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Utilization of Shrimp Skin Waste into Membrane Filtration

Isef Fahlendra[1], Doni Kusuma[2] & Sigit Baskoro[3]

[1]Isef Fahlendra, M.Si., [2]Doni Kusuma, M.Si. & [3]Sigit Baskoro, M.Si.
[1]Sakti Polytechnic, Surabaya
[2,3]Cakrawala College of Engineering, Surabaya
Indonesia

Abstract: *Indonesia is a maritime country that is rich in marine products, but utilization is less than the maximum. Waste from freezing shrimp varies, generally ranging between 30-75% of the weight of the shrimp depends on its type. The shrimp in the form of chitin (C8H13NO5) n is a natural polymer that can be found anywhere from the bark beetle up spider web, all that is around us ranging from plants and animals can be found chitin. Chitosan derivative of chitin by deacetylation process. Chitosan is a compound that is not soluble in water, strong alkaline solution, slightly soluble in HCl and HNO3 and H3 PO4, and does not dissolve in H2SO4. Chitosan is non-toxic, readily biodegradable. Chitin can be obtained from shrimp shells by deproteinasi and demineralization. chitin and chitosan can be used to mix some products, sewage treatment, antibiotics, dietary supplements, food, cosmetics, animal food supplements and can form a film / membrane or lens in the world of photography. The concentration of chitosan in this solvent is acetic acid with a variation of 40%, 30%, 20%, and variation of operating time of 60 minutes, 90 minutes, 120 minutes and the temperature variation of 30 0C, 79 0C, 99 0C. Comparisons between the raw material to the solvent acetic acid (ratio) is 1: 5 and 1:10. From the research results indicated that the high viscosity values obtained from the treatment of acetic acid concentration of 40%, the operating time for 60 minutes, and an operating temperature of 300C and the ratio of 1: 5. animal food supplements and can form a film / membrane or lens in the world of photography. The concentration of chitosan in this solvent is acetic acid with a variation of 40%, 30%, 20%, and variation of operating time of 60 minutes, 90 minutes, 120 minutes and the temperature variation of 30 0C, 79 0C, 99 0C. Comparisons between the raw material to the solvent acetic acid (ratio) is 1: 5 and 1:10. From the research results indicated that the high viscosity values obtained from the treatment of acetic acid concentration of 40%, the operating time for 60 minutes, and an operating temperature of 300C and the ratio of 1: 5. animal food supplements and can form a film / membrane or lens in the world of photography. The concentration of chitosan in this solvent is acetic acid with a variation of 40%, 30%, 20%, and variation of operating time of 60 minutes, 90 minutes, 120 minutes and the temperature variation of 30 0C, 79 0C, 99 0C. Comparisons between the raw material to the solvent acetic acid (ratio) is 1: 5 and 1:10. From the research results indicated that the high viscosity values obtained from the treatment of acetic acid concentration of 40%, the operating time for 60 minutes, and an operating temperature of 300C and the ratio of 1: 5. Comparisons between the raw material to the solvent acetic acid (ratio) is 1: 5 and 1:10. From the research results indicated that the high viscosity values obtained from the treatment of acetic acid concentration of 40%, the operating time for 60 minutes, and an operating temperature of 300C and the ratio of 1: 5. Comparisons between the raw material to the solvent acetic acid (ratio) is 1: 5 and 1:10. From the research results indicated that the high viscosity values obtained from the treatment of acetic acid concentration of 40%, the operating time for 60 minutes, and an operating temperature of 300C and the ratio of 1: 5..*

Keyword: *Chitin, chitosan, deproteinasi, demineralization & deacetylation.*

I. INTRODUCTION

Indonesia is a maritime country that is rich in marine products, but utilization is less than the maximum. Nevertheless, these marine resources can be a source of income, one of which is shrimp. In the last decade, commodity shrimp is excellent fisheries subsector for nearly 50% of the total export value comes from shrimp to maintaining and increasing export of shrimp that have a large enough market opportunity, it is necessary improvement. Shrimp in the international market demand is particularly high in Japan, America, Singapore, Hong Kong and Europe.

Chitin is a polymer that can be found anywhere from the bark beetle up spider web, all that is around us ranging from plants and hewanpun we can find chitin. Chitin-like cellulose because it has a similar molecule, hydroxyl-containing cellulose and chitin-containing asetamid. Because many sea creatures were created to have skin that contain these polymers, it is conceivable that the sea is full of chitin. While chitin found in the market which is in the form of chitosan. Chitosan is formed by a process called deacetylation. Chitin and chitosan only differ on a course that chitosan-containing molecular amine groups.

Many countries using chitin and chitosan in a variety of products or to mix some products. In Japan, chitosan originally used for waste treatment as it can absorb metal, but is now in use for antibiotics, dietary supplements, weight loss, food, cosmetics also for animal food and clothing as well as socks. In the United chitin and chitosan is used for animal food supplements and for water purification, as hair care products and supplements to the diet. Moreover, it can also be used in the manufacture of paper because it contains a hydroxymethyl, a proton conductor containing polymers that can be used for the manufacture of batteries. Chitin and chitosan can also be used for photography because it can be formed into multiple types of lenses and able to form a film.

1.1. Background

Shrimp shells containing chemical compound chitin and chitosan is a waste that is easily obtainable and available in large numbers, which have not been utilized optimally.

This time with a pond shrimp cultivation has grown rapidly, because shrimp is an export commodity that can be reliable in increasing exports of non -migas and is one of the marine species of high economic value. Indonesian shrimp are generally exported in the form of frozen shrimp that had been thrown head, skin and tail.

Waste generated from the freezing process shrimp, canned shrimp and prawn crackers processing ranged between 30% - 75% of the weight of the shrimp. Thus the number of parts discarded from shrimp processing business is quite high. Increasing the number of shrimp waste is still a problem that needs to be resolved utilization efforts. This not only adds value to the shrimp processing business, but also be able to address the problem of environmental pollution caused, especially the odor problems as well as environmental aesthetics are not good.

Currently in Indonesia fraction of shrimp waste is already utilized in the manufacture of crackers, paste, paste, and mixing ingredients of animal feed. While in developed countries like the United States and Japan, shrimp waste has been utilized in the industry as the manufacture of chitin and chitosan. The benefit in many modern industries awful lot like the pharmaceutical industry, biochemistry, biotechnology, biomedical, food, paper, textile, agriculture, and health.

With the properties of chitin and chitosan are associated with amino and hydroxyl bound, causing chitin and chitosan have reactivity high chemical and causes the nature of polyelectrolyte cations that may act as ion exchangers (ion exchanger) and can act as an absorbent for metals weight in waste water, Hirano [1]. Because acting as ion exchangers and as absorbents then chitin and chitosan from shrimp waste has the potential to solve environmental pollution problems with the absorption of water is cheaper and readily available ingredients.

Most waste from shrimp comes from the skin, head and tail. The shrimp skin function in animals shrimp (class of invertebrate animals), namely as protector.

Table 1 Skin Ingredients Shrimp

No.	Contents	Percent (%)
1	protein	25-40
2	Calcium carbonate	45-50
3	khitin	15-20

Table 2 The content of the skin Crab

No.	Contents	Percent (%)
1	protein	15.60 to 23.90
2	Calcium carbonate	53.70 to 78.40
3	khitin	18.70 to 32.20

The content of chitin in shrimp shells less than the shells of crabs, but the shells more easily obtainable and available in large quantities as waste.

1.2. Research purposes

Producing chitosan from shrimp shell waste as raw material for the filter.

1.3. Scope

This study only discusses the making of chitosan from shrimp shell waste originating from New Market Surabaya, and support parameters to achieve the ultimate goal to form the filter medium.

II. RESEARCH METHODS

2.1 Shrimp Waste Producers As chitin and Chitosan

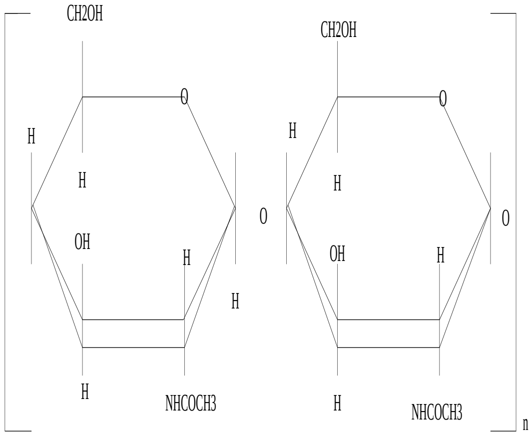
2.1.1 Khitin

Chitin is derived from a Greek word meaning clothes iron chain, was first investigated by Bracanot in 1811 in the residue of mushroom extract called fungiue. In 1823 Odins isolate a compound insect cuticle extra Janis called chitin name.

Chitin is a very important organic constituents in animal orthopoda group, annelids, mollusk, corlengterfa, and nematodes. Khitin usually berkonyugasi with protein and not only found in the skin and skeleton, but also present in the trachea, the gills, the intestinal wall, and on the inside skin of the cuttlefish. The presence of chitin can be detected by the color reaction Van Wesslink. In this way khitin reacted with I2-KI which gives a brown color, and when added to the sulfuric acid change color to violet. The color changes from brown to violet indicates a positive reaction the chitin.

Belonged polysaccharide chitin having a high molecular weight and is a straight-chain polymer molecule with another name □- (1-4) -2-acetamide-2-dioksi-D-glucose (N-acetyl-D-Glucosamine), [2]. Chitin structure similar to cellulose in which the bonds between the monomer strung glycoside bond at position□- (1-4). The difference with cellulose are hydroxyl groups attached to the carbon atoms is replaced by a second khitin acetamide group (NHCOCH2) so that chitin into a polymer berunit N-acetylglucosamine.

Chitin has the molecular formula C8H13NO5 an amorphous solid substance (amorphous), insoluble in water, dilute inorganic acid, dilute alkali and acid, alcohol, and other organic solvents but insoluble in mineral acids are concentrated. Chitin is less soluble than the cellulose and the N-glucosamine that terdeasetilasi slightly, while chitosan is chitin which terdeasetilasi as much as possible.



Picture 1 Chemical structure of chitin

2.1.2 Chitosan

Chitosan which is also called the □-1,4-2 amino-2-dioksi-D-glucose is a derivative of chitin by deacetylation process. Chitosan is also a multifunctional polymer because it contains three types of functional groups that amino acids, primary and secondary hydroxyl groups.

Chitosan is a compound that is not soluble in water, strong alkaline solution, slightly soluble in HCl and HNO3 and H3 PO4, and does not dissolve in H2SO4. Chitosan is non-toxic, readily biodegradable and are polielektrolitik, [1]. Besides, chitosan can easily interact with other organic substances such as proteins. Therefore, chitosan is relatively more widely used in various industrial fields of applied and health industy (Muzzarelli, 1986).

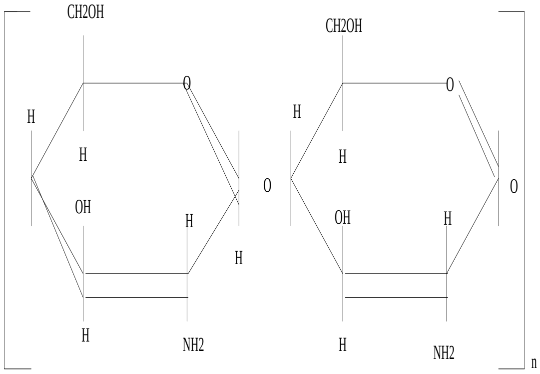


Figure 2 Chemical Structure of Chitosan

2.1.3 Application Chitosan

Chitosan is used in various industries, such as high quality adhesives, purification of drinking water (having power coagulation), a chelating compound, improves the dye in the paper industry, the textile and pulp because it is better to prevent shrinkage. Chitosan can also be used as a carrier (carrier) and component drug operation tools such as gloves, yarn operation, the membrane on plastic surgery, figure [3].

The use of chitosan as a coagulant in the circulation of waste water treatment will be re-used in the food industry has been officially used in Japan. Chitosan also has an effective ability to separate petroleum from waste, Brezski [4].

Chitosan has potential for use in industry and healthcare. The quality of chitosan depends on its use, for example for the chitosan used in waste water purification process is not in need of high quality but for use in the health sector needed a material with a high purity Bastaman [5]. The quality standards are based on the specifications of Protan, one distributor chitin / khitin largest in Japan, for handling liquid waste, toxic metal binder and other implements are in Table 3.

Table 3 Appropriate Chitosan Quality Standards Protan

Parameter	Value
The water content (% db)	<10
The ash content (% db)	<1.5
color solution	<2.0
The degree of deacetylation (%)	<70
Viscosity (cps)	> 200

III. MATERIALS AND TOOLS

3.1 material

The main material used in this study is the shrimp shells, especially shrimp in New Turi Market, Surabaya.

3.2 Tool

- 250 0C is appliance thermometer to determine the temperature at the reaction conditions
- Acid space is the room where the reaction takes place
- Hot plate is a tool to adjust the rotation speed and temperature to find the reaction conditions
- pH Meter Metrohm brand is a tool for measuring the pH of the solution
- Viscosity Brook Field is a tool for measuring the viscosity / viscosity of the solution
- The heater is a device for regulating the temperature of the reaction during the reaction
- Oven Wte Blinder is a tool for drying samples
- The condenser is a tool that is used to reduce evaporation during the reaction
- Mettler analytical balance is a tool for weighing samples to be taken
- Motor which is a tool to stir the solution during the reaction
- Three neck flask Duran is a tool for reacting solution
- Sip pumpkin 500 ml Pyrex to filter solution
- Vacuum Pumps brand DVR 1 is a tool that is used to filter the solution
- Other equipment that supports the research:
  - Pyrex beaker 100, 250 and 500 ml
  - Spatula
  - bottle Aquadest
  - Witeg reaction tube 50, and 100 ml

3.3 Solution

The solution used is:

- NaOH 3%
  NaOH in this study serves to eliminate the proteins that there may be skin shrimp
- HCl 3%
  HCl is used other minerals such as Ca
- concentrated NaOH
  Concentrated NaOH used to transform chitin into chitosan through the deacetylation
- Acetic acid
  This acid is selected to dissolve chitosan because it is regarded as a good solvent based on previous research.

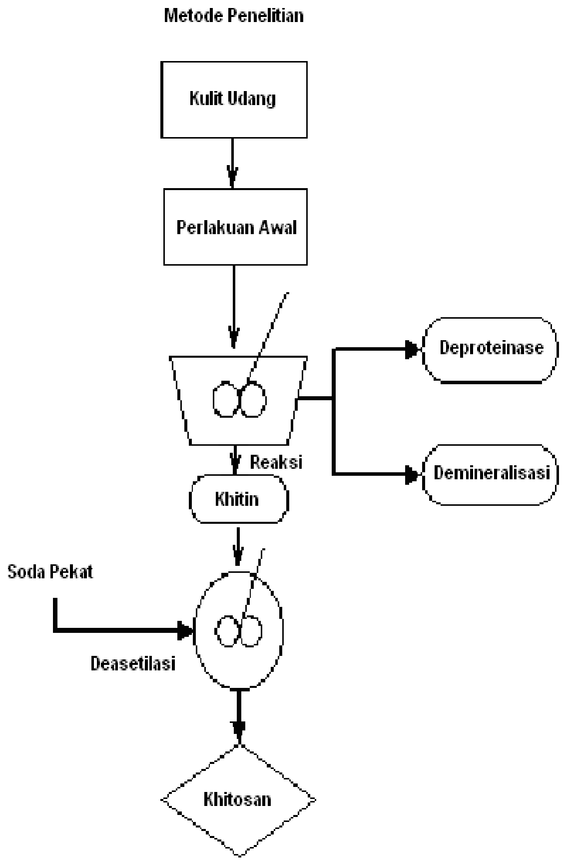


Figure 3. Preparation of Chitosan Methodology

IV. TEST METHODS

4.1 Treatment Early

Samples obtained in the form of shrimp shells in the market and then dried by drying or oven with a temperature of 1050C. The purpose of this is to avoid drying of samples contaminated with bacteria that can addle shrimp shell, an indicator of shrimp shells have bacterial contamination is with a pungent odor.

After the sample has been dried and then chopped / cut so that the resulting sample of shrimp shell powder to facilitate further processing.

4.2 Extraction of chitin

Skin shrimp protein content, calcium carbonate, and chitin. To obtain chitin protein and calcium carbonate must be removed. Based on earlier research method used is deproteinasi and demineralization.

4.3 Removal of Protein (deproteinasi)

Shrimp shell weighed and then dissolved in caustic soda (NaOH) 3% in a three-neck flask, then heated at a temperature of 70 - 900C with old heating 30-60 minutes after the measured pH and filtered to take solids.

4.4 Removal of Mineral (demineralization)

After the skin through deproteinasi process, the skin is then filtered. Taken solids and then diluted with Hydrochloric Acid (HCl) 3% in a three-neck flask and then heated at a temperature ranging between 70 - 900C with heating times 30-60 minutes, after which the measured pH and filtered to take the solids, then washed to pH neutral , Manufacture chitin from shrimp shells are listed in Figure 4.

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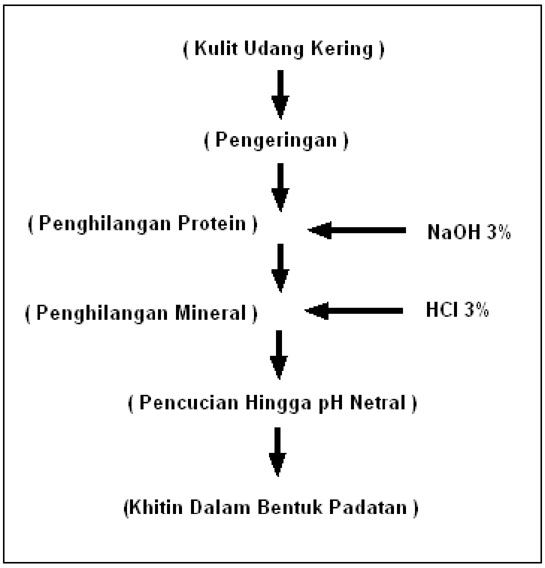

Figure 4 Making Process Flow Diagram khitin

4.5 Extraction of Chitosan

Chitosan is obtained from chitin which is acetylated by adding concentrated sodium hydroxide according to treatment were selected from previous research that is 50-60%. Then mixed in a three-neck flask and heated to temperatures ranging from 110 - 1400C by prolonged heating 1-2 hours. Once the process is done and finished the solidification process. To facilitate the solidification need to know the level of viscosity. Viscosity is a way to measure the viscosity of a substance. The higher the viscosity values mean more particles are dissolved. To be able to measure the viscosity, chitosan dissolved in a solvent selected from previous research that acetic acid. Chitosan manufacturing process flow diagram in Figure 5.

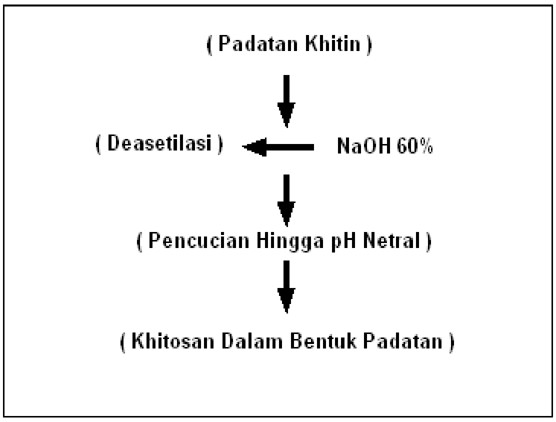

Figure 5 Chitosan Extraction Process Flow Diagram

V. RESULTS AND DISCUSSION

5.1 Treatment of Early Skin Shrimp

Shrimp fisheries in Indonesia is already intensively cultivated. In general, the shrimp utilized without heads or without the head and skin. Waste from freezing shrimp varies, generally ranging between 30-75% of the weight of the shrimp depends on its type.

Deproteinasi and demineralization is done to remove the proteins and minerals that bind to chitin in shrimp waste. Break the bond between the chitin with protein and minerals should be in accordance with the character of chitin association with proteins and minerals. Deproteinasi can be done before or after demineralization. Deproteinasi done first if the dissolved protein to be used further.

The separation of proteins from shrimp shells can be done by using NaOH 3.5% with the comparison between solvent with shrimp shells are 6: 1 and heated at a temperature of 70-75 0C for one hour, [5]. Deproteinasi can be made by dissolving it in 3.5 N NaOH at a ratio of 1:10 (w / v) and then do the heating at 90 0 C for one hour. 3% NaOH solution is used to wash and remove the proteins by comparison with shrimp shells solvent 6: 1, and then heated at a temperature of 80-85 0C by heating 30 minutes. Deproteinasi study was conducted by dissolving the shrimp waste using 3% NaOH solution with a ratio of 1: 8 (w/ v) and heated at a temperature range of 80-950C for 30 minutes. During deproteinasi, lye will go into the crevices of shrimp waste to sever the bond between chitin and protein.

Mineral separation using 1.25 N HCl in the ratio of solvent and shells 10: 1 and heated at a temperature of 70-75 0C for 1 hour [5]. Demineralization can be carried out by dissolving in HCl 1 N ratio of 1: 7 (w / v) with a temperature of 90 0C for 1 hour. Shrimp shells that have undergone deproteinasi mixed with HCl 1.5 N with a ratio of 7: 1 (w / v) at 90 0C for one hour, Fauzan [6].

Demineralization can be made by dissolving materials deproteinasi process results using a solution of HCl 3% with the ratio of 1: 8 (w / v) and heated at a temperature range of 80-950C for 30 minutes, then separation and water washing process results with distilled water until reaching pH neutral. In order for the demineralization run perfectly, cultivated during the demineralization constant stirring. Constant stirring will result in a solution of HCl reacted with shrimp waste. At the time of demineralization, calcium carbonate (CaCO3) will react with a solution of HCl to form calcium chloride (CaCl2), CO2 and H2O2.

5.2 Chitosan

The process of making chitosan from chitin in a process called deacetylation, namely the removal of the acetyl group (-COCH3) contained in the chitin. The elimination of the acetyl group can be performed using concentrated NaOH solution (50%) with a ratio of 1:20 (w / v) at a temperature of 120-140 0 C for one hour. Preparation of chitosan can be made by dissolving chitin using NaOH solution with a concentration of 60% with a ratio of 1: 5 (w / v) and heated at 110-1400C for 120 minutes. Then filtering and washing with water until neutral pH distilled water.

During the reaction by using evaporation condenser can be minimized while without using evaporation condenser is very large so it is necessary that the addition of NaOH solution is not depleted and this can lead to a solution with a solids ratio will change. Achievement of the maximum temperature is 1210C but when we do without receipts condenser temperatures can reach 1400C, because the conditions were not great stable due to evaporation. The air bubbles will occur when the temperature reached 1200C. Air distilled water required to neutralize the pH of about 1000-1500 ml. To separate chitosan with NaOH solution using a filter or vacuum. Things proved that chitosan is formed is not soluble in water, strong alkaline solution but soluble in acetic acid.

5.3 Viscosity

5.3.1 Acetic Acid Concentration

From the test results shown that chitosan dissolved in acetic acid 40%, the highest viscosity. The data were also obtained, with increasingly dense concentration higher viscosity whereas the more dilute concentrations found that the lower the viscosity. In the manufacture of a membrane viscosity of a solution is needed. Standard quality good viscosity according Protan chitosan is > 200 cps.

Table 4 Against Acetic Acid Concentration Viscosity

Parameter	A1B1C1	A2B1C1	A3B1C1
Chitosan Weight (Gram)	20 (1: 5)	19 (1: 5)	15 (1: 5)
As.asetat levels (%)	40	30	20
As.Asetat volume (ml)	100	95	75
Brook field viscosity (cps)	12600	7800	280
Bubbles	Fewer air bubbles	Many air bubbles	Large air bubbles arise
Temp. Operations (0C)	99	99	99
Operating Time (Mins)	90	90	90

5.3.2 Operating Temperature

Table 5 Temperature Reaction To Viscosity

Parameter	A1B1C1	A1B2C1	A1B3C1
Chitosan Weight (Gram)	20 (1: 5)	19 (1: 5)	20 (1: 5)
As.asetat levels (%)	40	40	40
As.Asetat volume (ml)	100	95	100
Brook field viscosity (cps)	12600	9520	31600
Bubbles	Fewer air bubbles	At the beginning of the air bubbles arise	Fewer air bubbles
Temp. Operations (0C)	99	79	30
Operating Time (Mins)	90	90	90

Stirring the solution at room temperature (300C) is nice to be done, it is proved by the results obtained the highest viscosity compared with viscosity results performed by heating. It also suggests a solution of cellulose acetate is similar to a good operation when the temperature is low.

5.3.3 Uptime

Table 6 Operation Time Against Viscosity

Parameter	A1B1C1	A1B1C2	A1B1C3
Chitosan Weight (Gram)	20 (1: 5)	20 (1: 5)	20 (1: 5)
As.asetat levels (%)	40	40	40
As.Asetat volume (ml)	100	100	100
Brook field viscosity (cps)	12600	21 520	11720
Bubbles	Fewer air bubbles	Fewer air bubbles	After 1 hour of air bubbles appear
Temp. Operations (0C)	99	99	99
Operating Time (Mins)	90	60	120

To obtain a high viscosity results when conducting agitation should not be too long. This can be seen through the results of an experiment, where the longer time stirring the lower the viscosity value. From the data in the know that the optimal time is 60 minutes stirring.

5.3.4 By comparison Solid Solution (Ratio)

a. Ratio relations and Acetic Acid Concentration Against Viscosity

Table 7 Against relationship and Concentration Ratio Viscosity

Ratio	Viscosity (cps)		
	A1B1C1	A2B1C1	A3B1C1
1: 05	12600	7800	280
1: 10	718	263	235

Comparison between the solution with chitosan affects the level of viscosity, the smaller the ratio of chitosan solution and the greater the viscosity value. And for a dense concentration levels still produce a high viscosity.

b. Ratio and Operating Temperature relationship Against Viscosity

Table 8 Relations Ratio and Temperature on Viscosity

Ratio	Viscosity (cps)		
	A1B1C1	A1B2C1	A1B3C1
1: 05	12600	9520	31600
1: 10	718	585	360

At a ratio of 1: 5 The optimum temperature is 30 0C temperature, while the ratio 1:10 optimum temperature is 90 0C. This is possible due to the large ratio requires heat to speed stirring as the process in general.

c. Relations Ratio and Operating Time Against Viscosity

Table 9 Relations Ratio and Operating Time Against Viscosity

Nisbah	Viskositas (cps)		
	A1B1C1	A1B1C2	A1B1C3
1:05	12600	21520	11720
1:10	718	285	300

With the time difference turned out the optimum ratio to the ratio of 1:10 is 90 minutes, while the optimum time for a ratio of 1: 5 is 60 minutes.

VI. CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusion

a. Chitosan is formed because it is not soluble in water, but soluble in an alkaline solution of acetic acid
b. The viscosity of the highest chitosan produced from products with room temperature (300 C) and the lowest viscosity is obtained from the product with a solvent concentration of 20%.
c. Comparison of ratio 1: 5 resulted in a higher viscosity value of the ratio of 1:10

5.2 Suggestions

Necessary to test the quality of chitin and chitosan quality.

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