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DEVELOPMENT OF HIGH-CALCIUM CHICKEN NUGGETS FORTIFIED WITH VARIOUS CITRIC ACID - EXTRACTED CHICKEN EGGSHELLS POWDER

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***Abstract**. Chicken nuggets are ready-to-eat frozen processed meat products that are ground, steamed, molded, coated, frozen, and fried. Because chicken nuggets have a low calcium content, it must be done with the addition of chicken eggshells powder. Chicken eggshells powder contains natural calcium in the form of calcium carbonate. The current study aims to develop nuggets fortified with citric acid- extracted chicken eggshells powder. The purpose of this research was to determine the effect of fortified calcium citrate from chicken eggshells powder on the physicochemical properties of nuggets. This study used a completely randomized design with 6 treatment levels of chicken eggshells addition: 0%, 1%, 2%, 3%, 4% and 5%, replicated 3 times, so and 18 experimental units. Parameters observed were physico-chemical properties; moisture content, pH, protein and calcium content. The results showed that the citric acid extracted eggshell powder had a significant effect on moisture content, pH, protein content and calcium content of chicken nuggets. The best treatment was the addition of 3% eggshell powder with moisture content of 58.83%, pH value of 6.49, protein 17.23%, and calcium content of 129.99 mg/100g. It is recommended that further research can be conducted to investigate the effect of adding shell calcium on the quality and shelf-life of chicken nuggets during storage with various packaging and temperatures.*

***Keywords:** eggshells powder; calcium; citric acid; fortification; chicken nugget,*

1. Introduction

Eggs are used extensively around the world, and food industries produce thousands of tonnes of discarded chicken eggshells, which pose a severe threat to the environment by complicating trash disposal and increasing pollution. Therefore, efforts to study and commercialize calcium-fortified foods have begun in order to improve the daily recommended intake of calcium for humans, which is now close to 1000 mg (National Institutes of Health, 2020). Calcium from a variety of sources, including calcium phosphate, calcium carbonate, calcium from dairy products, and cattle bone meal, is used to fortify foods (Ray *et al*., 2017; Holkem *et al*., 2017; Trindade & Grosso, 2000; Kobus-Cisowska *et al*., 2020). Currently, the most popular food type for calcium fortification is cereal. Unfortunately, anti-nutritional elements like phytic acid, which can inhibit calcium absorption in the intestine and result in calcium insufficiency, prevent the bioavailability of the calcium found in cereals and many other food products (Aditya *et al*., 2021; Das Lala *et al*., 2021; Kobus-Cisowska *et al*., 2020; Waheed *et al*., 2019).

A nugget is an example of a food item that satisfies these criteria. Nuggets are a type of

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processed meat that is made to keep its quality over time by grinding, seasoning, shaping in specific molds, steaming, wrapping in flour, sprinkling in breadcrumbs, parboiling, and then freezing. (Aditya *et al.,* 2021). They can also be cooked to perfection (fried return) to meet customer demands.

Chicken eggshells are the most significant source of calcium and have considerable commercial potential as a dietary supplement. In order to increase the calcium content of products, chicken eggshells can be utilized as a powder that is added during production. They can also be converted into calcium supplement tablets (Gaonkar & Chakraborty, 2017; Aditya *et al*., 2021; Das Lala *et al*., 2021; Umesh *et al*., 2021). Previously, researchers used chicken eggshell powder as a calcium fortification in foods such as soy milk (Safitri *et al*., 2014), cookies (Rahmawati & Nisa, 2015), wet noodles (Asviani & Ninsix, 2017), cheese sticks (Miranti *et al*., 2019), karasi cakes (Ardin *et al*., 2019). It has been demonstrated that adding chicken eggshells to culinary goods increases their calcium content.

Higher calcium will result from the use of citric acid solvent in the production of chicken eggshells because the acid solution causes the shell pores to open, making it easier for the solvent to enter the gaps created and effectively release chemicals that bind to calcium Holkem *et al.* (2017). The findings of Santoso *et al.* (2015), which shown that citric acid was able to raise calcium levels in mondol stingray bone gelatin, lend further credence to this.

According to Lamadiko *et al*. (2018), acid solvents also contribute to the softening of the shells to make them easier to treat. Citric acid will react with calcium carbonate in chicken eggshells to create calcium citrate, which has a higher level of solubility and bioavailability (Paula *et al*., 2014). Therefore, the aim of this research was to investigate the inclusion of chicken eggshell, which was created by soaking chicken nuggets in citric acid, in order to produce high-calcium chicken nuggets with favorable physico-chemical properties.

2. Methods

2.1. Materials

The materials used in this study were chicken eggshells, citric acid, HNO_3, $HClO_4$, selenium, H_2SO_4, NaOH, bromocresol green 0.2% and methyl red 0.1%, as indicators, boiling stone, filter paper, buffer solution, distilled water, chicken meat, wheat flour, panir flour, shallots, garlic, salt, pepper, chicken eggs, margarine and cooking oil. The equipment used in this study included analytical balances, distillation apparatus, oven, ICP-OES (Inductively Coupled Plasma – Optical Emission Spectrometry) Model of the equipment (Merk, spec)

2.2. Experimental design

The experimental design used was a complete randomized design (CRD) with the addition of chicken eggshell powder to the total weight of the material used, each consisting of 6 levels with 3 replications. In this study, the treatments were: P0: Without any addition of chicken eggshell powder as a control, P1: 1% of chicken eggshell powder P2: 2% of chicken eggshell powder, P3: 3% of chicken eggshell powder, P4: 4% of chicken eggshell powder and P5: 5% of chicken eggshell powder respectively.

2.3. Preparations of chicken eggshell powder

Chicken eggshells that have been collected were cleaned with running water and the eggshell membranes were discarded. Then the chicken eggshells were boiled at 100°C for 15 minutes to killing pathogenic bacteria in the chicken shells and dried under the sun light for 3 days. Furthermore, citric acid was used to soak eggshells with a concentration of 0.75%, a shell : solvent ratio of 1:2 (w/v), at 60°C for 3 hours. The dried chicken shells were ground using a hummer mill and sieved with a 120 mesh-sieve to produce eggshell powder. Then the eggshells were cleaned, drained and then dried using an oven at 50°C for 3 hours

2.4. Preparations of chicken nugget

After removing the bones, the chicken breast meat was weighed at 300g and ground in a food processor. It was smoothed out and combined with 17 g of eggs, 15 g of flour, 5 g of garlic, 5 g of shallots, 5 g of salt, 3 g of pepper, and previously prepared shell powder in accordance with the treatment. The dough was pressed uniformly into a baking sheet that has been greased with margarine, steamed in a hot steamer (100°C) for 25 minutes, then removed and allowed to cool. After being molded to a size of 2 x 3 x 1 cm, the cold dough was dipped in flour, egg white, and breadcrumbs until smooth. Then the dough was pre-fried with an oil heated to temperature of 180°C for 15 seconds, then the chicken nuggets were removed and allowed to cool. Furthermore, the chicken nuggets were stored in the freezer at -18°C. Then the nuggets were fried until cooked at a temperature of 150°C for 2 minutes in a state of deep frying.

2.5. Determination of Moisture content

The oven method was used to assess moisture content according AOAC methods (AOAC, 2005). The cup was first heated to 105 °C in the oven for 1 hour, then cooled in a desiccator for 15 minutes, and finally weighed with an analytical balance (W_0). After the sample has been weighed at a maximum of 2 g (W_1), it was placed in a cup and heated to 105 °C in the oven for 4 hours. After being baked, samples were weighed after spending 15 minutes in the desiccator.

The sample was then placed back in the oven for a further 30 minutes in order to achieve a constant weight (W_2). The sample's moisture content is determined using the formula (1).

$$\text{Moisture content (\%)} = \left(\frac{W_1 - W_2}{W_1 - W_0}\right) \times 100\% \quad (1)$$

Where: W_0 = The empty cup's weight (g)

W_1 = The empty cup's weight + sample before drying (g)

W_2 = The empty cup's weight + dried sample (g)

2.6. Determination of pH

10 g of chicken nugget samples were weighed, mashed, and combined with 10 ml of distilled water, then well mixed. This procedure was done in order to determine the pH level of the nuggets. To calibrate the pH meter, a buffer with a pH of 7 was first added. The electrode's tip was dipped into a homogenous solution containing the nugget sample in order to take measurements. The figures displayed on the pH meter screen are used to calculate pH.

2.7. Determination of Protein content

The three phases of destruction, distillation, and titration are used in the AOAC (2005) method for protein content analysis. The nugget sample, weighing 0.3 g, was first placed in the destruction flask. 5 mL of concentrated H_2SO_4 were poured to a tube containing a grain of selenium. A heating device was then used to warm the tube in a fume closet until the color of the concentrated black fluid turns clear.

The clear solution was chilled before being mixed with 20 ml of 40% NaOH and 90 mL of distilled water. In an Erlenmeyer with 25 mL of 0.3N H_2SO_4 and 3 drops of mixed indicator (0.2% bromocresol green and 0.1% methyl red), the distillation results were obtained. 100 mL of filtrate, the product of the distillation, are ready. Then, the 0.3N NaOH in the burette was used to titrate the Erlenmeyer flask holding the filtrate. Iterations of the solution were made till the pink color turned Tosca green. To determine how much protein was in the nuggets using the formula (2).

$$\%\ \text{Crude protein} = \frac{(Vb - Va) \text{ x Normality NaOH x } 0{,}014 \text{ x } 6{,}25}{A} \text{ x } 100\% \qquad (2)$$

Where A : weigh of sample (mg)

Vb: standard volume (mL)

Va : Sample volume (mL)

2.8. Determination of Calcium content

Wet ash was used to remove the samples, which were weighed at up to 5 g each and placed in an Erlenmeyer, for the analysis of the calcium levels in chicken nuggets using ICP-OES (Inductively Coupled Plasma - Optical Emission Spectrometry (Apriyantono *et al*., 1989). Nitric acid (HNO_3) and perchloric acid ($HClO_4$) were then added in a concentrated solution, which was left to stand for 12 hours. The solution is then heated for 4 hours at 100-180 °C until it turns yellow or colorless. Finally, the solution was chilled and allowed to cool completely. Distilled water was added then, the mixture was heated for 15 minutes to boiling, and then it was allowed to cool. The solution was then filtered using 42 Whatman paper, dissolved till the 50 mL volumetric flask was labeled, and read by ICP-OES.

3. Results and Discussion

3.1. Physicochemical characteristics

Physicochemical elements play a significant role in defining the quality of food since they have an impact on handling, durability, and quality standards. They are also crucial in determining how long food goods will stay fresh on the market. Table 1 shows the average value of physicochemical characteristics of chicken nuggets with eggshell powder extracted using citric acid.

Table 1. The average value of physicochemical characteristics of calcium fortified chicken nuggets.

Eggshell Powder (%)	Moisture content (%)± SD*	pH± SD*	Protein (%)± SD*
0	59.91 ± 0.73^{cd}	6.34 ± 0.03^{a}	22.21 ± 1.77^{d}
1	59.58 ± 0.25^{cd}	6.40 ± 0.02^{ab}	20.77 ± 1.37^{bcd}
2	59.35 ± 0.80^{bcd}	6.47 ± 0.06^{c}	18.40 ± 2.60^{bcd}
3	58.83 ± 0.68^{bc}	6.49 ± 0.04^{cd}	17.23 ± 1.80^{abc}
4	58.24 ± 1.06^{ab}	6.55 ± 0.03^{de}	15.22 ± 2.82^{ab}
5	57.38 ± 0.40^{a}	6.57 ± 0.04^{e}	12.88 ± 1.82^{a}

Note: According to the DNMRT test and the standard deviation at various concentrations of adding, these numbers followed by lowercase letters were not significantly different at the 5% level.

According to Table 1, based on the analysis of the moisture content of chicken nuggets, the amount of citric acid added to eggshell powder throughout the production process has a direct correlation with how much water is in each batch of nuggets produced. This is because adding eggshell powder, which is high in calcium, will reduce wheat flour's ability to hold water (Abidin *et al*., 2016). The larger quantity of chicken shell powder reduces the amount of water in the nugget dough, resulting in nuggets with a lower water content. This study is similar to recent studies by Asviani & Ninsix (2017) who discovered that shell powder possesses properties that prevent it from absorbing water. As a result, adding eggshell powder to wet noodles will reduce the amount of water in the finished noodles. According to Syadeto*et al*., (2017), the calcium Ca^{2+} particles in tilapia bone meal will bind to OH^- particles, from water components (H_2O), and reduce the moisture content of cookies. The water compound's H^+ bond is broken during this reaction, making it weaker and more susceptible to evaporation during the pre-frying procedure. As a result, the moisture content of the resultant nuggets is decreased.

Based on the data, Table 1 indicated the pH in average of chicken nuggets and it was demonstrated that the pH increased with the quantity of citric acid added in the soaked shell flour. This was due to the slightly acidic properties of shell powder soaked in citric acid; hence, the more the quantity of shell flour, the higher the pH of the final nuggets. This study was supported by Khalida (2018) research who found that the presence of calcium carbonate, which will ionize in water to form Ca^{2+} and Ca^{3+} ions, is the cause of the higher pH value of guava jelly sweets. The presence of calcium carbonate ($CaCO^3$) in water (H_2O) will react to produce ($Ca(OH)^2$) and carbon dioxide, according to Hanafi *et al*., (2016). (CO_2). In order to produce chicken nuggets that include alkaline calcium, the Ca^{2+} element reacts with OH^- to form alkaline calcium hydroxide $Ca(OH)^2$, while carbon dioxide (CO_2) is released as a gas into the atmosphere. The quantity of OH^- ions released into solution increases with the amount of Ca^{2+} components in the nuggets, raising the pH of the finished chicken nuggets.

According to the protein content analysis results shown in Table 1, the amount of citric acid added to eggshell during the production of chicken nugget products affects the amount of protein obtained. Chicken eggshell has a relatively low protein content of 5.04%, according to Ray *et al*. (2017). Lower protein levels in chicken nuggets will result with the incorporation of a higher percentage of eggshell powder; It was assumed that it was caused by a protein-calcium reaction. According to Lesmana *et al*. (2008), Calcium acts as a cation that interacts with the carboxyl groups of proteins to form powerful bonds known as calcium bridges. According to a study by Manab *et al*., (2017) a strong protein calcium salt bridge can make a protein resistant to high temperatures. The protein content of the chicken nuggets decreases because the cross-links between calcium and protein prevent the protein from being broken down into simple forms during the cooking process.

3.2. Calcium content

In the body, calcium plays a critical role in the development of bones and teeth and helps to prevent osteoporosis. Table 2 shows the typical calcium content in chicken nuggets with the addition of eggshell powder soaked in citric acid.

Table 2. Average value for the calcium content of chicken

Chicken Eggshell Powder (%)	Calcium content (mg/100g) ± SD*
0	8.17 ± 0.45
1	68.23 ± 1.25
2	109.89 ± 0.75
3	129.99 ± 2.56
4	200.96 ± 5.85
5	255.51 ± 1.15

Note: **SD*** =Standard Deviation

It could be seen that the calcium content of the nuggets increased with the proportion of eggshell added. Chicken nuggets without the addition of citric acid-soaked eggshell powder displayed the lowest value of calcium content as much as 8.17 mg/100g, while nuggets with the addition of 5 displayed the highest calcium content of 255.51 mg/100g.

Since chicken eggshells are mostly composed of calcium carbonate ($CaCO_3$), which accounts for 94% of their composition (Wulandari, 2018), adding eggshell powder into nuggets can raise the amount of calcium in the final product. This study was supported by the findings of Qolis *et al.* (2020), who found that eggshell crackers had increased calcium contents when the more shell flour was added to the recipe.

This study's increase in calcium content was more than that of Merta *et al.* (2020), which found that adding 20% eggshell powder to the production of nuggets resulted in calcium content of just 33.34 mg/100g. As a result, eggshell powder produced by soaking citric acid has a higher calcium content than without soaking. According to Yonata *et al.* (2017), this is due to the acid solution opening the shell pores,making it easier for the solvent to access the gaps created and enable the optimal release of chemicals that bind to calcium.

The body requires 1000 mg of calcium per day, according to the Republic of Indonesia's Minister of Health's Regulation No. 28 of 2019 regarding the suggested nutritional adequacy rate for Indonesians. Consuming 100 g of nuggets with the addition of eggshell powder that has been soaked in 5% citric acid can satisfy 25.55 percent of the body's calcium requirements while still staying under the acceptable nutritional adequacy rate. Food products' calcium concentration has a significant impact on their organoleptic quality, according to Lesmana *et al.* (2008). The nugget will have a gritty texture depending on how much calcium it contains.

4. Conclusions

Based on the physic-chemical properties of chicken nuggets with the addition of eggshell powder soaked in citric acid, it had a significant effect on the product properties of moisture content, pH, protein and calcium content. The best proportion for adding eggshell powder was 3%, with moisture content of 58.83%, a pH of 6.49, a protein content of 17.23%, and a calcium content of 129.99 mg/100g.

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