Synthesis and characteristics of nano calcium oxide from duck eggshells by precipitation method

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Abstract. This research aims to synthesize and characteristics nano calcium oxide from duck eggshells by precipitation method. The eggshell powder was calcined with 1.000ºC for 2 hours into calcium oxide. Calcium oxide solution 20 ml (5 mol/L) added with lactic acid solution 30 ml (8 mol/L) with ratio 1:1.5 (v/v) and mixed for 30 minutes at 50ºC with speed of 500 rpm/minutes. The mixed solution was added with ethanol 50% up to 20 ml (v/v), dried in the oven at 105ºC for 48 hours, mashed with blender, and then calcined with 1.000ºC for 2 hours into nano calcium oxide. The characteristics of calcium oxide and nano calcium oxide were analyzed by x-ray diffraction, Fourier transform infrared, scanning electron microscopy, energy dispersive x-ray, and particle size analysis. The XRD and FTIR showed that CaO was formed from the two samples supported by EDX results with the highest chemical elements, namely Ca and O. Regular morphology with uniform crystal size was obtained in the precipitation sample. The PSA obtained calcined calcium oxide and nano calcium oxide resulted by precipitation of 13,229 nm and 262 nm, respectively.

1. Introduction

Calcium is one of the important macronutrients needed by the body [1] which is abundant in bones and teeth [2]. Calcium deficiency in food is a common problem [3] which can cause osteoporosis [1]. Osteoporosis can be prevented as early as possible by consuming calcium-rich foods such as milk and milk products [4]. However, people usually do not consume it in the right amount by clinical guidelines and when consuming calcium tablet supplementation is expensive [3]. Therefore, natural mineral sources are becoming more popular [5,6]. Eggshells can be used as an alternative source of natural calcium with a higher level of solubility [7].

Eggshells are solid waste that contributes to environmental pollution [8] with the production of several tons every day [9]. The main sources of eggshells come from household waste, restaurants, bakeries [9], poultry farms, and hatchery [10]. Eggshells are currently known to be widely applied in the industry [11]. Eggshells have been applied as catalysts [12], adsorbents [11], biomedicine [13], and food supplement ingredients [3,9].

Eggshells are rich in calcium carbonate [10]. The content of calcium carbonate eggshell is around 96-97% and organic matter around 3-4% [14]. Calcium carbonate eggshell can be used as the main ingredient for the synthesis of nano calcium oxide [8] one of which is a duck eggshell. Commercial calcium oxide is known to have high prices [15]. Therefore, calcium carbonate which is synthesized into nano calcium oxide can increase the economic value of eggshell waste.
Material synthesized in nano size has a better performance with an increase in a surface area [8]. calcium oxide is a type of metal oxide that has been widely applied as a catalyst [16], antibacterial agent [17], and drug delivery system [18]. The manufacture of nano calcium oxide through precipitation methods is considered cheap, easy, and environmentally friendly [8]. The purpose of this study was to determine the characteristics of nano calcium oxide synthesized by precipitation method from duck eggshells.

2. Materials and Methods

2.1. Materials
The materials used in this study were duck eggshells from the hatchery waste, distilled water, lactic acid, and ethanol.

2.2. Synthesis of Nano Calcium Oxide
The duck eggshell soaked in hot water for 10 minutes, cleaned from egg membrane, dried in oven at 105°C for 12 hours and then mashed with sample mill. The eggshell powder was calcined with 1.000°C for 2 hours into calcium oxide. Calcium oxide solution 20 ml (5mol/L) added with lactic acid solution 30 ml (8 mol/L) with ratio 1:1.5 (v/v) and mixed for 30 minutes at 50°C with speed of 500 rpm/minutes. The mixed solution was added with ethanol 50% up to 20 ml (v/v), dried in oven at 105°C for 48 hours, mashed with blender, and then calcined with 1.000°C for 2 hours into nano calcium oxide.

2.3. Characterization
Calcined calcium oxide powder and nano calcium oxide of duck eggshell by precipitation were characterized using x-ray diffraction (XRD), fourier transform infrared (FTIR), scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDX), and particle size analyzer (PSA).

3. Results and Discussion

3.1. X-Ray Diffraction (XRD)
The results of x-ray diffraction (XRD) test are used to determine the degree of crystalline of a material. The x-ray diffraction pattern is monitored at 2θ = 5-90°. The results of XRD test from calcium oxide powder and nano calcium oxide duck eggshell are presented in Figure 1.

(a) (b)

Figure 1. XRD from (a) calcium oxide (b) nano calcium oxide
In standard CaO, peaks appear at $2\theta = 18.0205^\circ$, $34.1210^\circ$ and $50.8473^\circ$\cite{19} and in pure CaO, the peak appears at $2\theta = 32.2^\circ$, $37.3^\circ$, $53.8^\circ$, $64.1^\circ$ and $67.3^\circ$\cite{20}. Calcined calcium oxide has a diffraction angle of $2\theta$ with peaks of $17.9578^\circ$, $34.0622^\circ$ and $50.8167^\circ$, while precipitation samples of nano calcium oxide have a diffraction angle of $2\theta$ with peaks of $34.1037^\circ$, $37.3695^\circ$, $53.8756^\circ$. Calcined calcium oxide samples appear to have peaks that tend to be the same as standard CaO, whereas in nano calcium oxide the results of precipitation tend to be the same as pure CaO. This indicates that both samples have the same phase.

3.2. Fourier Transform Infrared (FTIR)
The results of Fourier transform infrared (FTIR) test are used to determine the functional groups of a compound. The FTIR analysis was carried out at wavelengths of 4000-400 cm$^{-1}$. The results of FTIR test from calcium oxide powder and nano calcium oxide of duck eggshell are presented in Figure 2.

![Figure 2. FTIR from (a) calcium oxide (b) nano calcium oxide](image)

Figure 2 shows the peaks that appear on calcined calcium oxide and nano calcium oxide on precipitation results which are generally almost the same. The OH band appears at about 3600 cm$^{-1}$\cite{21}. The band of the OH group appears very sharply at wave numbers 3619.96 cm$^{-1}$ and 3678.91 cm$^{-1}$ in calcined calcium oxide samples, whereas in the nano calcium oxide samples from the precipitation process appears at wave numbers 3620.67 cm$^{-1}$, 3649.91 cm$^{-1}$ and 3680.07 cm$^{-1}$. OH groups with sharp peaks are characteristic of standard CaO\cite{21}, so that the emergence of OH groups shows that there is a peak match between the two samples analyzed with standard CaO.

3.3. Scanning Electron Microscopy (SEM)
The results of scanning electron microscopy (SEM) tests are used to determine the morphology of a material\cite{22}. The results of SEM test from calcium oxide powder and nano calcium oxide of duck eggshell are presented in Figure 3.
The results of SEM test with a magnification of 5000x showed different morphological shapes of calcium oxide crystals and nano calcium oxide of duck eggshell. Calcined calcium oxide has a regular morphology with non-uniform crystal sizes and nano calcium oxide has a regular morphology with a uniform size. This shows that the precipitation process can make the crystal structure of nano calcium oxide become better and more orderly.

### 3.4. Energy Dispersive X-Ray (EDX)

The results of energy dispersive x-ray (EDX) test are used to determine the elements of a material. The EDX results from calcium oxide powder and nano calcium oxide of duck eggshell are presented in Figure 4.

The results of EDX test showed that the elements contained in calcined calcium oxide were C 5.04%; O 39.55%; Na 0.29%; P 0.59%; Cl 0.17%; and Ca 54.36%. The elements contained in nano calcium oxide produced through the precipitation process are C 3.08%; O 36.19%; Na 0.35%; Mg 0.41%; P 0.7%; and Ca 59.27%. The elements Ca and O are the highest chemical elements in number. This shows that the results of calcination and precipitation processes are together formed of calcium oxide (CaO).
3.5. **Particle Size Analysis (PSA)**

The results of particle size analysis (PSA) test are used to determine the size of a material. The results of measurements of calcined calcium oxide and nano calcium oxide of duck eggshell using particle size analyzer are presented in Figure 5.

![Figure 5](a) Particle size from (a) calcium oxide (b) nano calcium oxide

The PSA results show that the particle size of calcined calcium oxide and nano calcium oxide of duck eggshell by precipitation are 13,229 nm and 262 nm, respectively. The precipitation process can change the particle size from microns to nano meters. These results are like previous studies that to get nano meter sized particles can be done by the precipitation method [18,22–24]

4. **Conclusion**

The XRD and FTIR showed that CaO was formed from the two samples supported by EDX results with the highest chemical elements, namely Ca and O. Regular morphology with uniform crystal size was obtained in the precipitation sample. The PSA obtained calcined calcium oxide and nano calcium oxide resulted by precipitation of 13,229 nm and 262 nm, respectively.

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