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ARTICLE REVIEW OF FISH SKIN GELATIN

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ABSTRACT

The purpose of this review article is to examine the potential of fish skin as a raw material for gelatin production, the method of extracting gelatin from fish skin and the quality of fish skin gelatin from the results of research conducted in Indonesia and the application of gelatin. Based on a review of various articles and other literature, it can be concluded that Indonesia has a relatively large potential for fish skin as a raw material for gelatin. The stages of the method of making gelatin consist of immersion in an acid solution, extraction using water and finally drying. The quality of fish skin gelatin as a result of research conducted in Indonesia varies greatly depending on the type of fish skin and the method of extraction. Gelatin can be applied both for food and non-food products.

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INTRODUCTION

Gelatin can be said to be a protein obtained from the process of collagen hydrolysis from bone and skin materials of animals. Gelatin is one type of protein made from natural collagen found in the skin and bones of animals. Gelatin can be made from collagen-containing ingredients, such as skin, scales, and bones. Chen et al. (2016) states that collagen content in the skin and scales is higher than bones.

The benefits of gelatin are as diverse as being able to bind water, as a film shaper, having the ability to emulsify and make foam, as well as making it a versatile ingredient in the food, pharmaceutical, photography and cosmetic industries (Gomez- Guillen, Gimenez, Lopez-Caballero, &Montero, 2011). Hastuti and Sumpe (2007) stated that there are some advantages in the process of making gelatin made from fish skin such as faster process that is by soaking acid, while the manufacture of gelatin from hard raw materials such as bones and

scales have a longer process with alkaline soaking.

Indonesia always imports gelatin from China, Japan, France, Australia, India and other new countries. While the overall gelatin raw materials are imported, almost 90% is produced from raw materials of pig skin, cowhide and cow bones. Raw materials used from pig skin will cause conflict, especially for people in Indonesia because most of the people are Muslims. In addition, it will cause conflict also for hindus if they use raw materials from cattle to make gelatin (Gudmundsson 2002). Therefore, gelatin products are needed based on fish skin, because it will minimize the conflict that will be caused. The purpose of this review article is to study the potential of fish skin as a raw material for gelatin decay, gelatin extraction method from fish skin and quality of fish skin gelatin from research conducted in Indonesia as well as gelatin application.

POTENTIAL OF FISH SKIN AS GELATIN MATERIAL IN INDONESIA

The need for gelatin in Indonesia is increasing, which is more and more fulfilled than imports. The use of gelatin in Indonesia for food reached 63% and while the pharmaceutical field reached 30% and the rest for other needs. The advantages of using gelatin in an industry are usually to improve the power, texture, and stability, for example in the food industry namely meat products, gelatin is used to increase the binding power of water. According to Karim and Bhat (2008) arrange that the use of gelatin in the pharmaceutical field is usually used in the manufacture of hard capsule. For the field of cosmetics, gelatin is used as an emulsifier and softener material (smoothing agent*)* which is usually used in the form of creams and lotions and becomes the main ingredient "protein" in the manufacture of shampoos and "protein" hair conditioners. In the field of photographic film, gelatin can be used for fastening mediums and protective colloids for image-forming materials.

Parts of fish such as skin, fish bones, fish heads, and internal organs are usually left wasted and considered as waste that can pollute the environment when if studied more deeply the skin and bones of fish can be used as raw materials to make gelatin because it contains collagen. According to Agustin (2012) skin waste is composed of collagen which when hydrolyzed will produce gelatin. Other limbs such as skin, bones, and bubbles swimming fish if utilized properly will provide an advantage because it can be a fairly high selling point. The bones and skin of this fish is very potential as a source of raw materials for making gelatin because it covers 10-20% of the total body weight of the fish.

DEFINITION OF GELATIN

The term gelatin comes from the Latin word *gelatos* which means stiff, gelatin is a natural biopolymer or polymer that exists in nature which has a faintly dark or dull nature, can be translucent, colorless and odorless which is obtained from collagen fibrous protein from collagen animal products (Rehman *et al*. 2016). Gelatin is derived from partial hydrolysis of collagen. Hydrolysis can be carried out with either alkaline or acid collagen.

During hydrolysis, the cross-ties between the polypeptide chain bonds of the collagen are broken (Devi *et al*. 2016). Gelatin is also a polypeptide which has a high molecular weight and is an important hydrocolloid.

According to Wulandari (2019) hydrocolloid is a polymer component derived from animals, vegetables and microbes which generally have a hydroxyl group component, which can be found in animal and vegetable sources which are used as food additives to increase the quality and value of a product. The functions of hydroxylide are as emulsifier, adhesive, and gelling agent. Other hydrocolloids differ from gelatin hydrocolloids because most of their function as polysaccharides, while gelatin is a digestible protein containing all essential amino acids except tryptophan, there are two types of gelatin, Type A gelatin derived from acid processing and has an isoionic point of pH 7.9 to 4 and Type B are derived from alkalis with an isoionic point pH of 4.8 to 5.5 (Devi *et al*. 2016).

The use of gelatin is found in many facial and health care products, whether it is used in cosmetic products or in other products that use gelatin as a gelling agent in shampoos, hair sprays, air bubbles, bath salts, sunscreens, face creams, and lotions. In addition to health products, gelatin is also used for additives to food products that produce elasticity, stability and consistency and use in photography. Due to its functional, gelatin has increased interest in the industrial sector (Devi *et al*. 2016). According to Mariod (2013) gelatin can be produced from a variety of different collagen sources. Beef bones, fish and pork skin are the main commercial sources. In addition, the source of gelatin can come from:

1) Mammalian gelatin, which is derived from the constituent connective tissue and bones of vertebrates that can be studied from cows and pigs

2) Fish gelatin, derived from fish skin and bones, fish skin extraction is a step to reduce the main waste generated from the fish processing industry

3) Insect gelatin, which is the type of insect *Aspongopus viduatus* and *Aspongopus pubescens*. There are three types of extraction methods used to extract gelatin from *A. viduatus* and *A. pubescens*, mild acid and distilled water extraction methods, distilled water extraction methods and extraction with hot water, and only extraction with hot water.

GELATIN EXTRACTION METHOD

According to Rehman *et al.* (2016) the production principle of gelatin is to remove the disturbing parts and convert collagen that is insoluble in water into dissolved gelatin. The result of gelatin depends on parameters such as degree of acidity (pH), pressure, time and temperature. The general stages of gelatin production (Figure 1) according to Rehman *et al* (2016) are:

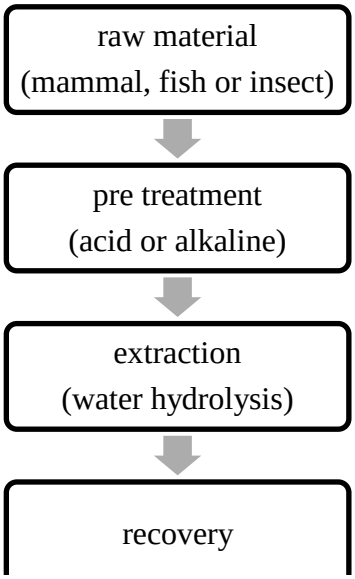

Figure 1. General stages of gelatin production

(Source: Rehman *et al*. 2016)

The raw material can be mammals, fish or insects. In the pretreatment raw materials are washed clean to remove contaminants, the bones are processed differently such as after washing, grinding and rewashing, the crushed bones are added to acid solution (4-7% HCl) for a minimum of two days. The sample is then treated with acids or alkalis to weaken the collagen framework by breaking the intramolecular cross-ties. The skin is treated with acids while bones are treated with alkalis. Gelatin produced using acids will produce Type A gelatin while those using alkalis will produce Type B gelatin. Citric acid is usually chosen as the most preferred acid because it does not smell like acetic acid and does not give color. After acid treatment, the samples were washed under running water and neutralized. Meanwhile, the bone alkaline treatment is demineralized and left in a liming vat for 20 days and can be extended up to 60 months (depending on the sample).

Furthermore, the extraction stage for samples treated with acid and alkaline, the extraction process using water with a controlled temperature ranging from 50-100^{o}C in this process will produce a water-soluble collagen arrangement or called dissolved gelatin. In the recovery and repair process, the gelatin solution obtained after extraction is clarified using a lamellar clarifier to remove particulate matter, and is filtered. The filtrate is then deionized using ion exchangers and concentrated to achieve a standard viscosity. The concentration is sterilized with plate heat exchangers and steam sterilizers. This sterilized gelatin is then cooled to form a gel that produces gelatin noodles by drying and crushing. So that in the end, we obtained powdered gelatin with a moisture content that varied from 8-12% (Haug *et al*. 2009 in Rehman 2016). According to Devi *et al*. 2016, making gelatin in a nutshell through an extraction process using a pretreatment of acid and alkaline extraction with distilled water and a drying process. Each extracted gelatin has different physicochemical characteristics.

GELATIN QUALITY

Gelatin production basically has to follow quality standards, in Indonesia based on the national standardization 01-3735-1995 (1995) (table 1). Basically, the color that is characteristic of gelatin is that it has no color and is dull to a yellowish color, water content is one of the factors that affect storage capacity because it is related to metabolic activity. The value of water content according to SNI (1995) is a maximum of 16%. The ash content to determine the purity of gelatin and the mineral content therein according to SNI (1995), the maximum gelatin ash content was 3.25%. Protein in food is used as a measure of nutrition that is beneficial to the body according to SNI (1995). The protein content contained in gelatin is expected to be 87.25% and the degree of acidity is an important parameter in the production of gelatin for the food and non-food industries. The degree of acidity is expected to be close to neutral (pH 7) because it will affect the application of the gelatin.

Table 1. Characteristics of gelatin

Characteristics	Terms
Color	Colorless to yellowish
Water content	Maximum 16 %
Ash content	Maximum 3.25 %
Protein	87,25%
Gel strength	50-300 bloom
pH	4.5-6.5

Source: BSN (1995)

CHARACTERISTICS OF GELATIN FROM FISH SKIN

The characteristics of gelatin in general are faintly dark or dull, can be translucent, colorless and flavorless obtained from fibrous protein collagen from collagen animal products (Rehman *et al.* 2016). Several studies have been conducted to determine the characteristics of gelatin, especially fish gelatin. Fish gelatin can be made from ingredients that contain collagen such as bones, skin and scales (Nurilamala 2017). The manufacture of fish-based gelatin, among others, has been carried out by Nurilmala *et al* (2017) using yellowfin tuna skin as a raw material for making fish skin gelatin, fish skin is an option because usually the skin is used as waste that has not been utilized properly and fish skin contains large amounts of collagen. The treatment was given to extract fish skin gelatin by giving different temperatures (55, 65 and 75 ^{o}C). This shows that the gelatin produced from this method has gel strength above the average commercial gelatin. The pH value of gelatin was not affected by the extraction temperature where the best extraction temperature was 75 ^{o}C.

Research conducted by Nasution *et al* (2018) on the characterization of gelatin from catfish skin using acid and alkaline extraction methods. In the acid extraction process, the raw material in the form of catfish skin is given sulfuric acid (pH 3) and soaked for 12 hours then dried at a temperature of 55^{o}C to produce solid gelatin which is then turned into gelatin powder. In the extraction process with alkaline, the fish skin was added with 0.8 N NaCl solution which was then added with a 0.2 N NaOH solution then dried and produced gelatin powder. The test results obtained the characteristics of the extracted catfish skin gelatin, namely the gelatin solution through an alkaline process produced a more cloudy color than the acidic process, catfish gelatin by acid-

ic method could not form gel because the collagen hydrolysis process that occurred resulted in shorter polypeptide chains. Meanwhile, the alkaline method forms a gel and has a gel strength value or also called Bloom with a moderate value (100-200 Bloom), the amino acid content in the acidic method is lower than the alkaline method. However, it can be concluded that the catfish skin gelatin has better characteristics with an alkaline method because it has a gel strength value.

Another research was conducted on catfish skin by Saputra *et al*. (2015) regarding the physical and chemical characteristics of catfish skin gelatin with a combination of various acids and temperatures, there were 3 acids that were treated, namely: acetic acid, citric acid and hydrochloric acid while the temperature treatment given there are 2: 45^{o}C and 55^{o}C. There are 2 categories of characteristic parameters observed, the first physical analysis includes result test, viscosity test and gel strength test, while chemical analysis is the test of acidity (pH), water content test, ash content, protein, fat and amino acid content.

The results obtained in catfish gelatin were that the result test had a significant effect on the temperature of 45^{o}C, the result value was greater so that the best treatment was the use of temperature of 45^{o}C while the type of acid had no significant effect. The viscosity test obtained between 2.03 - 4.13 the value meets SNI (1.5-7), the viscosity value depends on the use of temperature. The average gel strength ranges from 105.05-140.57 Bloom, this value is in accordance with SNI (50-300 Bloom). pH value the average pH measurement of catfish skin gelatin in this experiment ranged from 3.71 - 4.27. The moisture content obtained ranged from 9.09% - 10.74%. The water content value of the gelatin extracted from various types of acids and the treatment temperature was still within the range of SNI moisture content maximum of 16%, the gelatin ash content ranged from 0.52% - 1.24%, this value is still in the range of ash content permitted by SNI maximum of 3.23%. The protein content obtained was 82.06% - 87.55%, the highest protein content was obtained in 45 ^{o}C hydrochloric acid treatment and the lowest was at 55 ^{o}C citric acid. Fat content values for various types of acids and treatment temperatures ranged from 0.17% - 1.14%. The value of hydrochloric acid with a temperature of 45^{o}C shows the highest treatment result value compared to other treatment interactions (acetate or citrate), the use of different temperatures results in different amino acid values, the increase in temperature gets the smaller the amino acid concentration value.

Agustin *et al* (2015) conducted a research on tuna fish gelatin to determine the characteristics of good gelatin with differences in acetic acid concentrations. Research was based on the fact that tuna has waste in the form of skin, this has become an idea to use skin waste into gelatin which is expected to increase economic value and become an alternative raw material for gelatin that is safe and halal and reduce the dependence of industry in Indonesia on imported gelatin. Indonesia is mostly imported from Europe and America. The percentage of gelatin application in the food sector reaches 60% and 40% in non-food. Gelatin product in this research used acetic acid and research variables to determine its characteristics result, pH value and organoleptic test. The re-

sults obtained were that the concentration of acetic acid given 15% to the sample gave the most result and the resulting pH concentration was 4.5 and was still included in the standard acid pH range 4-7. Organoleptic characteristics obtained that the acid produced gelatin has a slightly coarse texture and is not uniform or irregular, colorless to yellowish and has no smell and taste.

Another research was conducted by Jaziri *et al* (2019) regarding the characteristics of chicken-chicken fish skin gelatin with pretreatment of citric acid concentrations. His research uses the asm-base method because it can provide better quality than thermal and enzymatic treatments. The objective of extracting gelatin with citric acid was to obtain the physicochemical properties of gelatin from chicken-chicken fish skin. The concentration of treatment given was different, the provision of citric acid 0.2 M, O, 4 M and 0.6 M. The characteristics seen were in the form of result percentage, viscosity value, gel strength, melting point, gel point, color, degree of acidity, level protein, moisture content, fat content, ash content and amino acids. The results obtained were the best result value in the 0.6 M treatment with a result of 8.83% indicating that the higher the concentration of the acid solution given, the higher the result percentage produced, this is because acidic compounds can make the gelatin structure easier to break down during the oxidation process due to the process hydrolysis that occurs. The pH value ranges from 5.48 to 5.81 and still meets the standards, in the viscosity measurement which aims to determine the viscosity level of gelatin, the best results are at the citric acid concentration of 0.2 M which is the highest.

The next parameter is the strength of the gel which indicates the ability of gelatin to form a gel, the best concentration is obtained at a concentration of 0.2 M citric acid, this indicates that the higher the concentration of citric acid used, the lower the strength of the gel. The melting point which is the temperature at which the gel melts ranges from 18.50 - 19, 28^{o}C. The gel point value ranges from 9.90 - 10.29 ^{o}C protein content ranged from 79.15 to 79.37% below the SNI (85-90%). The obtained moisture content ranged from 9.92-10.30%, according to SNI (max. 16%). The best fat content in the 0.6 M treatment indicates that the higher concentration of acid solution given, then the percentage of fat is getting lower, the lower fat content indicates the high quality of gelatin (max. 5%) and finally the ash content obtained ranges from 1.53 – 1.60% indicated that the gelatin ash content of the chicken fish met the SNI standard (max. 3.2%).

GELATIN APPLICATION

The growth of the fish processing industry in Indonesia is currently experiencing an increase, a kind of frozen fish fillet industry which creates processing waste in the form of fish bones. Until now, fish bones have only been used as animal feed, so that the economic value has only slightly increased, especially when fish bones are generally just thrown away. Based on this matter, there must be an effort to use fish bone waste to be something that is more useful, one of which is to digest fish bone waste into gelatin.

Fish bones and skin have great potential as an ingredient in agar because they cover 10% to 20% of the fish body weight. Fish skin consists of epidermis and dermis which are the two main layers. The dermis is a tissue that contains a lot of collagen and is very thick. The dermis is the main part of the skin needed for ingredients to make Gelatin, because this layer is mostly (about 80%) consisting of a network of collagen fibers formed by binding tissue. Fish skin contains 26.9% protein, 0.7% fat, 2.5% ash, and 69.6% water. Gelatin has a function that is still difficult to replace in the food and pharmaceutical industry. This is because gelatin is versatile, it can act as a filler, emulsifier, adhesive, sediment, and nutrient enhancer. It is also flexible and can form a thin elastic layer to form a transparent and strong layer. An important feature is its high digestibility (Hastuti and Sumpe, 2007).

Generally, gelatin products are used as a thickener and coagulant in food, usually elastic, emulsifier, stabilizer, foaming, avoiding syneresis, water binding, increasing consistency, thin coating, rich in nutrients, preservatives, etc. Non-food benefits include stabilizing lotions in shampoos, skin toners and protectors (creams), soaps (especially liquid emulsion), lipsticks, nail polish, shaving foam, sunscreens, face masks, etc.

The results of the study (Atma *et al*. 2018) regarding the physical and chemical characteristics of catfish bone gelatin extracted with pineapple waste were carried out in two stages, namely gelatin extraction and analysis of their physical and chemical properties. Gelatin extraction was divided into two stages, namely pretreatment and main extraction. In this study, some of the physical and chemical properties of fishbone gelatin can be compared with commercially available gelatin and other fish bone gelatin. The strength of the fishbone gelatin gel was extracted with pineapple residue 64.83 g bloom, hardness 4.96, cohesion 0.88, elasticity 1.03, elasticity 4.36, and elasticity 2.78. The viscosity and pH of the gelatin solution obtained were 3.17 cP and 4.52, respectively. The chemical properties of gelatin include water content of 8.59%, ash content of 0.95%, crude protein 47.60%, and fat of 7.71%. Some of the physical and chemical properties of fishbone gelatin in this study can be compared with other commercially available fishbone gelatin.

Based on the results of research (Hidayah *et al*. 2017) which discusses the physical and sensory characteristics of ice, to ensure the best recipe and to recognize the comparison of sensory features and microstructure of ice cream with the best recipe dumbo catfish bone gelatin with commercial ice cream. continues to be large, the gelati concentration of dumbo catfish bones, the overrun value continues to increase and the melting rate decreases, the accumulation of gelatin concentration does not affect the color, aroma and taste, but affects the texture and overall The best recipe for ice cream is with dumbo catfish bone gelatin 0 , 4% and 0, 5%.

Based on other research. The results showed that the addition of crusted gelatin to the characteristics of jelly candy was effective. The treatment method in this study was to add 14% gelatin on different scales (lac, milkfish and pickles) and repeated 3 times. The results showed that the difference between gelatin and fish scales was significant ($P < 0.05$), the highest gel strength value was 350 ± 5.50 g.cm2, the lowest water content

was 15.81 ± 0.17%, and the highest ash content. . 2.12 ± 0.10%, the lowest Aw value was 0.72 ± 0.11, the lowest pH value was 4.40 ± 0.08, and the hedonic value was in the interval 8.0 <μ <8.2. The addition of seaweed scales, gelatin, milkfish and fish curry had a significant effect on gel strength, moisture content, ash, Aw and pH test. The best jelly candy formula, with the addition of gelatin with the addition of curisi fish scales based on the hedonic test with formulation D, namely the addition of gelatin with curisi fish scales.

Research (Irash *et al* 2018) regarding the effect of gelatin accumulation from milkfish bones on the manufacture of jelly candy from rosella flowers, the results of the study can be said that the concentration of gelatin is one aspect, especially in gel making. The very low concentration of gelatin will cause the gel to become soft or even less likely to create gel. This matter was intertwined in the treatment of 10% and 12% gelatin concentrations, where no gel was created at all but only a thick solution was created. But on the accumulated gelatin concentration of 14% and 16% a soft gel was created. At 18% accumulated gelatin concentration, the gelatin accumulated was not very soft and not very hard, the elasticity of jelly candy at this concentration was preferred by panelists. In contrast to the accumulation of gelatin concentration of 20%, this accumulation obtained a hard gel, so the panelists did not like it. Thus, jelly candy that has a chewy texture that is not very hard can be said to be favored by the panelists. Gelatin from milkfish bones affects the water content, color, aroma, taste and texture of rosella jelly candy. Continue to be a lot of gelatin that is added until it becomes a lot of water content from the jelly candy and affects the color, aroma, taste, texture (chewiness) of the jelly candy. To obtain good quality for jelly candy from roselle flowers, an accumulation of gelatin concentration of 18% is required, where in this accumulation a water content of 8.76% is obtained and the thickness is favored by the panelists.

Based on the results of the study by Dewantoro *et al* (2019) the effect of gelatin accumulation. Tilapia agar is resistant to pineapple syrup, which includes pineapple syrup with different concentrations, stability, hedonic properties, color and pH value, respectively 0%, 3%, 5%, and 7%, each with 3 replications. Obtaining the results of the analysis of the raw material which proved that the gelatin concentration had a significant effect on the highest pH value of pineapple syrup with 7% gelatin concentration, which was significantly different from the pineapple syrup pH value of 0% and 3%. Increasing the concentration of gelatin added in the formulation of pineapple syrup causes the pH value to increase. This is related to the method used to make gelatin. Acidic processes tend to produce a low pH, whereas alkaline processes, will have a tendency to create a large pH. The pH value of the gelatin produced ranged from 3.82 - 5. This value still meets the gelatin standard, which is between 3.8 -5. Hijriah *et al* (2017), reported that the formation of an increase in pH with the increasing concentration of gelatin added could be due to the presence of a ratio of various gelatin concentrations. Continue to increase the concentration of gelatin added until the pH of the juice is about to increase. The trigger factor for sour taste is H+ ion, if the hydrogen ion concentration (acidity) increases until the pH is about to drop and vice

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versa.

CONCLUSION

Based on a review of various articles and other literature, it can be concluded that Indonesia has a relatively large potential for fish skin as a raw material for gelatin. The stages of the method of making gelatin consist of immersion in an acid solution, extraction using water and finally drying. The quality of fish skin gelatin as a result of research conducted in Indonesia varies greatly depending on the type of fish skin and the method of extraction. Gelatin can be applied both for food and non-food products.

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