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Utilization of Shrimp Shell Waste for Glucosamine

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ABSTRACT

This article aims to examine the manufacture of glucosamine from shrimp shells as an effort to utilize waste from the shrimp freezing industry. Based on the literature study, information was obtained that the manufacture of glycosami can be carried out through chemical hydrolysis, enzymatic hydrolysis and pressurized hydrolysis methods. The stages of the process of making glycosamine are 1) shrimp shell is converted into chitin then further processed into glycosamine or 2) shrimp shell is converted into chitin, chitin becomes chitosan then further processed into glycosamine.

Keywords : Hydrolysis, method, enzymatic, chemical, chitosan.

INTRODUCTION

Based on FAO (2016), world shrimp export activities are carried out in the form of 80-90% frozen shrimp without heads and skins (peeled). Waste generated from the production of shrimp processing including heads, skins, tails, and legs produces about 35-50% of the initial weight (Swastawati et al., 2008). Meanwhile, in 2020 the Ministry of Maritime Affairs and Fisheries reported that in Indonesia, the unutilized solid waste of shrimp crustaceans was 56,200 metric tons per year. From the large amount of waste produced, it will gradually accumulate in the environment in very abundant quantities, if it is not processed further it will become a source of contaminants or a place for bacteria to live so that it can pollute the environment.

According to Marganov (2003), shrimp shells contain 25-40% protein, 45-50% calcium carbonate, and 15-20% chitin, but the amount of these components depends on the type of shrimp and where they live. The amount of protein content in shrimp shells is large enough so that it has the potential to be used as glucosamine. This article aims to examine the manufacture of glucosamine from shrimp shells as an effort to utilize waste from the shrimp freezing industry.

Glucosamine

According to Anderson et al. (2005), Glucosamine is a compound that is naturally found in the body, especially in connective tissue and cartilage tissue. Glucosamine can even be found in almost all soft tissues in the human body, but the highest concentration is in cartilage. Glucosamine is produced from the hydrolysis of chitin, which produces glucosamine which is an amine sugar, chitin is a copolymer of N-acetyl-D-glucosamine and glucosamine (Miller, 2011). Glucosamine is found in various forms such as glucosamine sulfate, hydrochloride, N-acetylglucosamine or chlorohydrate salts, and dextraoratory isomers (Persiani et al., 2005).

Glucosamine has a very important role for joint health and flexibility (EFSA, 2009). Because the body produces synovial fluid which functions as a lubricant for cartilage. Therefore, this material has an important role in the field of joint health and flexibility. In this aspect, the consumption of glucosamine hydrochloride and sulfate types has an influence on joint pain (Kulkarni et.al, 2012). According to Anderson et al. 2005, in connective tissue and cartilage Glucosamine has been shown to stimulate cartilage production and inhibit changes in bone metabolism in patients with osteoarthritis (Towheed et al. 2005; Clegg et al. 2006).

Glucosamine Production Method

According to Ernawati (2012), there are two methods in producing glucosamine, including chemical hydrolysis and pressurized hydrolysis. The hydrolysis of chitosan into glucosamine can be carried out by several methods including chemical hydrolysis, enzymatic, fermentation, and various mixtures of these methods (Cahyono et. al., 2014).

a. **Chemical Hydrolysis Method**

According to Ernawati (2012), the chemical hydrolysis method has a fairly complicated procedure, using relatively expensive chemicals with a high hazard in the direct stirring process. The process requires strong alkali solution with high concentration, high temperature, and long time. In addition, the chemicals used can pollute the environment. Meanwhile, the advantages of chemical hydrolysis are that the materials needed tend to be easier to obtain, the production of glucosamine is relatively fast, and the production can be carried out on a large scale. (Dutta et al., 2004).

a. **Enzymatic Hydrolysis Method**

Enzymatic production of glucosamine is more environmentally friendly, but has limitations on enzyme stability and the cost of enzyme extraction is quite expensive (Dutta et al., 2004).

a. **Pressure Hydrolysis Method**

While the pressurized hydrolysis method has a high level of safety, the production process is easy to do, does not require a long time and affordable production costs.(Ernawati, 2012). The pressurized hydrolysis method is commonly referred to as the autoclave method because it uses an autoclave. The pressurized hydrolysis method is a working system that combines the functions of pressure and acid. Pressure plays an important role in the process of cutting polymer bonds into smaller units. Acid solution or HCl plays a role in the formation of bonds with the amine group–NH2 after the acetyl group –COCH3 is cut (Ernawati, 2012).

Glucosamine Production Stages

The production of glucosamine hydrochloride from chitin is carried out after the deacetylation and depolymerization process followed by hydrolysis by immersion in hydrochloride solution to become glucosamine hydroloride (Mojarrad et al., 2007). According to Ernawati (2012), glucosamine hydrochloride from chitin is insoluble in water, which means that chitin has not been hydrolyzed to glucosamine, while glucosamine hydrochloride from chitosan is completely soluble in water.

The process of making glucosamine using the pressurized hydrolysis method, based on the method used by Afridiana (2011) with modifications. Parameters tested in this phase I study include testing the yield of glucosamine (AOAC, 2005), solubility test (Ernawati, 2012), water content analysis (AOAC, 2005). 2007), protein content (Bradford, 1976), and ash content (AOAC, 2007) and analysis of the degree of chitin deacetylation using FT-IR (Kasai, 2008 and Khan et al. 2012) and Glucosamine Hydrochloride content using a SpectrophotomUV-Vis etri. The process of stage II Padap process stage II is carried out based on the best treatment stage I. The process is carried out the same as the stage I process, which begins with processing tiger prawn shells (Penaeus monodon) into chitin which will then be hydrolyzed using the best concentration of the stage I process and continued with the manufacture of glucosamine. The parameters tested in this phase II study include testing the yield of glucosamine (AOAC, 2005), solubility test (Ernawati, 2012), pH (SNI, 2004).

a. Stage 1, the process of making chitin

Stage 1 in the manufacture of chitin from shrimp shell waste are as follows:

1. Wash the skin and head of the shrimp thoroughly
2. Dry in the sun for 2 days
3. Puree with a dry blender
4. Shrimp shell and head flour Added and mixed with 1.0 M HCl solution (pa) at a ratio of 1:10 (w/v)
5. Heated at 75°C for 2 hours and stirred Washed with distilled water to neutral pH Dryed in an oven at 80°C for 24 hours
6. Cooled, weighed and added 3.5% NaOH solution (pa) with a ratio of 1:10 (w/v) Heated at 80°C for 2 hours and stirred
7. Washed with distilled water to neutral pH, and dried in an oven at 80°C for 24 hours

b. Stage 2, Glucosamine manufacturing process

After the chitin is extracted, the next step is to hydrolyze glucosamine from chitin. The process includes the following:

1. Chitin added with HCl concentration 23, 30, or 37%, stirred for 4 hours at a temperature of 90±5°C
2. Centrifuged at 4000 rpm for 15 minutes
3. The precipitate was washed with ethanol solution. Centrifuged at 4000 rpm for 15 minutes. The precipitate was dried in an oven at 40°C for 4 hours. Glucosamine hydrochloride

Segmentation of Glucosamine in the Market

Glucosamine can be found, both in offline stores (pharmacies, etc.), as well as online stores (amazon, Shopee, Tokopedia, Lazada, and other online shop platforms), in the form of supplements for joints. But unfortunately almost all products from glucosamine have a relatively high price, so they still have not reached the market widely. Here are some examples of Glucosamine products from shrimp shell waste that are sold in the market, and online shops:

a. Doctor Best Glucosamine Chondroitin

Figure 1. Glucosamine Products, Doctor Best Glucosamine
Source: tokopedia.com

Doctor best Glucosamine Chondroitin is a glucosamine product from shrimp shells sold in the market, has a price range of IDR 255,000 –595,000. depending on the store that sells the product. Suggested Use i.e. Adult Use Take 2 capsules daily with food, or as recommended by a nutritionally-informed physician. For other ingredients contained in this product, namely, Gelatin (capsule), microcrystalline cellulose, magnesium stearate (vegetable source), silicon dioxide. Contains clams (crab shells and prawns).

b. Nutrilite, Glucosamine With Boswellia

Figure 2. Glucosamine Products, Nutrilite
Source: tokopedia.com

Nutrilite Glucosamine with Boswellia is a glucosamine product from shrimp shells sold in the market, with a price range of IDR 255,000 –475,000. depending on the store that sells the product. The recommended consumption of Nutrilite Glucosamine is 1 capsule 3 times a day. The ingredients of these products include Glucosamine HCI from shrimp shells, boswellia herbs, acerola cherry concentrate, citrus bioflavonoids. Nutrilite Glucosamine with boswellia has several benefits including, Anti-inflammatory (inflammation), helps normal function of connective tissue, joint structure.

Glucosamine Quality Based on Various Research

Based on research conducted by Hardoko et al 2018, that the 4-hour hydrolysis treatment with a technical HCl concentration of 37% was chosen as the best stage I treatment in the production of glucosamine-HCl. The use of technical HCl at a concentration of 37% resulted in glucosamine HCl levels of 7511.46 mg/kg. At a technical HCl concentration of 37%, a temperature of 80°C and a duration of hydrolysis of chitin in tiger prawn shells for 4 hours, the highest glucosamine was produced, which reached 10519.79 mg/kg with a solubility of 89.65%, pH 3.82, and a reddish yellow color.

Based on research by Zaeni et al 2017, using the conventional pressure hydrolysis method (hotplate) resulted in FTIR which showed glucosamine hydrochloride produced by microwave was similar to that produced from a hotplate for 90 minutes. Based on the research of Meata et al 2019 with the acid hydrolysis process of shrimp shell chitosan accompanied by ultrasonication can produce glucosamine hydrochloride with relatively high yields. With a hydrolysis temperature of 80 °C and an ultrasonication time of 40 minutes, the yield is 0.13±0.67%.

Uses of Glucosamine Products

Glucosamine in the body produces synovial fluid which functions as a lubricant for cartilage. Therefore, this material has an important role in the field of joint health and flexibility. In this aspect, the consumption of glucosamine hydrochloride and sulfate types has an effect on joint pain (Kulkarni et.al, 2012). According to Anderson et al. 2005, in connective tissue and cartilage Glucosamine has been shown to stimulate cartilage production and inhibit changes in bone metabolism in patients with osteoarthritis (Towheed et al. 2005; Clegg et al. 2006).

Conclusion

Based on the literature study, information was obtained that the manufacture of glycosami can be carried out through chemical hydrolysis, enzymatic hydrolysis and pressurized hydrolysis methods. The stages of the process of making glycosamine are 1) shrimp shell is converted into chitin then further processed into glycosamine or 2) shrimp shell is converted into chitin, chitin becomes chitosan then further processed into glycosamine.

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