium point (amount of CO<sub>2</sub> adsorbed and equilibrium pressure) was plotted to produce an isotherm. The amount of CO<sub>2</sub> adsorbed was expressed in mmol CO<sub>2</sub> per gram CaO. Meanwhile, for the CO<sub>2</sub> adsorption onto the wetted sample, the degassing process was skipped to avoid removal of water vapour from the sample. The water content in a wetted sample was expressed as  $R_w$  (weight ratio of water to CaO sample). Further, Zheng et al. (2012) mentioned that it is necessary to place the adsorption system in a vacuum condition initially since each isotherm will start at a pressure reading of zero. Accordingly, the wetted sample was cooled to - 20 °C to minimize the loss of water, due to the vaporization step. Subsequently, the chamber temperature was raised to 2 °C and the effects of water contents ( $R_w$  of 0 to 3.7) towards the CO<sub>2</sub> adsorption were analyzed.

## 3. Theory

A wide variety of equilibrium isotherm models have been formulated to describe the experimental adsorption data (Loganathan et al., 2015). Five isotherm models (Langmuir, Freundlich, Redlich-Peterson (R-P), Toth and Sips) are used to analyze the experimental data. Amongst these models, the Langmuir is the simplest one to describe the adsorption onto the homogeneous surface, and there are definite and energetically equivalent numbers of the adsorption sites. The Langmuir equation is given by Eq(1) below:

$$q_e = \frac{q_{max}k_L P_s}{1 + k_L P_s} \quad (1)$$

where,  $q_e$  is an amount of CO<sub>2</sub> adsorbed at equilibrium (mmol/g),  $q_{max}$  is the maximum-monolayer adsorption capacity of the adsorbent (mmol/g),  $P_s$  is an equilibrium pressure of the gas adsorbed (bar), whilst  $k_L$  is the Langmuir adsorption constant that relates to the free adsorption energy (1/bar) (Li and Hitch, 2015). The Freundlich isotherm model is the earliest known relationship which describes a non-ideal and reversible adsorption process (Chen, 2015). Opposite to the Langmuir model, this model is applicable to the multilayer adsorption (Fil et al., 2012). The Freundlich model is based on an assumption that the adsorption energy will exponentially decrease with an extent of the adsorption process (Al-Anber, 2011). The Freundlich isotherm equation can be expressed by Eq(2) (Li and Hitch, 2015):

$$q_e = k_F P_s^{1/n_F} \quad (2)$$

where  $k_F$  is the Freundlich isotherm constant (mmol/g.bar)<sup>1/n<sub>F</sub></sup> and  $n_F$  is heterogeneity factor that represents a deviation from the linearity of adsorption, and is also known as the Freundlich coefficient. As the  $k_F$  value increases, the adsorption capacity of adsorbent for a given adsorbate will increase too. The  $n_F$  parameter indicates type of the adsorption process, whether the adsorption is linear ( $n_F = 1$ ), a chemical process ( $n_F < 1$ ) or a physical process ( $n_F > 1$ ). The adsorption capacity or surface heterogeneity is determined from the value of slope 1/n, which are ranging from 0 to 1, whereby it becomes more heterogeneous as its value becomes closer to zero (Al-Anber, 2011). Contrary to the Freundlich and Langmuir model, the Redlich-Peterson (R-P)

that has been introduced in 1959 is a three-parameters adsorption isotherm model. The isotherm equation can be expressed by Eq(3):

$$q_e = \frac{k_R P_s}{1 + \alpha_R P_s^\beta} \quad (3)$$

where  $k_R$  (L/g) and  $\alpha_R$  (1/mmol) are R-P isotherm constant whilst R-P isotherm exponent is presented by  $\beta$  value. To gain a deep insight on the nature of adsorbents' surface, the Sips isotherm model that combines the Langmuir and Freundlich isotherm is analyzed. The difference between the Langmuir and Sips models is due to an additional parameter "n", which characterizes the system heterogeneity (García et al., 2013), whereby if the parameter  $n$  is unity, then the Langmuir model will be applicable to describe the surface (Delavari-Amrei et al., 2008). This Sips isotherm model is expressed by Eq(4):

$$q_e = q_{max} \frac{(b_s P_s)^{1/n}}{1 + (b_s P_s)^{1/n}} \quad (4)$$

where  $b_s$  constant is related to the energy of adsorption. Besides, the Toth isotherm model which is a modified Langmuir equation is studied, as this model is capable to reduce the error between the experimental data and predicted value of the equilibrium adsorption capacity (Subramanyam and Ashutosh, 2012). In addition, the Toth equation is best suited to the multilayer adsorption, and can be expressed by Eq(5) (Saha et al., 2011):

$$q_e = q_{max} \frac{b_t P_s}{(1 + (b_t P_s)^t)^{1/t}} \quad (5)$$

where  $b$  and  $t$  represents the Toth constant (bar/g) and exponent, respectively. The parameter  $t$  in the Toth model is used to depict the heterogeneity of the system, whereby lower  $t$  value implies a more heterogeneous system. Then, the isotherm parameters in these isotherm models are estimated using a non-linear technique. The non-linear method is a superior way to obtain the isotherm parameters as compared to a linearized method, and therefore, should be primarily adopted to determine the isotherm parameters (Chowdhury and Saha, 2011). For a non-linear method, trial and error procedures have been implemented, whereby the errors are minimized whilst maximizing the coefficient of determination ( $R^2$ ) between the experimental and predicted data, via a solver add-in in Microsoft Excel (Kumar and Sivanesan, 2006). To quantitatively compare the suitability of these isotherm models in fitting the experimental data, a hybrid fractional error function (HYBRID) (Gulipalli et al., 2011) and non-linear  $R^2$  (Kumar and Sivanesan, 2006) were calculated. This HYBRID method is developed to improve the fit squares of the error function at the lower pressure values (Sreńscek-Nazzal et al., 2015), and is expressed by Eq(6):

$$HYBRID = \frac{100}{n-p} \sum_{i=1}^n \left[ \frac{(q_{e,exp} - q_{e,cal})^2}{q_{e,exp}} \right] \quad (6)$$

where  $q_{e,exp}$  and  $q_{e,cal}$  are the measured and calculated amount of adsorbate adsorbed at an equilibrium point (mmol/g), respectively;  $n$  is the number of data points whilst  $p$  is the number of parameters in the isotherm equation. Besides, the suitability of these models is evaluated by the coefficient of regression ( $R^2$ ) that varies between 0 to 1. The  $R^2$  equation is expressed as Eq(7), whereby  $\overline{q_{e,exp}}$  is an average of  $q_{e,exp}$ . (Kumar and Sivanesan, 2006).

$$R^2 = \frac{\sum (q_{e,cal} - \overline{q_{e,exp}})^2}{\sum (q_{e,cal} - \overline{q_{e,exp}})^2 + \sum (q_{e,cal} - q_{e,exp})^2} \quad (7)$$

## 4. Results and discussion

### 4.1 CO<sub>2</sub> adsorption measurement

The CO<sub>2</sub> adsorption isotherms on the synthesized CaO with various amounts of water at 2°C are illustrated in Figure 1. The adsorption capacities in the wetted samples are dependent upon the amount of water content, due to prominent changes in the adsorbent's textural structure through the addition of water (Abanades García et al., 2011). Referring to Figure 1, there is a huge impact on the CO<sub>2</sub> uptakes in the presence of water ( $R_w$  of 0.30 to 0.67), in which at  $R_w$  of 0.67, the amount of CO<sub>2</sub> adsorbed is 8.9 higher than the amount adsorbed by the dried sample at 36 bar. According to Zhang et al. (2014), the increment in water content in pore structures, the hydrate formation will take place and accordingly, will promote the CO<sub>2</sub> separation from the gas mixtures. Based on their experimental findings, the CO<sub>2</sub> adsorption (2.49-2.81 mmol/g) is higher when the water content on the activated carbon is around 19.23 to 30.41 wt%, compared to only 2.24 mmol/g in absence of the water.

In addition, it has been reported that the metal oxides surrounded with water will assist in the CO<sub>2</sub> sorption, due to interaction between the particle with CO<sub>2</sub> and produced CO<sub>3</sub><sup>2-</sup> ions and H<sup>+</sup> ions. Subsequently, the free metal ion reacts with CO<sub>3</sub><sup>2-</sup> to form the metal carbonate (Kumar and Saxena, 2014). Besides, at lower amount of water addition ( $R_w = 0.3$ ), the adsorption isotherm resembles the sorption isotherm of the dried sample, and no inflection point has been observed. The lack in the inflection point is due to insufficient amounts of water for the hydrates formulation. Meanwhile, at the optimum  $R_w$ , there is a presence of the inflection point at the pressure of about 24 bar. Likewise, Billemont et al. (2013) who observed the inflection point at pressure of 2 to 3 MPa suggested the formation of CO<sub>2</sub> hydrates (clathrates) at this point, whereby the ordered-structured of the clathrates consist of the trapped CO<sub>2</sub> in crystal lattice of the water molecules. Despite of the potential of the water addition towards the CO<sub>2</sub> sorption, too much water addition is undesired due to the pore blockages (Fernández Bertos et al., 2004). In the present study, the increasing water addition ( $R_w$  of 0.73 to 3.73) shows a decreasing trend towards the CO<sub>2</sub> uptake. Kumar and Saxena (2014) reported that the metal carbonates formation will build an impervious layer surrounds the unreacted metal oxide and thereby, hinders further CO<sub>2</sub> diffusion. In fact, this concept has been agreed by Morales-Flórez et al. (2014) who clarified that the hydration and carbonation concept involved two regimes, whereby the first step is a rapid reaction whereas the second step is a slow reaction, due to impervious by-products layer creation that tends to block pores, and prevent the unreacted CaO to further react with the adsorbate molecules. Therefore, optimizing the water addition into the porous material is significant in order to improve the gas uptake via the hydrates formation, without imposing a gas diffusion problem that is caused by the thick layers' formation that will reduce the CO<sub>2</sub> sorption capacity.

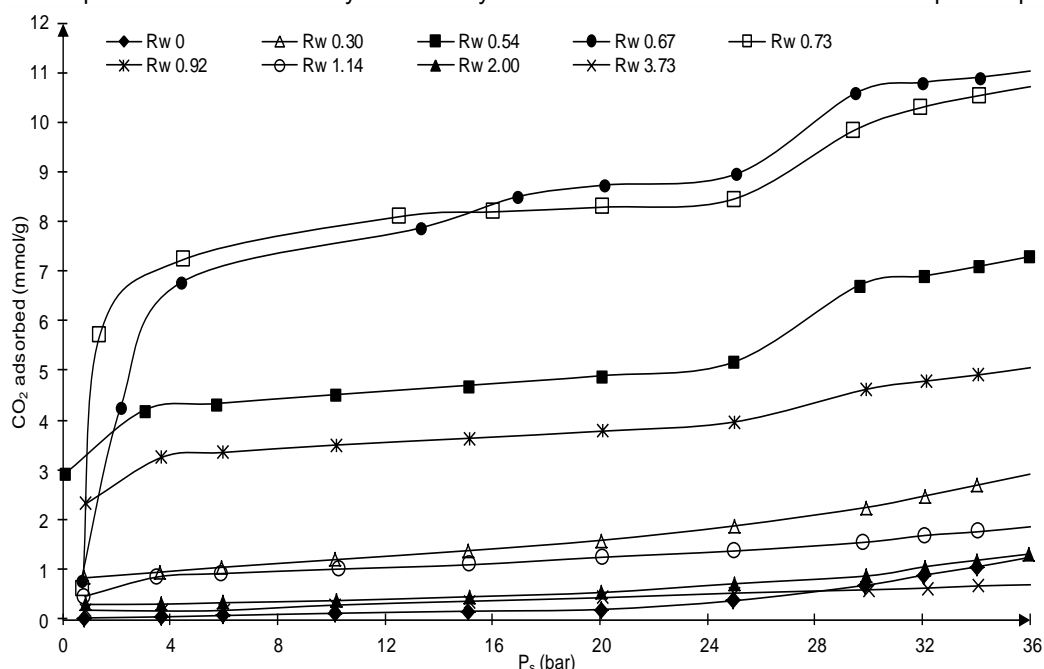


Figure 1: CO<sub>2</sub> uptakes on synthesized CaO at different amount water ( $R_w$ ) at 2 °C

#### 4.2 Comparison of adsorption isotherm models

In single component isotherm study, determining the best-fitting model is the key analysis to mathematically describe the adsorption system and, accordingly to explore the related theoretical assumption. To understand the characteristics of these adsorbent, the CO<sub>2</sub> experimental equilibrium data were analyzed by the Langmuir, Freundlich, R-P, Toth and Sips isotherm model. The isotherm parameters of these various models towards the dried ( $R_w = 0$ ) and wetted ( $R_w = 0.67$ ) synthesized CaO at temperature of 2 °C are tabulated in Table 1. With respect to the  $R^2$  values, the suitability of these models in predicting the sorption behaviour towards the dried CaO follows the order of Freundlich > Langmuir > R-P > Sips > Toth. Further, the computed value which is  $n_F < 1$  implies that the CO<sub>2</sub> adsorption onto the dried CaO is a chemisorption process, whereas if the value is larger than 1, it suggests a physisorption process (Aljeboree et al., 2014). In fact, the chemical interaction between the CO<sub>2</sub> and CaO will result in the calcium carbonates (CaCO<sub>3</sub>) formation, thereby, align with the Freundlich constants.

Besides, it has been reported that lower  $n$  values indicates a presence of the high-energy active sites (Arshadi et al., 2014). Moreover, the estimated  $1/n_F$  which is way beyond than unity describes a cooperative adsorption (Foo and Hameed, 2010), which implies favourability of the active site to retain the sorbate molecules (Arshadi

et al., 2014). Meanwhile, for the wetted CaO, the R-P isotherm model fits the experimental data due to closer  $R^2$  value to unity, and followed by Langmuir, Sips, Freundlich, and lastly is the Toth model. Referring to Table 1, the constant  $\beta$  value which is almost 1 (0.995) shows a close resemblance of the sorption behaviour to the Langmuir model (Foo and Hameed, 2010), and is further proven by a small difference in the  $R^2$  value between the Langmuir and R-P isotherm model.

Table 1: The optimized parameter values obtained from different adsorption isotherm models at different  $R_w$

Isotherm model	Parameter / Error	Water ratio, $R_w$	
		0	0.67
Langmuir	$q_{max}$	$9.090 \times 10^3$	12.090
	$k_L$	$7.892 \times 10^{-7}$	0.176
	HYBRID	0.113	0.136
	$R^2$	0.331	0.940
Freundlich	$n_F$	0.367	1.999
	$k_F$	$3.644 \times 10^{-5}$	1.938
	HYBRID	0.007	0.297
	$R^2$	0.989	0.914
R-P	$a_R$	1.455	0.180
	$k_R$	0.018	2.142
	$\beta$	0.000	0.995
	HYBRID	0.127	0.153
	$R^2$	0.331	0.941
Sips	$q_{max}$	0.014	13.622
	$b_s$	1.391	0.114
	$1/n$	0.286	0.933
	HYBRID	$2.636 \times 10^{-8}$	$8.859 \times 10^{-9}$
	$R^2$	0.320	0.935
Toth	$q_{max}$	0.454	9.936
	$b_T$	0.006	0.145
	$t$	7.405	2.665
	HYBRID	$3.557 \times 10^{-7}$	$1.150 \times 10^{-7}$
	$R^2$	0.308	0.900

## 5. Conclusions

The remarkable difference was observed in the CO<sub>2</sub> adsorption behaviours on the dried and wetted CaO. The CO<sub>2</sub> uptake rapidly increased in the presence of water, since CO<sub>2</sub> hydrates are developed in porous CaO structure, and accordingly, at an equilibrium pressure of 36 bar, the maximum CO<sub>2</sub> uptake (11.03 mmol/g) attained by the wetted CaO ( $R_w$  of 0.67) is significantly higher than the amount obtained in the dried CaO. The Freundlich model was found to give the closest fit to the experimental isotherm data in the dried sample. On the other hand, the Redlich-Peterson (R-P) model provides the best fit for the wetted CaO at the optimum  $R_w$  of 0.67 owing to the non-linear regression approach.

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