UTILIZATION OF SHRIMP SHELLS FOR NON-FOOD PRODUCTS

Junianto[1], Adhiestyrahma Syakira Davy[2], Nur Aini Azhar Firdaus[2], Paramita Yuniazahra[2], Wulan Yulianti[2], Ami Damayanti[2] and Anisa Dwi Putri [2]

1) Lecturer staff of the department of Perikanan_ Padjadjaran University
2) Students of Fisheries Study Program – Padjadjaran University

ABSTRACT

This article aims to review the use of shrimp shells into non-food products. Based on the results of literature studies, information was obtained that shrimp shells, industrial waste from freezing and canning shrimp can be utilized into value-added products. The product is chitosan, which is deproteined, deminerasylated and acetylated shrimp shells. The chitosan produced can be used as raw materials in non-food products, namely filtration membranes, biopepticides, drug delivery materials in biomedicine and hand body cream.

Keywords: chitosan, biopeptide, membrane filtration, body cream, added value.

INTRODUCTION

Shrimp shell waste in Indonesia comes from processing plants, namely shrimp freezing and canning plants. These factories produce waste in the form of heads, skins, tails and legs with a percentage of about 35%- 50% of the weight of shrimp.

Shrimp exports that are increasing every year have resulted in a large amount of shrimp shell waste in Indonesia. Like waste in general, shrimp skin waste also has a negative impact if it is not used. The negative impact is polluting the environment, causing unpleasant odors.

Shrimp shells contain protein (25%-40%), chitin (15%-20%) and calcium carbonate (45%-50%). Through the right technological approach, this potential waste can be further processed into chitin [(C8H13NO5)n]. This chitin can be further processed into chitosan [(C6H11NO4)n] and glucosamine (C6H13NO5). These three products have biodegradable properties and do not have toxic properties so they are very friendly to the environment.

Chitosan is widely used in various fields, namely the field of nutrition (lowering cholesterol levels, weight, fiber sources), food (nutritional, flavor preservatives), biomedicine (bone pain, burns, anti-tumor, osteoarthritis, AIDS inhibitors), cosmetics (hair care, *moisturizing creams and lotions) and* in the environmental field (cain waste treatment). Glucosamine, which is a monomer of chitosan, also functions in the pharmaceutical field, namely to overcome rheumatic diseases, is a fairly vital component in the mobility and flexibility of bone preparations.

This shrimp shell waste needs to be utilized optimally. This is important in order to reduce environmental pollution due to the unpleasant odor caused by unused shrimp shells. In addition, this is also important because it can educate the public about the potential use of waste and can provide new business opportunities for the community by recycling it into a new, more useful product. This article aims to review the use of shrimp shells into non-food products.

Some of the uses of shrimp skin into non-food products are a) shrimp skin as raw material for ultrafiltration membranes b) shrimp skin as raw material for biopesticides c) shrimp skin as raw material for introducing drugs in biomedicine or pharmaceuticals. d) shrimp skin as raw material in making *hand body cream* and e) shrimp skin as raw material for making bioplastics.

Shrimp shells in order to be used as raw materials for the products mentioned above, it needs to be converted into chitosan. The process of converting shrimp shells into chitosan consists of the stages of deproteination, deminerasilization and deacetylation. The deproteination stage takes place as follows: The shrimp skin is mashed and then soaked in a 3.5% NaOH solution at 65° C for 120 minutes. After that, the shrimp shells are washed with water or aqueous to a neutral pH. Then the proteinized shrimp shells are dried in the oven at 65 ° C for 24 hours. The next stage is demineralization. Deproteinized shrimp shells are soaked in a 4% HCL solution, stirred and heated with an electric stove to a temperature of 30° C for 60 minutes. After that, the demineralized shrimp shells are washed with aquades to a neutral pH, and dried in the oven at 65 ° C for 24 hours, then chitin is obtained. The next stage is the deacetylation of chitin to become chitosan. Chitin is soaked in a 50% NaOH solution for 4 hours at 100° C while stirring. After that, the solid material, namely chitosan, is washed with aquaades to a neutral pH, then dried in the oven and chitosan is obtained. Chitosan is ground to obtain chitosan in the form of a fine powder.

The yield of chitosan is determined based on the percentage of the weight of chitosan produced against the weight of the raw material of shrimp shells before processing. Based on the results of the research of Setha *et al.* In 2019, chitosan amendments were obtained in the range of 5.12- 5.63%. . The amendments obtained from the research of Zahiruddin *et al.* (2008) ranged from 13.89%- 17.55%. The yield of chitosan is influenced by the concentration of chemical compounds used and the duration and temperature of the extraction process.

The quality of chitosan from shrimp shells can be seen from several parameters, one of which is ash content. Ash content is a parameter to determine the minerals contained in a material that characterizes the success of the demineralization process carried out. Low ash content indicates a low mineral content. The lower the ash content produced, the higher the quality and purity of chitosan. The results of the analysis of ash content from chitosan resulted from the research of Zahiruddin *et al.* (2008) ranged from 0.17%-0.31%. This shows that the chitosan produced has met the quality standards of chitosan ash content set by Protan Biopolymers, which is < 2%.

Apart from ash content, water content is also one of the parameters that are very important for determining the quality of chitosan. Protan Biopolymers set the quality standard for chitosan moisture content to be ≤10% (Bastaman 1989). The results of the analysis of the water content of chitosan produced are known that the water content of chitosan ranges from 8.91%-11.14%.

Next there is a nitrogen level, the nitrogen level determines the chitosan properties that interact with other groups. The presence of other compounds in chitosan including the form of the amine group (NH2) causes chitosan to have a fairly high chemical reactivity, so that chitosan is able to bind water and dissolve in acetic acid (Benjakula and Sophanodora 1993). According to Protan Biopolymer the quality standard of chitosan nitrogen content that has been set is ≤5%. The results of the analysis of chitosan nitrogen levels from shrimp shells from several studies have met the established standards. The resulting nitrogen content has a range between 3.16%-5.36%.

The next parameter there is a degree of deacetylation that indicates the percentage of the acetyl group that can be removed from chitin so that chitosan is produced. A high degree of deacetylation indicates that the acetyl group contained in chitosan is low. The less the acetyl group in chitosan, the stronger the interaction between ions and hydrogen bonds from chitosan. The results showed that in general the degree of deacetylation of shrimp skin chitosan is between 73.73%-84.61%. The quality standard for the degree of deacetylation of chitosan set by Protan Biopolymers is ≥70%.

CHITOSAN FOR ULTRAFILTRATION MEMBRANE MATERIALS

Ultrafiltration is a process of filtration or filtration through a membrane whose pore size ranges from 0.001–0.02 μm. This method is commonly used to separate colloids, reduce the concentration, purification and fractionation of macromolecules such as proteins, dyestuffs and other polymeric materials.

Membrane technology using the ultrafiltration method has good prospects in the field of food processing. Ultrafiltration is widely used in various processes and industries, including wastewater treatment, food industry and biotechnology sectors. In recent times ultrafiltration is widely used for bio-macromolecules, including proteins such as recombinant therapy and industrial enzymes.

Ultrafiltration membranes that are often used in water treatment processes are membranes made of cellulose acetate, polysulfone and polyacrylonitrile, which are quite expensive. Therefore, an alternative raw material is needed that is relatively easy and cheap by utilizing other waste as membranes. Chitosan on shrimp shells can be used as a membrane with the addition of acetic acid and other variations of composition.

The manufacturing process of ultrafiltration membranes made from chitosan raw materials is as follows: Chitosan powder is dissolved with acetic acid and poured in molds. After forming a layer of wet film the mold is ventilated until the film becomes dry. To remove the film from the mold, a 4% NaOH solution is required, the dry membrane that is still on the mold is immersed in the NaOH solution until the membrane is detached from the mold. Next, the membrane is cleaned with aquadest by rinsing. Once it becomes a membrane, make sure that the membrane has dried completely.

The advantages of chitosan as an ultrafiltration membrane material are that it is easy to obtain, affordable, not dissolved in water but able to bind water, is anti-bacterial, not carcinogenic, able to absorb metal elements and is easily decomposed or degraded properly. According to Setiawan *et al*. (2015), the higher the chitosan concentration, the smaller the membrane pore size, this can happen because the higher the chitosan concentration level, the denser the particle density level which results in the smaller membrane pore size so that the performance of this ultrafiltration process is better.

CHITOSAN FOR BIOPESTICIDES

Biopesticides are biochemical pesticides composed of natural, non-toxic compounds used to control Plant Disruptive Organisms. Besides being non-toxic, biopesticides are natural pesticides that are also friendly or safe to the environment. Commonly used definitions of biopesticides are those from the U.S. *Environmental Protection Agency* (USEPA). Biopesticides are defined as pesticides of natural origin composed of animals, plants, bacteria, and minerals. Biopesticides also include living organisms that can control Agricultural Crop Disruptive Organisms (Mishra *et al*. 2015).

The use of chitosan in agriculture is that it can be used as a natural biopesticide to protect plants from bacterial and fungal attacks and as a coating material on various plant seeds. In addition, chitosan can also act as a source of carbon for microbes in the soil, accelerating the process of transforming organic compounds into inorganic compounds and helping the root system in plants to absorb more nutrients from the soil. From various studies, chitosan has been shown to inhibit the growth of *in vitro* fungi from many pathogenic fungi, for example, *Botrytis cinerea*, *Alternaria alternata*, *Colletotrichum gloeosporioides* and *Rhizopus stolonifer*.

Chitosan can act as a carrier and protective agent of other antimicrobial compounds such as essential oils. Essential oils have shown antimicrobial activity but are highly volatile. The incorporation of chitosan as a coating can ensure better resistance to the active material on the surface and maintain a high concentration of active molecules.

Several studies have shown the effectiveness of chitosan in protecting plants from biotic stress by direct and/or indirect action. So it can be concluded that chitosan has many possible applications in agriculture with the aim of reducing or replacing chemical pesticides that damage the environment.

The process of making biopesticides using chitosan is as follows: Chitosan is mixed with water and then stirred. After that it is sprayed on the target plant.

Chitosan as a biopestide has the advantage that it can act as a carrier and protective agent for antimicrobial compounds. The incorporation of chitosan as a coating can ensure better resistance to the active material on the surface and maintain a high concentration of active molecules. Several studies have shown the effectiveness of chitosan in protecting plants from biotic stress by direct and/or indirect action.

CHITOSAN FOR DRUG DELIVERY MATERIALS IN BIOMEDICINE

The drug delivery system, especially through the lungs (pulmonary drug delivery system), is one of the appropriate drug *delivery alternatives*. This delivery system is considered to be able to deliver drugs well so that their bioavailability can reach 100% because the drug does not experience the first cross-metabolism in the liver. One of the promising drugs to be administered through this lung route is *diltiazem hydrochloride*. In addition to good delivery, a relatively thinner barrier and high vascularity that envelops part of the lungs make the drug easily absorbed and enter the systemic circulation (Paranjpe and Goymann 2014). In this conduction system, chitosan microparticles are used as the conducting material.

Chitosan as a drug delivery material is carried out by making chitosan microparticles. Chitosan microparticles can be performed by evaporation of solvents, dry spray and ionic gelation.

This method of evaporation of solvents has been widely used to create microparticles. Some variables that can affect the characteristics of the microparticles produced include the solubility and morphology of the active substance, the type of solvent used, temperature, composition and viscosity of the polymer and *drug loading* (Muhaimin 2013).

The manufacture of chitosan microparticles by this solvent evaporation technique is carried out in a solution medium as a mobile phase. A coating material is dispersed into a volatile solution and does not mix with its mobile phase. While the core material to be encapsulated is dispersed into a polymer solution as a coating material. The mixture of core materials and coating materials is then agitated in the mobile phase solution to produce microparticles (Sahil *et al.* 2011).

The *spray drying* technique is practically carried out by dispersing the core material into the coating material, then the mixture is atomized through pipes into a stream of hot air that provides latent heat of evaporation (Muhaimin 2013). An advantage of this technique is that either water-soluble or water-insoluble compounds can be introduced into particles.

He *et al.* (1999) has made microparticles from both cross-spliced and non-cross-spliced chitosan materials as a conductor for cimetidine, famotidine and nizatidine. From his research, the results of spherical particles with particle sizes varying between 4 – 5 μm for chitosan that are not cross-spliced and sizes of 2 – 10 μm for cross-spliced chitosan. The particle size will increase when the spray flow rate is increased by increasing the nozzle size and will decrease at a higher air flow rate.

The ionic gelation method is a commonly used method because the process is simple, does not use organic solvents and can be easily controlled for the formulation of microparticles or nanoparticles using polysaccharide polymers. The particle formation process occurs due to complexation due to different charges between polysaccharides and counter ions so that they undergo ionic gelation and precipitation to form spherical particles.

In acidic solutions, the –NH2 group of chitosan (polysaccharide) will be protonated to NH3+ and interact with gelation agents with different charges. A gelation agent that is often used is *tripolyphosphate* (TPP) which results in an interaction between the positive charge of the protonation group in chitosan and the negative charge of TPP to form a complex with sizes in the nanoparticle range.

In the process of introducing the drug into chitosan microparticles, it is divided into two ways depending on the solubility properties of the drug. The process is as follows;

1. For water-soluble drugs, the drug entry process is carried out by *incorporation (incorporation*) where the drug is added during the manufacture of microparticles, in this case the drug is introduced into a chitosan solution mixed until homogeneous, then the microparticles are made by a predetermined method.
2. For drugs that are insoluble in water, the drug entry process is carried out by *incubation (incubation*) where the drug is introduced into microparticles after the microparticles are formed by soaking the microparticles into a drug-saturated solution (Agnihotri *et al.* 2004).

In terms of pharmaceutics and biomedicine, chitosan microparticle systems can provide several advantages and disadvantages. The advantages of microparticles include (Dubey *et al.* 2009; Park *et al.* 2002 in Cahyaningrum 2014) : a. Covering up the unpleasant taste and smell. b. Protects the drug against environmental influences c. Reduce the particle size to increase the solubility of drugs that are difficult to dissolve. d. Produce slow-release and controlled release products and drugs with targeted release. e. Protects toxic compounds. f. Improving powder flow rate

CHITOSAN IN THE MANUFACTURE OF HAND BODY CREAM

Hand & body lotion is a cosmetic whose use is applied to the skin of the hands and body. The benefits of the content contained in *hand & body lotion* are to soften, brighten and protect the skin from sun exposure. The use of natural ingredients is still very rarely used for the manufacture of cosmetic products, so its use is used only for a few purposes. Chitosan has properties as an adsorbent that can be used as an exogenous antioxidant ingredient. Chitosan compounds can be combined with other hydrocolloid compounds obtained from natural materials such as *Spirulina* sp.

Hand body cream or *lotion* is an emulsion preparation whose application is topical on a daily scale. The emulsion used on the skin can be oil in water or water in oil (Allen *et al.* 2014). The consistency of *hand body cream* or *lotion* in the form of a liquid that allows its use evenly and does not take long when applied to the skin. The characteristics of a good hand body cream are that it has values in accordance with national standards, including having a homogeneous appearance; pH value between 4.5-8.0; viscosity between 2,000-5,000 cPs; and has a maximum total plate number value of 102 . *Hand body creams* or *lotions* generally use anti-bacterial ingredients for their products as preservatives. The use of anti-bacterial ingredients that are widely used is BHT (*Butylated hydroxytoluene*). In addition to anti-bacterial ingredients, BHT is also widely used as an antioxidant

Chitosan in the field of cosmetics has been applied as a humectant, thickening agent, stabilizer and moisturizer (Lang and Clausen 1989). According to Rinaudo (2006), chitosan has a moisturizing and softening effect on the skin**.**

The procedure for making hand body cream made from chitosan is as follows (Apriadi, 2004): Weigh chitosan (2g), Dissolve chitosan with 1% acetic acid with a ratio of 1:10 (w/v). Add aquades until they reach 100 mL. Homogenizing for 60 minutes. Aqueous phase material consisting of propylene glycol 2.5 g; triethanolamine 0.2 g; glycerin 3.5 g; 2% chitosan solution is added 1 mL; 25 ml of water is heated at 75°C and stirring is performed. Oil phase material consisting of 1.5 g of lanolin; olive oil 8.0 g; and 3.0 g of stearic acid was heated at 75°C and stirred was performed. Put the water phase material into the oil phase material slowly by stirring continuously until the dough is homogeneous. Stirring is stopped at 35°C and cooled until it reaches room temperature. After cooling, *hand body cream* is obtained.

The advantage of using chitosan as a raw material for *hand body cream* is in mixing manufacturing materials such as acetic acid, chitosan and 1% dissolved acetic acid. This is because chitosan is a weak base that is slightly soluble in water and organic solvents, but soluble in acidic solvents. The application of chitosan in the non-food field has been widely used. One of the reasons chitosan is widely used is because chitosan has antimicrobial properties (Helander 2001). In addition, chitosan is also used as a source of antioxidants. The antioxidant properties of chitosan are evidenced by the ability to reduce free radical activity by binding free radicals (Lin and Chou 2004).

CONCLUSION

Based on the results of literature studies, information was obtained that shrimp shells, industrial waste from freezing and canning shrimp can be utilized into value-added products. The product is chitosan, which is deproteined, deminerasylated and acetylated shrimp shells. The chitosan produced can be used as raw materials in non-food products, namely filtration membranes, biopeptides, drug delivery materials in biomedical and hand body creams.

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