Advance Sustainable Science, Engineering and Technology (ASSET)
Vol. 6, No.4, October 2024, pp. 0240403-01 ~ 0240403-08
ISSN: 2715-4211 DOI: https://doi.org/10.26877/asset.v6i4.788

Preparation of Calcinite Fertilizer from Golden Snail Shells by Calcination and Crystallization Processes

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Abstract. The golden apple snail is a significant pest that damages crops and can lead to crop failure because it has a habit of consuming various soft plants, including young rice plants. Golden snail shells have a high calcium carbonate content of around 60.56%. Large calcium content can be used as a source for the production of calcium nitrate fertilizer. The stages in making calcinit fertilizer are washing the shell of gold snails and drying for 1-2 days. After that, size reduction is carried out to 50 mesh. After that, the calcination process was carried out with a variable temperature of 700,750,800,850,900 °C for 4 hours. The calcined shell is dissolved with HNO_3 with a variable of 1-5 N for 1 hour. After that the solution is filtered from impurities and neutralized to pH 7. After that the solution is crystallized into white crystals. The largest Ca and N content was obtained at a calcining temperature of 900 and HNO_3 5 N concentrations, namely Ca of 21.94% and N of 16.52%. The results showed that the higher the calcining temperature and the higher the HNO3 content, the higher the Ca content and N content

Keywords: calcium nitrate, sustainable agricultur, fertilizer production

(Received 2024-07-03, Accepted 2024-07-27, Available Online by 2024-08-16)

1. Introduction

Plants need nutrients according to their needs. The nutrition referred to Ca (calcium) and N (Nitrite). Gold snail is one of the animals whose shell contains calcium carbonate. The golden apple snail is a significant pest that damages crops and can lead to crop failure because it has a habit of consuming various soft plants, including young rice plants [1]. According to the Directorate of Food Crop Protection, in 2022, pest problems in crops will result in reduced yields in the agricultural sector. The population of carp snails is quite large, causing damage to plants up to 20 percent. Because of its high calcium content, it can be used as a material for making calcium nitrate fertilizer. The crystallization process is used for the formation of solid calcium nitrate fertilizer.

Research conducted by Fazriyati in 2022 with the title "Making Calcinit Fertilizer from Cow Bone and HNO_3 with Calcination and Precipitation Process", cow bone is calcined using temperature variations of 600; 650; 700; 750; 800 °C with a calcination time of 4 hours. After that, the precipitation

process was carried out using variations in HNO_3 concentration of 1N; 3N; 5 N. Based on the results of the experiment, the largest CaO content was obtained at a calcination temperature of 800 ℃ by 74.6 % and the largest Nitrogen content at a concentration of HNO_3 5 N by 49.6 % [2]. In 2023, Hamzah conducted research on the production of calcium nitrate fertilizer from chicken eggshells and nitric acid by reacting the eggshells with HNO_3 in varying volumes of 10, 15, 20, 25, to 30 ml at a temperature of 60 ℃. The optimal results were obtained with a nitric acid volume of 30 ml and a reaction time of 50 minutes [3].

Based on the above, considering several studies that have been done before, researchers will make calcinite fertilizer from gold snail with variations in calcination temperature and HNO_3 concentration that can meet the existing calcinite fertilizer quality standards. The selection of gold snail as the material for calcinite fertilizer is because based on previous research, most of the use of gold snail is used for the production of liquid organic fertilizer. Therefore, research was conducted on the manufacture of calcinite fertilizer from gold snail by calcination and precipitation methods.

1.1 Calcinit Fertilizer

Calcinit or calcium nitrate fertilizer is a fertilizer that contains two nutrients, calcium and nitrate. This fertilizer is water soluble and is classified as a supplement. Calcium nitrate fertilizer can help increase crop yields, make plants less susceptible to diseases and pests, and long fruit storage periods [4]. Calcium (Ca) ranks as the third most abundant vital nutrient in plants, following nitrogen (N) and potassium (K), and its levels are nearly equivalent to those of phosphorus (P) within plant tissues. Notably, mitochondria contain the greatest concentrations of Ca. This element plays a crucial role in the processes of cell division and growth [5]. In addition, nitrogen contained in calcinite fertilizer is useful for chlorophyll synthesis and plays an important role in the photosynthesis process [6]. Calcinite fertilizer can significantly increase soil pH and can effectively reduce cd sorption by soil because it has a high adsorption capacity after being calcined [7].

Table.1 Characteristic Calcium Nitrate

Specifications	Description
pH	6
Content	15,5 % N, 19-22% Ca, < 1,5% NH_4
Water Solubility	1200g/L

1.2 Golden Snail and Shell Content

The golden snail (*Pomacea canaliculata L.*), also known as the mulberry snail, is a major pest of rice plants. This pest prefers young rice plants, and the intensity of damage varies from 10% to 100%, depending on the population level in each field. The extent of damage is highly dependent on the size of the snails; even when they measure 31-40 mm, their destructive power reaches 97.38% [8]. Gold snail is one of the molluscca animals that contains high protein which is often found in rice fields or in plants that are quite wet, usually in swamps, rice fields, and areas that are always flooded and can also survive in extreme environments such as lack of oxygen and pollution. Gold snails can reproduce again if they receive irrigation after surviving for approximately 6 months in the soil [9].The meat is a good source of protein for animals as it contains 54 to 62 % protein [10]. Therefore, gold snails can be used as an alternative supplementary feed for ducks in order to increase egg production. The utilization of gold snails is generally as fish or livestock feed.

Gold snail shells have not been widely utilized, but the most content of gold snail shells consists of calcium carbonate. Other contents include calcium phosphate, silicate, magnesium carbonate, iron and organic substances that make up the rest of the structural protein composition, and phosphorus compounds [11].

Table.2 Golden Snail Shell Content

Compounds	%
$CaCO_3$	60,56
SiO_2	6,72
$Ca_3(PO_4)_2$	11,82

1.3 Calcination

Calcination is the treatment of materials for the decomposition of compounds that are chemically bonded to the material [12]. The initial stage of the calcination process is a decomposition reaction in order to release gases in the form of carbonates or hydroxides so as to produce powders in the form of oxides with high purity [13]. The optimum time for calcination is about 4 hours [14]. The calcination process is carried out by heating at temperatures that vary depending on the type of carbonate compound present. However, for calcium carbonate, a high temperature required for decomposition. This is because the chemical bonds in crystal water are quite strong [15]. The calcination temperature affects the structural changes in materials. When a material is heated at a constant rate, physical changes occur, such as phase transitions and an increase in energy that allows atoms to vibrate at greater interatomic distances. The alteration of material structure due to temperature arises because heating a material leads to an increase in energy, enabling atoms to vibrate at larger interatomic distances [16].

Calcination is necessary to decompose compounds in the form of salts or dihydrates into oxides, forming a crystalline phase. The events that occur during the calcination process are:

1. The release of free (H_2O) and bound (OH) water takes place around 100 °C to 300 °C.
2. Release of gases, such as: CO_2 takes place around 600 °C and at this stage is accompanied by a significant weight reduction.
3. At higher temperatures, around 800 °C, the crystal structure has been formed, at which point the bonds between the particles are not yet strong and are easily separated. [17]

1.4 Crystallization

Crystallization is a formation of a solid/crystal. It occurs in two stages, namely, nucleation and crystal growth. What causes these stages is the condition of supersaturation. Supersaturation condition is a state where in a solution the solute is more than the solvent. Crystal formation, generally called nucleation. There are usually three different mechanisms:

1. Homogeneous nucleation states that very high supersaturation is required before crystals form. In general discussions of the nucleation of new phases, for example in liquid materials, it is assumed that the new phases form as clusters. The rate at which clusters continue to grow is often referred to as the nucleation rate.
2. Heterogeneous nucleation Crystals form at heterogeneities or other small crystals in solution. These heterogeneities can be formed by adding certain elements to the solution. This nucleation mechanism is usually treated by considering the gap formed on the flat plane of the substrate.
3. Crystal multiplication the third way in which crystals are formed is by the splitting of existing crystals. This process is known as crystal multiplication. The crystal multiplication process is then spontaneously accelerated [20]

There are 4 ways to become supersaturated: temperature reduction, solvent evaporation, chemical reaction, and changing the solvent composition. The step to supersaturation by decreasing the temperature is better known as Cooling. If a saturated solution is lowered in temperature, the saturated concentration of the solution will drop, so that crystals begin to form [18]. The water content in the product decreases due to the heating process resulting in water evaporation [19]. For evaporation crystallization step is to evaporate the solvent with a temperature of more than 100 °C according to the temperature of water evaporation.

2. Methods

The materials used in this study are gold snail shells, 68 % HNO_3 solution, aquadest, NH_4OH, filter paper, pH meter paper.

2.1 Procedures

The golden snail shells are washed thoroughly and then dried in the sun for 1-2 days. The dried shells are reduced in size to 50 mesh. After that the shells are calcined at a temperature of 700, 750, 800, 850, 900 ℃. The calcined shells are tested for content. Calcination carried out on the goldfish conch shell will free the CO_2 compound from the $CaCO_3$ compound to produce CaO. The process is a decomposition reaction, with the reaction:

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)} \quad (1)$$

The calcination process has a complex mechanism and involves several stages starting with heat transfer to the surface of the particles and passing through the outermost layer. Heat is absorbed by the material so that the CO_2 produced migrates to the surface and then spreads within the heating chamber. After the shell is calcined, the compound content in the shell is reacted with HNO_3 reagent with variable concentration 1, 2, 3, 4, 5 N to produce calcium nitrate solution. The reaction is carried out in a beaker glass accompanied by stirring. Stirring aims to accelerate the reaction so as to maximize the resulting product.

$$CaO_{(aq)} + 2HNO_{3(aq)} \rightarrow Ca(NO_3)_{2(s)} + H_2O_{(l)} \quad (2)$$

After mixing for 1 hour, the solution was filtered to separate impurities. After that, the neutralization process was carried out using NH_4OH solution. During the neutralization process a precipitate is formed, which will be filtered before the solution is crystallized. After dissolution, the material that has been calcined is adjusted to a pH of 6 (neutral) and then checked using pH paper The precipitate formed during the neutralization process is filtered using filter paper. The calcium nitrate solution formed is crystallized by heating with a temperature of 150 ℃, the solvent contained in the solution will evaporate to reach supersaturation conditions so that crystalline solids can be formed during the heating process. The solids formed are white calcium nitrate crystals.

3. Results and Discussion

3.1 Analysis of Content CaO

Table.3 CaO content

Temperature Calcination (℃)	Content CaO (%)
700	86,15
750	90,60
800	94,80
850	98,52
900	98,55

Based on table.3, it can be seen that the higher the calcination temperature, the higher the CaO content produced. This is because the higher the calcination temperature, the more perfect the $CaCO_3$ decomposition process [20]. The test results are used to determine the amount of material reacted, so that the higher the CaO content in the material, the less weight of CaO is needed.

3.2 Calcinite Fertilizer Content

Figure.1 Calcinit Fertilizer

The results of the research in the form of calcinite fertilizer were analyzed to determine the nitrogen content with the kjeldahl method, Ca content with the AAS (Atomic Absorption Spectrophotometry) method in the laboratory of the Industrial Research and Consultation Center, Ketintang, Surabaya.

Table.4 Calcinit Fertilizer Content

Suhu (℃)	Konsentrasi HNO_3 (N)	%Ca	%N
700	1	14.6	11.05
	2	15.23	11.35
	3	15.82	11.81
	4	16.65	12.47
	5	17.01	12.8
750	1	16.9	13.25
	2	17.07	13.37
	3	17.37	13.54
	4	17.68	13.77
	5	17.95	14.05
800	1	17.01	15.32
	2	17.73	15.76
	3	18.09	16.28
	4	18.56	16.55
	5	19.11	16.75
850	1	18.85	16.9
	2	19.02	16.94
	3	19.23	16.98
	4	19.72	17.02
	5	20.15	17.09
900	1	19.9	17.15
	2	20.08	17.18
	3	20.11	17.2
	4	20.19	17.21
	5	20.23	17.24

Based on table 3.2, it shows that the best results were obtained at a calcination temperature of 900 ℃ and an HNO_3 concentration of 5 N with a Ca content of 20.23 % and an N content of 17.24 %. This is in accordance with the SNI for calcinite fertilizer for a Ca content of 19 % - 22 % and a minimum N of 15.5 %. Meanwhile, research conducted by Fazriyati (2022) was also in accordance with SNI where the largest CaO content produced was 74.6 % and N content was 49.6 %

This is due to differences in materials and manufacturing methods in these two studies. Research conducted by Fazriyati (2022) used beef bone as material and the process used was calcination and precipitation with the material reacted with HNO_3 then allowed to stand and the sediment dried using an oven. Meanwhile, this research used golden snail shell material and the process used was calcination and crystallization where the material was reacted with HNO_3 without a precipitate forming, then the solution was neutralized and crystallized. Based on the standard calcium nitrate fertilizer

content, the results obtained have met the standards but are still much smaller than research conducted by Fazriyati (2022).

3.3 Effect of Calcination Temperature on Ca Content

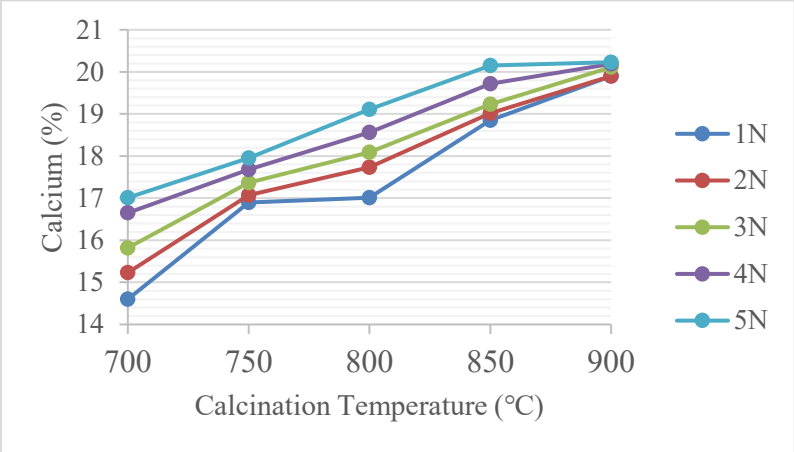

Figure.2 Graph of the effect of calcination temperature on Ca content

Based on Figure 3.2 The graph above shows the relationship between calcination temperature and Ca, the calcium content value ranges from 14.6 % to 20.23 %. There is an increase in Ca content with every increase in temperature. The best calcium content is found at a temperature of 900 °C with a concentration of 5 N with a calcium content of 20.23 %. These results meet the SNI for calcium nitrate fertilizer, namely 19 % - 22 %. The calcium content is influenced by the calcination temperature, the higher the calcination temperature, the more completely $CaCO_3$ is decomposed into CaO and CO_2. Based on these results, a higher CaO content can produce a more optimal calcium content in calcium nitrate fertilizer. It can be seen in the graph that the Ca content starts to become constant at a temperature of 850 °C – 900 °C, this is because the reagents that have reacted into products have been completely converted, so that a constant Ca content is obtained [20]. The Ca content begins to be constant at temperature because at that temperature the decomposition process of $CaCO_3$ is more perfect.

3.4 Effect of Concentration HNO_3 on N Content

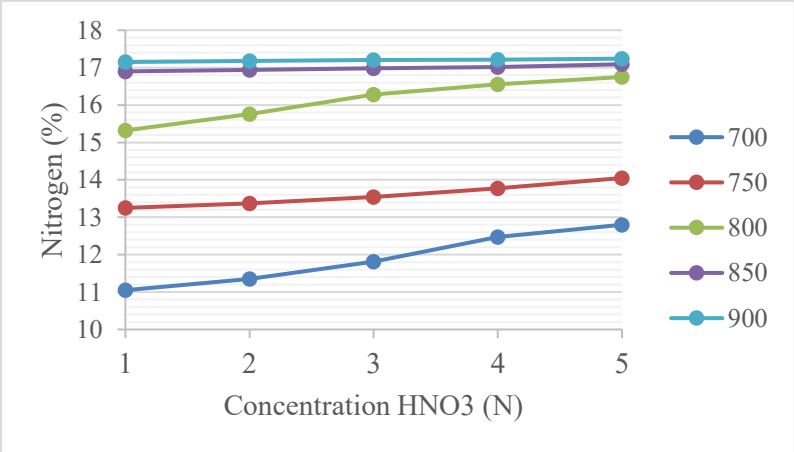

Figure.3 Graph of the effect concentration HNO_3 on N Content

Based on (Figure 3) Graph of the Effect of HNO3 Concentration on the Nitrogen Content of Calcinite Fertilizer, the Nitrogen content value ranges from 11.05 % - 17.24 %. As the concentration of HNO_3 increases at each calcination temperature, the nitrogen content also increases. However, at calcination temperatures of 850 and 900, the nitrogen content remains relatively constant despite changes in HNO_3 concentration. The highest nitrogen content, 17.24 %, was

obtained at a concentration of 5 N with a calcination temperature of 900 ℃. The results of the nitrogen content are in accordance with SNI, namely a minimum of 15.5 %. The nitrogen content can be influenced by the concentration of HNO_3 used. The higher the concentration of HNO_3, the more reactants will react to become calcium nitrate fertilizer so that the nitrogen content will be greater. In accordance with research conducted by Fazriyati (2022), the greater the concentration of HNO_3 used, the greater the nitrogen content contained [2].

4. Conclusion

Based on research that has been done, making calcinite fertilizer from gold snail shells and HNO_3 with a calcination and crystallization process produces products The best calcium and nitrogen levels are obtained at a calcining temperature of 900 °C and HNO_3 concentration of 5 N, for calcium levels obtained by 21.94 % and nitrogen levels obtained by 16.52 % where this is in accordance with SNI calcinit fertilizer which has a calcium content of around 19 – 22 % and a nitrogen content of at least 15.5 %. Calcium nitrate fertilizer in this study can be used as a plant supplement because it already meets the specified standards It is hoped that in future research, the optimal conditions for the crystallization process can be determined.

Acknowledgements

The authors would like to thank all those who contributed to this research. Especially to the lecturers who have helped and provided many suggestions regarding our research.

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