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Preliminary study of carbon dioxide (CO_2) adsorption using chicken eggshell

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Abstract. Carbon dioxide (CO_2) emission is a major concern nowadays due to its contribution to global warming scenarios. Therefore, valorization of inexpensive and green material to adsorb the CO_2 prior to emission has been emphasized. In this research study, calcined chicken eggshell waste had been tested as a potential CO_2 adsorbent. Specifically, calcined eggshell at 700°C, 800°C, and 900°C has been used in subsequent carbonation reaction at 650°C for 1 hr. The result shows that increasing the calcination temperature improves the eggshell decomposition (weight loss) and CO_2 adsorption capacity (weight gain). Specifically, the weight gain by the calcined eggshell at 900°C is roughly 61 wt.%. Both pristine and calcined eggshells are characterized by the Fourier-Transform Infrared Spectroscopy (FTIR), thermogravimetric analysis (TGA), Scanning Electron Microscopy (SEM), and N_2 physisorption. Overall, utilization of the chicken eggshell waste is indeed promising as this can contribute to both environmental and economic advantages.

Introduction

The climate change specifically due to anthropogenic carbon dioxide (CO_2) emission has become a major issue amongst the researchers, policy makers, and other related professionals, due to these arising problems: global warming, ecological imbalance, socio-economic issue, and other climate-related disasters. Due to these, carbon reduction has become a prominent global focus these days. It is worth noting that calcium looping (CaL) technology is one of the promising short-term method for CO_2 capture [1, 2]. Fundamentally, two reactions are involved in this process, i.e., calcination and carbonation, as described in Eq. (1) and (2), respectively.

$$Endothermic\ calcination: CaCO_3 \leftrightarrow CaO + CO_2, \Delta H = 178\ kJ/mole \quad (1)$$

$$Exothermic\ carbonation: CaO + CO_2 \leftrightarrow CaCO_3, \Delta H = -178\ kJ/mole \quad (2)$$

To date, limestone has been extensively used as a source of calcium oxide (CaO), due to its low prices and wide availability. Nevertheless, there has been a great concern on the mineral limestone extraction and mining process, which will jeopardize the environment [3, 4]. Due to ecological destruction, it is worthy to shift to the greener calcium-based feedstock i.e., chicken eggshell waste. Her et al. [5] reported that the eggshell has high resemblance to the limestone, in which it possesses >95% calcium carbonate ($CaCO_3$) as well. Being used as a main commodity in Malaysia, it is expected that approximately 70,000 tons of eggshells will be produced annually.

Since the eggshell waste is traditionally useless, majority of this calcium-rich wastes are dumped in the landfill without any pretreatment, thus, it will result in serious environmental problems [6]. Furthermore, Jayasankar et al. [7] reported that the accumulation of eggshell waste

will attract worms and rats, in which leading to health problems. Therefore, transformation of the discarded eggshell wastes to value-added material (i.e., CO_2 sorbent) is promising as it could be a novel and valuable approach in the solid waste management, and at the same time, to reduce CO_2 emission.

Materials and Methods

Materials. The waste chicken eggshells were obtained from burger stalls and cafeteria in Universiti Teknologi PETRONAS. Upon washing with tap water several times, these eggshells were oven-dried at 105°C for 24 hr. The dried wastes were then crushed and pulverized by using agate mortar and grinder, respectively, before being screened to < 80 μm. The samples were kept in an air-tight container to prevent any reaction with the surroundings, prior to the further experimentation. In addition, high purity CO_2 (99.8% purity) and nitrogen (N_2, 99.9% purity) tank were supplied from Linde Malaysia Sdn. Bhd.

Calcination-carbonation process. Following López-Periago et al. [8], the calcination-carbonation testing of the chicken eggshell had been carried out by using a tubular furnace. In calcination process, ~25 g of eggshell was weighted inside a ceramic crucible and then placed in the central part of the tube furnace. In the process, the samples were heated to the desired calcination temperature (700-900°C) with fixed heating rate of 10°C/min under N_2 flow rate of 200 mL/min. The weight loss in the calcination process was calculated, following Eq. (3) [9]. Meanwhile, carbonation process was carried out by heating the calcined samples to 650°C, in presence of CO_2 flow. The carbonation process was maintained for 1 hr upon reaching the desired temperature. Further, weight gain that corresponds to CO_2 adsorption was measured by following Eq. (4) [10].

$$\text{Weight loss (calcination)} = \frac{m_o - m_f}{m_o} x100\% \quad (3)$$

$$\text{Weight gain (carbonation)} = \frac{m_f - m_o}{m_o} x100\% \quad (4)$$

Referring to Eq. (3) and (4), m_o and m_f represents the initial and final weights, respectively.

Characterizations. The decomposition profile of the pristine eggshells was investigated by using a Perkin Elmer thermal analyzer under purified N_2 atmosphere, at heating rate of 10°C/min. Further, the functional groups of the bio-calcium were analyzed using the Perkin Elmer Fourier Transform Infrared (FTIR) spectrometer within the range of 4000-400 cm^{-1}. The surface area and porosity analysis of both raw and calcined eggshell were measured by the Micromeritics ASAP 2020. Prior to analysis, the samples were outgassed at 250°C. Lastly, the exterior morphology of these samples were observed by using the Scanning Electron Microscope (SEM), coupled with the Energy Dispersive X-ray (EDX) spectroscopy.

Results and Discussion

Calcination-carbonation studies. The suitable temperature for the calcination is deduced from the thermal decomposition analysis from ambient temperature to 800°C. Referring to Fig. 1, a minor weight loss (~5 wt.%) at temperature of < 300°C is attributed to the loss of moisture and volatile organic substance, while a significant decomposition (~40 wt.%) at the temperature of >650°C is attributed to the $CaCO_3$ conversion to CaO [11-13]. Salauddeen et al. [14] reported that the CO_2 release is taken from the point where a significant weight loss is observed till the end of analysis.

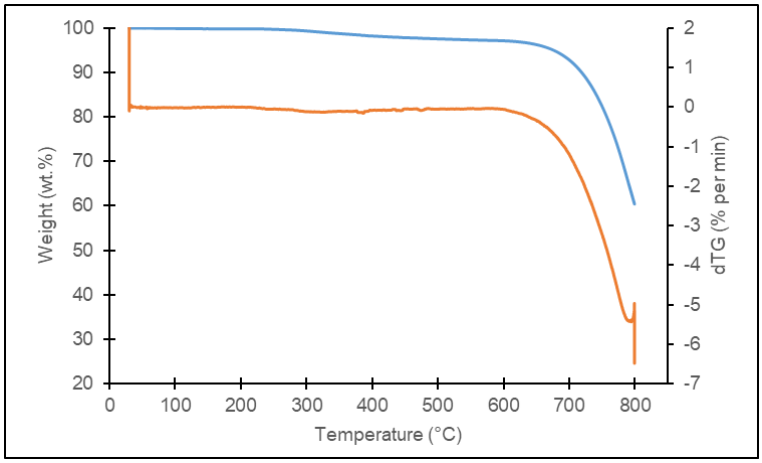

Fig. 1. TG-dTG curve of raw chicken eggshell

Similarly, Rohim et al. [11] observed that the decomposition of eggshell has two distinct stages, which is at < 640°C and 640-840°C. The decomposition behavior of eggshell is further validated by using the furnace, where the sample is heated from ambient to 700-900°C. In this study, 700°C is taken as the minimum point, as Gao and Xu [15] previously agreed that temperature of <700 °C do not contribute to the CaO formation. Further, calcination temperature should not be excessively high as it may result in particle sintering and attrition [14], hence, explains why 900°C is taken as the maximum point. Referring to Fig. 2, the calcination temperature is directly proportional to weight loss, where weight loss of 5.96% and 45.00% has been encountered at 700°C and 900°C, respectively. This behavior is expected owing to the endothermic reaction of calcination, as described in Eq. (1). Besides, accelerating decomposition at higher temperatures is due to increment in kinetic energy of the particles, which will enhance the calcination rate. On top of that, higher calcination temperatures are found to positively correlate with weight increase of CaO (Fig. 2), which is plausibly due to the changes in textural and chemical compositions. Moreover, it shows that at the calcination temperature of 900°C, color of eggshell that has transformed to white color (Fig. 3) indicates more formation of metal oxide.

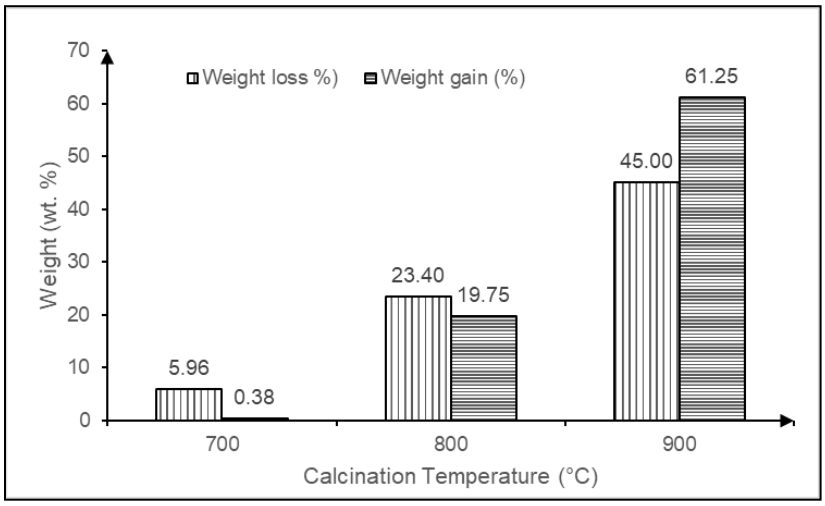

Fig. 2. Weight loss and weight gain at different calcination temperatures. (Note: The weight loss measures the degree of calcination (decomposition) while weight gain corresponds to carbonation conversion)

Fig. 3. Chicken eggshell powder before calcination (a), and after calcination at (b) 700°C and (c) 900°C

Likewise, similar experimental findings have been obtained by Mohadi et al. [16] and Commey and Mensah [17]. Besides, it has been reported that in an atmospheric condition, the calcination temperature of ~950°C is considered as an optimal condition as it does not contribute to sorbent decay even at prolong calcination time [18]. Future work may incorporate the surface area and porosity analysis as well as elemental compositions at each calcination temperatures. In addition, a comparative work with the commercial CaO has been conducted, at which the weight gain (CO_2 adsorption capacity) is approximately 12 wt.%.

Functional group analysis: The FTIR spectra of calcined and carbonated eggshell are illustrated in Fig. 4. Based on Fig. 4, it demonstrates that the calcinated eggshell consists of the hydroxyl O-H stretching, where there is a large peak at ~3600 cm^{-1}. Meanwhile, for the carbonated eggshell, sharp peaks are observed at 1427 and 873 cm^{-1}, which indicative the presence of C-O stretching and bending of $CaCO_3$, respectively [6, 11]. Other noticeable peaks for the carbonated eggshell that are at 2515, 1798, and 712 cm^{-1} indicates the presence of $CaCO_3$ [19, 20].

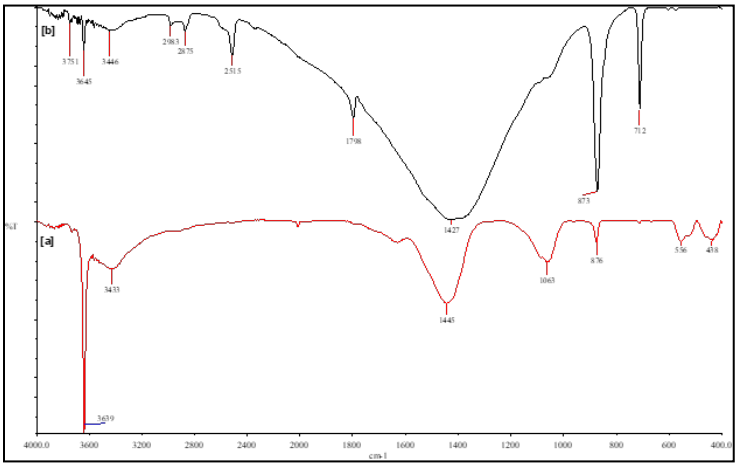

Fig. 4: FTIR spectra of (a) calcined eggshell at 900°C and (b) carbonated eggshell waste

SEM-EDX analysis: The exterior surface of raw and calcined eggshell at 900°C is shown in Fig. 5. In reference to Ghouti and Salih [21], raw eggshell is composed of irregular-shaped particles and in agglomerated form. In contrast, calcined eggshell has a porous structure, which is plausibly due to release of gases (i.e., CO_2) that occupy the pores and complete transformation to metal oxide (CaO), as supported by the EDX analysis. From analysis, it shows that this calcined eggshell is merely composed of calcium (55 wt.%) and oxygen (45 wt.%) content. Likewise, Sree et al. [22] also reported that the calcined eggshell predominantly contains 65 wt.% calcium and balanced by oxygen compositions.

Surface area and porosity analysis: From the N_2 physisorption analysis, BET surface area and total pore volume of calcined eggshell is found to be 1.18 m^2/g and 0.003 cm^3/g, respectively. Herein, these textural characteristics are similar to Viriya-empikul et al. [23], who previously reported that the calcined eggshell has surface area of 1.1 m^2/g and total pore volume of 0.005 cm^3/g. Further, the calcined eggshell at 900°C is mesoporous in nature, where the average pore diameter is 10.13 nm. It is noteworthy to mention that the surface properties are not appealing for the CO_2 adsorption, hence, this sorption process is most likely due to intrinsic nature of calcined eggshell.

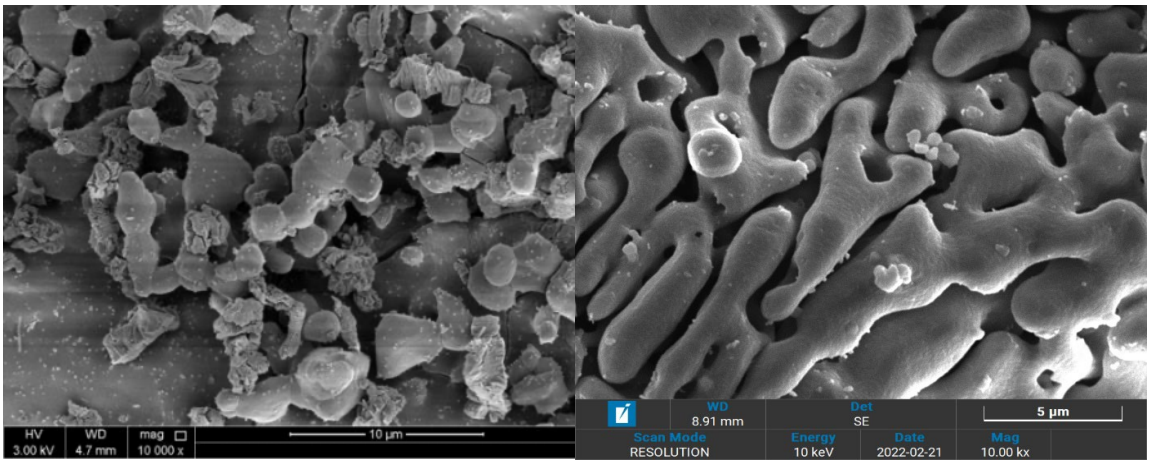

Fig. 5. SEM micrography of raw eggshell waste (left) and calcined eggshell at 900°C (right)

Conclusions

The results prove the suitability of eggshell wastes as potential substitute for the limestone in the CaL process, wherein the maximum CO_2 uptake of around 61 wt.% has been attained by calcined eggshell at 900°C. Further, CO_2 adsorption capacity by eggshell derived CaO that is higher than commercial CaO (~60% vs. 12%) is attractive due to its inexpensiveness and environmental-friendly properties. Upon calcination, eggshell is found to be primarily composed of calcium and oxygen, thus verifies the CaO formation. Further, based on structural analysis, the calcined eggshell follows the Type II isotherm while the surface morphology indicates that it has a porous and irregular structure. In terms of the carbonation process, the calcite formation can be noticeably observed from the functional groups.

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