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Preparation of Calcium Nitrate ($Ca(NO_3)_2$) from Egg Shells

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ABSTRACT: The Indonesian people's consumption of eggs increases every day which causes wasted eggshells to also increase. The shells from eggs that have been thrown away will become waste which can cause the surrounding environment to become polluted and unhealthy. Eggshell waste can be used as a basic ingredient for making calcium nitrate ($Ca(NO_3)_2$) because it contains high calcium carbonate of 98.2 %. The egg shells used in this study were broiler chicken, free-range chicken, duck and quail egg shells. The process of making calcium nitrate from eggshells uses the lime method with a leaching process, before being used the eggshells are prepared first by soaking using 5 % NaClO and then made into calcium nitrate powder. The formed calcium nitrate was tested qualitatively and quantitatively. The qualitative test of calcium nitrate was carried out using a turbidity meter while the quantitative test was carried out by titrating a solution of calcium nitrate using an EDTA solution. The highest conversion value obtained was in the quail shell sample, which was 89.95 % gram with a yield weight of 1.15 gram. Based on the results obtained, the quail eggshell contains a high content compared to other eggshell samples.

Keywords: Calcium Nitrate, Eggshell, Leaching, Waste

1. Introduction

Indonesia is one of the countries in Southeast Asia where the majority are livestock breeders, the results of the 2013 Agricultural Census (ST2013) show that the number of households livestock farming in Indonesia almost reaching 13 million households. Meanwhile, in 2021, livestock and animal health statistical data show that the largest breeders in Indonesia are poultry breeders, the poultry population consists of chickens, ducks, geese and quail, this is because poultry is the most promising commodity, not only meat. can be bought and sold, but derivative products such as eggs are very promising, it is no wonder that Indonesia is one of the countries with egg production activities with an average of 5.16 million tons [1].

Poultry egg production in Indonesia is relatively high, with production increasing from year to year. Poultry eggs are a food that is popular with Indonesian people. Apart from being able to be processed into various kinds of food, eggs are also relatively cheap. With this, eggs can be consumed by all groups, both by small children and adults. Most of the poultry eggs produced in Indonesia come from chickens, ducks and quail.

Consumption of chicken eggs increases every day, causing the shells of chicken eggs to be wasted to also increase. Shells from chicken eggs that have been thrown away will become waste for the environment. Egg shell waste that is simply thrown away by people around the environment can cause the surrounding environment to become polluted and unhealthy. Many food traders in street food areas just throw away egg shell waste without processing it further, because they feel it is not useful.

Egg shells have a high nutrient content, namely 97% [2]. This high calcium content is known as a calcium carbonate compound which is very good as a raw material for making POC and can increase the pH of soil and water media. Broiler chicken eggshell waste also contains $CaCO_3$ of 97%, 3% phosphorus, 3% magnesium, sodium, potassium, zinc, manganese, iron and copper [3]. The egg shell has several layer structures, the transparent protein that covers the surface of the egg shell is the cuticle which is the first layer of the egg shell, the foam layer which is the largest component in the egg shell is the second layer. In the second layer there are proteins, potassium carbonate, calcium phosphate, magnesium carbonate, and magnesium phosphate which is a layer of lime. The third layer, namely the mammary, is the thinnest layer and consists of woven proteins and minerals. The fourth layer is the innermost layer of the membrane [4].

There is a lot of egg production in Indonesia, but the amount of egg shell waste is increasing, apart from polluting the environment and causing an unpleasant odor, egg shell waste also contains Coliform fecal bacteria [5]. This bacteria is found in egg shells attached to poultry feces, therefore efforts are needed to reduce egg shell waste, one of which is taking the calcium nitrate $(Ca(NO)_3)_2$ contained in egg shells, calcium nitrate can be used to make NPK fertilizer, as an additive in making concrete and for waste water treatment plants, apart from that, crafts from egg shells also have high value when marketed.

The use of egg shells as calcium nitrate has several benefits, namely, firstly, the production of calcium nitrate can reduce dependence on imported raw materials and has the potential to save the country's foreign exchange. Second, the function of calcium nitrate itself, for example as fertilizer, can increase agricultural yields and overall plant productivity. Third, egg shell waste can be used to make valuable materials, thereby reducing negative impacts on the environment.

This research aims to study the effect of variations in egg shell types on the process of making calcium nitrate ($Ca(NO_3)_2$). Eggshells from different types of eggs have different chemical compositions, and understanding these differences can provide valuable insight into waste processing and calcium nitrate production.

2.2 Methodology

2.2.1 Raw Material Preparation.

The egg shells used in this research were the egg shells of free-range chicken, broiler chicken, duck and quail eggs which had been used as waste. Before use, the egg shell samples are washed and cleaned. After that, the egg shells are soaked using 5% NaClO which aims to remove impurities and pathogenic bacteria that stick to the egg shells, then oven the egg shells overnight to

remove the water content in the shells egg. The dried egg shells are mortared until they become powder.

2.2.2 Research Methods.

The formation of calcium nitrate from egg shells was carried out using the lime method by reacting egg shell powder with HNO_3 4N through a heating process. Nitric acid is used to destroy egg shells and remove organic material to obtain calcium minerals. The reaction between egg shells and nitric acid will produce CO_2 gas. Next, the egg shells that have gone through the heating process are filtered to obtain the filtrate and residue. The filtrate obtained is then concentrated in a fume cupboard until calcium nitrate crystals form. The crystals were desiccated overnight to remove steam from the calcium nitrate crystals.

2.2.3 Calcium Nitrate Analysis

The calcium nitrate formed was tested qualitatively and quantitatively. Qualitative tests for calcium nitrate were carried out using turbidy meter. Qualitative tests of potassium nitrate products were carried out using sodium carbonate (Na_2CO_3), oxalic acid ($C_2H_2O_4$), and sodium sulfate (Na_2SO_4). Each of these solutions is mixed into a calcium nitrate solution which is made by diluting 1 gram of calcium nitrate crystals with 50 mL distilled water. Meanwhile, the quantitative test was carried out by titrating the calcium nitrate solution using 0.01 M EDTA ISO 3238:1975 solution.

3. Results and Discussion

3.1 Formation of Calcium Nitrate

The lime method in the process of forming calcium nitrate is carried out by reacting eggshells containing calcium carbonate with HNO_3 4M as much as 100 mL. This method is carried out by reacting the calcium carbonate lime found in egg shells with nitric acid. In the formation of calcium nitrate, the reaction that occurs follows equation (1):

$$CaCO_{3(s)} + 2HNO_{3(l)} \rightarrow Ca(NO_3)_{2(s)} + H_2O_{(l)} + CO_{2(g)}\ [6] \quad (1)$$

From this reaction, calcium nitrate ($Ca(NO_3)_2$) that is formed is still mixed with residue in the form of water (H_2O). This residue can be removed by evaporation process while CO_2 gas some will evaporate and some will dissolve in water. After dissolving it with nitric acid, the solution is then filtered with filter paper and left to stand. Then continue concentrating until a white precipitate forms. After that, leave it overnight in a desiccator until calcium nitrate powder is obtained. The yield results obtained are as follows:

Table 1. Yield and Conversion Data

No	Shell Type	Yield (gram of result/grams of sample)	Conversion (%)
1	Free-range chicken eggs	1.67	64.55
2	Broiler chicken eggs	1.84	88.55
3	Quail eggs	1.15	89.95
4	Duck eggs	1.93	89.00

From the table above it can be seen that the largest conversion value obtained was for the quail shell sample, namely 89.95% grams with a yield weight of 1.15 grams. The significant difference in conversion results lies in the free-range chicken egg shell sample, which produces the smallest conversion value, namely 64.55%. This is because at the calcium nitrate preparation stage the egg shell samples used were still dirty, the large amount of mucus contained on the surface of the egg shells caused the resulting conversion to be small, besides that the

structure of the free-range chicken egg shell samples was thinner compared to the structure of the egg shell samples used other [7].

3.2 Qualitative Test

The calcium nitrate powder that has been synthesized is each tested qualitatively using a turbidity meter which aims to measure turbidity (quantified in Nephelometric Turbidity Units, NTU) [8]. Where in this test a calcium nitrate solution is used which is then reacted with a sodium carbonate solution (Na_2CO_3), oxalic acid ($C_2H_2O_4$), and sodium sulfate (Na_2SO_4).

This qualitative test was carried out by taking 1 gram of calcium nitrate then dissolving it in 50 mL of distilled water. After that, take 10 mL of calcium nitrate solution 3 times and place it in 3 test tubes (A, B, C). After that, take 10 mL of Na_2CO_3 then put it in test tube A, take 10 mL of solution $C_2H_2O_4$ and put it in test tube B, and take 10 mL of Na_2SO_4 solution and put it in test tube C. Observe the changes that occur in each test tube and measure the turbidity value. From the qualitative tests above, the turbidity values for each sample are obtained which are presented in the following table:

Table 2. Turbidity Values from Free-range Chicken Egg Shell Samples

Sample	Observation	Turbidity Value (Ntu)
Solution O	Clear yellowish	183.3
Solution A	Cloudy white, little sediment	272.2
Solution B	White, lots of sediment	272.2
Solution C	Clear	5.6

Table 3. Turbidity Values from Broiler Chicken Egg Shell Samples

Sample	Observation	Turbidity Value (Ntu)
Solution O	Cloudy clear	10.8
Solution A	Cloudy white, little sediment	272.1
Solution B	White, lots of sediment	272.1
Solution C	Clear	0

Table 4. Turbidity Values from Quail Egg Shell Samples

Sample	Observation	Turbidity Value (Ntu)
Solution O	Cloudy clear	66.2
Solution A	Cloudy white, little sediment	103.5
Solution B	White, lots of sediment	103.6
Solution C	Clear	0

Table 5. Turbidity Values from Duck Egg Shell Samples

Sample	Observation	Turbidity Value (Ntu)
Solution O	Cloudy clear	0
Solution A	Cloudy white, little sediment	272.1
Solution B	White, lots of sediment	272.1
Solution C	Clear	0

Based on the table above, it can be seen that the calcium content contained in several shell samples after being reacted with sodium carbonate, oxalic acid and sodium sulfate changes the color of the solution, which means the samples contain calcium. When mixing calcium nitrate

solution with sodium carbonate solution, the reaction that occurs follows equation (2):

$$Ca(NO_3)_{2(l)} + Na_2CO_{3(s)} \rightarrow CaCO_{3(s)} + 2NaNO_{3(aq)} \quad (2)$$

When mixing a calcium nitrate solution with an oxalic acid solution, the reaction that occurs follows equation (3):

$$Ca(NO_3)_{2(l)} + Na_2C_2O_{4(s)} \rightarrow CaCO_{3(s)} + 2NaNO_{3(aq)} \quad (3)$$

When mixing calcium nitrate solution with sodium sulfate solution, the reaction that occurs follows equation (4):

$$Ca(NO_3)_{2(l)} + Na_2SO_{4(s)} \rightarrow 2NaNO_{3(s)} + CaSO_{4(l)} \quad (4)$$

3.3 Quantitative Test

The quantitative test for calcium nitrate is carried out by titration using EDTA solution. EDTA is a substance that can be used to form complex compounds. This salt will form a complex with a number of metal ions in solution [9]. Therefore, titration using this salt can be used to determine Ca levels in egg shells. Every use of the titration method always uses an indicator. The indicators used in this analysis are *Eriochrome Black T* (EBT). The use of EBT in a sample solution containing calcium will show a change in the colour of the sample solution to pink at a pH of 10.

This quantitative test was carried out by taking 25 mL of calcium nitrate sample solution, adding 250 mg of NaCN, measuring the pH at 10 ± 0.1, adding 2-3 drops of buffer solution, and adding one end of a spoonful of EBT indicator. After that, it is titrated with EDTA solution until the colour changes from pink to light blue. This can also indicate that all the calcium in the sample has become complex. This titration process was carried out 3 times. The following is data from calculating the percentage of calcium levels in each type of egg shell sample.

Table 6. Calcium Nitrate Percentage Result Data

Egg Type	Calcium Levels (%)
Free-range Chicken	16.50
Broiler Chicken	24.79
Quail	28.34
Duck	2.83

From the table above, it can be seen that the highest percentage of calcium levels is found in quail egg shell samples, namely 28.3%. This is influenced by the fact that the membrane in quail egg shells is thinner than chicken and duck egg shells [10].

Calcium Nitrate precursors from egg shells (Free-range Chicken, Broiler Chicken, Quail and Duck) have been successfully synthesized. Calcium Nitrate precursor can be reacted with Nickel Sulfate ($NiSO_4$), Cobalt Sulfate ($CoSO_4$) or Manganese Sulfate ($MnSO_4$) to produce Nickel Nitrate ($Ni(NO_3)_2$), Cobalt Nitrate ($Co(NO_3)_2$) or Manganese Nitrate ($Mn(NO_3)_2$), the reaction can be seen in equation (5-7). Where this material can be applied as a raw material for making lithium ion batteries such as NMC, which is usually used in the sol gel, combustion, spray pyrolysis methods [11].

$$NiSO_{4\ (aq)} + Ca(NO_3)_{2\ (aq)} \rightarrow Ni(NO_3)_{2\ (aq)} + CaSO_{4\ (s)} \quad (5)$$

$$CoSO_{4\ (aq)} + Ca(NO_3)_{2\ (aq)} \rightarrow Co(NO_3)_{2\ (aq)} + CaSO_{4\ (s)} \quad (6)$$

$$Mn(SO_4)_{(aq)} + Ca(NO_3)_{2\ (aq)} \rightarrow Mn(NO_3)_{2\ (aq)} + CaSO_{4\ (s)} \quad (7)$$

4. Conclusion

The yield results obtained from the calcination process in this research are as follows:

Table 7. Calcium Nitrate Percentage Result Data

Egg Type	Calcium Levels (%)
Free-range Chicken	16.50
Broiler Chicken	24.79
Quail	28.34
Duck	2.83

Based on the results obtained, it can be concluded that quail egg shells have the highest calcium content compared to other egg shell samples, namely 28.3% and have the highest conversion compared to other egg shells, namely 89.95%. In this research, the method used is the lime method using a leaching process. In the preparation stages, such as cleaning, drying and crushing the egg shells, it can influence the yield results.

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Author Contributions

Chofifah Indar Parawangsyah, Khaerul Anwar, Nadiyah Zalfa, Sri Tria Rahmawati carried out the experiment. Enni Apriliyani and Khikmah Nur Rikhy Stulasti wrote the manuscript with support Soraya Ulfa Muzayanha. The final report was committed by all contributors.

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