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Research Article

The Effects of the Preparation Factors on the Properties of CO_2 Capture Sorbent Derived from Local Waste Eggshell

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Abstract

In this study, the CaO adsorbent was prepared by using local waste eggshell as a raw material. The influence of preparation parameters including calcination temperature, calcination time and particle size of eggshell powder on the adsorption surface area were investigated. By means of statistically experiment design, the interesting parameters were investigated by a full 2^3 factorial design. The prepared sorbent material was characterized by X–ray diffraction (XRD), Scanning electron microscopy (SEM) and the Brunauer–Emmet–Teller (BET). The results showed the particle size of eggshell powder greatly affected the BET surface area. By applying the prepared condition of 149 µm in particle size, 6 h of calcination time and 1,000ºC calcination temperature, the obtained CaO adsorbent yielded the highest in BET surface area of 5.023 $m^2\ g^{-1}$. The CO_2 performance test in the fluidized bed reactor with 12% V/V CO_2 in N_2 balance also revealed that the local waste eggshell can be used as CO_2 adsorbent. The CO_2 carrying capacity of the highest BET surface area sorbent was 0.011 g $CO_2\ g^{-1}$ sorbent at 700°C carbonation temperature.

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Introduction

As the prediction of United Nations in 2019, the growing in global population is assumed to be over 9 billion by 2045. This situation has led to a massive increasing in natural resource consumption and waste production. The environmental problems such as global warming, the damage in marine habitat also came from the inefficient waste management. The circular economy approach is highly practical approach to decrease the amount of waste and the natural resources consumption whereas raise the production efficiency [1]. By recycle and reuse of waste materials as the raw material for preparation of other materials and chemicals are the sustainable ways for applying the circular economy approach. Hydrothermal carbonization, enzymatic pretreatment, ultrasonic pretreatment are the examples of useful techniques to convert biobased waste into the value-added materials [2].

The impact of global warming issue provokes social responsibility and urges associated authorities to launch the CO_2 reduction policy. In order to diminish the CO_2 releasing to the atmosphere, several technical solutions have been recommended. The CO_2 capture and storage technology are proposed to play an important role in reducing the CO_2 volume worldwide. This technology can be applied in both pre–combustion and post–combustion systems. Post-combustion capture is concerned the CO_2 capture of the high temperature flue gas produced from the fossil fuels combustion. This approach can be employed with the existing power plant. Normally, the CO_2 concentration in flue gas stream has a low concentration with 3%–33% vol and a low CO_2 partial pressure with 0.03–5 bar [3].

Recently, several CO_2 capture technologies for post-combustion capture have been developed such as liquid absorption, solid adsorption and membrane absorption. Among them, liquid absorption and membrane absorption

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have challenges in large-scale operation such as solvent degradation, high cost and the corrosive nature of sorbents [3–4].

The using of solid adsorbent is the promising technology as it can be operated at a wide range of temperature (ambient–700°C). Also, it has been considered applicable for separating CO_2 from the high temperature stream of flue gas as a post-combustion process. The calcium oxide (CaO) is the interesting adsorbent for the CO_2 adsorption through the calcium looping cycle. CaO adsorb the CO_2 to form the $CaCO_3$ at the reaction temperature around 600–700°C. Then the adsorbent can be regenerated by heating at 900°C to release the CO_2. The mechanism of the CO_2 on the CaO surface is chemisorption which is the gas–solid non-catalytic reaction. The reaction rate considerably depends on the carbonation temperature. The CaO conversion in the carbonation can be separated into two stages which are the kinetic-controlled carbonation (initial rapid surface reaction rate) and the diffusion-controlled carbonation (slow reaction rate). In the diffusion-controlled step, it is suggested that the coverage of $CaCO_3$ product molecules on the CaO surface inhibit the active CaO surface and pores from the contact of incoming CO_2 molecules. Then, the gas diffusion is limited resulting in the extremely decline of the reaction rate. Therefore, the sorbent performance could be governed by the sorbent pores and surface area. However, the advantages of CaO adsorbent are high selectivity with fast reaction rates, the obtainable of low cost natural CaO precursors such as limestone, eggshell and marine organism shell and low waste generation due to the recyclable of adsorbent [5–7].

Since eggs are the main ingredient in the food production processes and there are a lot of eggshells left over from these processes. The preparation of CaO from these waste eggshells is very interesting. Since it will coincide with the concept of green process by utilizing renewable material, reducing the waste and the disposal cost, the environmental-friendly adsorbents are subsequently generated. In this study, the local waste eggshells were gathered to be a raw material for CaO adsorbent. The effects of sorbent preparation parameters on the adsorption surface were investigated. The most influence parameter and the interaction of parameters would be explored systematically via the 2^k experi-mental design methodology. And the CO_2 adsorption capability of the prepared CaO was also performed in the fluidized bed reactor for the possibly practical application.

Experimental

1) Materials

Different types of waste eggshell material, including chicken, quail and duck eggshells, were gathered from fresh market of Prachuap Khiri Khan province, Southern of Thailand. All samples were washed several times and dried naturally. Then, they were grinded into fine powder and further determined the particle size by size sieving. The physical appearance of the fine powder depended on the source of waste eggshells which were similar to the previous reported [8–9]. To obtain the sorbent materials, the eggshell powder with specific size was calcined in the furnace at a particular calcination temperature and time.

2) Experimental design methodology and statistical analysis of sorbent preparation

To investigate the preparation parameter that might significantly affect the sorption capability, a full 2–level, 3–factors (2^3) factorial design experiment was performed, randomly. The calcination temperature, the calcination time and the particle size before calcination (in term of the U.S. mesh size) were selected as the considering variables. The full 2^3 factorial design is shown in Table 1 as a sorbent preparation conditions. The levels were displayed in a coded value with dimensionless coordinates as +1 (high) and 1 (low). Since high CO_2 adsorption would be reflected by the high surface area material, the BET surface area was, then, served as a response factor [10]. All experiments were replicated and statistically analyzed with the 5% significance level of the test (P–values <0.05).

3) Eggshell powder and sorbent material characterization

Before calcination, all types of eggshell powder were conducted the element analysis by X–Ray fluorescence (S4 Pioneer wavelength dispersive fluorescence spectrometry) to select the suitable material for performing the 2^3 factorial design experiments.

After calcination, the surface area of the calcined eggshell powder of all conditions was evaluated by BET (ASAP 2020 V4.00) using N_2 adsorption at liquid nitrogen temperature.

The prepared sorbents from calcined eggshell powder were assessed the morphology both before and after CO_2 adsorption test by scanning electron microscopy (QUANTA 450 scanning electron microscope, FEI). The surface of the raw material before calcination was also investigated.

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Table 1 Experimental variables in coded and actual units for 2^3 factorial design

Factors	Variables	Low (-1)	High (+1)	Unit
A	Calcination temperature	800	1000	°C
B	Calcination time	3	8	h
C	U.S. mesh size (converted to micron)	50 (297)	100 (149)	- (micron)

The crystalline structures of the prepared sorbent before and after CO_2 adsorption test were characterized by X–ray diffraction technique (Bruker AXS–D8 Advance machine using Cu K α radiation). The diffraction patterns were collected between 10–80° at the scanning rate of 2° min^{-1}.

4) CO_2 capture performance test

The CO_2 capture performance test was performed in the lab–scale, fluidized–bed reactor as shown in Figure 1. The reactor column was made of quartz with inside diameter 0.025 m and 0.8 m height. The column was heated up to the 700°C before adding 20 g of sorbent material from the top of column. Then, the carbonation test was operated by flowing the mixed gas (12% V/V CO_2 in N_2) into the column with the flow rate of 2.5 L min^{-1}. The CO_2 adsorption behavior was observed by measuring the output CO_2 content at the top of column with the online CO_2 sensor (K33 BLG 30% CO_2 + RH/T Data Logging Sensor, CO_2 Meter). The carbonation test was conducted without reversible reaction (without regeneration process for the used sorbent material).

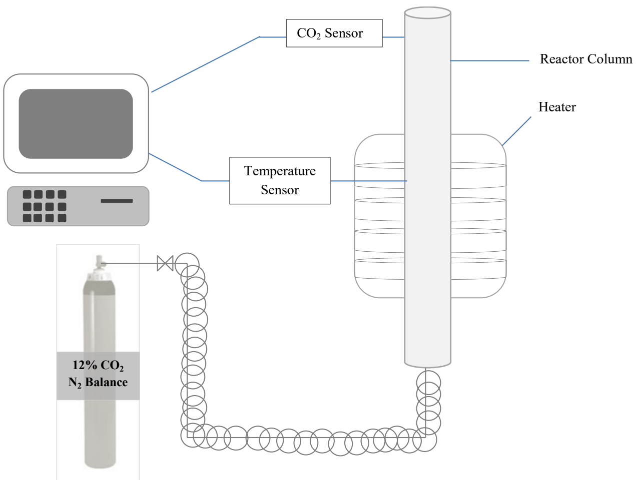

Figure 1 A schematic diagram of the fluidized bed reactor for the carbonation test.

Results and discussion

1) Composition analysis of raw materials

The elements content among chicken, quail and duck eggshell were quite different due to the genetic and environmental parameters [8]. Thus, the element analysis of raw materials was performed by XRF to screen the suitable raw material for preparing the sorbent. The analysis results in the Table 2 showed that all types of eggshells contain various elements apart from calcium. Because the prepared sorbent was calcium–based type, the calcium content of the raw materials was prior to be considered. From data, the calcium content of chicken and duck eggshell were quite similar (98.76 and 98.45% weight, respectively). However, when considering the impurity and the availability in the local area, the chicken eggshell was selected to further study the effect of preparation parameters.

Figure 2 presents the SEM images of the chicken eggshell powder morphology. Before the calcination process, the eggshell powder displayed rough and gnarled surface. The irregular shape of crystal structure was also observed. After the calcination process, the eggshell powder structure showed the interconnected skeleton structure with voids between each skeleton. The results were consistent with the previous report [9].

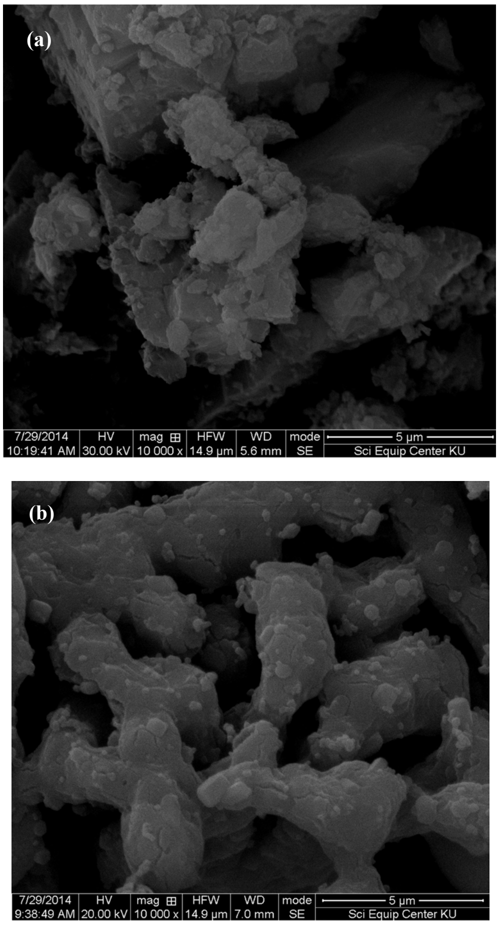

Figure 2 SEM images of chicken eggshell powder (a) before and (b) after calcination.

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Table 2 Element analysis of some eggshell types by XRF

Elements	Weight %		
	Chicken eggshell	Quail eggshell	Duck eggshell
Ca	98.760	97.460	98.450
Mg	0.556	0.896	0.300
P	0.198	0.737	0.305
S	0.189	0.422	0.285
Na	0.131	0.180	0.146
K	0.073	0.130	0.070
Sr	0.090	0.081	0.399
Si	0.003	0.045	0.025
Fe	-	0.037	0.009
Al	-	0.012	0.011

Table 3 Textural analysis results for 2^3 factorial design

Standard order	A*	B*	C*	BET surface area ($m^2\ g^{-1}$)	Total pore volume ($cm^3\ g^{-1}$)	Adsorption average pore width (nm)
Experimental data						
1	-1	-1	-1	2.358	0.002	3.318
2	+1	-1	-1	1.079	0.00003	0.113
3	-1	+1	-1	2.430	0.002	3.084
4	+1	+1	-1	1.245	0.0003	1.036
5	-1	-1	+1	2.462	0.003	4.244
6	+1	-1	+1	2.954	0.002	2.911
7	-1	+1	+1	4.001	0.004	3.752
8	+1	+1	+1	5.023	0.004	3.565

Remark: * experimental variables and conditions can be referred from Table 1

2) 2^3 factorial design and statistical analysis

In this work, the 2^3 factorial design was applied to screen the important parameters in the step of sorbent preparation that might influence on the properties of the sorbent. The interesting parameters such as calcination temperature, calcination time and particle size were counted into the experiment. As the BET surface area is one of the factors that indicates the capability of CO_2 adsorption, then, it was used as the response factor. After randomly performing the experiments, the results are shown in Table 3.

Figure 3(a) represents the effect of calcination temperature on the BET surface area of prepared sorbent. From the figure, the increasing of calcination temperature resulted in the decreasing of BET surface area of sorbent material for large particle size (U.S. mesh no. 50) eggshell. On the contrary, it was observed the opposite trend in case of small particle size (U.S. mesh no. 100), when raising the calcination temperature. During the calcination process, the eggshell particles ($CaCO_3$ source) were converted to CaO sorbents by releasing CO_2 and created some pores inside the particles.

This different trend could be suggested by the fact that the increasing of reaction temperature would normally retard the reaction rate of the exothermic process like the calcination. While the effect of the surface area of eggshell particle on the reaction rate should be considered since the calcination process was the heterogeneous phase reaction. Generally, the increasing of surface area provides the raising of the reaction rate [11]. Thus, in case of small particle size eggshell powder which yields the high BET surface area might compensate the drawback of increasing the calcination temperature. However, from the statistical results, the calcination temperature exhibited the insignificant effect on the BET surface area.

Figure 3(b) shows the influence of the calcination time on the BET surface area. From the figure, it can be seen that the increasing of the calcination time led to the increasing of the BET surface area. When extending the residence time at constant temperature and constant eggshell particle size, the complete conversion of $CaCO_3$ to CaO might occur. More CO_2 molecules were released and generated pores inside the particles [12]. Consequently, the increasing of BET surface area was initiated.

In term of the effect of eggshell particle size, the results were expressed in Figure 3(c). As the number of U.S. mesh size increased (providing a smaller particle size), the BET surface area was increased. This could be explained by the fact that for the large eggshell particle, heat may not completely penetrate through the particle. Then, it could release less CO_2 molecules and generated less pores inside the particle [13]. Therefore, smaller porosity particles were obtained.

The analysis of variance (ANOVA) at a 95% confidence interval was expressed in Table 4. Based on P–Value, any main effects or interaction effects that presented their probability less than 0.05 have a significant influence on the response [14]. For the preparation of CO_2 sorbent from the waste eggshell, only the particle size of eggshell powder (factor C) significantly influenced the BET surface area of the prepared sorbent material.

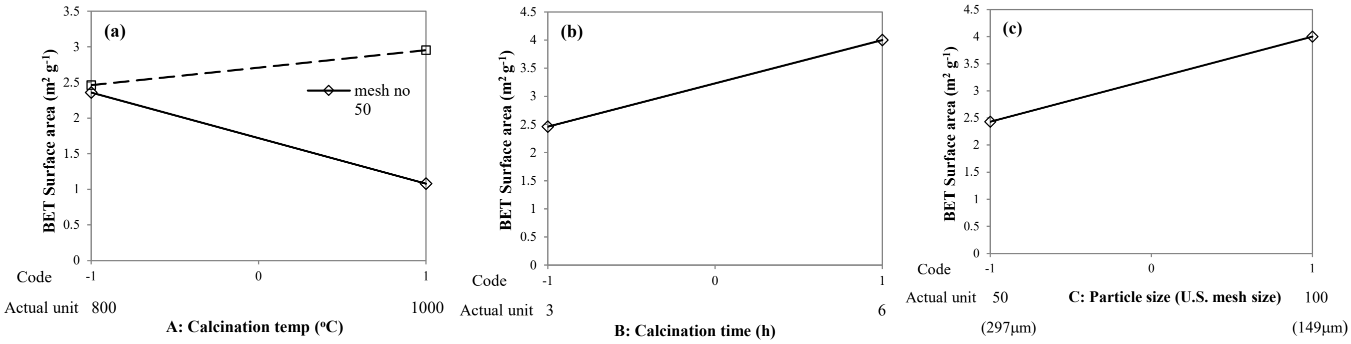

Figure 3 Main effect plots for the BET surface area of 2^3 factorial design showing the effects of (a) calcination temperature, (b) calcination time, and (c) eggshell particle size.

Table 4 Analysis of variance (ANOVA) for the 2^3 factorial design

Source	Sum of squares	DF	Mean square	F–value	P–value
Model	12.120	6	2.020	84.38	0.0831
A	0.110	1	0.110	4.71	0.2748
B	1.850	1	1.850	77.20	0.0721
C	6.710	1	6.710	280.41	0.0380
AB	0.049	1	0.049	2.03	0.3894
AC	1.980	1	1.980	82.60	0.0698
BC	1.420	1	1.420	59.32	0.0822
Residual	0.024	1	0.024		
Cor Total	12.140	7			

Remark: $R^2 = 0.9980$

3) The carbonation test

From the results in Table 3, the best condition for preparing the sorbent were 1000°C in calcination temperature, 6 h of calcination time and 100 U.S. mesh particle size (149 micron) due to the highest in the BET surface area of 5.023 $m^2\ g^{-1}$. Moreover, the pore size distribution also affects the CO_2 capture capacity. The capacity of sorbents with the large pore size is generally improved because of the decreasing of the mass transfer resistance [5, 15]. When optimizing between the surface area and the pore size of the sorbent, the best condition in the work which yielded the adsorption average pore width of 3.565 nm was selected to further investigate the CO_2 adsorption capability.

The CO_2 adsorption test was performed in the fluidized bed reactor. The adsorption took place at 700°C in the quartz column and the adsorption experiments were repeated. The CO_2 removal fractional breakthrough curve as a function of time was showed in Figure 4.

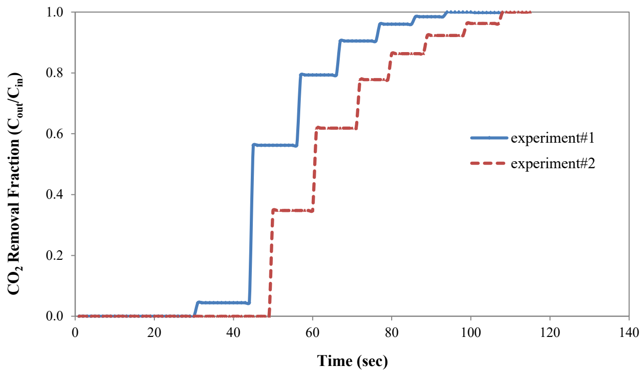

Figure 4 CO_2 removal fractional breakthrough curve as a function of residence time of sorbent prepared from chicken eggshell in fluidized bed reactor at 700°C carbonation temperature in 12% v/v CO_2 with N_2 balance.

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From the figure, the prepared sorbent expressed the complete CO_2 adsorption within 30 s before losing the sorption ability after 100s. The adsorption capability was found to be 0.011 g CO_2 g^{-1} of sorbent. Thus, from the results, the sorption material prepared from waste chicken eggshell can be used to adsorb CO_2. When comparing with the other study of CO_2 capture eggshell sorbents, the adsorption capacity evaluated by thermogravimetry technique at 100 second of the first adsorption cycle was slightly higher than the reported value of this study [10]. However, the residence time of sorbents in the turbulent fluidization process were normally too short in each cycle, the prepared sorbents then showed the plausible results for application in the fluidized bed adsorption system. Furthermore, the comparison of the CO_2 capture capability of the CaO-based sorbents from various sources were disclosed in Table 5. As compare to the previous works, the CO_2 capacity of CaO adsorbent of this work was significantly lower. The reason may be because of the lower carbonation temperature, the lower concentration of CO_2 input stream and different types of test reactors. Also, the adsorbent of this work was used without any surface modification. The further study of the dominant variables in the fluidized bed reactor such as the adsorbent quantity, carbonation temperature and the flow rate of CO_2 should be conducted to the enhance the optimal condition for CO_2 capture of this prepared sorbents.

The morphology of prepared sorbent after the CO_2 adsorption were investigated by SEM and showed in Figure 5. It can be seen that, the prepared sorbent after the first carbonation remained porous and connective skeleton. Also, there were some small in the shape of tubular structures occurred on the surface of sorbent material. This might be the calcite crystal polymorphs of $CaCO_3$. Moreover, the crystalline structure of the prepared sorbent before and after the CO_2 adsorption were evaluated by XRD technique as presented in Figure 6. It could be observed that 2-theta values of the sorbent material before CO_2 adsorption contained 32.2°, 37.5°, 53.9°, 64.2° and 67.4° which are the characteristic of CaO crystal structure. This XRD pattern indicated that after calcination process, the $CaCO_3$ crystalline structure in the eggshell powder completely converted to CaO phase. After CO_2 adsorption, the characteristic peak of 29.5° was the major different peak of calcite phase being found in the XRD pattern. From these results, therefore, confirmed that the carbonation reaction occurred in the CO_2 adsorption process.

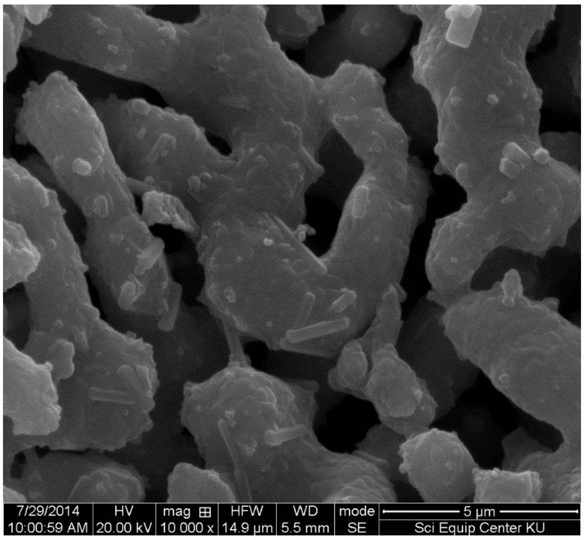

Figure 5 SEM image of sorbent prepared from chicken eggshell after CO_2 adsorption test.

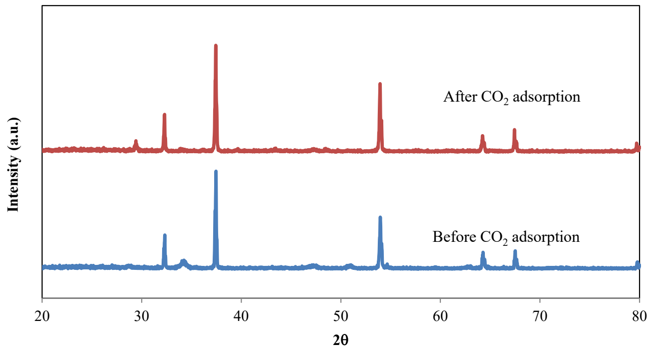

Figure 6 XRD patterns of sorbents prepared from chicken eggshell before and after CO_2 adsorption experiments.

Table 5 Comparisona of the CO_2 capture capability of the CaO-based sorbents from various sources

Sources of CaO adsorbents	Test reactor	CO_2 (%)	Carbonation temperature (°C)	Adsorption capability (g CO_2 g^{-1} sorbent)	Reference
Sea salt doped mussel shell	Fixed bed reactor	n/a	850	0.16	[16]
Oyster shell blende with polymethyl methacrylate	TGA	15	750	0.19	[17]
Raw eggshell	TGA	15	700	0.19	[18]
Synthetic CaO with eggshell precursor	TGA	n/a	750	0.23	[6]
Raw chicken eggshell	Fluidized bed reactor	12	700	0.011	This study

Conclusion

Waste chicken eggshell showed the highest in calcium composition with the lowest impurities among other types of studied eggshell. After going through the process of cleaning, drying and crushing, the eggshell powder was calcined to obtain the CO_2 sorbent material. Because the parameters in the calcination process influenced the adsorption ability of prepared materials, the full 2^3 factorial design was introduced to the experiment for scrutinizing. In this experiment, the BET surface area was chosen to represent the adsorption capability of the prepared sorbent. The results revealed that the variation of particle size of eggshell powder significantly affected the BET surface area value. The highest BET surface area adsorbent (5.023 $m^2 g^{-1}$) obtained from the condition of 149 µm in eggshell particle size, 6 h of calcination time and 1000°C calcination temperature. After applying the prepared sorbent in the fluidized bed reactor with 12% v/v CO_2 with N_2 balance, the results also showed that the carbonation could be possibly occurred in this system and yielded the adsorption capacity of 0.011g CO_2 g^{-1} sorbent at 700°C operating temperature.

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