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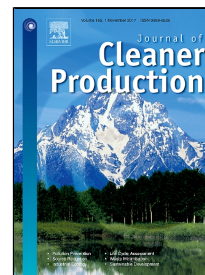
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1 Effect of water onto porous CaO for CO₂ adsorption:
2 Experimental and extended isotherm model

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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 CO₂ 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 CO₂ capture were investigated. The adsorption equilibrium of CO₂ 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 CO₂ 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 CO₂ 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 R² 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 CO₂ adsorbent for gas
19 adsorption applications.

20 **KEYWORDS:** *CO₂ sorption, Calcium oxide, Isotherm model, Water sorption isotherm, Non-*
21 *linear regression*

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 CO₂ emissions in China's commercial sector has
16 been predicted to be 1942 Mt by 2030, which is huge and about half of the CO₂ emissions in year
17 2014 (Wang and Lin, 2017). In Malaysia, around 288.1 MtCO₂ has been emitted, contributing
18 0.67% to global emissions in year 2012 (World Resources Institute, 2015). The increasing
19 concentration of atmospheric CO₂ due to carbon emissions will continuously lead to a significant
20 impact on global climate.

21 The increasing amount of CO₂ 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 CO₂ 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 CO₂ 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 CO₂ reductions by 2050 (IEA, 2014).
5 It is crucial to develop the CCS technologies to cope with the global demand of CO₂ 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 CO₂ 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 CO₂ present
14 in flue gas or in atmosphere. There are three basic types of CO₂ 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 CO₂ such as absorption, adsorption, cryogenic, membrane and gas hydrate
18 formation. The CO₂ separation with solid sorbents has become a promising technology that can be
19 integrated with existing CO₂ emitting plants (Benedetti et al., 2015). In this retrospect, CO₂
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 CO₂ is caused by van der Waals attraction between the CO₂ molecule and adsorbent
23 surface. It is caused by pole-ion and pole-pole interactions between the quadruple of CO₂

1 molecules and the ionic and polar sites of the CO₂ 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 CO₂ separation is a new technology by which the exhaust gas containing CO₂
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 CO₂ from the hydrate in
16 an energy efficient manner; efficient capture of CO₂; 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 CO₂ 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 CO₂ should be explored to ensure the world
22 sustainability. Improved technologies for CO₂ capture are necessary to achieve low energy
23 penalties and low cost process. It is suggested to allow formation of CO₂ 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_x, SO_x and water vapor significantly impact the
3 performance of CO₂ 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 CO₂ by adsorption process and techniques to introduce
8 water on these materials, allow more CO₂ can be adsorbed. An ideal CO₂ adsorbent should exhibit
9 a higher CO₂ 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 CO₂ 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 CO₂ supersaturation sites in the porous media
17 and decrease in the induction time needed for hydrate formation thus increasing the amount of CO₂
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 CO₂ in industrial
20 gas streams especially for high CO₂ 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 CO₂ 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 CO₂ due to their reactivity with CO₂, 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 CO₂ 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 CO₂ 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 (CaCO₃) (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, CaCO₃ liberate CO₂ 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 CO₂ hydrate
4 inside the pores. The sorption behavior of CO₂ 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 CH₄ and C₃H₈ hydrates has been reported by Handa and Stupin (Handa
7 and Stupin, 1992). They found that the equilibrium pressures of CH₄ and C₃H₈ 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 CH₄, C₃H₈ and CO₂ 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 CO₂ and CH₄ 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 CO₂ and CH₄; respectively to indicate hydrate
14 formation in the system. Zheng and his co-workers have reported that the formation of CO₂
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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ gas streams. Therefore, the main objectives of this work were to
4 measure the CO₂ 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_w 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 N₂ 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 CO₂ 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. CO₂ adsorption measurement

The CO₂ 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, CO₂ hydrate formation region. The details of CO₂ analysis has been discussed in previous paper (Azmi et al., 2016). The capability of porous CaO derived from waste cockle shell for CO₂ capture has been measured and compared with commercial CaO. The degree of effectiveness of the proposed system was evaluated by comparing the amount of CO₂ 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, β | 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); β : 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 CO₂ 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 CO_2 ; α 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 α_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 α_2
 3 is larger than that α_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 CO₂ 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 ² /g | cm ³ /g | Å |
| Commercial CaO | < 0.1 | 7.27 | 3.88 x 10 ⁻² | 213.34 |
| | < 0.1 | 8.79 | 1.72 x 10 ⁻² | 78.16 |
| Synthesized CaO | 0.1 – 0.25 | 4.38 | 1.07 x 10 ⁻² | 98.61 |
| | > 0.5 | 2.86 | 1.20 x 10 ⁻² | 172.68 |

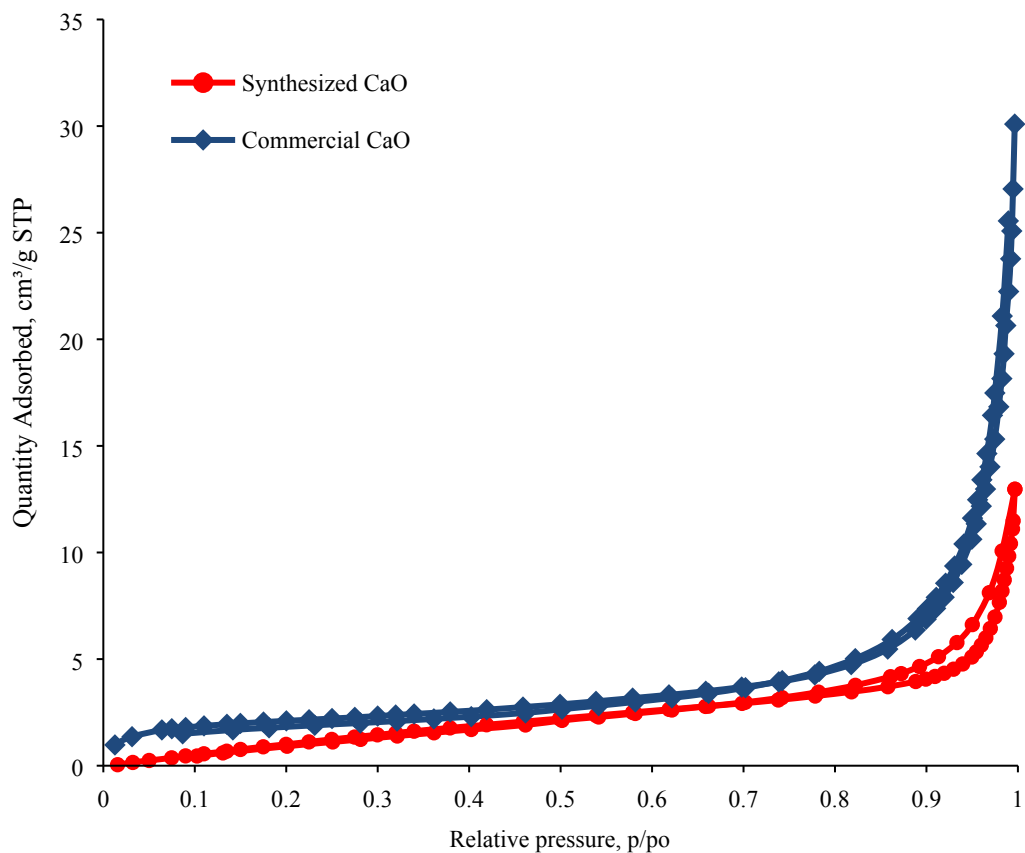
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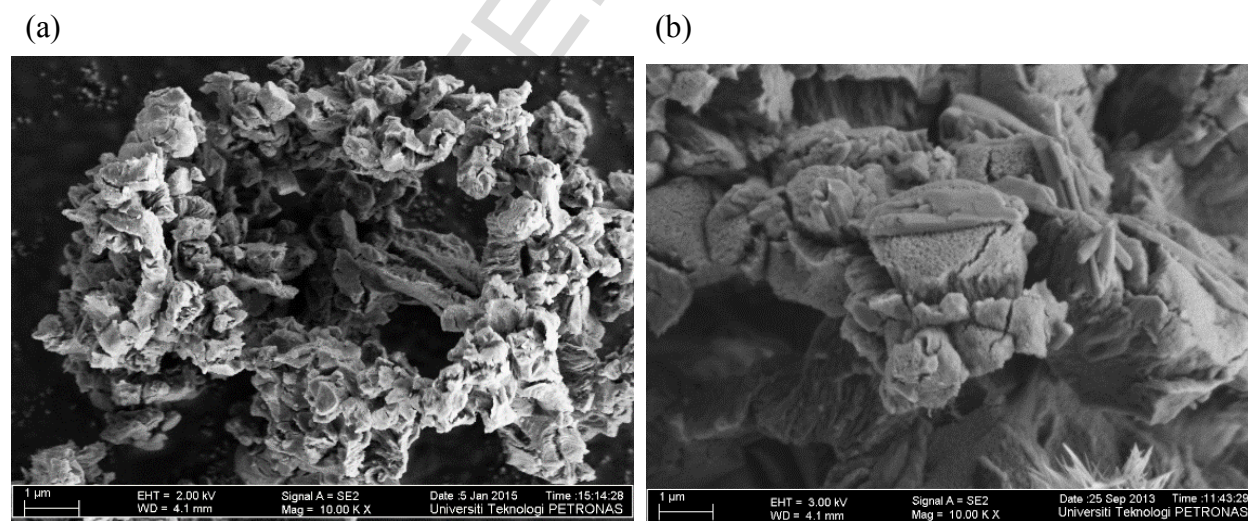
14 Table 2 summarizes the properties of the porous calcium oxide. From the presented values, it
 15 is shown that synthesized CaO with smaller particle size (< 0.1 mm) offers the highest specific
 16 surface area compared with the others sizes. Differ for average pore width, the values are directly
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

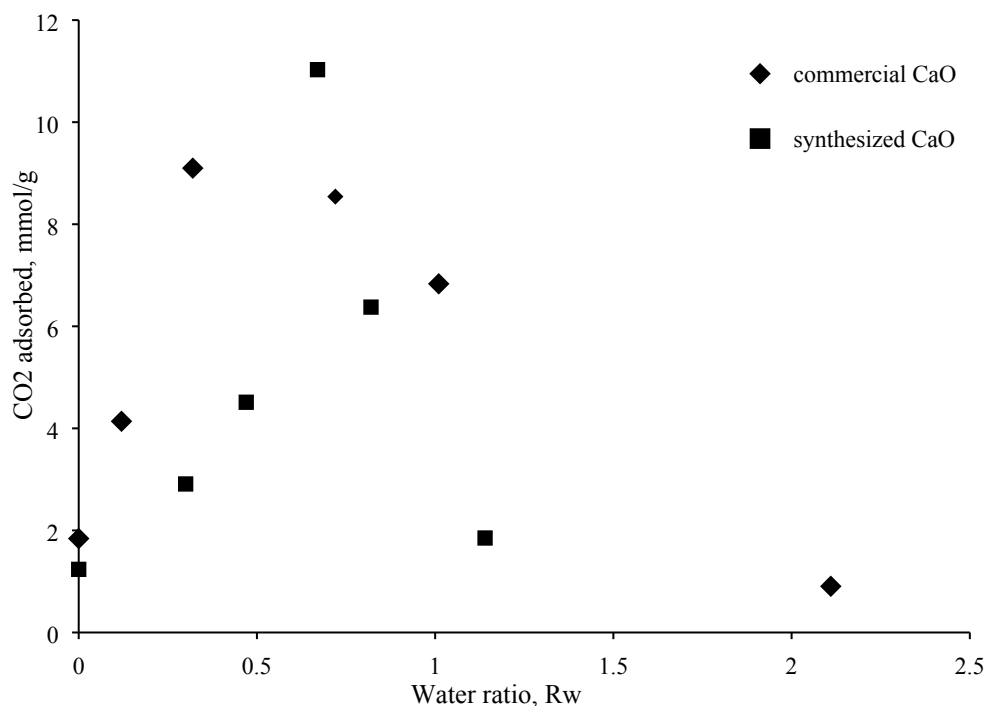


1

2 **Fig. 1.** N₂ 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. CO₂ adsorption isotherm



5
 6 **Fig. 3.** Effect of water ratio on CO₂ sorption at 36 bar for calcium based sorbents at 2 °C

7 Fig. 3 illustrated the effects of water content on CO₂ 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 CO₂
 9 adsorbed in the materials was expressed in mmol of CO₂ 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 CO₂
 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 CO₂ on dry and wetted porous CaO

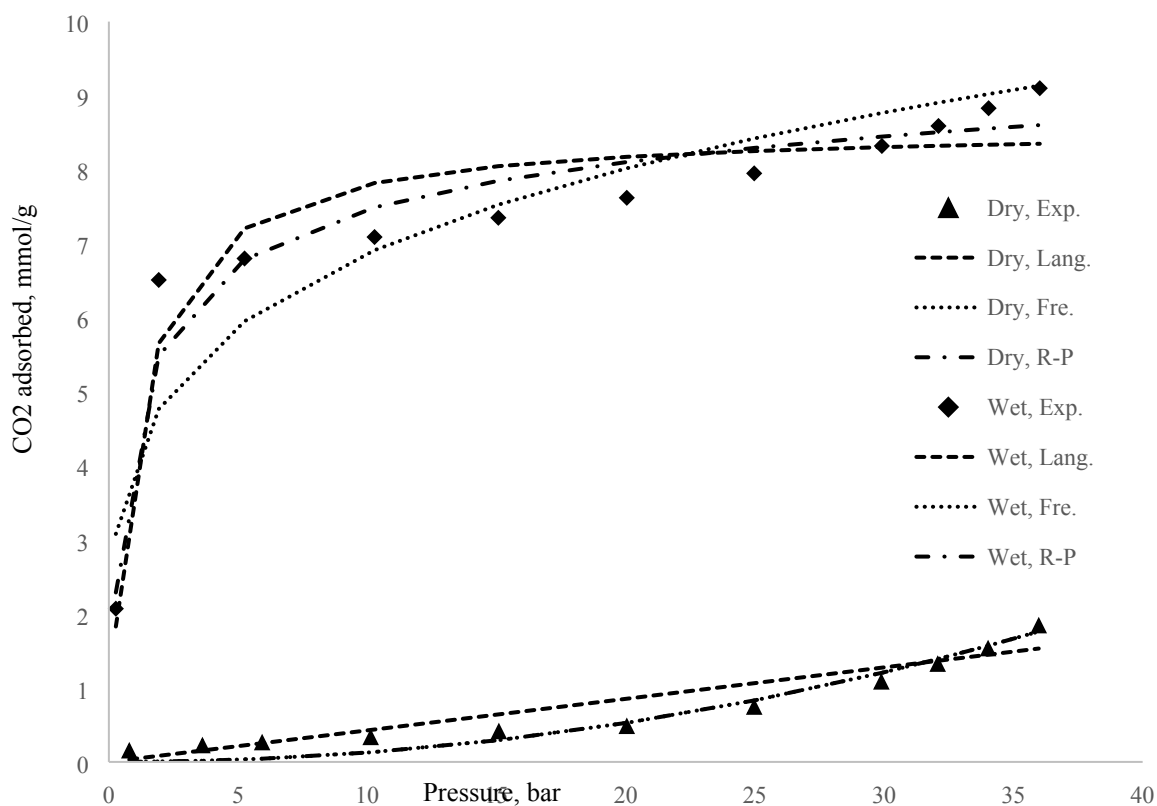
| P (bar) | Amount adsorbed, q (mmol/g) | | | |
|---------|-----------------------------|-----------------------|--------------------|-----------------------|
| | Comm. CaO | | Syn. CaO | |
| | R _w = 0 | R _w = 0.32 | R _w = 0 | R _w = 0.67 |
| 1 | 0.15 | 2.07 | 0.02 | 0.77 |
| 5 | 0.22 | 6.51 | 0.04 | 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 CO₂ 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 CO₂ hydrate. However, the amount of CO₂ 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, $\text{Ca}(\text{OH})_2$.

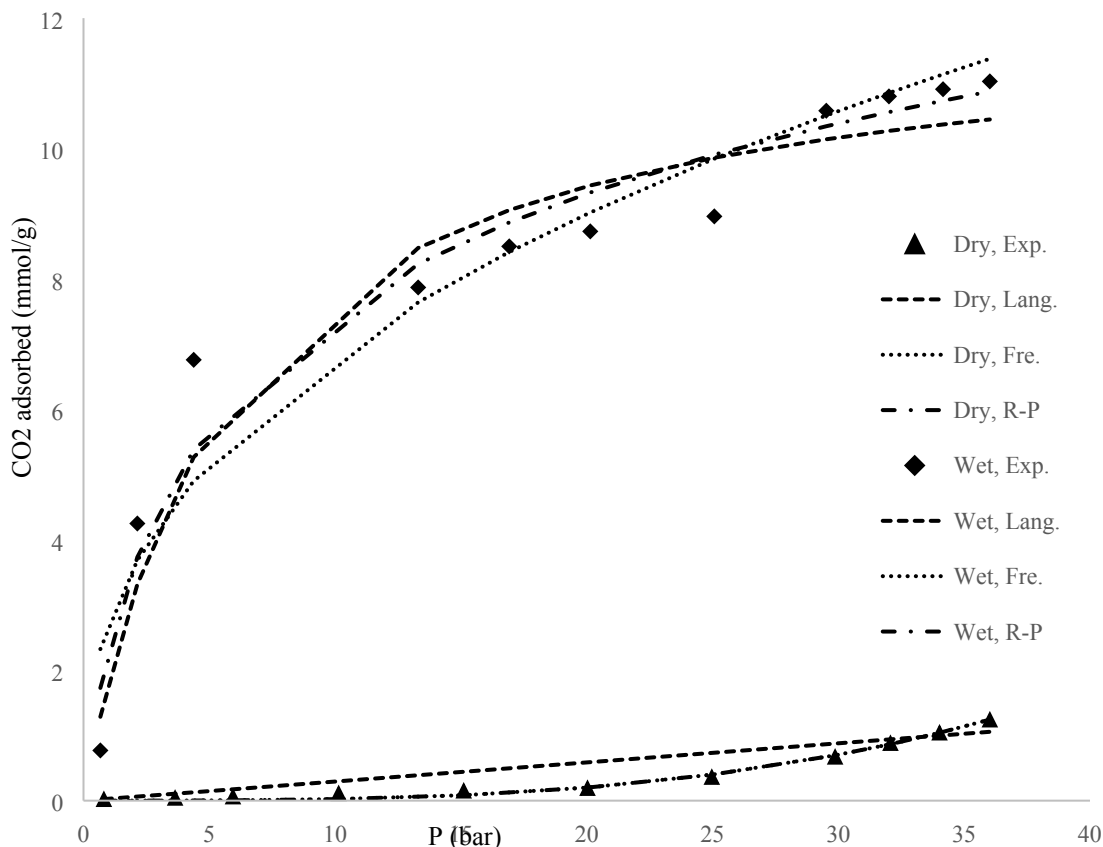
6 A solid hydrate was formed when gas CO_2 was in contact with sufficient amount of water in the
 7 system in which a CO_2 molecules occupy the center of a cage surrounded by water molecules
 8 (Premlall et al., 2014). CO_2 was dissolved in hydroxide ions that react with Ca^{2+} ions to form
 9 calcium carbonate. As the reaction proceeds, 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.** CO₂ adsorption isotherms for dry and wetted commercial CaO
 2 (Exp. = Experimental; Lang. = Langmuir; Fre. = Freundlich; R-P = Redlich-Peterson)



3
 4 **Fig. 5.** CO₂ 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 | 8.008×10^{-6} | 0.999 | 1.125×10^{-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 | 1.805×10^{-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 | 4.684×10^3 | 2.107 | 1.437×10^3 | 0.180 |
| | k_R | 171.433 | 13.799 | 25.625 | 2.142 |
| | β | 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 CO₂ 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 CO₂ 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 CO₂ on CaO. In fact, the chemical interaction between the CO₂ and CaO
2 will result in the calcium carbonates (CaCO₃) 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 R² values 0.944 and
10 0.941 for CO₂ adsorption on commercial and synthesized CaO. The constant β 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 R² 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 CO₂ 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 (α_1) is less than the value of size in mesopore (α_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).

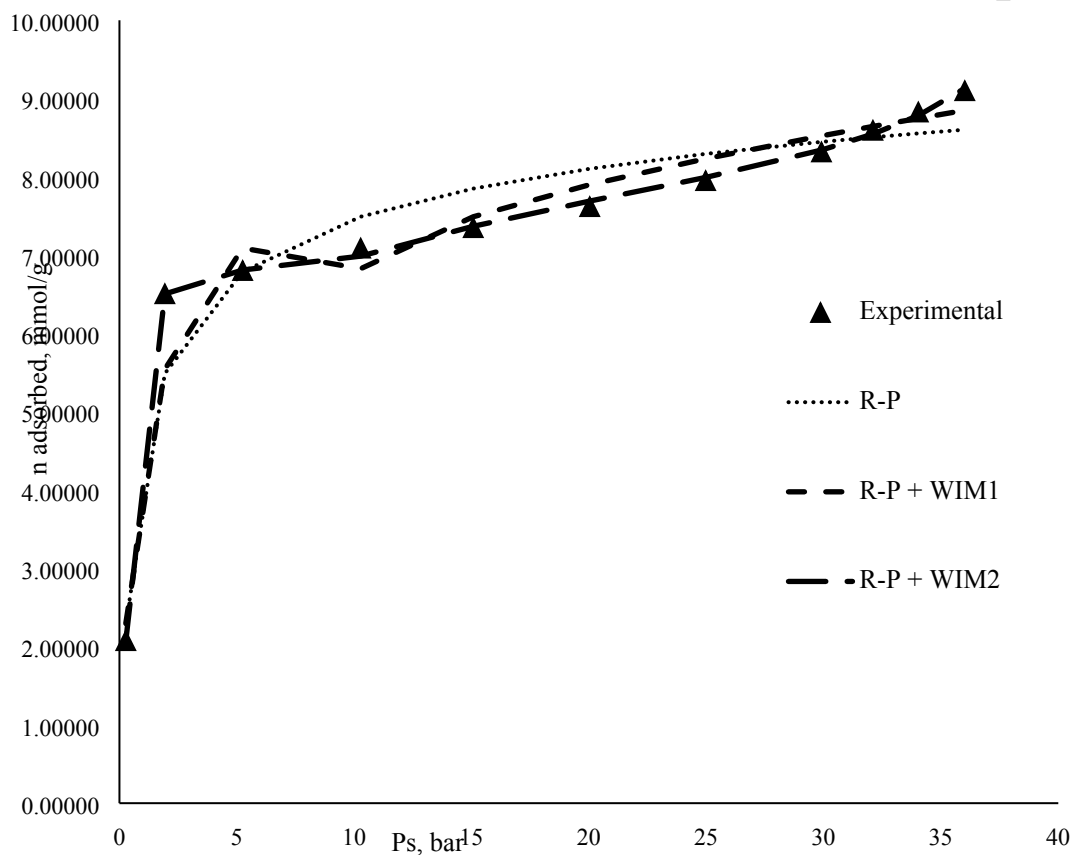
7 **Table 5**

8 The optimized parameter values obtained from WIM1 and WIM2 for CO₂ adsorption on porous
 9 CaO at optimum water ratio

| Isotherm models | Parameter | Adsorbent | |
|-----------------|-------------|-------------------------------|------------------------------|
| | | Comm. CaO ($R_w = 0.32$) | Syn. CaO ($R_w = 0.67$) |
| WIM1 | $q_{\mu s}$ | -0.76 | -1.11 |
| | $K_{\mu s}$ | -2585.49 | -2374.52 |
| | α_1 | 5.00 | 4.00 |
| | K_f | 0.00 | 0.00 |
| | S_o | 793.02 | 12691.59 |
| | HYBRID | 0.04 | 0.23 |
| | R^2 | 0.96 | 0.98 |
| WIM2 | $q_{\mu s}$ | -1.63 | -2.78 |
| | $K_{\mu s}$ | 26375.91 | 155.30 |
| | α_1 | 5.00 | 4.00 |
| | q_m | 1.02 | 1.32 |
| | K_m | -1727.20 | 2.14×10^{14} |
| | α_2 | 8.00 | 12.00 |
| | K_f | -0.84 | -0.48 |
| | S_o | -0.22 | -1.96 |
| | HYBRID | 0.00 | 0.33 |
| R^2 | 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 CO_2 may condense in small pores and
10 react with water to form HCO_3^- , which leads to more 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 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, 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 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 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 CO_2 molecules to form CO_2 hydrate. Whereas an excess
22 amount of water prevents 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_2 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_2 adsorption on commercial
5 CaO

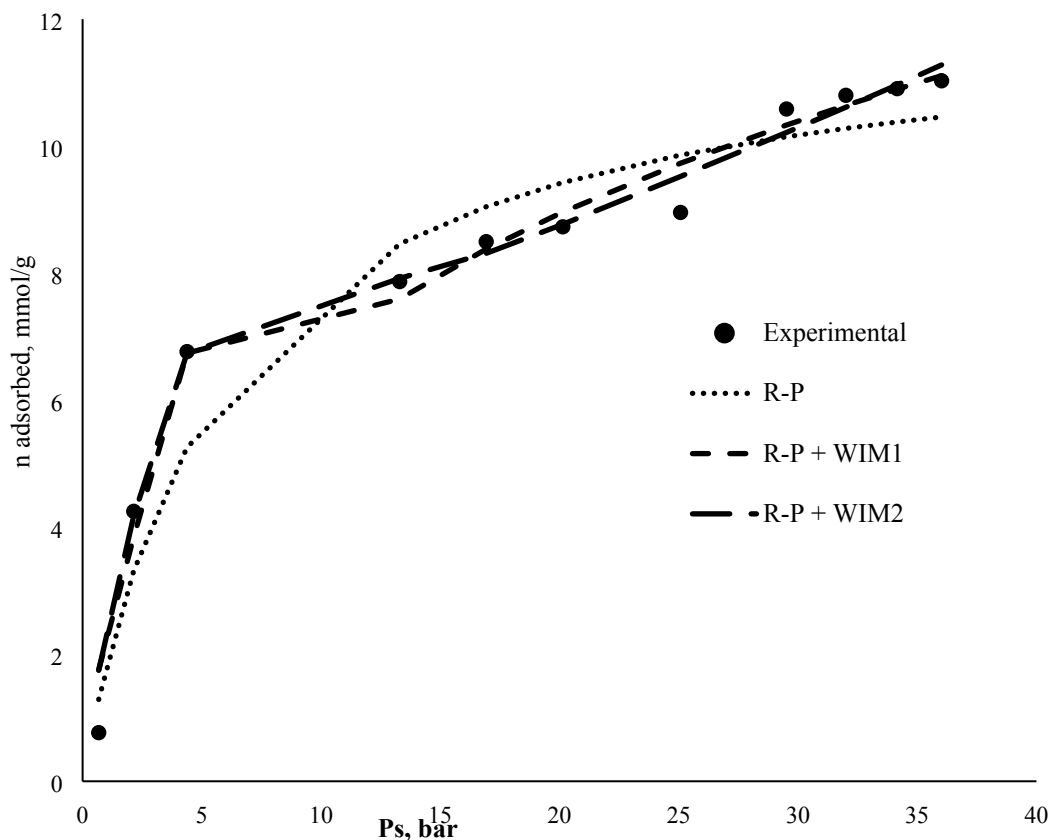


Fig. 7. Comparison of experimental and predicted isotherm data of CO₂ adsorption on synthesized CaO

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 CO₂ 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 CO₂ 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 R², perfectly describe that multilayer adsorption has occurred during sorption of CO₂ 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 CO₂ adsorbent in a commercial system due**
5 **to its availability and cheaper in cost. This greener and cleaner approach of formation of CO₂**
6 **hydrate inside the pores with sufficient equilibrium data provides a reliable route for designing a**
7 **large-scale CO₂ 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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