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Synthesis and Characterization of Nanoparticle Calcium Oxide (CaO) from Blood Calm Shell by Precipitation Methods

Aisy Aulia Amri*, Zahranisa Shorea, Caecilia Puji Astuti

Departement of Chemical Engineering, Faculty of Engineering, Universitas Pembangunan Nasional "Veteran" Jawa Timur, Jln. Raya Rungkut Madya, Gunung Anyar, Surabaya, 60294, Indonesia.

*20031010001@student.upnjatim.ac.id

Abstract. Blood Clam (Anadara granosa) contains high calcium carbonate which can be utilized in various fields by being used as nanotechnology. The shell contains 98.7% $CaCO_3$ making it a sustainable material source. The research aims to synthesize and characterize of calcium oxide nanoparticles by precipitation methods. This method begins with crushing the shell into 100 mesh as sample. Each sample is mixed with HCl solute. After mixing, each filtrate is precipitated with KOH solute to multiple pH (7 ; 9 ; 11). The method continues with neutralizing the precipitate with water until it reach pH 7 and drying it with oven in 100°C for 1 hour. The sample will be calcinated for 3 hours in various temperature (300°C ; 500°C ; 900°C). Samples will be analyzed with SEM-EDX and XRF Analysis. Research indicates that The degree of acidity and calcination temperature do not have a significant effect on calcium oxide content. The calcium oxide content is ranged between 82,58% - 87,47% with the sizes being ranged between 550 nm - 20µm.

Keywords: Calcium oxide, Nanotechnology, Blood clam shells, Precipitation, sustainable material.

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1. Introduction

Indonesia is a country known for its abundant marine resources. The marine life found in the Indonesian Sea is not limited to fish, but also many types of shellfish. One type of shellfish that is abundant in Indonesia is the blood clam (Anadara granosa). This blood clam (Anadara granosa) is considered to have a high economic price to be developed. The price of blood clams in the Indonesian market reaches Rp. 20,000/kg [6]. The potential of blood clam shells are also many because they contain high calcium carbonate which can be utilized in various fields by being used as nanoparticle technology [2]. One of the fields that favor nanoparticle technology is the manufacture of green catalysts from calcium oxide nanoparticles. This green catalyst from CaO nanoparticles can be a catalyst that is biodegradable, non-toxic, renewable, and stable in acidic and alkaline conditions [11]. Calcium oxide also is one of the main ingredient of dolomite as the adsorbent of heavy metal waste [17].

The abundance of blood clams in Indonesia according to the Directorate General of Capture Fisheries of Indonesia in 2012 was 48,994 tons. Given the composition of the shells that are more than the meat, which is about 70% shell and 30% meat [12]. The dara mussel shell itself contains 98.7% CaCO3, 0.05% Mg, 0.9% Na, 0.02% P and 0.2% other elements. Reviewing the amount of CaCO3 content in blood clam shells, this shell waste has the potential to be synthesized and characterized into calcium oxide (CaO) nanoparticles. Nanoparticle synthesis itself attracts more attention from researchers today because of the increase in surface area and absorption power. The results of the synthesis of Calcium Oxide from the shell of this pigeon mussel can be considered nanoparticles when they are very small, namely 10^{-9} m.

The synthesis and characterization system of calcium oxide nanoparticles from blood clam shells consists of various methods. The method that can be done is the heating/thermal method that has been done by Ghiasi and Malekzadeh in 2012. In this method, they synthesized nanocalcium oxide by heating calcite at 900oC for 5 hours and then hydrolyzing it with lime. This process can produce calcium oxide nanoparticles with an average particle size of 50 nm [10]. Another prior research provide fact that from shell, the content of Calcium oxide in the product is 87,39% [13].

Another method that can be used is the Precipitation method. This precipitation method uses the help of chemicals to dissolve and precipitate the desired substance. This precipitation method only requires acidic chemicals for dissolution, and basic properties for the precipitation process and then dried at 100ºC for 1 hour and calcined at 300ºC;500ºC;700ºC for 3 hours. Calcinating method is required for the sample to lose its mass, so it can be known that $CaCO_3$ has turned into CaO [14].

Using a solvent in the form of HCl and a KOH precipitator will get a by-product in the form of KCl. This KCl can be reprocessed into one of the raw materials for making *Chromolaena odorata* liquid fertilizer to increase the yield of Black Madras purple rice [7]. Considering the shortcomings and advantages of the available methods, the Synthesis and Characterization of Calcium Oxide (CaO) Nanoparticles from Blood Clam Shells by Precipitation method was carried out.

2. Methods

2.1. Research Method

The materials used were blood clam shell waste obtained from Kenjeran Beach, Surabaya, and solvents in the form of HCl and KOH precipitators obtained from a chemical supply store located on Jalan Tidar, Surabaya.

2.2. Procedures

The precipitation method is the mixing of acids with bases that produce crystalline solids and water [8]. The dissolution reaction that occurs during the dissolution process of CaCO3 in blood clam shells with a solvent of hydrochloric acid (HCl) is

$$CaCO_{3(s)} + 2HCl_{(l)} \rightarrow CaCl_{2(l)} + H_2O_{(l)} + CO_{2(g)}$$

This reaction occurs during the dissolution process of CaCO3 in 25gr pigeon shell powder with 250 mL of 5N hydrochloric acid. Conch shells have substances other than CaCO3, so that in the dissolution process, Calcium oxide will be dissolved while other substances will precipitate [4]. The reaction that occurs in the precipitation process using Calcium Hydroxide solution is:

$$CaCl_{2(l)} + 2KOH_{(l)} \rightarrow Ca(OH)_{2(s)} + 2KCl_{(l)}$$

In this process, the reaction that occurs is that the dissolved Calcium chloride precipitated with calcium hydroxide will form a Calcium hydroxide solid. This solid will precipitate, and the resulting solution is Potassium chloride which is a by-product of the precipitation process. First, the blood clam shells were reduced in size to 100 mesh and then 20 grams of blood clam shell powder was taken. The 20 grams of blood clam shell sample was then dissolved with 250 mL of 5N HCl in a beaker glass with 250 rpm stirring within 10 minutes. After dissolving, filtration was carried out and then the filtrate was precipitated with 3N KOH solution slowly and then measured the degree of acidity with a pH Indicator according to the variables. Precipitation method for each degree of acidity took 1 hour of stirring with 90 rpm. This method is based on [15] which states that smallest nanoparticle size could be achived with 90 rpm stirring velocity. Then filtration is carried out where the filtrate will be stored as a by-product while the precipitate will be neutralized with water until the pH becomes neutral to be free from impurities. The neutral precipitate will be dried in an oven at 100ºC for 1 hour. After drying, the precipitate is transferred to a porcelain cup and then calcined in a furnace for 3 hours. The consideration for calcination time is based from [16] which use 3 hours per sample for its research to obtain CaO. The variable temperatures of 300ºC; 500ºC; and 900ºC. Precipitation is done until each sample got into pH 7, 9, and 11. Each pH will be calcined with the variable temperature. The sample that are taken for analysis are pH 7 on 300ºC, pH 9 on 500ºC, and pH 11 on 900ºC.

3. Results and Discussion

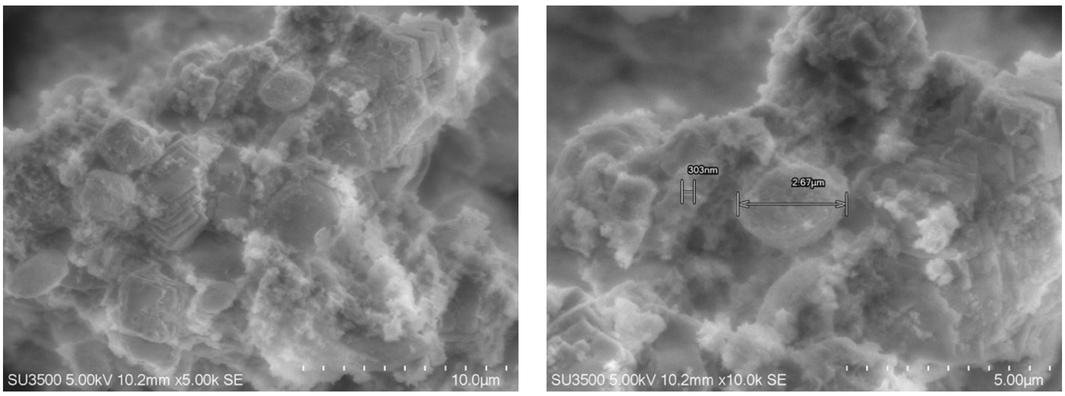
In the raw material of blood clam shell powder, initial analysis is carried out in the form of XRF and SEM-EDX methods. This initial analysis was carried out to determine the levels contained in it, the shape, and particle size.

Table 1. Results of Analysis of Content in Blood Clam Shells

Component	Concentration
Al2O3	0,333%
SiO2	0,644%
P2O5	0,0879%
SO3	0,122%
Cl	0,0386%
K2O	0,0712%
CaO	49,7%
Fe2O3	0,394%
SrO	0,134%
Balance	48,4%

Source: Unit Pelaksana Teknis (UPT) Laboratorium Terpadu Universitas Diponegoro

Based on the results of the analysis of the component content in the blood clam shell, which is 49.7%. So it is known that in 100 grams of shell powder raw material, there are about 35 grams of calcium oxide content. This shows that blood clam shells can be used as raw material in the synthesis of Calcium oxide (CaO).



(a) Magnification of 5000 times (b) Magnification of 10000 times

Figure 1. SEM Analysis Results of Blood Clam Shell Powder Raw Material

Based on the results of SEM analysis that has been carried out on the raw material, it can be seen that the particle morphology of the pigeon shell powder is calcite. The particle size obtained varies and ranges from 303 nm – 2,67μm. The results of this analysis will be used as a comparison of the synthesis of calcium oxide nanoparticles.

It is produced by dissolving 50 grams of blood clam shell powder in 250 ml of hydrochloric acid at various concentrations. The stirring speed used is 250 rpm. It can be seen that the weight of the residue is getting less with increasing concentration. This is because the powder from the blood clam shells dissolves more into the hydrochloric acid used. As well as the degree of acidity (pH) of the resulting solution decreased because hydrochloric acid is a strong acid. As the concentration of hydrochloric acid increases, the pH of the solution will decrease.

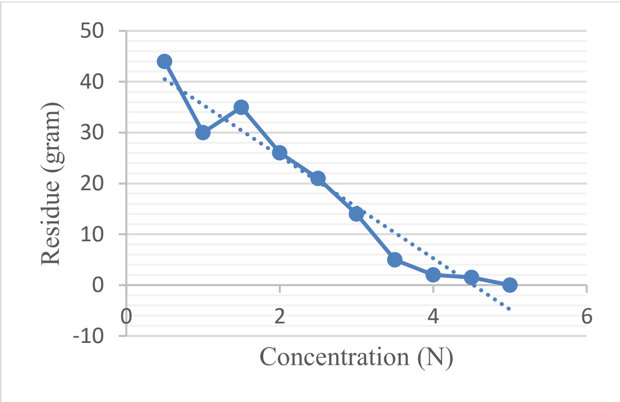


Figure 2. Correlation between Hydrochloric Acid Concentration and Residue of Blood Clam Shell Powder

After the dissolution data is plotted on the figure, it can be seen that the relationship between concentration and residue of blood clam shell powder is inversely proportional. The higher the concentration used, the lower the residue produced, this is because more blood clam shell powder dissolves in hydrochloric acid if the concentration is increased. It can be ascertained that the more blood clam shell powder dissolved, the higher the calcium content dissolved in hydrochloric acid.

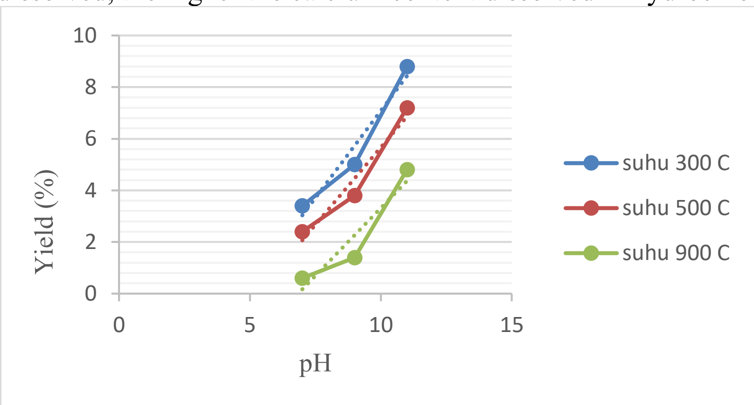


Figure 3. Correlation between Yield and pH of Calcium Oxide by Precipitation Method at Various Calcination Temperatures

Based on the results of figure 3, it can be seen that the relationship between pH and yield is directly proportional. If the pH is higher, the yield produced is also higher, which means that the higher the pH, the more calcium oxide is produced. The decomposition process of $CaCO_3$ into CaO is not only influenced by time, but also by temperature. Research on the effect of calcination time on CaO yield resulted in 4 hours as the optimal time at 900°C. Calcination prefers high temperatures because the $CaCO_3$ decomposition reaction is an endothermic reaction, which is a reaction that requires energy from outside in the form of heat to break the chemical bonds in the sample so that the reaction will free CO_2.

It can be seen that the release of CO_2 is directly proportional to the formation of CaO. A constant yield value will be obtained if the calcination temperature is 900°C with a time of 4 hours. If the final weight value and the initial weight are not much different, then the release of CO_2 is still low, so the CaO formed is also still small. Yield is a comparison of the number of samples of decomposition reaction results expressed in percent (%), the higher the yield value, the $CaCO_3$ has not been decomposed completely [3]. Based on the results of the analysis of calcium oxide (CaO) nanoparticles from blood clam shells using XRF and SEM-EDX tests, the results obtained are the % composition, shape, and size of calcium oxide particles shown as follows.

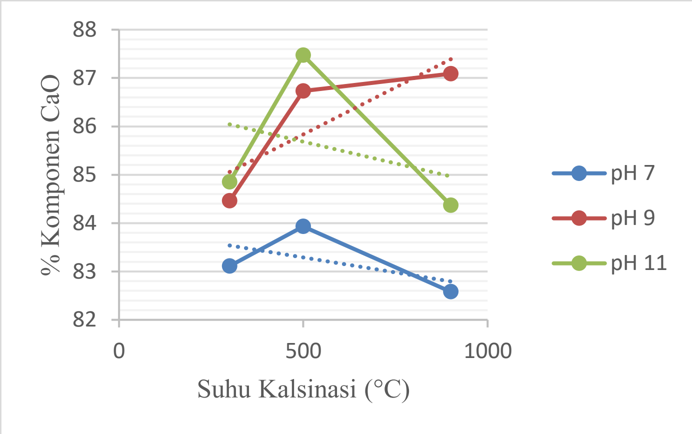
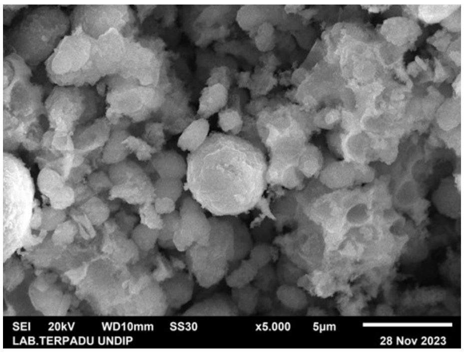
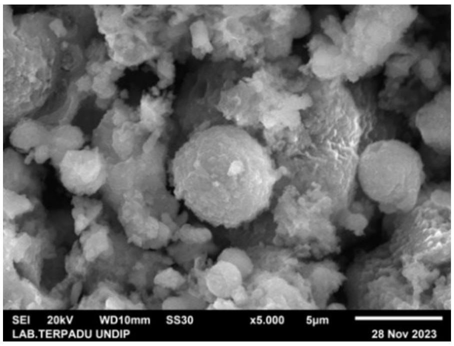


Figure 4. Correlation of Calcination Temperature with % CaO Component at Various pH

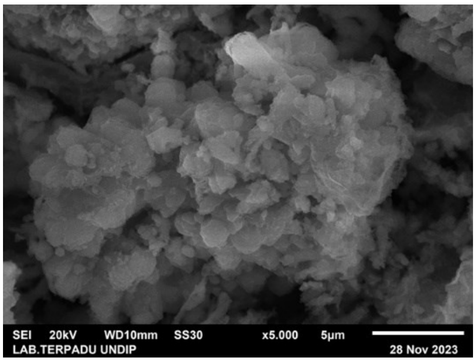
Based on the results of the XRF analysis test on the resulting product, it shows that the largest component is CaO with a number above 80%. The best calcium oxide nanoparticle results are at pH 11 with a calcination temperature of 500°C within 3 hours, with a CaO yield of 87.47%. This result is suitable according to [13]. However, according to [18], this result is lower. This could happen because during neutralization process, the sample is not clean enough, resulting the content of CaO a little bit low. The higher the pH used, the more CaO will be formed. According to [1], basic compounds added in the solution, namely KOH, can increase the concentration of OH- ions, thus causing the formation of metal hydroxide compounds that are difficult to dissolve in water. According to [3], CaO begins to form at temperatures >500°C and at temperatures ≥900°C the CaO formed will be more active so that if used as a catalyst it will be more optimal.



(a) pH 7 300°C



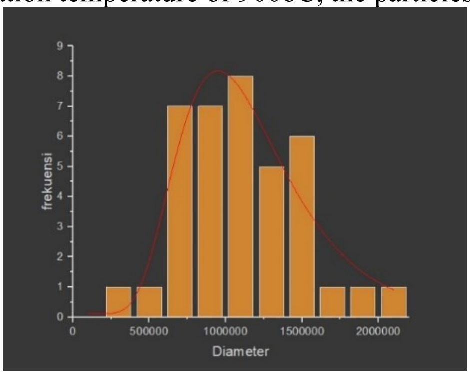
(b) pH 9 500°C



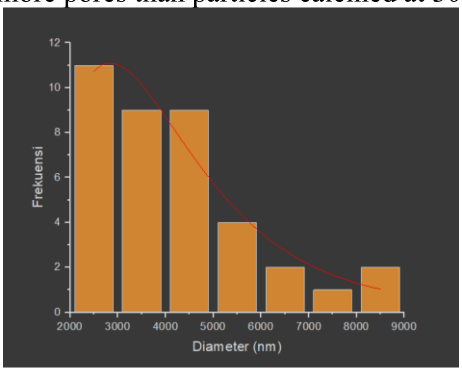
(c) pH 11 900ºC

Figure 5. SEM-EDX Analysis of Calcium Oxide (CaO) Nanoparticles from Blood Clam Shells

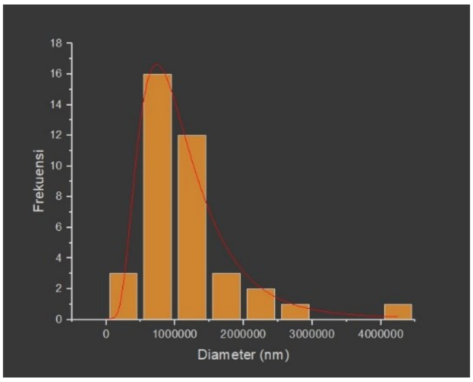
The morphological shape of the resulting CaO crystals is spherical or spheric. This form is in accordance with previous research conducted by [10] with the same method and eggshell raw materials that the shape of the resulting CaO is spherical. This is also suitable from prior research [19], in which the morphology of the product is shaped as spherical ball. The results of this morphology are also in accordance with the characterization of nanocalcium oxide from green mussel shells with the precipitation method by [1] where the morphology of calcium oxide precipitation results in a spherical shape. The higher the calcination temperature, the particles also have many pores. It can be seen that at a calcination temperature of 900oC, the particles have more pores than particles calcined at 300oC.



(a) pH 7 300ºC



(b) pH 9 500ºC



(c) pH 11 900ºC

Figure 6. SEM Analysis for Particle Size Distribution of Bloodshell Calcium Oxide Powder

Particle size at pH 7 with a calcination temperature of 300ºC produces particles with sizes ranging from 5 – 20μm with the most spread in size 10μm. The particle size of calcium oxide with pH 9 with a calcination temperature of 500ºC produces particles with sizes ranging from 650nm-750nm with the most spread in size 750nm. The particle size of calcium oxide with pH 11 with a calcination temperature of 900°C produces particles with sizes ranging from 500 nm - 4 μm, with the highest distribution at the size of 650nm. The sizes of the product is not suitable from prior researches. Based on [20], the nanoparticles that is achieved within the range of 7 – 41 nm.

The distribution of particles is known to be uneven and too big. This can be caused by the high calcination temperature which increases crystal growth activity so that it tends to form new bonds and crystal transformation occurs [8]. The results of the synthesis of calcium oxide from the virgin clam shell using this precipitation method cannot be considered as nanoparticles because the size is not in accordance with the provisions. According to [5], nanoparticles are particles with sizes between 1 - 100 nm, while the size of the particles produced is still greater than the provisions.

4. Conclusions

The degree of acidity and calcination temperature do not have a significant effect on calcium oxide content. The difference in the amount of Calcium Oxide components produced in the product is only slight. The synthesis of calcium oxide from blood clam shells produces a yield of 2.4% - 13.6% depending on the variation of acidity (pH) and calcination temperature used. SEM-EDX analysis results showed that the particle size formed in the product was 550 nm - 20μm with the dominant constituent elements C, O, and Ca. The results of XRF analysis showed that the CaO content obtained was 82.58% - 87.47%. The product has the same size when compared with the results of calcium oxide synthesis with other materials and the same method. For future reference, variable for solvent concentrate which is used for dissolution and precipitation could be changed to be mor varied. Also, stirring time in precipitation process could be changed to prove whether it would change the result on the CaO content.

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