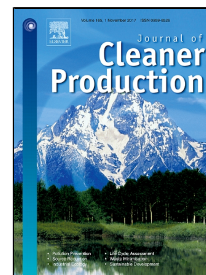


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Effect of water onto porous CaO for CO<sub>2</sub> adsorption: Experimental and extended isotherm model



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1 Effect of water onto porous CaO for CO<sub>2</sub> adsorption:  
2 Experimental and extended isotherm model

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1 **ABSTRACT:** Tremendous increment of carbon dioxide in atmosphere has posed devastating  
2 impacts to global climate change. The phenomenon has become one of the great challenges need  
3 to be considered for achieving techno-economic system. This paper presents an alternative  
4 approach for capturing high concentration of CO<sub>2</sub> by combination of two separation processes,  
5 adsorption and gas hydrate. Potentials of waste seashell from cockle for producing low cost porous  
6 calcium oxide for CO<sub>2</sub> capture were investigated. The adsorption equilibrium of CO<sub>2</sub> on porous  
7 calcium oxide with presence of water was measured using a static volumetric technique at 2 °C for  
8 pressures up to 36 bar. The CO<sub>2</sub> uptakes of 9.1 mmol/g and 11.3 mmol/g were obtained for  
9 commercial and synthesized CaO at 36 bar. At optimum water ratio, the equilibrium data were  
10 simulated first with three different isotherm models: Langmuir, Freundlich and Redlich-Peterson.  
11 The Freundlich model adequately describe the CO<sub>2</sub> adsorption on dry samples and Redlich-  
12 Peterson gives the best fitted for wet samples at optimum water ratio. The Redlich-Peterson model  
13 having the highest R<sup>2</sup> was further extended by incorporating water isotherm model to determine  
14 the occurrence of water inside the sample. The curve obtained from the extended isotherm model  
15 shows an increment of coefficient from 0.94 to 0.99 and 0.94 to 0.98 for commercial and  
16 synthesized CaO. The findings revealed the potential of waste cockle shell as a viable and  
17 sustainable materials for preparation of calcium oxide for gas adsorption applications. This novel  
18 technology will go a long way in amassing the impacts of water in CO<sub>2</sub> adsorbent for gas  
19 adsorption applications.

20 **KEYWORDS:** *CO<sub>2</sub> sorption, Calcium oxide, Isotherm model, Water sorption isotherm, Non-*  
21 *linear regression*

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## 1 1. INTRODUCTION

2 The issues of global warming and climate change have become a subject of intense interest all  
3 over the world since the last decade. Warming of the climate system is now evidenced from  
4 observations of increasing temperature, diminishing ice and increased sea level, in which will  
5 undoubtedly give rise to destruction to ecosystem, biodiversity and human economic activities  
6 both in short and in long term (Fang et al., 2017). The anthropogenic (human-caused) driver of  
7 climate change is the increasing concentration of greenhouse gases (GHG) in the atmosphere (Wee  
8 et al., 2008). Among these GHG, carbon dioxide is the largest contributor in regard of its amount  
9 present in atmosphere, where it contributing to 65% of global warming effects, primary from fossil  
10 fuel and industrial processes (Yamasaki, 2003). The atmospheric content of carbon dioxide can  
11 reach 570 ppmv, rise in sea level of 3.8 m and a rise in global mean temperature of about 2 °C by  
12 the year of 2100, as predicted by the International Panel of Climate Change (IPCC) (Sreenivasulu  
13 et al., 2015). It has been reported that the six largest emitting countries / regions were China (29%),  
14 the United States (15%), the European Union (EU27) (11%), India (6%), the Russian Federation  
15 (5%) and Japan (4%) (Olivier et al., 2013). The CO<sub>2</sub> emissions in China's commercial sector has  
16 been predicted to be 1942 Mt by 2030, which is huge and about half of the CO<sub>2</sub> emissions in year  
17 2014 (Wang and Lin, 2017). In Malaysia, around 288.1 MtCO<sub>2</sub> has been emitted, contributing  
18 0.67% to global emissions in year 2012 (World Resources Institute, 2015). The increasing  
19 concentration of atmospheric CO<sub>2</sub> due to carbon emissions will continuously lead to a significant  
20 impact on global climate.

21 The increasing amount of CO<sub>2</sub> in the atmosphere initiate numerous research activities around  
22 the globe to capture these high carbon dioxide concentration. High research effort is necessary to  
23 find ways to reduce the large amount of CO<sub>2</sub> emitted to the atmosphere and keep at manageable

1 levels. Carbon capture and sequestration (CCS) has become an attracting technology that is being  
2 explored to meet CO<sub>2</sub> reduction targets. The costs of GHG emission mitigation measures would  
3 be more than doubled as the reduction target cannot be met without CCS. The cycle of CCS  
4 technology can contribute around 14% of total energy related CO<sub>2</sub> reductions by 2050 (IEA, 2014).  
5 It is crucial to develop the CCS technologies to cope with the global demand of CO<sub>2</sub> reduction.  
6 There are variety of CCS technologies can be applied in the power generation sectors as well as in  
7 industry, where 15 large scale CCS projects have entered in operations since 1972 (Jakobsen et  
8 al., 2017). Recently, this technology is still mainly on pilot or demonstration scales due to several  
9 factors such as cost, political uncertainties and public acceptance. Therefore, focus on development  
10 of CCS technology to the establishment of larger scale projects is more on reducing the costs and  
11 identifying the storage capacity (Wennersten et al., 2015). The process of capturing CO<sub>2</sub> at large  
12 point sources, typically coal-fired power plants is the first step in CCS technology. Carbon capture  
13 involves the development of separation technologies that can effectively capture the CO<sub>2</sub> present  
14 in flue gas or in atmosphere. There are three basic types of CO<sub>2</sub> capture: pre-combustion, post-  
15 combustion and oxyfuel with post-combustion (Olajire, 2010).

16 A variety of conventional technologies are presently being suggested for separating a  
17 concentrated stream of CO<sub>2</sub> such as absorption, adsorption, cryogenic, membrane and gas hydrate  
18 formation. The CO<sub>2</sub> separation with solid sorbents has become a promising technology that can be  
19 integrated with existing CO<sub>2</sub> emitting plants (Benedetti et al., 2015). In this retrospect, CO<sub>2</sub>  
20 captured by solid adsorbents might offer a couple of advantages, in which the selection of most  
21 suitable adsorbent is the key for excellent separation (Figuerola et al., 2008). The selective  
22 adsorption of CO<sub>2</sub> is caused by van der Waals attraction between the CO<sub>2</sub> molecule and adsorbent  
23 surface. It is caused by pole-ion and pole-pole interactions between the quadruple of CO<sub>2</sub>

1 molecules and the ionic and polar sites of the CO<sub>2</sub> adsorbents surface (Samanta et al., 2011). The  
2 process of molecules to adsorb onto the adsorbents basically occurs in three main steps. The first  
3 step involves the diffusion of adsorbate molecules from the major body of the gas streams to the  
4 external surface of the adsorbent particles. Next, it shows that the adsorbate migrates from the  
5 relatively small area of the external or boundary surface to the pores or active sites within each  
6 adsorbent particle. These active sites consist of homogeneous and heterogeneous forms, where the  
7 bulk of adsorption normally occurs since there is where the majority of surface area is available.  
8 Finally, the contaminant molecules adhere to the surface of the active sites and the complete  
9 adsorption process have occurred.

10 Hydrate-based CO<sub>2</sub> separation is a new technology by which the exhaust gas containing CO<sub>2</sub>  
11 is exposed to water under high pressure forming hydrate (Leung et al., 2014). In gas hydrate  
12 formation system, the basic mechanism of the process is the selective partition of target  
13 components between the hydrate and gas phases. As main process solvent required for hydrate  
14 based technology is water, which provides the process with abundant (cheap) and green raw  
15 chemical. Potential barriers to this technology are: the ability to release CO<sub>2</sub> from the hydrate in  
16 an energy efficient manner; efficient capture of CO<sub>2</sub>; stable pre-hydrate; and trace contaminants  
17 interfere with hydrate formation (Wong and Bioletti, 2002). The need to accelerate the hydrate  
18 formation rate and increase the gas capacity has restricted the use of hydrate-based CO<sub>2</sub> capture  
19 technology (Yang et al., 2013).

20 By virtue of the world's dependency on oil and gas as the main source of energy is expected to  
21 rapidly increase, an alternative approach of capturing CO<sub>2</sub> should be explored to ensure the world  
22 sustainability. Improved technologies for CO<sub>2</sub> capture are necessary to achieve low energy  
23 penalties and low cost process. It is suggested to allow formation of CO<sub>2</sub> hydrate inside the porous

1 materials to overcome earlier mentioned disadvantages of the current technologies. In adsorption  
2 process, presence of impurities such as NO<sub>x</sub>, SO<sub>x</sub> and water vapor significantly impact the  
3 performance of CO<sub>2</sub> adsorbents such as zeolites, activated carbons and metal organic frameworks  
4 (MOFs) (Spigarelli and Kawatra, 2013). The presence of water vapor, which is an inevitable  
5 component in flue gas, may negatively affect the capacity of the sorbent and reduces the  
6 availability of the active surface area (Samanta et al., 2011). An alternative approach requires the  
7 development of porous materials to capture CO<sub>2</sub> by adsorption process and techniques to introduce  
8 water on these materials, allow more CO<sub>2</sub> can be adsorbed. An ideal CO<sub>2</sub> adsorbent should exhibit  
9 a higher CO<sub>2</sub> uptake and selectivity, faster kinetics of adsorption/ desorption, mild conditions for  
10 regeneration, stability during extensive adsorption–desorption cycling, tolerance to the presence  
11 of moisture and other impurities in the feed and adequate mechanical strength of adsorbent  
12 particles (Raganati et al., 2015). Thus, it is necessary to cater the limitation of the current technique  
13 for capturing high CO<sub>2</sub> content in gas streams. The addition of water on porous media creates  
14 plenty of voids among and inside the porous media particles, which provide an efficient contact  
15 between water and gas (Adeyemo et al., 2010). Moreover, the porous structure can increase the  
16 rate of hydrate formation due to the increase on local CO<sub>2</sub> supersaturation sites in the porous media  
17 and decrease in the induction time needed for hydrate formation thus increasing the amount of CO<sub>2</sub>  
18 separated from the gas stream. It is our believed that the combined hydrate and adsorption  
19 processes through the use of wetted porous materials is a way forward for capture CO<sub>2</sub> in industrial  
20 gas streams especially for high CO<sub>2</sub> concentration streams.

21 In order to have the successful combination effect of the proposed system, the porous material  
22 use must be wetted with water and has tendency to perform at operating conditions of CO<sub>2</sub> hydrate.  
23 However the cost of porous materials is become a crucial factor to be considered for the potential

1 application of the proposed system. Calcium based materials are good adsorbent candidates for  
2 capturing CO<sub>2</sub> due to their reactivity with CO<sub>2</sub>, high capacity and low material cost (Wang et al.,  
3 2011). The calcium based sorbents are mainly derived from natural CaO compounds such as  
4 limestone, magnesite and dolomite (Wang et al., 2013). However, mining large quantities of raw  
5 materials such as limestone result in extensive deforestation and top soil loss (Mehta, 2001). In  
6 Marine industry, the seashell wastes such as mussel, oyster, clam and cockle denote an extensive  
7 amount of by-products. From the viewpoint of eco-friendly and economic disposal, these residues  
8 are claimed to be a reliable potential biomass source which can be converted into high value-added  
9 products for industrial application (Lu et al., 2015). For example, mussel shell accounts for 95 –  
10 99% by weight of calcium carbonate, which is a major substance for CO<sub>2</sub> adsorbent (Barros et al.,  
11 2009).

12 In Malaysia, the production of cockle is very high with three main cockle cultivation centers  
13 (Juru at Penang, Kuala Selangor at Selangor and Matang at Perak) while other places like in Jarum  
14 Mas at Perak, and Kapar at Selangor, also accelerate their effort to increase the production (Izura  
15 and Hooi, 2008). Cockles are quite common to be served in daily dishes of Malaysia's cuisine.  
16 The shells have no utilization and normally been dumped, left untreated at the dumping site. Thus,  
17 waste cockle shells are abundantly available in Malaysia and its utilization as CO<sub>2</sub> adsorbent  
18 should be expanded in this work. Calcium oxide (CaO) can be extracted from the shells via  
19 calcination process as it contains a large amount of calcium carbonate (CaCO<sub>3</sub>) (Castilho et al.,  
20 2013). The decomposition process of cockle shell uses heat to decompose the material and cause  
21 volatile removal or phase transition. During the process, CaCO<sub>3</sub> liberate CO<sub>2</sub> and generate CaO  
22 when treated at high temperature in furnace.

23



1 In this study, it is crucial to ensure the porous material use is be wetted with water in order to  
2 have successful combination effect of hydrate formation and adsorption. Recently, activated  
3 carbon and silica gel are two porous materials widely been used for formation of CO<sub>2</sub> hydrate  
4 inside the pores. The sorption behavior of CO<sub>2</sub> showed a significance effect of pore dimension on  
5 activated carbon with the presence of water. The first study on the effect of porous media on the  
6 equilibrium pressures of CH<sub>4</sub> and C<sub>3</sub>H<sub>8</sub> hydrates has been reported by Handa and Stupin (Handa  
7 and Stupin, 1992). They found that the equilibrium pressures of CH<sub>4</sub> and C<sub>3</sub>H<sub>8</sub> hydrates in silica  
8 gel pores were higher than those of bulk hydrates. Uchida and his co-workers experimentally  
9 determined the equilibrium pressures of CH<sub>4</sub>, C<sub>3</sub>H<sub>8</sub> and CO<sub>2</sub> hydrates in porous glasses of different  
10 pore sizes (Uchida et al., 2002). Wang and his co-workers have measured the sorption behavior of  
11 CO<sub>2</sub> and CH<sub>4</sub> on activated carbon with a wide pore-size distribution at 275 K in different amount  
12 of water (Wang et al., 2008). They observed that there were an inflection pressures at about 1.5 –  
13 2.0 MPa and at 3 MPa on sorption isotherms of CO<sub>2</sub> and CH<sub>4</sub>; respectively to indicate hydrate  
14 formation in the system. Zheng and his co-workers have reported that the formation of CO<sub>2</sub>  
15 hydrates were influenced by the quantity of pre-sorbed water and pore size distribution of the silica  
16 gel (Zheng et al., 2012). Only the pores with a definite size are suitable for hydrate formation as  
17 the impetus of pore space for hydrate formation disappears if the pore size is too large (Zheng et  
18 al., 2012).

19 The benefits from this approach are three-fold, based on from the current separation  
20 techniques. Firstly, from the large quantities of residual and untreated seashell, the calcium based  
21 materials can be utilized as CO<sub>2</sub> adsorbent. Secondly, the use of cheap raw material and water,  
22 lead to reduction of operational cost and better in term of cycle analysis. Thirdly, the chances of  
23 CO<sub>2</sub> with water dispersed in the porous materials, yield better stability for sequestration in the deep

1 sea. It is believed the combination of adsorption and CO<sub>2</sub> hydrate formation in a single step as a  
2 separation process is an innovative advancement towards a venture for exploration and production  
3 of natural gas from high CO<sub>2</sub> gas streams. Therefore, the main objectives of this work were to  
4 measure the CO<sub>2</sub> uptake of the derived CaO and compare with the commercial CaO at 2 °C on dry  
5 and wet analysis. The sorption isotherm data at optimum water ratio, R<sub>w</sub> were further correlated  
6 with isotherm models: Langmuir, Freundlich and Redlich-Peterson (R-P). The water isotherm  
7 models have been included to study the effect water inside the pores.

## 8 **2. Materials and methods**

### 9 **2.1. Material preparation and characterization**

10 The commercial calcium oxide was purchased from Sigma Aldrich and has been used without  
11 further treatment. The full detailed synthesis of CaO from a waste cockle shell can be found  
12 elsewhere (Azmi et al., 2014). The adsorption / desorption isotherm of N<sub>2</sub> was performed on  
13 Micromeritics ASAP 2020 Accelerated Surface Area and Porosimetry by degassing 0.3 g sample  
14 at 350 °C for 4 h and has been analyzed in liquid nitrogen at -196 °C. Three different particle sizes  
15 have been evaluated for synthesized CaO. The surface morphology structures were observed and  
16 analyzed by +FESEM (Zeiss Supra 55 VP). All gases used in this work were supplied by Linde  
17 Malaysia with the following mole fraction purities: He 0.999, compressed air 0.999 and CO<sub>2</sub> 0.999.  
18 He and compressed air were used as a carrier gas in adsorption measurement for degassing and  
19 purging processes. Mixture of glycol and water was used to provide the desired temperature for  
20 vacuuming process of wet sample.

21

22

23

## 2.2. CO<sub>2</sub> adsorption measurement

The CO<sub>2</sub> equilibrium data was obtained using a static volumetric technique where the measurements were performed by using High Pressure Volumetric Analyzer (HPVA II), a series of gas adsorption analyser. The HPVA was used to obtain isotherm at low temperature and high pressure, CO<sub>2</sub> hydrate formation region. The details of CO<sub>2</sub> analysis has been discussed in previous paper (Azmi et al., 2016). The capability of porous CaO derived from waste cockle shell for CO<sub>2</sub> capture has been measured and compared with commercial CaO. The degree of effectiveness of the proposed system was evaluated by comparing the amount of CO<sub>2</sub> uptakes on dry and wetted materials.

## 3. Theory

In adsorption equilibrium study, the adsorption isotherm is often used to express the results of adsorption. The capacity of the sorbent can directly obtain from the isotherm and the parameter of model is used to explain the surface properties and affinity of the sorbents. In order for researchers to discover novel adsorbents in retrieving an ideal adsorption system, it is crucial to establish the most suitable adsorption equilibrium correlation that is desirable for predicting of adsorption mechanism pathways, expression of the surface properties and capacities of adsorbent and effective modelling design of the adsorption system (El-Khaiary, 2008; Foo and Hameed, 2010). In this study, the Langmuir, Freundlich and Redlich-Peterson isotherm model were employed as listed in Table 1. The full description of the studied isotherm models with the procedures to determine the parameters are described elsewhere (Azmi et al., 2016).

1 **Table 1**  
2 List of isotherm models

Adsorption Isotherm	Models	Adjustable parameters	Ref.
Langmuir	$q_e = \frac{q_{\max} K_L P_S}{1 + K_L P_S}$	$q_{\max}, K_L$	Li and Hitch, 2015
Freundlich	$q_e = K_F P_S^{1/n_F}$	$K_F, n_F$	Li and Hitch, 2015
Redlich-Peterson (R-P)	$q_e = \frac{K_R P_S}{1 + a_R P_S^\beta}$	$K_R, a_R, \beta$	Foo and Hameed, 2010

3  $q_e$ : amount of adsorbate adsorbed at equilibrium (mmol/g);  $q_{\max}$ : maximum-monolayer  
4 adsorption capacity of the adsorbent (mmol/g);  $P_s$ : equilibrium pressure of gas adsorbed  
5 (bar);  $K_L$ : Langmuir adsorption constant related to the free energy adsorption (1/bar);  
6  $K_F$ : Freundlich isotherm constant (mmol/g.bar);  $n_F$ : heterogeneity factor;  $K_R$ : R-P isotherm  
7 constant (L/g);  $a_R$ : R-P isotherm constant (1/mmol);  $\beta$ : R-P isotherm exponent.

8  
9 The presence of water on the porous calcium oxide has to be counted to understand the interactions  
10 of water with the adsorbent by implementing the water adsorption isotherm. **It is crucial to include**  
11 **the water adsorption since water is used as a probe for surface chemistry and pore structure**  
12 **characterization of porous carbon materials (Velasco et al., 2016). Water, being a very small**  
13 **molecule with kinetic diameter of 0.28 nm, can easily enter pores smaller than 0.4 – 0.5 nm, in**  
14 **which the pores cannot be “seen” by CO<sub>2</sub> for the given sufficient time (Lodewyckx, 2010). Do et**  
15 **al. have developed a new water isotherm model to describe the adsorption and desorption branches**  
16 **of water adsorption in activated carbon (Do et al., 2009). The water isotherm model is described**  
17 **in Eq. (1):**

18

$$1 \quad q_e = q_{\mu s} \frac{K_{\mu s} \sum_{n=\alpha+1} \left(\frac{P}{P_0}\right)^n}{K_{\mu s} \sum_{n=\alpha+1} \left(\frac{P}{P_0}\right)^n + \sum_{n=\alpha+1} \left(\frac{P}{P_0}\right)^{n-\alpha}} + S_o \frac{K_f \sum_{n=1} n \left(\frac{P}{P_0}\right)^n}{1 + K_f \sum_{n=1} \left(\frac{P}{P_0}\right)^n} \quad (1)$$

2 where  $q_{\mu s}$  is the saturated amount of adsorbate adsorb (mmol/g);  $K_{\mu s}$  is the equilibrium constant  
 3 for adsorption;  $P/P_0$  is the reduced pressure of  $\text{CO}_2$ ;  $\alpha$  is the critical size of water cluster;  $S_o$  is the  
 4 amount of the functional groups on the surface;  $K_f$  is the equilibrium constant for adsorption per  
 5 unit functional group. In the present work, this type of water isotherm will be identified as water  
 6 isotherm model 1 (WIM1).

7 Do et al. have assumed that the functional groups and the micropore units are randomly distributed  
 8 where each functional group interacts with one water molecule in their proposed isotherm model  
 9 (Do et al., 2009).

10 In recent year, a new adsorption-desorption model for water adsorption in synthesized mesoporous  
 11 carbons materials have been proposed by Horikawa et al. as an extension of the previous model  
 12 (Horikawa et al., 2011). The previous model as discussed earlier has been further extended by  
 13 adding an additional term to account for adsorption in mesopores as described in Eq. (2):

$$14 \quad q_e = q_{\mu s} \frac{K_{\mu s} \sum_{n=\alpha_1+1} \left(\frac{P}{P_0}\right)^n}{K_{\mu s} \sum_{n=\alpha_1+1} \left(\frac{P}{P_0}\right)^n + \sum_{n=\alpha_1+1} \left(\frac{P}{P_0}\right)^{n-\alpha_1}} + q_m \frac{K_m \sum_{n=\alpha_2+1} \left(\frac{P}{P_0}\right)^n}{K_m \sum_{n=\alpha_2+1} \left(\frac{P}{P_0}\right)^n + \sum_{n=\alpha_2+1} \left(\frac{P}{P_0}\right)^{n-\alpha_2}} +$$

$$15 \quad S_o \frac{K_f \sum_{n=1} n \left(\frac{P}{P_0}\right)^n}{1 + K_f \sum_{n=1} \left(\frac{P}{P_0}\right)^n} \quad (2)$$

16 where  $q_{\mu s}$  is the saturated amount of adsorbate adsorb in the mesopore (mmol/g);  $K_m$  is the  
 17 equilibrium constant for adsorption for mesopore adsorption and  $\alpha_2$  is the water cluster sizes inside  
 18 mesopore. In the present work, this extended water isotherm will be identified as water isotherm  
 19 model 2 (WIM2).

1 Horikawa et al. have assumed that the critical water cluster size for adsorption in mesopores is  
 2 different from that for adsorption in micropores (Horikawa et al., 2011). The water cluster size  $\alpha_2$   
 3 is larger than that  $\alpha_1$  in micropores for the water molecules to be stabilized in mesopores. As  
 4 synthesized CaO used in this work is classified as mesoporous, it is crucial to evaluate the WIM1  
 5 and WIM2 against the experimental data. The calculated water adsorption will be further added to  
 6 existing isotherm model to study a mechanism for water adsorption in CO<sub>2</sub> adsorption process.

7

## 8 4. RESULTS AND DISCUSSION

9

### 4.1. Material characterization

10 **Table 2**

11 Summary of physisorption analysis for samples with different particle sizes

Sample	Particle size	BET surface area	Pore volume	Average pore width
	mm	m <sup>2</sup> /g	cm <sup>3</sup> /g	Å
Commercial CaO	< 0.1	7.27	3.88 x 10 <sup>-2</sup>	213.34
	< 0.1	8.79	1.72 x 10 <sup>-2</sup>	78.16
Synthesized CaO	0.1 – 0.25	4.38	1.07 x 10 <sup>-2</sup>	98.61
	> 0.5	2.86	1.20 x 10 <sup>-2</sup>	172.68

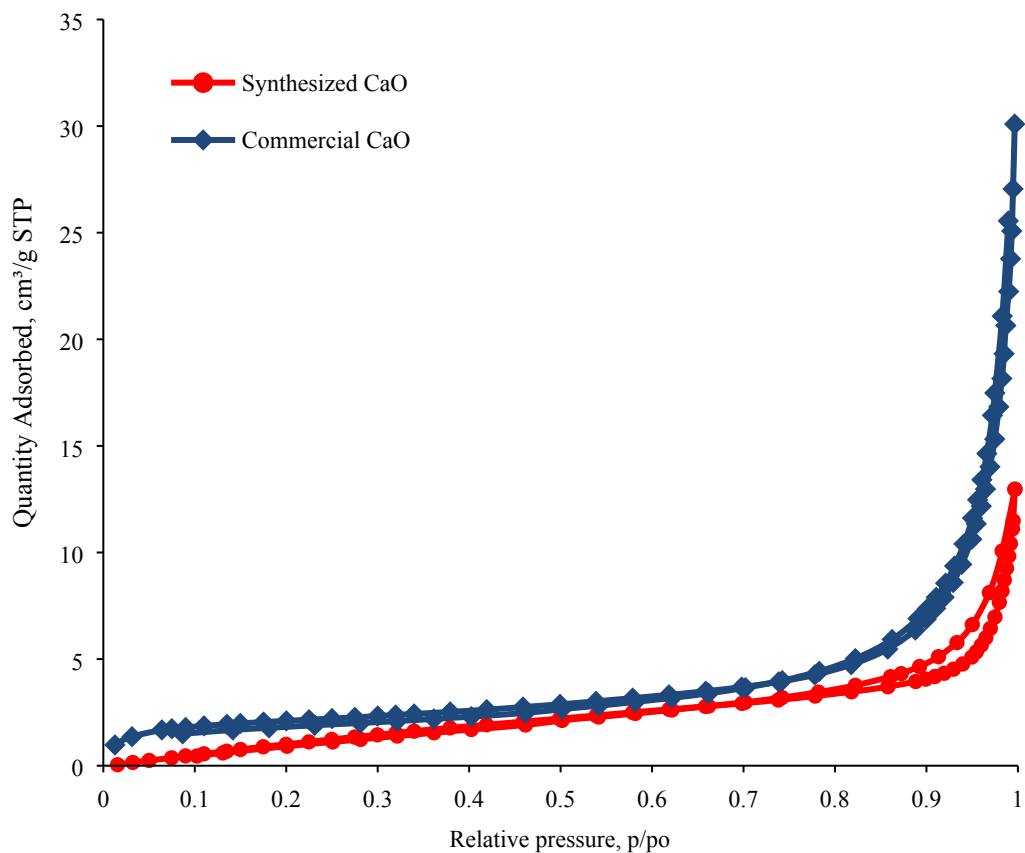
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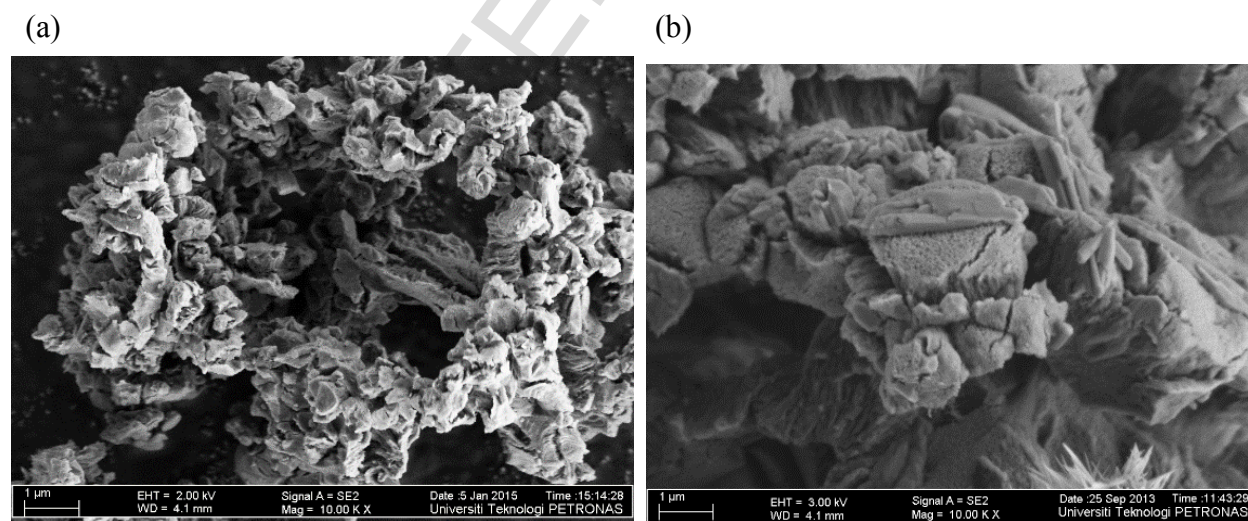
14 Table 2 summarizes the properties of the porous calcium oxide. From the presented values, it  
 15 is shown that synthesized CaO with smaller particle size (< 0.1 mm) offers the highest specific  
 16 surface area compared with the others sizes. Differ for average pore width, the values are directly  
 17 proportional with the particle sizes. The phenomenon is observed as particle size may introduce

1 mass and heat transfer limitation during calcination process. The same particle size of synthesized  
2 and commercial CaO gives more surface area as tabulated in Table 2.

3 In order to measure the surface area and porosity of the samples, nitrogen molecules act as the  
4 adsorbate where they will fill in and resides on the pores and covers all the areas of the sample.  
5 The nitrogen adsorption and desorption isotherms for commercial and synthesized CaO with  
6 particle size  $< 0.1$  mm are shown in Fig. 1. Type of the sorbent materials can be estimated through  
7 this isotherm plot. Both commercial and synthesized CaO are type II isotherms according to BET  
8 classification in the range of measurements indicating adsorption of gases in mesoporous  
9 adsorbents. The adsorption of  $N_2$  at 77 K on both samples showing hysteresis loop on desorption  
10 and the amount of gas adsorbed of each sample is similar. The total amount of gas adsorbed on  
11 commercial CaO is higher than synthesized CaO as approaching relative pressure to 1, implying  
12 that commercial CaO has higher macropores. From Table 2, the average pore width show that  
13 these two samples can be categorized as mesoporous material since it is in range of 20 – 500 Å.  
14 Zhou et al. have reported that microporous adsorbents with pore size less than 20 Å are not suitable  
15 for the wet storage method as it is needed a definite space for formation of water cages inside the  
16 pores (Zhou et al., 2005). The calcium based sorbents used in this work with a broad distribution  
17 in mesopore can be a better choice of adsorbent to capture  $CO_2$  in presence of water.



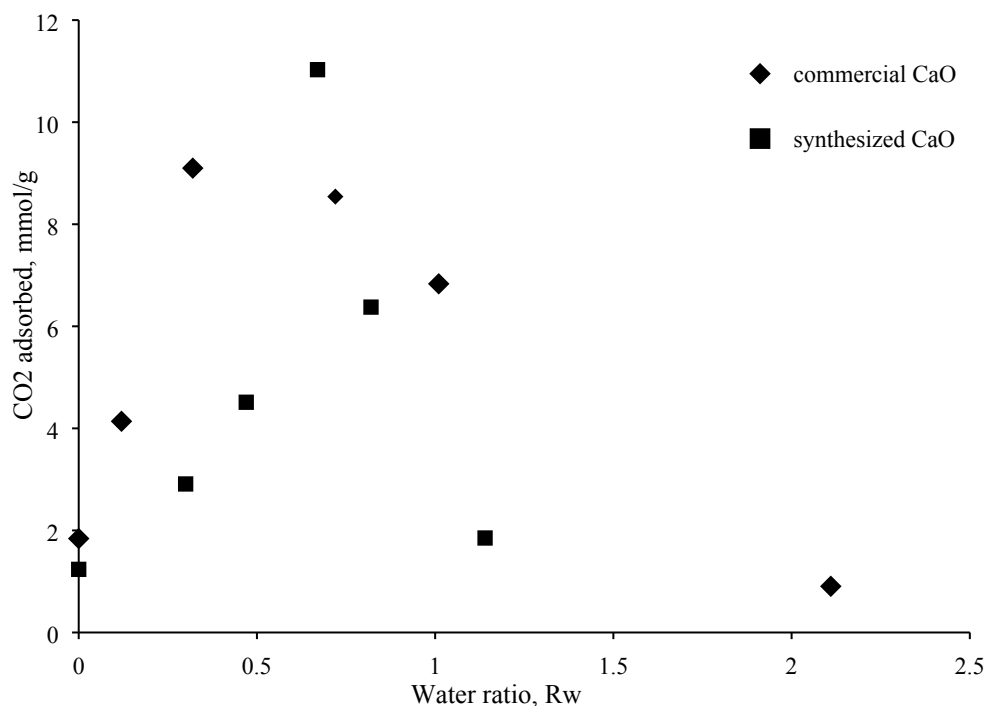
1

2 **Fig. 1.** N<sub>2</sub> adsorption and desorption isotherms for commercial and synthesized CaO3 **Fig. 2.** FESEM images of (a) commercial CaO; (b) synthesized CaO



1 FESEM images of commercial and synthesized CaO is depicted in Fig. 2. It can be observed that  
 2 the agglomerates of synthesized CaO are larger, rounded and profusely cracked (Fig. 2b). The  
 3 phenomenon may be observed due to sintering at high temperature during calcination process.

#### 4 4.2. CO<sub>2</sub> adsorption isotherm



5  
 6 **Fig. 3.** Effect of water ratio on CO<sub>2</sub> sorption at 36 bar for calcium based sorbents at 2 °C

7 Fig. 3 illustrated the effects of water content on CO<sub>2</sub> sorption amount at 36 bar. The water content  
 8 in a wet sample was expressed as  $R_w$ , the weight ratio of water to sample. The amount of CO<sub>2</sub>  
 9 adsorbed in the materials was expressed in mmol of CO<sub>2</sub> on the basis of per gram sample. At  
 10 2 °C, the pressure studied is limited only up to 36 bar, dependence on the temperature studied. It  
 11 is important to ensure that the pressure dosed is not greater than saturation pressure to avoid CO<sub>2</sub>  
 12 from condensed at high pressure. The adsorption capacities in wet sample were water content

1 dependence due to the remarkable changes in the sorbent's structure texture during the addition of  
 2 some amount of water (Martinez et al., 2011).

3 **Table 3**  
 4 Adsorption data of CO<sub>2</sub> on dry and wetted porous CaO

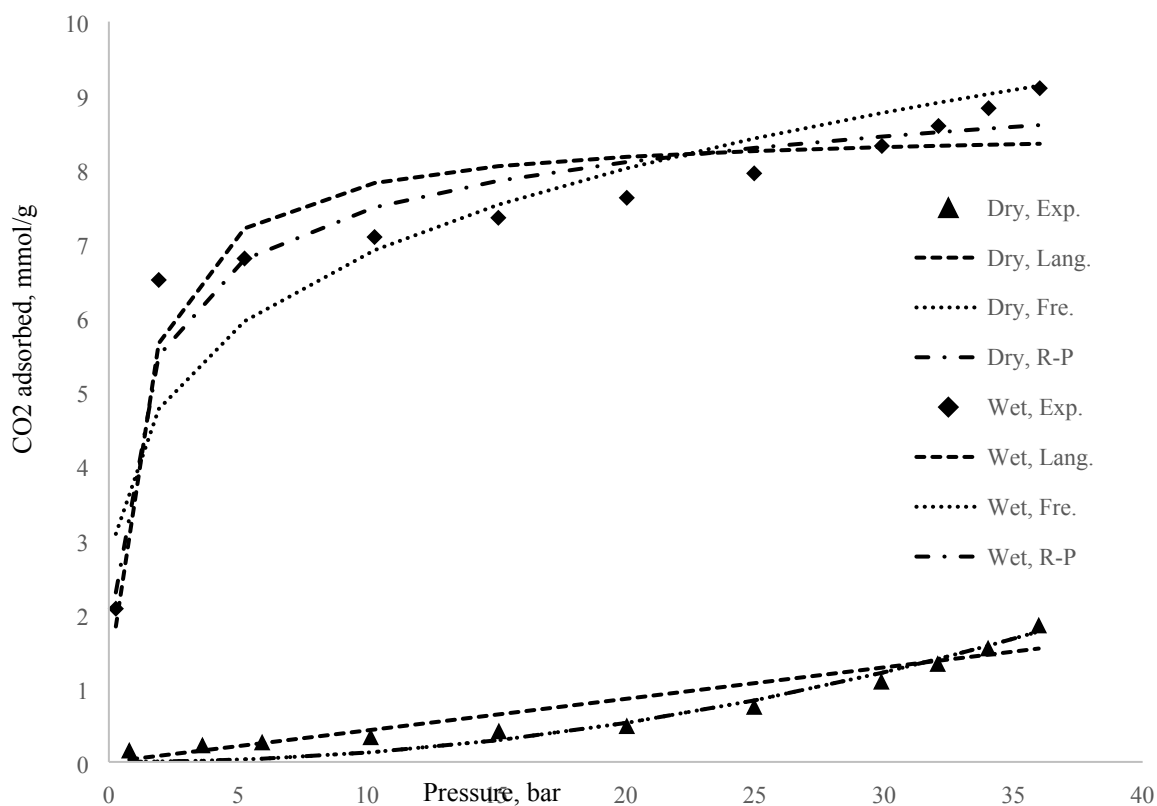
P (bar)	Amount adsorbed, q (mmol/g)			
	Comm. CaO		Syn. CaO	
	R <sub>w</sub> = 0	R <sub>w</sub> = 0.32	R <sub>w</sub> = 0	R <sub>w</sub> = 0.67
1	0.15	2.07	0.02	0.77
5	0.22	6.51	0.04	4.25
7	0.26	6.80	0.06	6.76
10	0.33	7.09	0.11	7.87
15	0.41	7.35	0.15	8.50
20	0.48	7.62	0.19	8.73
25	0.74	7.95	0.36	8.96
30	1.08	8.32	0.67	10.58
32	1.32	8.59	0.88	10.80
34	1.53	8.83	1.04	10.91
36	1.84	9.10	1.24	11.03

5  
 6 The highest CO<sub>2</sub> uptakes are observed at water ratio of 0.32 and 0.67, which is about 7.26 and 9.79  
 7 higher than the value of dry sample at 36 bar for commercial and synthesized CaO (Table 3). The  
 8 phenomenon is observed might due to the larger pore size of commercial CaO, less efficiency of  
 9 the solids as a carrier for formation of CO<sub>2</sub> hydrate. However, the amount of CO<sub>2</sub> decreased as  
 10 water content increased beyond this optimum value. The reaction was limited with an excess  
 11 amount of water due to the blockage of the pores in the solid (Bertos et al., 2004). As calcium

1 oxide is a sort of hydrophilic material, it is believed that the initial water adsorption occurs at the  
 2 functional groups of calcium surface was due to the strong chemisorption of water molecule with  
 3 the functional group (Do et al., 2000). Therefore, an additional amount of water will lead further  
 4 interactions of water molecules will occur on top of the chemisorbed water molecules via the  
 5 hydrogen bonding and resulting the formation of calcium hydroxide,  $\text{Ca}(\text{OH})_2$ .

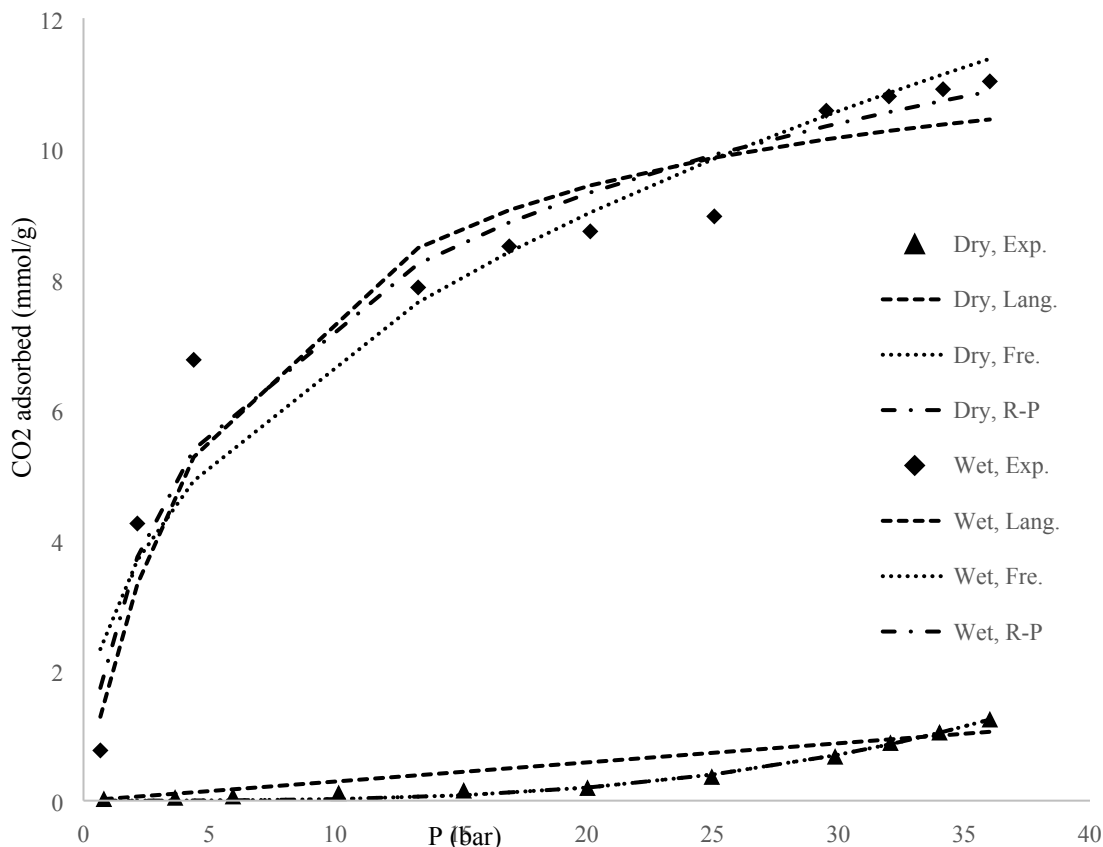
6 A solid hydrate was formed when gas  $\text{CO}_2$  was in contact with sufficient amount of water in the  
 7 system in which a  $\text{CO}_2$  molecules occupy the center of a cage surrounded by water molecules  
 8 (Premlall et al., 2014).  $\text{CO}_2$  was dissolved in hydroxide ions that react with  $\text{Ca}^{2+}$  ions to form  
 9 calcium carbonate. As the reaction proceeds,  $\text{Ca}^{2+}$  ions are consumed, but they are continuously  
 10 replenished by the suspended  $\text{Ca}(\text{OH})_2$  (Gupta and Fan, 2002).

11



12

1 **Fig. 4.** CO<sub>2</sub> adsorption isotherms for dry and wetted commercial CaO  
 2 (Exp. = Experimental; Lang. = Langmuir; Fre. = Freundlich; R-P = Redlich-Peterson)



3  
 4 **Fig. 5.** CO<sub>2</sub> adsorption isotherms for dry and wetted synthesized CaO  
 5 (Exp. = Experimental; Lang. = Langmuir; Fre. = Freundlich; R-P = Redlich-Peterson)

6 The plots of the experimental data and the predicted data from Langmuir (Lang.), Freundlich  
 7 (Fre.) and Redlich-Peterson (R-P) isotherm models on commercial and synthesized CaO are shown  
 8 in Fig. 4 and Fig. 5. The detailed isotherm parameters were listed in Table 4. **All the parameters in**  
 9 **the equation were determined by minimizing the error (HYBRID) and maximizing the respective**  
 10 **coefficient of determination ( $R^2$ ) between experimental data and predicted isotherm data using the**  
 11 **solver add-in with Microsoft's spreadsheet, Microsoft Excel. The calculation on these two error**  
 12 **functions have been discussed in the previous work (Azmi et al., 2016).**

1

2

3 **Table 4**

4 The fitted parameter values using different isotherms models on porous CaO

Sample		Comm. CaO		Syn. CaO	
		$R_w = 0$	$R_w = 0.32$	$R_w = 0$	$R_w = 0.67$
Langmuir	$q_{max}$	5317.789	8.582	26067.182	12.090
	$k_L$	$8.008 \times 10^{-6}$	0.999	$1.125 \times 10^{-6}$	0.176
	HYBRID	8.880	5.062	28.285	13.588
	$R^2$	0.868	0.924	0.760	0.941
Freundlich	$n_F$	0.001	4.496	0.322	2.504
	$k_F$	0.485	4.117	$1.805 \times 10^{-5}$	2.719
	HYBRID	7.888	12.832	2.312	43.100
	$R^2$	0.958	0.876	0.991	0.932
Redlich-Peterson	$a_R$	$4.684 \times 10^3$	2.107	$1.437 \times 10^3$	0.180
	$k_R$	171.433	13.799	25.625	2.142
	$\beta$	0	0.919	0	0.995
	HYBRID	7.387	4.031	12.108	15.285
	$R^2$	0.8131	0.944	0.462	0.941

5

6 The Freundlich adequately describes the adsorption data on dry basis for both studied samples

7 with the lowest values of HYBRID and the highest values of  $R^2$ . The Freundlich model describes

8 that the multilayer adsorption has occurred on porous CaO at 2 °C (Fil et al., 2012). The adsorption

9 capacity of CO<sub>2</sub> on commercial CaO is higher than synthesized CaO on dry basis (Table 3). The10 phenomenon is clearly explained by the Freundlich isotherm constant,  $k_F$ , the CO<sub>2</sub> uptake increases11 with increasing of  $k_F$  values. The  $n_F$  parameter in Freundlich model indicates the type of adsorption12 process whether the adsorption is linear ( $n_F = 1$ ), chemical process ( $n_F < 1$ ) or physical process ( $n_F$ 13  $> 1$ ). From the tabulated data,  $n_F$  parameter ( $< 1$ ) indicates that chemical process has occurred

1 during the adsorption of CO<sub>2</sub> on CaO. In fact, the chemical interaction between the CO<sub>2</sub> and CaO  
2 will result in the calcium carbonates (CaCO<sub>3</sub>) formation, thereby, align with the Freundlich  
3 constants. It has also been reported that lower  $n_F$  values indicates a presence of the high-energy  
4 active sites (Do and Do, 2000). Moreover, the estimated  $1/n_F$  which is way beyond than unity  
5 describes a cooperative adsorption, which implies favorability of the active site to retain the sorbate  
6 molecules (Do and Do, 2000). The Langmuir adsorption model deviates to accurately describe the  
7 adsorption data, primarily because it fails to account for the surface roughness of the adsorbate  
8 and multi-layered adsorption phenomenon (Rudzinski et al., 2001). In the case of wet sample at  
9 optimum water ratio, the Redlich-Peterson model gives the best fitted with R<sup>2</sup> values 0.944 and  
10 0.941 for CO<sub>2</sub> adsorption on commercial and synthesized CaO. The constant  $\beta$  values, approaching  
11 1 show a close resemblance of the sorption behavior to the Langmuir model, and is further proven  
12 by a small difference in the R<sup>2</sup> value between the Langmuir and R-P isotherm model (Do et  
13 a.2000).

14 The model has been further extended with addition of water isotherm models: WIM1 and WIM2  
15 to understand a mechanism of water adsorption in CO<sub>2</sub> adsorption process. The philosophy of  
16 correlate the adsorption equilibrium data with water isotherm model is to give better understanding  
17 about the surface characteristics of the wetted materials as well as improve the predicted data. The  
18 values of optimized parameters obtained from the fitting of model to the experimental data of CaO  
19 at optimum condition are tabulated in Table 5. From the tabulated table, it is clearly seen that the  
20 water cluster sizes in micropore ( $\alpha_1$ ) is less than the value of size in mesopore ( $\alpha_2$ ) and these values  
21 relatively small as compared with other studies. It is reported that water cluster sizes is dependent  
22 on the concentration of functional groups; the higher concentration the smaller of cluster size and  
23 vice versa (Horikiwa et al., 2011). **The existence of additional basic functional groups attached**

1 with calcium atoms during the calcination process has become advantage for water adsorption.  
 2 The fast reaction has been occurred between the basic sites of synthesized CaO and water  
 3 molecules, in which allow the formation of hydroxide groups on the surface of the calcium  
 4 adsorbent (Margaretha et al., 2012). The water molecules will easily adsorb in form of cluster and  
 5 only small value of cluster size is required with the presence of these functional groups (Do et al.,  
 6 2009).

7 **Table 5**

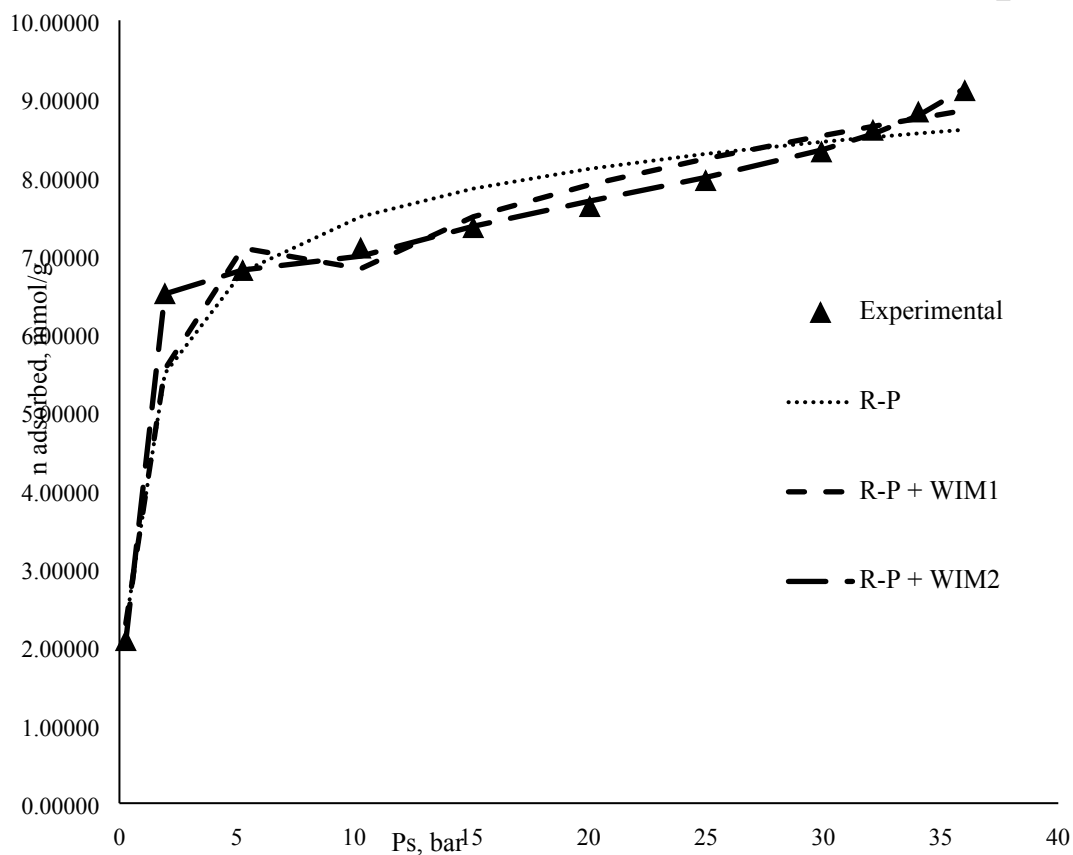
8 The optimized parameter values obtained from WIM1 and WIM2 for CO<sub>2</sub> adsorption on porous  
 9 CaO at optimum water ratio

Isotherm models	Parameter	Adsorbent	
		Comm. CaO (R <sub>w</sub> = 0.32)	Syn. CaO (R <sub>w</sub> = 0.67)
WIM1	q <sub>μs</sub>	-0.76	-1.11
	K <sub>μs</sub>	-2585.49	-2374.52
	α <sub>1</sub>	5.00	4.00
	K <sub>f</sub>	0.00	0.00
	S <sub>o</sub>	793.02	12691.59
	HYBRID	0.04	0.23
	R <sup>2</sup>	0.96	0.98
WIM2	q <sub>μs</sub>	-1.63	-2.78
	K <sub>μs</sub>	26375.91	155.30
	α <sub>1</sub>	5.00	4.00
	q <sub>m</sub>	1.02	1.32
	K <sub>m</sub>	-1727.20	2.14 x 10 <sup>14</sup>
	α <sub>2</sub>	8.00	12.00
	K <sub>f</sub>	-0.84	-0.48
	S <sub>o</sub>	-0.22	-1.96
	HYBRID	0.00	0.33
R <sup>2</sup>	0.99	0.98	

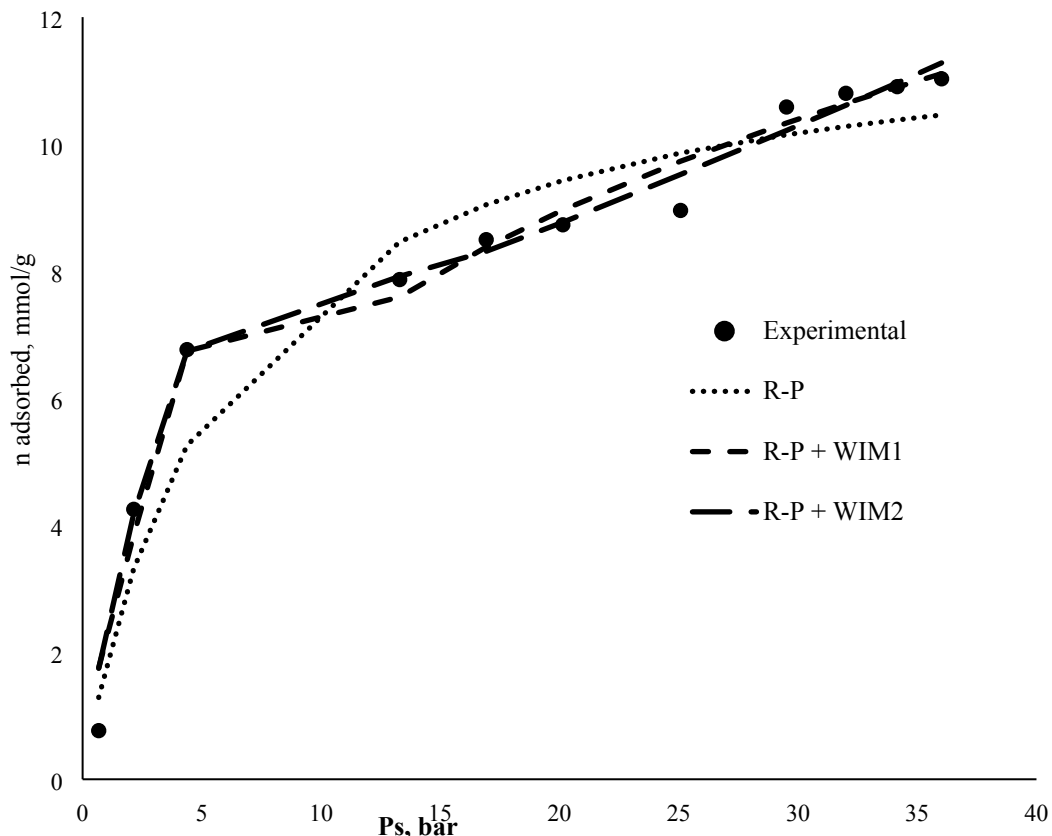
1  
2 Fig. 6 and 7 show the comparison between the predicted data from R-P, R-P + WIM1 and R-P +  
3 WIM2 with the experimental data on commercial and synthesized CaO. There are improvement  
4 of the predicted data obtained from combination of R-P and water isotherm models: WIM1 and  
5 WIM2 where the  $R^2$  value has increased from 0.944 to 0.963 to 0.999 on commercial CaO and  
6 from 0.941 to 0.979 to 0.983 on synthesized CaO. At the low pressure, the amount sorbed is  
7 slightly deviated in the existing isotherm model (R-P). However, the extended model R-P + WIM1  
8 and R-P + WIM2 describes reasonably well the experimental data of wet synthesized CaO at low  
9 pressure. The phenomenon is observed in porous CaO as  $\text{CO}_2$  may condense in small pores and  
10 react with water to form  $\text{HCO}_3^-$ , which leads to more  $\text{CO}_2$  molecules fixed at low pressure (Wang  
11 et al., 2008). It is also believed that the higher sorption amount is due to the higher solubility of  
12  $\text{CO}_2$  in water. As the pores are filled by the water, calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) is produced and  
13 only external surface is exposed to the adsorbing gas,  $\text{CO}_2$ . Wang et al. have reported that CaO  
14 particles will transform into small  $\text{Ca}(\text{OH})_2$  particles and a part of  $\text{Ca}(\text{OH})_2$  dissolves with the pore  
15 structure becoming loose (Wang et al., 2013). The extended models successfully predict the data  
16 at inflection point as the presence of water are included in the calculation. The formation of  $\text{CO}_2$   
17 hydrate in the system was indicated by increasing of sorbed amount to a much higher level, which  
18 were represented by inflection of isotherms at a definite pressure. The increment of  $\text{CO}_2$  uptake at  
19 this point was may due to coalescence of water clusters on the adsorption branch (Dong et al.,  
20 2011). In the case of  $R_w$  less than 0.67, the inflection point is not appeared due to insufficient  
21 amount of pre-adsorbed water to trap  $\text{CO}_2$  molecules to form  $\text{CO}_2$  hydrate. Whereas an excess  
22 amount of water prevents  $\text{CO}_2$  from getting into the pore spaces as both interior and exterior pore  
23 spaces between the sorbent particles have been totally occupied by extra water. **The most suitable**



- 1 adsorption equilibrium correlation is essential for describing the reaction of CO<sub>2</sub> with solid CaO
- 2 and optimizing the use of the materials that can be used for design purposes.



3  
4 **Fig. 6.** Comparison of experimental and predicted isotherm data of CO<sub>2</sub> adsorption on commercial  
5 CaO



**Fig. 7.** Comparison of experimental and predicted isotherm data of CO<sub>2</sub> adsorption on synthesized CaO

## 5. CONCLUSIONS

The adsorption capacities in solid CaO are depending on the amount of water presence inside the pores due to change of sorbent's structure texture during addition of water. By having water ratio at optimum values of 0.32 and 0.67, about 7.26 and 9.79 mmol/g increment of CO<sub>2</sub> uptake have been measured for commercial and synthesized CaO. An adequate quantity of water used for each materials have significantly been measured to ensure formation of CO<sub>2</sub> hydrate inside the pores.

In the case of dry analysis, the Freundlich model was found to give the best fitted with the highest values for R<sup>2</sup>, perfectly describe that multilayer adsorption has occurred during sorption of CO<sub>2</sub> on solid CaO at 2 °C. The Redlich-Peterson model shows the good agreement of predicted and

1 measured data for wet analysis of both materials. The existing R-P model was extended with water  
2 isotherm models: WIM1 and WIM2 to give the best fitted predicted data with the increment of  
3 coefficient from 0.94 to 0.99 and from 0.95 to 0.98 on commercial and synthesized CaO. **The**  
4 **untreated cockle shell has a considerable potential as CO<sub>2</sub> adsorbent in a commercial system due**  
5 **to its availability and cheaper in cost. This greener and cleaner approach of formation of CO<sub>2</sub>**  
6 **hydrate inside the pores with sufficient equilibrium data provides a reliable route for designing a**  
7 **large-scale CO<sub>2</sub> separation process by using the solid CaO.**

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### 16 **Notes**

17 The authors declare no competing financial interest.

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