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ARTICLE REVIEW: UTILIZATION OF SHRIMP SKIN FOR CHITOSAN

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Abstract

This paper aims to describe the manufacture of chitosan from shrimp shells and its use. Chitosan is a natural product, which is a derivative of the polysaccharide chitin. Chitosan has the chemical name poly D-glucosamine (β (1-4) 2-amino-2-deoxy-D-glucose), a white amorphous solid form of chitosan with a fixed crystal structure from the initial form of pure chitin. Chitosan can be extracted by several methods, namely by chemical methods and biological methods (proteolytic enzymes). To produce chitosan, several processes are needed, namely demineralization (removal of minerals), deproteinization (removal of protein), and deacetylation. Chitosan is widely used in industries such as the food industry as a coating for fruits to inhibit respiration, purifying fruit juices, as a source of fiber and antimicrobial compounds.

Key words: *Chitin, extraction, deproteination, deacetylation, demineralization*

Introduction

Shrimp shells have low economic value. Shrimp shells, if thrown away, will be hydrolyzed and produce a foul odor and increase the BOD (Biological Oxygen Demand) of water so that it can damage water quality (Cahyaningrum *et al.* 2008). Shrimp shell is one of the potential sources to be used in the manufacture of chitin and chitosan, which is a biopolymer that has commercial potential in the industrial sector. Shrimp shell contains 25-40% protein, 40-50% calcium carbonate, and 20-36.61% chitin, but the amount of these components depends on the type of shrimp and where they live. Chemically, chitin is a polymer of β-(1,4)-2-acetamide-2-deoxy-D-glucose which cannot be digested by mammals (Nurhikmawati 2014).

Chitosan can be used in various fields of biochemistry, medicine or pharmacology, food and nutrition, agriculture, microbiology, wastewater treatment, paper industries, membrane or film textiles, cosmetics, and so on (Suhardi 1992). Chitosan can be extracted by several methods, namely by chemical methods and biological methods (proteolytic enzymes). This paper aims to describe the use of shrimp shells for the manufacture of chitosan. In shrimp shells, chitin exists as a mucopolysaccharide bonded with inorganic salts, especially calcium carbonate ($CaCO_3$), proteins, and lipids including pigments. Therefore, obtaining chitin from shrimp shells involves the processes of protein separation (deproteination) and mineral separation (demineralization). Meanwhile, to get chitosan, it is followed by a deacetylation process (Krissetiana 2004).

The potential of the waste generated by the shrimp processing business is very promising. Therefore, this paper aims to describe the manufacture of chitosan from shrimp shells and its use.

Shrimp Processing Industry Waste

Shrimp in Indonesia are generally exported in frozen form abroad after removing the head, tail, and skin. Shrimp, as one of the export commodities, is divided into three types, namely (1) products consisting of the body and head as a whole, (2) the body without the head, and (3) the meat only (Abun 2009). If this fresh shrimp is processed into frozen shrimp, then 35%-70% of the whole weight will be shrimp waste in the form of heads, tails, and shells.

Waste from the shrimp processing industry contains an important and very useful element when processed, namely, chitin, which is further processed will produce chitosan which will be useful in various industries, for example as a food preservative (substitute for borax and formalin), waste treatment, slimming drugs and cosmetics, and so forth. Chitosan has an active group that can bind to microbes so that chitosan is able to suppress microbial growth. Developed countries such as Japan and the United States have been produced chitosan industrially.

Utilization of Shrimp Skin Waste

So far, shrimp shell waste in Indonesia has not been used optimally, because it is only used as an ingredient for shrimp paste, shrimp crackers, and shrimp shell flour. Shrimp shells can be used to produce chitin, chitosan, and glucosamine, which are widely used in various fields and certainly have a much better-added value.

Chitosan is widely used in various fields, namely nutrition (cholesterol-lowering, weight loss, fiber source), food (nutritional, flavor preservatives), biomedicine (bone pain, burns, anti-tumor, osteoarthritis, AIDS inhibitors), cosmetics (treatment of hair, moisturizing creams, and lotions) and the environmental field (liquid waste treatment) (Hanafi *et al.* 2000).

Chitosan

Chitosan is a natural product, which is a derivative of the polysaccharide chitin. Chitosan has the chemical name poly D-glucosamine (β (1-4) 2-amino-2-deoxy-D-glucose), a white amorphous solid form of chitosan with a fixed crystal structure from the initial form of pure chitin. If chitosan is stored for a long time in an open state (contact with air), decomposition will occur, the color will become yellowish and the viscosity of the solution will decrease (Krissetiana 2004).

Chitosan Making Process

Chitosan is one of the biomedically important polymers. demineralization, deproteinization, and deacetylation are the main steps to develop various forms of chitosan. Demineralization consists of the removal of minerals, mainly the disintegration of CaCO3 (calcium carbonate) into water-soluble calcium salts, and is usually carried out by acid treatment, whereas dilute hydrochloric acid is the most preferred acid among other mineral and organic acids.

To isolate chitin from crustacean shells, chemical processes for demineralization and deproteinization were applied using strong acids and bases to remove calcium carbonate and protein, respectively. In simple terms, the production process of chitosan using chemicals is by extracting chitin from crustacean shells by milling the shells to obtain crustacean shell flour, then chemical demineralization is carried out to remove minerals contained in crustacean shell flour, then chemical deproteination of demineralized material is carried out. After the chitin substance was obtained in this way, it was then deacetylated using NaOH, the residue from the deacetylation was then washed with distilled water until the pH was neutral and then dried at 45 °C overnight to obtain chitosan (Affes *et al.* 2019).

The chitosan deacetylation process can be carried out by chemical or enzymatic methods. Chemical processes use bases, such as NaOH, and can produce chitosan with a high degree of acetylation, reaching 85-93% (Tsigos *et al.* 2000). However, the chemical process produces chitosan with various molecular weights and its deacetylation is also very random (Tsigos *et al.* 2000), so that the physical and chemical properties of chitosan are not uniform. In addition, chemical processes can also cause environmental pollution, are difficult to control and involve many side reactions that can reduce yields (Tokuyasu *et al.* 1997). Enzymatic processes can cover the shortcomings of chemical processes. Basically, enzymatic deacetylation is selective and does not damage the chitosan chain structure, thus producing chitosan with more uniform characteristics in order to expand its application (Tokuyasu *et al.* 1997).

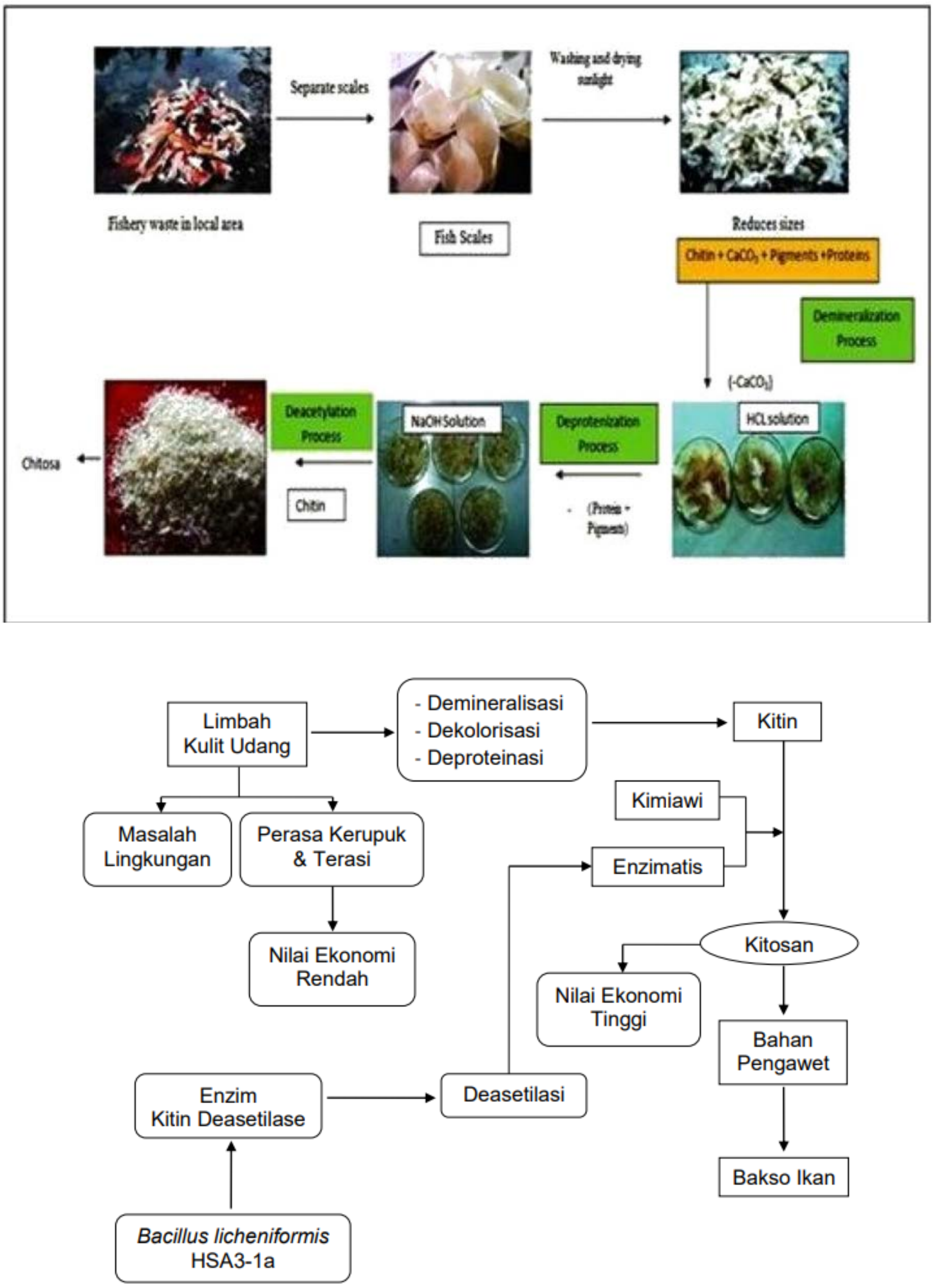

Figure 1. Chitosan Production Process (Source: Kumari *et al.* 2015)

However, the use of chemicals can cause partial deacetylation of chitin and hydrolysis of polymers resulting in inconsistent final physiological properties. The hydrolyzed protein components also become useless during the removal of this chemical protein. In addition, chemical treatment brings dangerous environmental problems such as wastewater disposal which makes this process ecologically aggressive and a source of pollution.

The use of proteolytic microorganisms or proteolytic enzymes can be used as an alternative to extract chitosan. That is by means of chitin obtained after deproteinization of shrimp shell waste and then deacetylated with enzymes from proteolytic microorganisms.

Chitosan Characteristics

Chitosan that has been produced is characterized by following the quality standard of SNI No. 7949 (2013) in Kusmiati and Nurhayati (2020), which includes chitosan color, moisture content, ash content, nitrogen content, and degree of deacetylation.

Table 1. Characteristics of Chitosan (Source: Kusmiati and Nurhayati 2020)

Parameter	SNI (No. 7949, Tahun 2013)
Warna	Coklat muda sampai putih
Kadar Air	≤12 %
Kadar Abu	≤ 5 %
Kadar Nitrogen Total	≤ 5 %
Derajat Deasetilasi	≥75 %

Potential and Utilization of Chitosan

Chitosan was found to be non-toxic, biodegradable, environmentally friendly, and reported by several researchers to have strong antimicrobial and antifungal activity (Aider 2010). Chitosan has been widely used in industry, for example, in the food industry as a coating for fruits to inhibit respiration, purification of fruit juices, a source of fiber, and antimicrobial compounds (Ghaout *et al.* 1992) Chitosan is a compound that has many benefits, so the biosynthesis of chitosan is a very important thing.

Chitosan Economic Value

The price of chitosan in the world market is around US$ 7.5/10g for chitosan with good standards. Currently, 90% of the world's chitosan market is controlled by Japan with the production of more than 100 million tons annually (Iason *et al.* 2000). Meanwhile, according to Triastiningrum and Purnomo (2016), the selling price of commercial chitosan in the market is Rp. 540,000.00/kg.

Conclusion

Chitosan is a natural product, which is a derivative of the polysaccharide chitin. Chitosan has the chemical name poly D-glucosamine (β (1-4) 2-amino-2-deoxy-D-glucose), a white amorphous solid form of chitosan with a fixed crystal structure from the initial form of pure chitin. Chitosan can be extracted by several methods, namely by chemical methods and biological methods (proteolytic enzymes). To produce chitosan, several processes are needed, namely demineralization (removal of minerals), deproteinization (removal of protein), and deacetylation. Chitosan is widely used in industries such as the food industry as a coating for fruits to inhibit respiration, purifying fruit juices, as a source of fiber and antimicrobial compounds.

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