Seminar Nasional Humaniora dan Aplikasi Teknologi Informasi (SEHATI) 2024, Vol.10 No.1
30 Oktoberr 2024

ISSN: 2477-0078

SYNTHESIS OF CALCIUM OXIDE UTILIZING CHICKEN EGGSHELL WASTE VIA A FOAM-FREE APPROACH

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Abstract

Chicken eggshells are an abundant, inexpensive, and potentially significant raw material source that can be transformed into calcium oxide nanoparticles. Various methods can be employed for the synthesis of calcium oxide nanoparticles, but the sol-gel method offers numerous advantages, including cost-effectiveness and the utilization of relatively low-temperature conditions under ambient pressure. The objective of this research is to utilize chicken eggshell waste as a source for CaO nanoparticles. In this study, CaO nanoparticles were successfuly produced from chicken eggshell waste using the sol-gel method with a foam-free approach. The eggshell powder was dissolved in an HCl solution to form a $CaCl_2$ sol, and the resulting foam was then separated and not used. NaOH solution was added dropwise to the $CaCl_2$ sol to form a $Ca(OH)_2$ precursor gel, which was then subjected to thermogravimetric analysis. The $Ca(OH)_2$ precursor was calcined at 900°C for 1 hour to form the CaO nanoparticle product. The product was then characterized using Infrared spectrum, X-Ray Diffraction (XRD), and X-Ray Fluorescence (XRF) instrumentation. The characterization analysis results confirmed the formation of CaO nanoparticles. This finding suggests that the synthesis of CaO nanoparticles from chicken eggshell waste using a foam-free approach can be a viable method, as it can minimize the formation of contaminant crystals, enabling development for various applications.

Keywords: Calcination, Chicken Eggshell Powder, Sol-gel Method, CaO Nanoparticles, $Ca(OH)_2$ precursor.

1. INTRODUCTION

The increasing volume of solid waste has emerged as an urgent challenge to achieve the target of public health status in Indonesia. Inadequate waste management can result in adverse consequences for public health and the environment. Industrialization and demographic expansion are the main drivers behind the increasing volume of solid waste [1]. The contribution of food service businesses and households plays a dominant role in the abundant of chicken eggshell waste [2]. The primary constituent of this waste is calcium carbonate, which is characterized by its diminutive porous structure [3]. This waste can be transformed into valuable products for various applications, as it contains a dominant $CaCO_3$ of up to 96% [4]. However, chicken eggshell waste can have an adverse impact on the environment, as it can produce foul odors due to decomposition by soil bacteria, so the ability to address this waste problem is necessary [5].

The synthesis of nanoparticles is receiving increasing attention due to the enhancement in their performance arising from the increase in their surface area [6]. Metal oxide nanoparticles have a wide range of applications in various fields. In the domain of healthcare, metal oxide nanoparticles are used for cancer treatment. For example, titanium dioxide nanoparticles can be used in photodynamic therapy, where the contribution of these nanoparticles is through light activation to generate reactive oxygen species that can eliminate cancer cells [7]. Furthermore, other metal oxide nanoparticles serve as heterogeneous catalysts, such as calcium oxide which is involved in the transesterification reaction for biodiesel production [8]. Similarly, zinc oxide nanoparticles are used in solar cells as a semiconductor material to enhance the efficiency of the conversion of solar energy into electricity [9].

The nanomaterial components that have been mentioned represent only a few of the many applications of metal oxide nanoparticles. Copper oxide, iron oxide, titanium oxide, magnesium oxide, aluminum oxide, silicon dioxide, and calcium oxide nanoparticles are among the most commonly used metal oxide nano-materials [10]. Metal oxide nanoparticles have been synthesized using various methods, such as the hydrothermal method [11], chemical precipitation, and thermal decomposition [12], ultrasonic [13], sol-gel [14], and many other methods.

However, these synthesis techniques often have drawbacks, including the use of additives, high temperature and pressure requirements, time-consuming procedures, high costs, and overall complexity. In contrast, the sol-gel method offers a promising approach to overcoming many of these limitations. This technique is simple, cost-effective, time-efficient, and does not require expensive equipment. Furthermore, it can be carried out at lower temperatures without the need for high pressure. Therefore, the sol-gel method is a viable and attractive choice for the synthesis of calcium oxide nanoparticles. This study aims to synthesize calcium oxide nanoparticles from discarded chicken eggshells using the sol-gel technique.

2. RESEARCH METHODOLOGY

This research was conducted at the Chemistry Laboratory of Tanjungkarang Health Polytechnic, Department of Medical Laboratory Technology, from July to September 2024. The materials used were chicken eggshells obtained from household waste; 0.1 M HCl, 0.1 M NaOH, 0.1 M $AgNO_3$ analytical grade solution (Merck). The equipment used includes; porcelain mortar, 100 mesh sieve, porcelain crucible, beacker glass, burette, dropper, macro centrifuge, oven, Analytical balance (BEL Model MW 333i type MWnn3i-M), Muffle furnace (Labomiz scientific), Thermogravimetric analyzer NEXTA STA (Hitachi STA200RV), and instrumentation for product characterization such as; X-Ray Fluorescence Spectrometers (Supermini200), Fourier Transform Infra-Red (Agilent Technologies Carry 630), X-Ray Diffraction (Shimadzu XRD-700).

2.1 Synthesis of CaO Nanoparticles from Chicken Eggshell Waste Powder

The chicken eggshells were ground using a porcelain mortar until they became a fine powder, then sieved using a 100 mesh sieve. Subsequently, 12.5 g of the chicken eggshell powder was mixed with 250 mL of 0.1 M HCl solution, and the formed foam was separated and not used.

It was then centrifuged at 2000 rpm for 10 minutes, the precipitate and solution were separated, and this process was repeated twice. The solution separated from the precipitate was then added with 250 mL of 0.1 M NaOH solution dropwise using a burette until a white mixture was formed. The white mixture was then allowed to settle for 24 hours, and then decanted [15].

The precipitate was then washed twice, the first wash using 1 liter of hot distilled water, and the second wash using 500 mL of hot distilled water. The clear solution was then tested with a few drops of 0.1 M $AgNO_3$ solution, and the formation of a brown color indicated that the washing with hot distilled water was complete. The decantation was then continued until only the precipitate remained [16].

The precipitate was then placed in a porcelain dish and dried in an oven at 80 ℃ until dry. After drying from the oven, the $Ca(OH)_2$ precursor is then analyzed by Thermogravimetry, and then calcined at a temperature of 900 ℃ for 1 hour. The calcination product obtained was then characterized using Fourier Transform Infra-Red (FTIR), X-Ray Diffraction (XRD), and X-Ray Fluorescence (XRF) instrumentation to verify the formation of the synthesized CaO nanoparticles.

2.2. Characterization of CaO Nanoparticles Products

The dried $Ca(OH)_2$ precursor at a temperature of 80 °C was characterized using a Thermogravimetric analyzer (NEXTA STA Hitachi STA200RV), furthermore, the calcined product was characterized using X-Ray Fluorescence spectrometers (Supermini200), Fourier Transform Infra-Red (FTIR Agilent Technologies Carry 630), and X-Ray Diffraction (Shimadzu XRD-700).

3. RESULTS AND DISCUSSION

As shown Figure 1, calcium oxide nanoparticles products were obtained through a series of processes. When hydrochloric acid solution was added, a hydrolysis chemical reaction occurred between $CaCO_3$ from the eggshell powder and HCl, forming a $CaCl_2$ sol, water, and CO_2 gas that appeared as foam. Subsequently, the $CaCl_2$ sol was added with sodium hydroxide solution to form a $Ca(OH)_2$ precursor gel due to the condensation reaction, which resulted in the formation of an inorganic network from small particles weakly bonded by covalent forces [17].

Figure 1. Synthesized CaO Nanoparticles

On the other hand, the foam was not used in the subsequent processes because it could hinder the formation of the $Ca(OH)_2$ precursor and NaCl when NaOH was added to the $CaCl_2$ sol. Washing with hot deionized water was intended to separate impurities such as Cl^- and Na^+ ion, and other organic compounds. The test with $AgNO_3$ solution was intended to determine whether the Cl^- ion was no longer present, as indicated by the formation of a brown precipitate, which is the AgOH compound [18].

The thermogravimetric analysis of the $Ca(OH)_2$ precursor shown in Fig 2 provided information that there was a reduction in mass due to the phase change of various compounds into gas according to the characteristics of each compound as a function of the applied temperature [19].

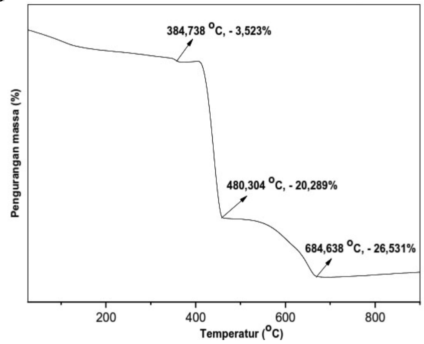


Figure 2. Thermogravimetric Analysis Results of the $Ca(OH)_2$ Precursor

The weight loss of 3.523% occurred at a temperature of 384.738 due to the vaporization of water molecules. At a temperature of 480.304, a mass reduction of 20.289% occurred as a result of the evaporation of organic compounds and the phase change of Ca2 to CaO, followed by weight loss of 26.531% at 684.638 due to the phase change of $CaCO_3$ to CaO.

The comparison of the infrared spectra between commercial CaO and the synthesized CaO, as shown in Fig.3, indicates that the synthesized CaO nanoparticle product contains a relatively high content of organic compounds.

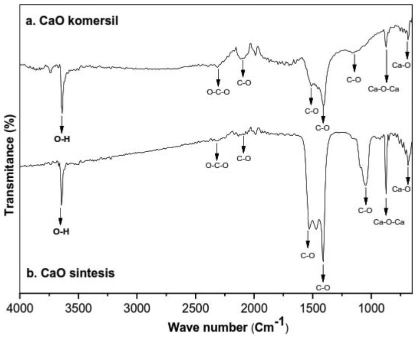


Figure 3. FTIR Analysis Results Show the Comparison of Synthesized and Commercial CaO

Furthermore, the peak positions in the FTIR analysis patterns of the commercial CaO and the synthesized CaO are relatively similar, with the peak at 3742.2 cm^{-1} indicating the presence of the O-H stretching functional group, the presence of O-C-O at 2310.9 cm^{-1}, and the peaks at 2117.1 cm^{-1}, 1990.4 cm^{-1}, 1513.3 cm^{-1}, and 1408.9 cm^{-1} representing the absorption peaks of the C-O bond. Additionally, the presence of the Ca-O group is shown at the wavenumber of 712 cm^{-1}, and the wavenumber of 880 cm^{-1} represents the peak of the Ca-O-Ca bond [20].

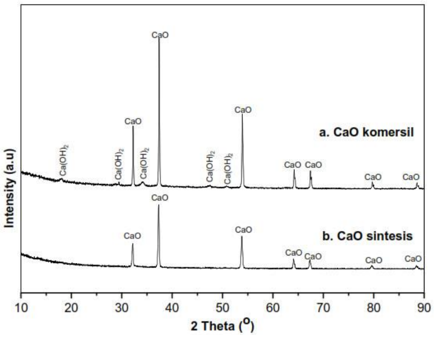


Figure 3. Comparison of XRD Analysis Results of Commercial and Synthetic CaO

The XRD analysis in Figure 3 provides information that the commercial CaO is similar to the results of previous research [21], with Crystallographic Open Data ID Number 101095. The three dominant peaks are at 2θ angles of 32.2°, 37.6°, and 53.8°. Additionally, the XRD analysis of commercial CaO still shows the presence of $Ca(OH)_2$ peaks at 2θ; 17.9°, 29.4°, 34.3°, 47.3°, and 50.9° [22].

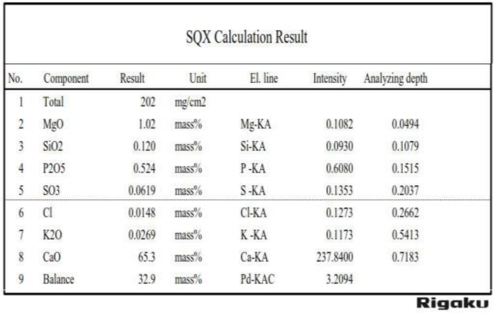
Furthermore, the X-ray diffraction characteristics of the synthesized CaO crystals have resembled the results of previous research by [21], with Crystallograph Open Data ID 9006694, which showed three dominant 2θ angles of 32.17°, 37.3°, and 53.8°, but no other impurity crystal peaks were found, and this analysis indicates that the CaO synthesized in this research has relatively fewer impurity crystals compared to commercial CaO [23].

The XRD data analysis can also be relatively used to inform the particle size of the synthesized CaO, as shown in equation 1 using the Debye-Scherrer formula [24].

$$D = \frac{k\ \lambda}{\beta\ cos\theta} \tag{1}$$

In which, D = crystal phase size (nm), k = shape constant valued at 0.9 – 1, λ = x-ray wavelength used= 1.542 nm, $\beta =$ Measurement result of half the maximum peak width height (in radians, $\alpha^{\circ}\ \frac{\pi}{180^{\circ}}\ x\ FWHM,\ \alpha^{\circ} =$ Bragg angle). The synthesized CaO crystal size obtained was 29.9 nm, where the calculation data used included a FWHM value of 0.28 and a 2θ angle of 37.3°.

Table 1. Results of XRF Analysis of CaO Nanoparticles



SQX Calculation Result

No.	Component	Result	Unit	El. line	Intensity	Analyzing depth
1	Total	202	mg/cm2			
2	MgO	1.02	mass%	Mg-KA	0.1082	0.0494
3	SiO2	0.120	mass%	Si-KA	0.0930	0.1079
4	P2O5	0.524	mass%	P -KA	0.6080	0.1515
5	SO3	0.0619	mass%	S -KA	0.1353	0.2037
6	Cl	0.0148	mass%	Cl-KA	0.1273	0.2662
7	K2O	0.0269	mass%	K -KA	0.1173	0.5413
8	CaO	65.3	mass%	Ca-KA	237.8400	0.7183
9	Balance	32.9	mass%	Pd-KAC	3.2094	

Rigaku

The XRF analysis results of the synthesized powder are tabulated in Table 1. The data in Table 1 shows that CaO is the largest quantity at 65.3%, which is better than the results of our previous research that synthesized CaO nanoparticles using a thermal decomposition technique, which produced 41% CaO nanoparticles [25].

4. CONCLUSION

CaO nanoparticles have been successfully synthesized from chicken eggshell waste through the application of the sol-gel method. The sol-gel technique has many advantages compared to other methods for synthesizing metal oxide nanoparticles, such as being simple, economical, not requiring expensive equipment, ambient temperature, and without pressure. The results of FTIR, XRD, and XRF analyses clearly confirm the formation of the synthesized CaO nanoparticles. The particle size obtained through calculations using the Debye-Scherrer formula from the XRD analysis data resulted in a size of 29.9 nm. The produced product is relatively pure, as evidenced by the XRD analysis results not showing any X-ray diffraction peaks from other crystals, but the CaO nanoparticle product yield of 65.3% can still be improved in the future by applying calcination at a temperature of 685℃ .

ACKNOWLEDGMENTS

The researchers express their gratitude to the Ministry of Health of the Republic of Indonesia through the Decree of the Director General of Health Resources Number: HK.02.03/F/2322/2023 for the funding and opportunity to complete this research. Additionally, the researchers also thank the Faculty of Mathematics and Natural Sciences of the University of Lampung for the support provided in completing this research.

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