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Utilization of Waste Eggshells as Humidity Adsorbent

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Abstract: The chicken and duck eggshell powders were prepared and heated at 1300°C for 4 h. The samples were analyzed by X-Ray Diffraction (XRD). It was found that Calcium Carbonate ($CaCO_3$) from chicken and duck eggshells completely transformed into Calcium Oxide (CaO). Then the samples were placed in a box installed with a hygro-thermometer for humidity adsorption test in the range of 20-75% RH at 25°C. Hydration rate for duck and chicken eggshells were 0.0625% RH min^{-1} (within 880 min) and 0.0482% RH min^{-1} (within 1140 min) respectively. The results show that CaO from the duck eggshells is a better adsorbent than that of chicken eggshells. Furthermore, after humidity adsorption, CaO obtained from both eggshells were partly transformed into portlandite ($Ca(OH)_2$ was confirmed by the Rietveld refinement method and Scanning Electron Microscope (SEM).

Key words: Calcium carbonate, calcium oxide, portlandite, humidity adsorption, hydration rate, adsorbent, eggshell

INTRODUCTION

Humidity causes a lot of problems to industries such as pharmaceutical and food products, where the humidity level must be limited to control quality of product. Thus, incorporation of a sorbent into product packaging to adsorb humidity has been commonly found in practice. Silica gel has been widely used as a sorbent because of its porous structure and very high surface area. Other sorbents such as natural clay, molecular sieve and calcium sulfate have been alternatively employed as well as natural materials having composition of Ca and O atom such as coral, eggshells and seashells (Donigian *et al*., 1999; Hladnik, 2004; Hladnik and Muck, 2002; Ridgway and Gane, 2004; Christensen *et al*., 2006; Bolukbasi *et al*., 2005).

The utilization of eggshell calcium carbonate has long been investigated due to the high content of calcium, magnesium and phosphorous. The eggshell carbonate can be employed as a fertilizer, soil conditioner or an additive for animal feed (Chmasrist and Harms, 1976; Amu *et al*., 2005). It can also be used as a source of Ca for human nutrition (Schaafsma *et al*., 2000). Due to the intrinsic pore structure of the eggshell, it was proposed as a low cost adsorbent as alternative to expensive activated carbon. Several studies proved the effectiveness of eggshell for the sorption of heavy metals such as Cr, Cd, Cu (Chojnacka, 2005; Otun *et al*., 2006) and the removal of dye effluents (Tsai *et al*., 2008). Chicken eggshell has been applied as a bio-filler for polymer composites (Toro *et al*., 2007) and the possibility of the use of powdered eggshells as a bone substitute has also been investigated by Dupoirieux *et al*. (1995) and Pankaew *et al*. (2010). In this study, CaO was prepared from chicken and duck eggshells. The hydration rate of CaO was investigated by X-ray Diffraction (XRD) and Scanning Electron Microscope (SEM) techniques.

MATERIALS AND METHODS

Sample preparation: The chicken and duck eggs were obtained from Charoen Pokphand Foods (CPF) public company limited, Bangkok, Thailand. The membranes of the eggs were removed and washed with distilled water to remove adhesion. The shells were dried in air for 2 day. Then, these shells were ground into powder using an agate mortar. Finally, both eggshells powders were heated at 1300°C for 4 h with a rate of 5°C min^{-1}.

Humidity test: For design of experimental system, a box with a dimension of 7×7×7 inch was constructed with acrylic sheets for investigation of humidity adsorption for the eggshells sample. Hygro-thermometer TH-802A was installed in the box for the experiment. Each side of the box was sealed with epoxy and the lid was supported with gum hinged to protect the environmental humidity into them.

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The hydration rate of synthesized CaO derived from chicken and duck eggshells was studied in the range of 75-20% RH at 25°C. The starting humidity was set to 75% RH within the box. In the experiment, 20 g of each eggshell was placed in a disc and inserted into the box. The humidity was recorded every 20 min until the humidity was reduced to 20% RH and the powders were weighed again to compare with initial weight.

Adsorbent characterization: The CaO obtained from chicken and duck eggshells before and after humidity adsorption test were characterized by X-ray powder diffractometer to identify the phases. These analyses were carried out on powdered samples by a Philips diffractometer using monochromatized CuK_α radiation. The X-ray tube was operated at 30 kV and 25 mA in the 2θ range of 20-80° with a scanning speed of 2% min^{-1}. Then the lattice parameters and atomic position were refined by the Rietveld method using FULL PROF SUITE-2000 software program.

The eggshells were scanned. The morphology was studied by scanning electron microscopy (Leo 1455 VP) with an accelerating voltage of 20 kV.

RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern of chicken and duck eggshells before and after humidity adsorption. It can be concluded that the eggshells were not completely transformed into Calcium Oxide (CaO) at the heating temperature from 700 up to 1000°C but at 1100°C and above it can be completely transformed. For certainty of the complete transformation of CaO, in present study, the temperature of 1300°C for 4 h was selected in order to use on CaO preparation. The chicken and duck eggshells were heated at 1300°C for 4 h. It is seen that Calcium Carbonate ($CaCO_3$) from both eggshells have completely transformed into CaO at 1300°C according to the chemical reaction (Rivera *et al*., 1999):

$$CaCO_3 \rightarrow CaO + CO_2 \quad (1)$$

The CaO at 1300°C obtained from chicken and duck eggshells was used for further humidity adsorption test. Figure 2 shows the result on the hydration rate of both eggshells in the range of 75-20% RH at 25°C. For comparison, silica gel was also tested. It is seen that, for duck eggshell the humidity decreased with a rate of 0.0625% RH min^{-1} within 880 min, whereas for chicken eggshell the humidity decreased with a rate of 0.0482% RH min^{-1} within 1140 min. However, for silica gel the humidity rapidly decreased with a rate of 0.25% RH mim^{-1} within 220 min.

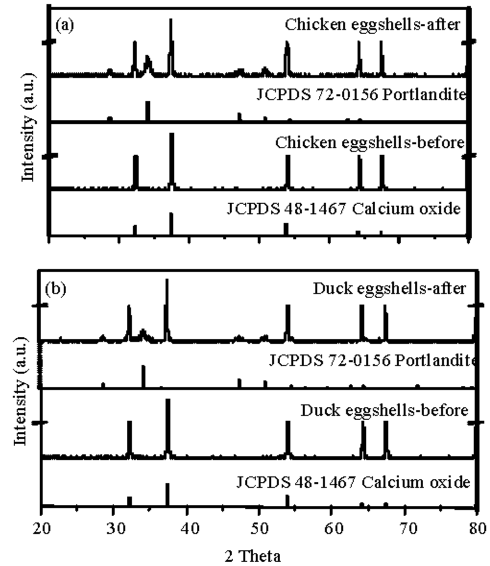

Fig. 1(a-b): X-ray diffraction patterns of (a) chicken and (b) duck eggshells before and after humidity adsorption experiment

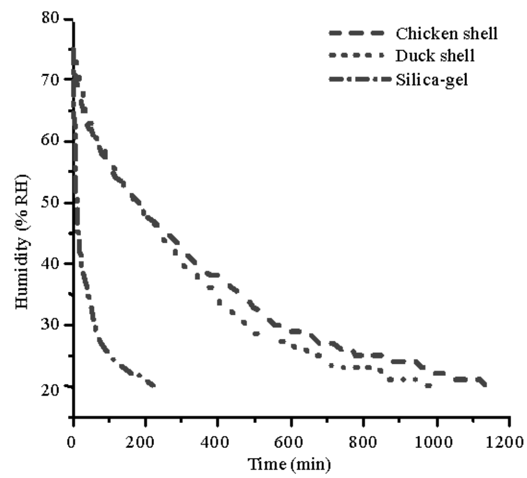

Fig. 2: Variations of the hydration rate of both eggshells and silica gel after moisture adsorption at 75-20% RH at 25°C

The XRD patterns in Fig. 1 present the peaks of CaO and $Ca(OH)_2$ during the hydration process. When the CaO phase of both eggshells adsorbed humidity, they produce portlandite. The reaction can be represented as follows (Montes-Hernandez *et al*., 2009).

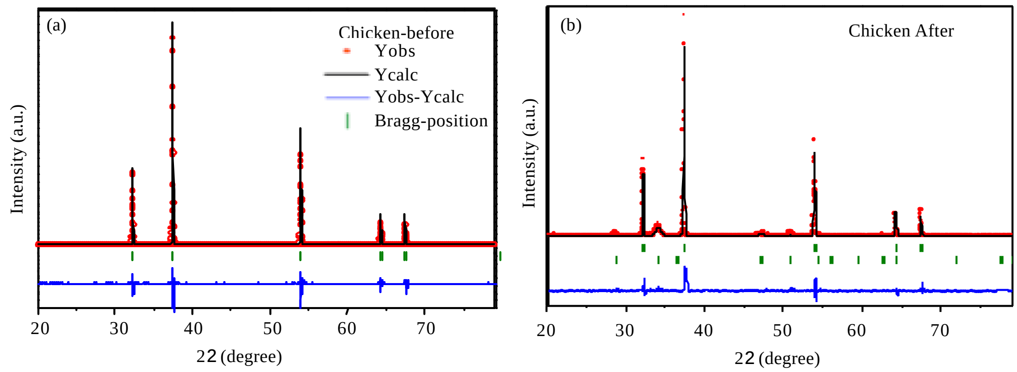

Fig. 3(a-b): X-ray powder diffraction profiles for Rietveld refinement pattern of CaO from chicken eggshells (a) before and (b) after humidity adsorption

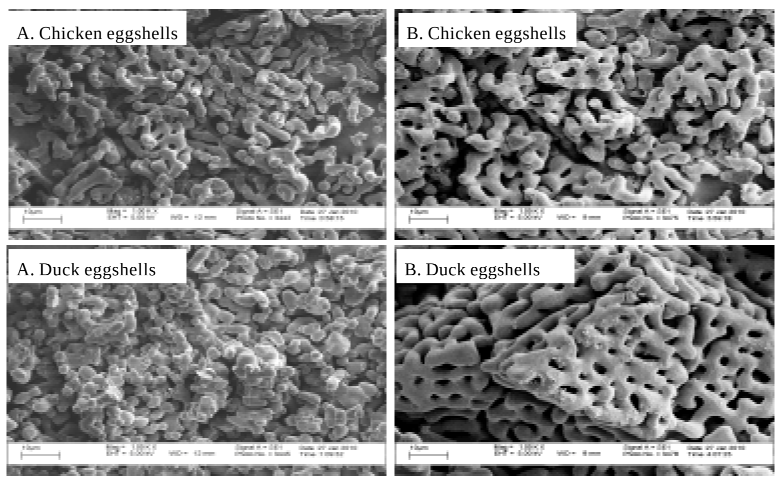

Fig. 4: SEM micrographs of calcium oxide derived from chicken and duck eggshells before and after humidity adsorption. (A: before and B: after)

Table 1: Relevant crystallographic data of chicken and duck eggshells established from powder X-ray diffraction refinements

Sample	Before Phase	Before Phase fraction (%)	After Phase	After Phase fraction (%)
Chicken eggshells	CaO	100	CaO	81.82
			$Ca(OH)_2$	18.18
Duck eggshells	CaO	100	CaO	91.77
			$Ca(OH)_2$	8.23

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad (2)$$

The intensity of $Ca(OH)_2$ for duck eggshells is less than that of $Ca(OH)_2$ for chicken eggshells. Indicating that transforming CaO to $Ca(OH)_2$ for duck eggshells is less than chicken eggshells.

Using the Rietveld refinement, the structural compositions of chicken and duck eggshells samples were analyzed qualitatively and quantitatively by fitting the experimental powder XRD profiles with respect to corresponding structural parameters (i.e., lattice parameters, atomic coordinates) and instrumental parameters. A summary of the refined lattice parameters and phase fractions of the chicken and duck eggshells sample are shown in Table 1. It shows fraction of $Ca(OH)_2$ from both eggshell, where CaO from duck eggshells is a better adsorbent. Figure 3 shows the final Rietveld refinement of powder XRD data for CaO from chicken and duck eggshell.

The morphologies of calcium oxide derived from chicken and duck eggshells of before and after humidity adsorption are shown in Fig. 4. It can be observed that the morphologies of both eggshells exhibit the uniform particles of grape-type granules. Before investigating the

Table 2: Weight change data of chicken and duck eggshells before and after humidity adsorption

Sample	Weight (g) Before	After
Chicken eggshells	20.0000	20.5138
Duck shells	20.0000	20.6514

humidity adsorption, the average particle size of duck eggshell is smaller than that of chicken eggshell. However, during the adsorption experiment, the size of particle from both types of eggshell were bigger than that of their original sizes, due to moisture adsorbed. From the above results, it was found that the hydration rate depends on the larger surface area of the particles and this result is also supported by the increase in the weight of duck eggshells after humidity adsorption as shown in Table 2.

CONCLUSION

The chicken and duck eggshells consist of $CaCO_3$ with calcite structure. The $CaCO_3$ from both eggshells completely transformed to CaO after heating at 1300°C for 4 h. The hydration rate for duck and chicken eggshells were 0.0625% RH min^{-1} (within 880 min) and 0.0482% RH min^{-1} (within 1140 min), respectively. CaO from both eggshells was partly changed to portlandite after adsorbing moisture. Both eggshells may become a promising material using as a humidity adsorbent.

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