



REVIEW ARTICLE : APPLICATION OF ALGINATE AS FOOD ADDITIVE

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ABSTRACT

Indonesia has great potential in producing alginate. Currently, alginate is widely used as a safe food additive. This review article aims to explain seaweed which can be used as alginate material, alginate extraction method, alginate quality and alginate application for food product development. Based on the results of the study that alginate can be extracted from the types of seaweed *Sargassum sp* and *Turbinaria Sp*. The alginate extraction method can be done in 7 methods. The quality of alginate is regulated in JECFA (*The FAO / WHO Joint Expert Committee on Food Additives*) standards. Alginate has been widely applied as a food additive in the manufacture of comaboko (as an emulsifier, ice cream (as a stabilizer) and dodol (as an edible coating to slow down food decline).

INTRODUCTION

Hydrocolloid is a colloid that dissolves in water, serves to thicken the solution and help the process of gel formation from the solution. Hydrocolloids can be added and used in food and non-food products. The use of hydrocolloids in the fisheries processing functions as a *thickening agent*, *emulsifier*, and adhesive (Herawati 2018). That can plays a role in producing products with good quality products, apart from optimal adhesion. Hydrocolloids that are safe for consumption are hydrocolloids extracted from natural raw materials.

Alginate is a hydrocolloid that comes from the anionic polysaccharide group, which comes from the cell walls of seaweed (Sze-kalska et al. 2016). The main content of the cell wall of seaweed is alginophyte. This compound is composed of guluronic and manuronic acids, binds to 1,4 β -D- manuronic acid and α -L-guluronic acid (Draget et al, 2005). Alginate is obtained from the extraction process.

Alginate has two forms, namely an acidic called alginic acid, and a salt called sodium alginate (Rasyid 2003). The three basic uses of alginates are their ability to increase the viscosity of the solution (when dissolved in water), the ability to form a gel (which will form when salt is added), and also the ability of alginates to form films (Subaryono 2010). In the food sector, alginate is used as a natural food additive which functions as a thickener, gelling agent, emulsion stabilizer and texture preserver (Dermawan et al., 2006). The role of alginate as a thickener and emulsifier is used in the manufacture of sweetened condensed milk. In making ice cream it is used as a *stabilizer*, in addition to that also to form ice crystals that are small and uniform in size so that the ice cream becomes softer. In fisheries, alginate is used as glazing in fish freezing, so that it can inhibit oxidation reactions. In the canning process it is used to increase viscosity (Dermawan et al., 2006). Therefore, the use of alginate as a food additive is very important in the processing of food products, so in this review this article aims to explain seaweed which can be used as alginate material, alginate extraction method, alginate quality and alginate application for food product development.

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SEAWEED THAT CAN BE USED AS RAW MATERIAL FOR ALGINATE

Marine resources in Indonesia has 28 species of brown seaweed with six genera, there are *Dyctyota*, *Padine*, *Hormonphysa*, *Sargassum*, *Turbinaria* and *Hydroclathrus*. Of the many species found, the seaweed that has been identified is *Sargassum* sp. as many as 14 species, 4 species of *Turbinaria* sp, 1 species of *Hormophysa* sp, 4 species of *Padina* sp, 5 species of *Dyctyota* sp and one species of *Hydroclathrus* sp (Yunizal 2004). Seaweed from *Sargassum* sp. such as *S. crassifolium* and *S. duplicatum* contains higher alginates than other brown seaweeds, such as *Padina* sp and *Turbinaria* sp (Mushollaeni and Rusdiana, 2011).

Sargassum sp is a seaweed that is included in the Phaeophyceae class or brown algae. *Sargassum* is found living attached to rocks or coral boulders. Seaweed *Sargassum* sp is easily found and distributed in Indonesian, such as in the Sunda Strait, Bangka Belitung, Karimunjawa, Lombok Beach, Bali Beach and the South Coast of Java Island (Kadi, 2005). The species of *Sargassum* sp is *Sargassum duplicatum*, *S. cymosum*, and *S. polycystum* are abundant in Permisan Beach, Cilacap, Central Java Province (Widyartini et al, 2012).

Sargassum duplicatum has a round talus on the main stem, and slightly flattened (flattened) at the branch, has a smooth surface. The dichotomous branching with the thallus has oval round leaves, with serrations at the edges. Vesicles are attached to the stems and leaves, are elliptical and small in size (Widyartini et al., 2012).

Sargassum polycystum has common characteristics. The length of the thallus 35 cm in the shape of a stem with a yellowish brown color, also vesicles that are oval in shape, cylindrical axis with *holdfast* in the form of *discoïd berrhizoid*. The length of the leaf thallus is 1.3-4.2 cm with a width of 0.25-1.15 cm. Shaped tapered, or rounded and serrated edges (Widyartini et al, 2012) .

Sargassum cymosum has a cylindrical thallus, and has a smooth texture, has a serrated edge that reaches in long 2.5 cm long and high 2 cm. Holdfast is disc-shaped, has clear crytostomata, spreads over the leaf sheet. *Sargassum cymosumovoid* has vesicles and has a receptacle that forms a special cylindrical and elongated (0.5 - 1.5 cm) branch (Widyartini et al, 2012).

Besides *Sargassum*, examples of types of seaweed that contain alginate are *Turbinaria*. *Turbinaria* is a brown macroalgae that has bioactive polysaccharides (Handayani 2014). *Turbinaria ornata* is a type of alginate-producing seaweed. *Turbinaria ornata* has a cylindrical trunk, erect, rough and holdfast in the form of small discs with radial roots and branches around the main stem. The difference between *Turbinaria ornata* and other types is that the leaves are shaped like a funnel with serrated edges (Handayani 2018). *Turbinaria* live in intertidal to subtidal waters, and have a high level of tolerance to environmental parameters such as drought, light intensity, salinity and temperature. The substrate wheregrows *Turbinaria* coral or igneous rocks (Atmadja 1996). Meanwhile, *Turbinaria ornata* and *Turbinaria conoides* grow in the reef flat area (Atmadja 1996).

Turbinaria are almost scattered throughout Indonesia's territorial waters. The areas with the highest diversity are Sumatra Island and its surroundings (seven species), Java Island and its surroundings (six species), Kalimantan Island and its surroundings have the lowest diversity with 1 species (Atmadja & Prud'home van Reine, 2014).

ALGINATE EXTRACTION METHOD

The first method is the Chapman extraction method. This method was used in research conducted by Pasanda et al (Pasanda et al 2017). Brown seaweed (*sargassum* sp) was collected and then the samples were washed with mineral water and then dried under the sun. The sample was dried again in an oven at 60 °C until constant weight. In order to facilitate the process of forming alginic acid, seaweed is soaked for 24 hours in a 2% (1: 30 w / v) formaldehyde liquid to remove pigment. After that, seaweed washed with distilled water then soaked again in a HCl 0.2 M (1: 30 w / v) in 24 hours. Then the sample was washed again with distilled water until it was neutral.

The next process was immersed in 2% (1: 10 w / v) Na₂CO₃ solution at a temperature of 70 for 5 hours while stirring. After that it is filtered with muslin cloth. The filtrate obtained is aerated for 3 hours, the end will be formed in two parts, the bottom part which is clear is separated from the filtrate by removing it. To see the formation of calcium alginate fibers, the filtrate was added with CaCl₂ 0.5 M then 0.1% (1: 10 w / v) technical NaOCl was added to give a bleaching effect.

After calcium alginate is formed, alginate is converted again to become alginate acid by immersing in 0.5 M (1: 10 w / v) HCl solution for 1 hour. In order for the water content to decrease in the alginate acid gel, the *pressed water* content is about 25%. The next process is the addition of sodium carbonate powder in a mixer so that the alginic acid gel is converted into sodium alginate in the form of a paste then immersed in technical ethanol and dried to a moisture content of 12% under sunlight for ± 12 hours. The last process was refining and analyzed the moisture content and viscosity value using the Brookfield viscometer and functional groups using FTIR.

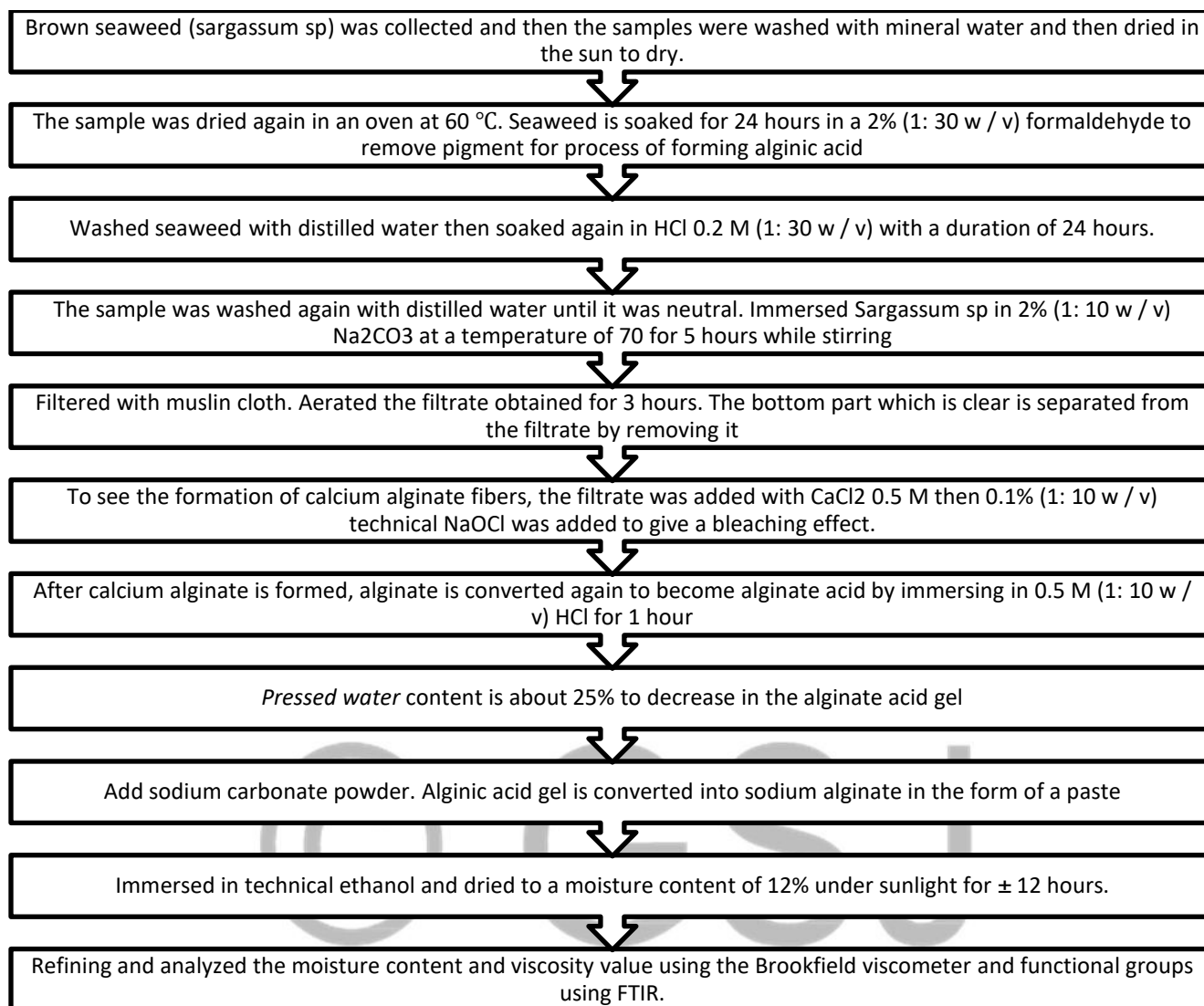


Figure 1. Chapman extraction method

The second method in the alginate extraction process is the Mc. Hugh method. The principle of this method is the separation of alginate from the filtrate through precipitation in the form of Ca-alginate. The first step is that the dried seaweed is soaked for 6 hours with a 0.4% formalin solution. Furthermore, seaweed is soaked in 1% HCL for 1 hour with a ratio (seaweed: HCL 1: 30 w / v). Seaweed is washed with clean water until the pH is neutral.

The extraction process uses a 1:30 (w / v) 2% Na₂ CO₃ solution at a temperature range of 60-70 for 60 minutes. Furthermore, the extract is filtered with nylon cloth measuring 30-40 mesh. The filter results are aerated for 3 hours and the clear bottom is removed. Addition of 0.5 M CaCl₂ to the aerated filtrate to form calcium alginate fibers. In the bleaching process, 0.1% effective chlorine of technical NaOCl is added to the calcium alginate fibers that have been formed. The conversion of calcium alginate to alginic acid was immersed in 0.5 M HCL solution (this activity was repeated 3 times).

To reduce the water level so that the aliginic acid gel is perfectly formed, it must be *pressed* until the water content is around 25%. Alginic acid is converted again to sodium alginate by adding sodium carbonate powder in a mixer. The resulting paste is soaked in technical ethanol and dried under the sun for about 12 hours until the water content remains 12%. The last step is grinding with a size of 60 mesh and the sodium alginate powder is finished.

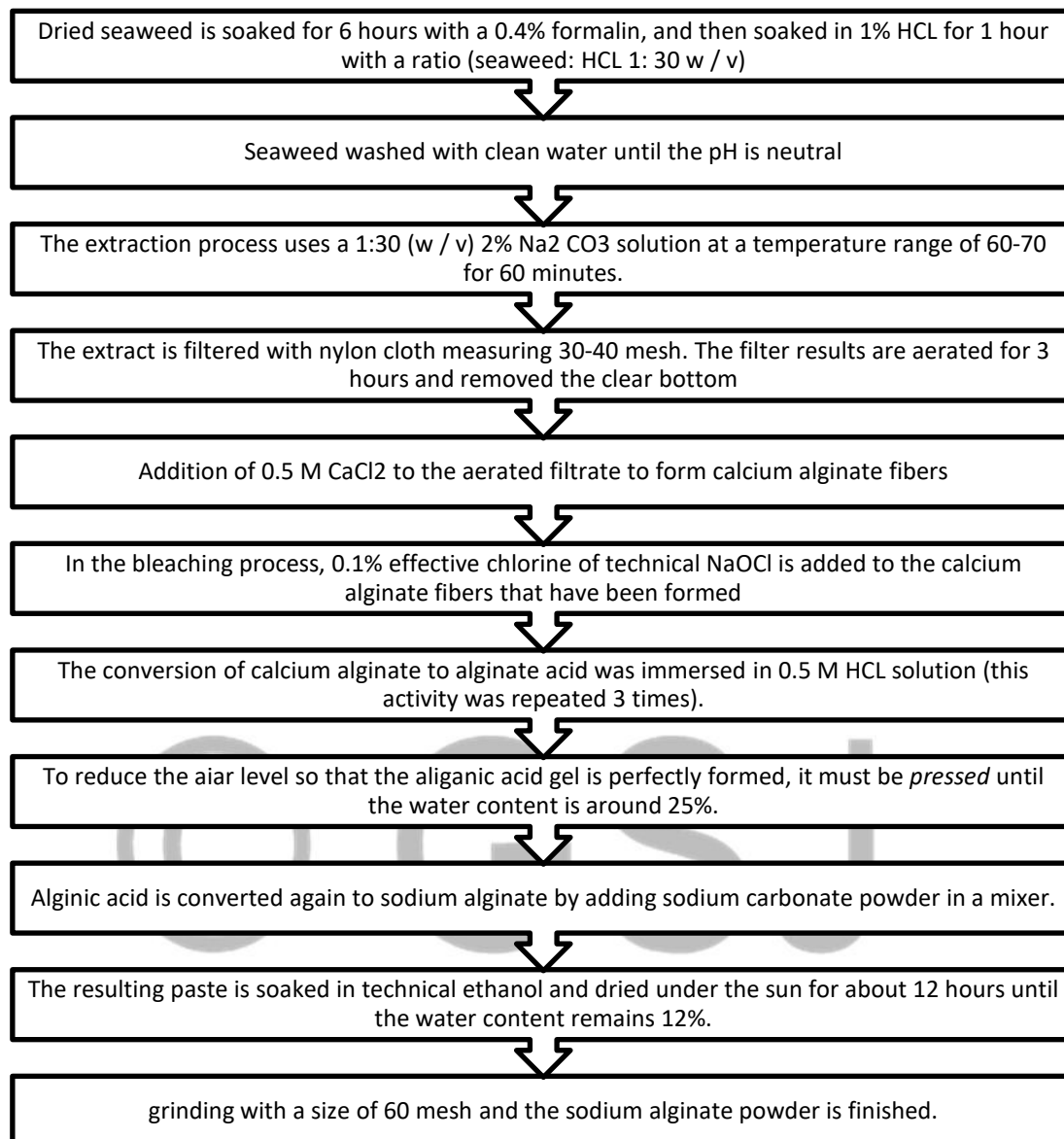


Figure 2. Mc. Hugh method

The third method is the extraction method through the alginic acid route which was developed at the Research Center for Product Processing and Marine Biotechnology in Jakarta. Seaweed that has been dried soaked in 1% HCL karutan for 1 hour with a ratio of seaweed: HCL is 1; 30 w / v. To neutralize the pH, the seaweed is washed with clean water. After the pH of the seaweed was neutral, the size was reduced and extracted using 2% Na₂CO₃ (ratio 1:30 w / v) at 60 - 70 for 60 minutes. The extract was filtered with a 150 - mesh vibrator.

The bleaching process is carried out by adding 4% NaOCl from the volume of the filtrate, then stirring for 30 minutes. To precipitate alginate acid, 10% HCL is added to the filtrate to pH 2.8-3.2. The precipitated alginic acid is separated and washed clean. The conversion process to sodium alginate is carried out by titrating 10% Na₂CO₃ to pH 7. To separate sodium alginate, the filtrate is poured gradually into isopropyl alcohol in the ratio (1: 2 v / v) while stirring and allowed to stand for 30 minutes. Drying the alginate fiber is carried out in the sun for approximately 12 hours so that the moisture content is 12%. The alginate fibers are ground to a size of 60 mesh. So that sodium alginate is formed.

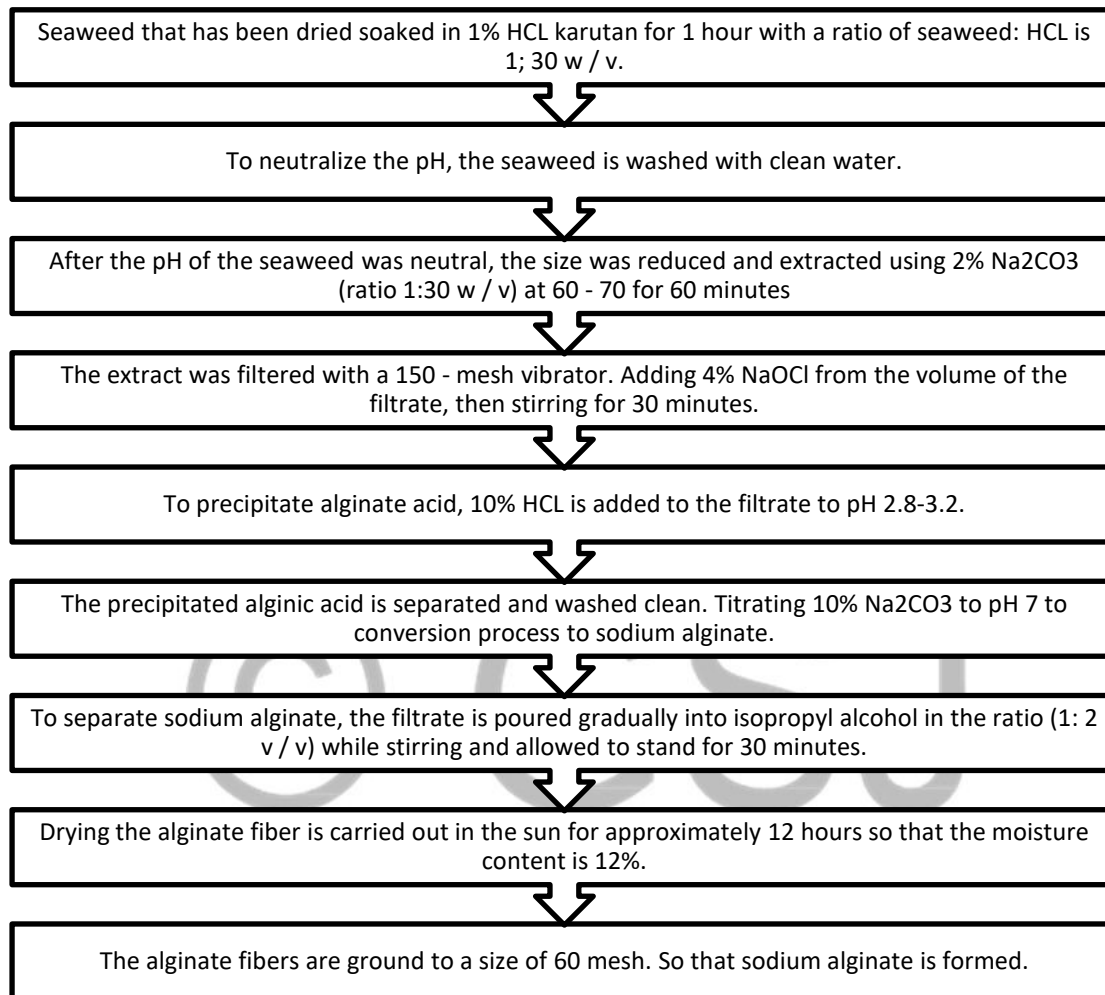


Figure 3. Extraction Method Through The Alginic Acid Route

The fourth method is the Vincent method. In this method, the dried seaweed is soaked with Ca (OH) 2 solution. Furthermore, soaking the dregs with a 0.2 N H₂SO₄ solution for 30 minutes

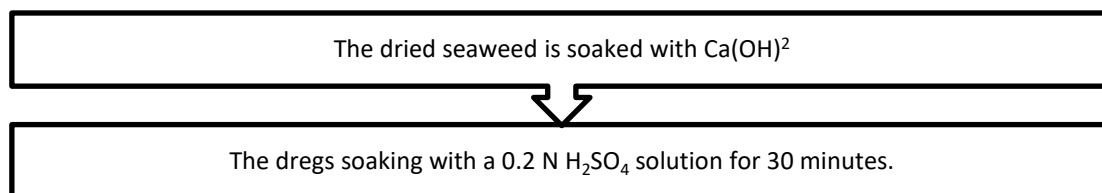


Figure 4. Vincent Method

The fifth method is the Herter method with initial immersion with CaCl₂ solution. For the next step , soaking the dregs with 0.5 N HCL for 60 minute.

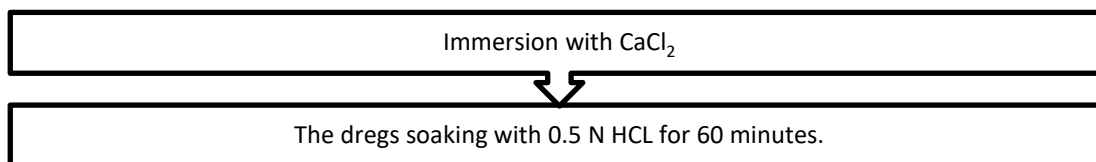


Figure 5. Herter Method

The sixth method, namely of this method is the Bashford method, washing was carried out at the beginning of the process with water, then immersed in H₂SO₄ at 50 for 60 minutes. Repetition of washing with water after centrifugation.

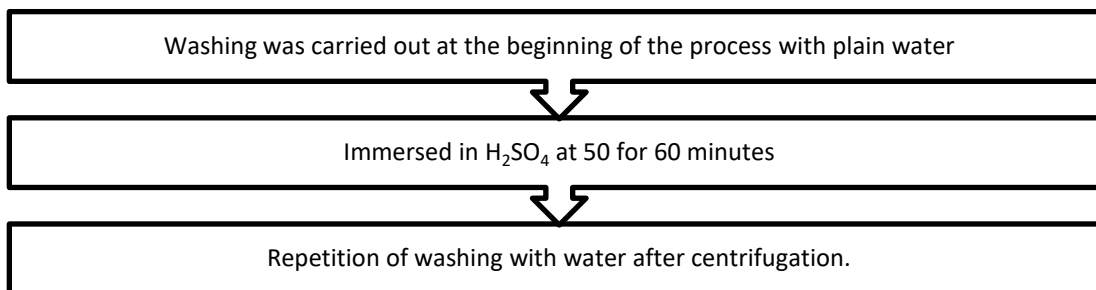


Figure 6. Bashford method

The seventh method from Husni *et al* (2012). Seaweed powder as much as 100 grams soaked in 1% HCl solution with a ratio (1:30 w / v) for 1 hour. Washing with running water to neutral pH. Seaweed is extracted at 60-70 for 2 hours using 2% Na₂CO₃ with a ratio of 1:30 then filtered with a vibrator with a mesh size of 150. The bleaching process is carried out with 4% NaOCl for 30 minutes until the color of the filtrate changes to ivory quinine. Alginate acid is precipitated by adding 10% HCl gradually and stirred slowly until an alginate acid precipitate has a pH of 2.8-3.2. To separate the alginate acid and the residue, it is filtered. The precipitate obtained is washed with distilled water. The conversion process of alginate to sodium alginate uses 10% Na₂CO₃ until the pH becomes neutral then the sodium alginate is separated by gradually pouring the filtrate into isopropyl alcohol with a ratio of 1: 2. The sodium alginate that has been obtained is dried under the sun to dry for approximately 12 hours until the water content of sodium alginate is <12%. If the alginate is dry then mash it in a blender and filter it with a filter size of 60 mesh

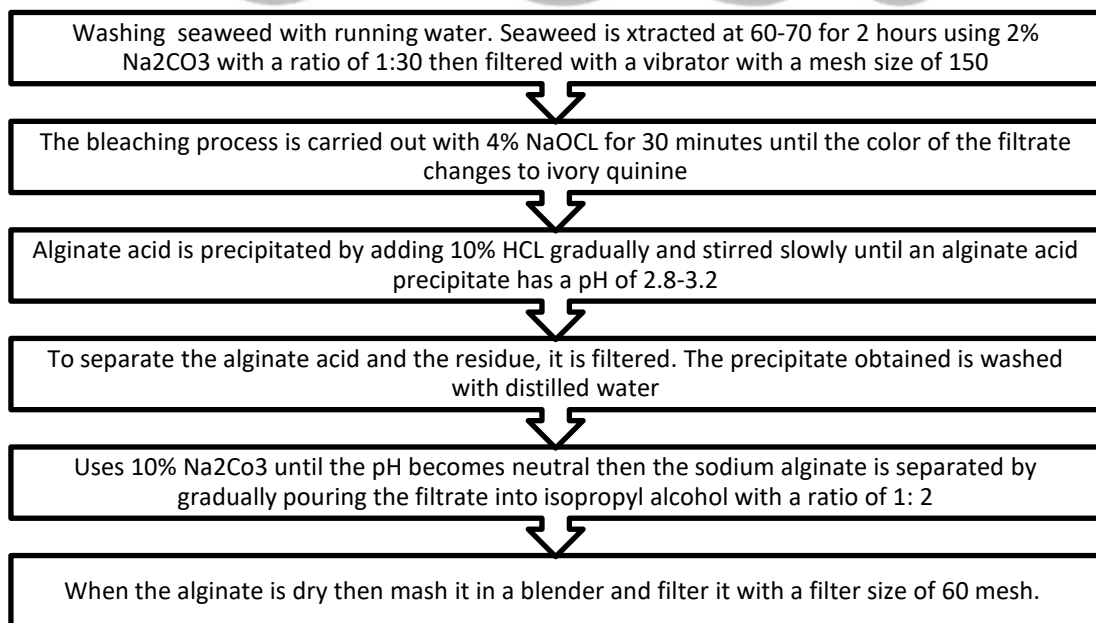


Figure 7. Method from Husni et al (2014)

ALGINAT QUALITY

As a complex organic compound, phycocolloid which is extracted from brown seaweed, alginate has a quality standard. Alginate quality standards can be seen in the table below :

Table 1. Alginate Quality Standards

Characteristics of	Sodium Alginat
Purity (% dry weight)	90,8 – 100 %
As (%)	< 3 ppm
Pb (%)	< 10 ppm
Hg (%)	< 0,04 %
Ash (%)	18 -27 %
Water (%)	< 15 %

Source: Winarno 1996

Table 2. Alginate Quality Standards

Characteristics of	Quality Standards Na-Alginat
Water (%)	< 15%
Ash (%)	18 - 27%
pH (%)	3,5 – 10
Viscosity (%)	10 - 5000cp
Yield (%)	>18%

Source: Food Chemical Codex 1981

Factors Affecting Alginate Quality

The quality of alginate may vary for each species. This difference can be caused by difference in the raw material for extraction, the age of the raw material, the location of the raw material and the extraction method used (Draget *et al.* 2005). The concentration of HCl and the concentration of Na₂CO₃ significantly affected the yield, ash content, moisture content and viscosity in the alginate extraction of *Padina* sp. (Susanto *et al.* 2001).

Types of seaweed that live in basin habitats (always inundated by sea water) have a higher water content than seaweed in tidal areas (Mushollaeni, 2011). *Turbinaria* has a higher water content than species *Sargassum*. In addition, the water content is also influenced by isopropanol which is added to the alginate extraction, including the refining process, the drying process and the storage after powdering.

Ash content indicates the presence of inorganic salts which are insoluble in water ranging from 15% -25% and soluble in water ranging from 75% -85%. Some types of seaweed are physically softer and thinner than other types. This type will crumble more easily during extraction than other types that are more hard-textured. This physical texture difference can result in the separation and purification process of impurities in the alginate solution varying according to the texture of the seaweed (Truss *et al.*, 2001). The more impurities in the alginate solution will increase the ash content it contains.

The purity of alginate is directly proportional to the yield it produces (Mushollaeni 2011). Seaweed species such as *Padina*, which only consist of thin sheets that are not dark in color and do not have strong roots and grow on corals in relatively clear waters, have low levels of purity and yield (Mushollaeni 2011).

The Pb and Hg content in alginate is an indication of the presence of Pb and Hg metals in the raw materials used. This metal comes from the environment where the seaweed lives (Salasa, 2002). The coast which is close to the industry has relatively high levels of Pb and Hg metals which are from hazardous waste.

Viscosity shows the degradation that occurs during the extraction process (Vold *et al.* 2006). The raw material for extracting alginate that grows in areas exposed to direct waves has strength and is strongly bound to its place of life, has a higher polyguluronate. Polyguluronate and the presence of hookon Ca²⁺ will determine the viscosity value (Ertesvag *et al.* 2009).

The pH value is one of the physical properties that determines the acidity level of sodium alginate. pH depends on the substances contained therein. Besides that, the concentration of the substance can also affect the pH value. The pH value will decrease the higher the concentration of acetic acid.

ALGINATE QUALITY IN SEVERAL STUDIES

Quality of alginate on an international scale is regulated in the JECFA standard (*The FAO / WHO Joint Expert Committee on Food Additives*) which contains alginate requirements as a food additive (FAO 2009). Extraction alginate from raw materials *Sargassum* sp greenharvested from BTDC Nusa Dua Beach Bali, with treatment differences in the concentration of acetic acid obtained are as follows (Aristya et al, 2017):

Table 3. The value of the average - average alginate best *Sargassum* sp treatment.

Konsentrasi Asam Asetat	Rendemen	Kadar Air	Kadar Abu	Viskositas	pH
0.0%	2,263	0,025	0,592	8,000	7,1
0.5%	2,810	0,030	0,351	8,000	6,4
1.0%	2,751	0,033	0,345	9,333	6,3
1.5%	2,897	0,037	0,374	12,000	6,0
2.0%	2,417	0,035	0,339	10,666	5,7
2.5%	2,903	0,036	0,416	8,000	5,6

Source: Aristya dkk. 2017

Based on these results, the extraction treatment using acetic acid which is sufficient to meet the standards of the *Food Chemical Codex* is a treatment with a concentration of acetic acid as much as 1.5%. However, the value of ash content and yield has a value below the quality standards than that which has been arranged.

Other research about physicochemical characteristics of sodium alginate from *Sargassum crassifolium*, *Sargassum polycystum*, *Padina* sp., And *Sargassum echinocarpum*, which grows on the coast of Gunung Kidul Yogyakarta, obtained the following results (Mushollaeni, 2011):

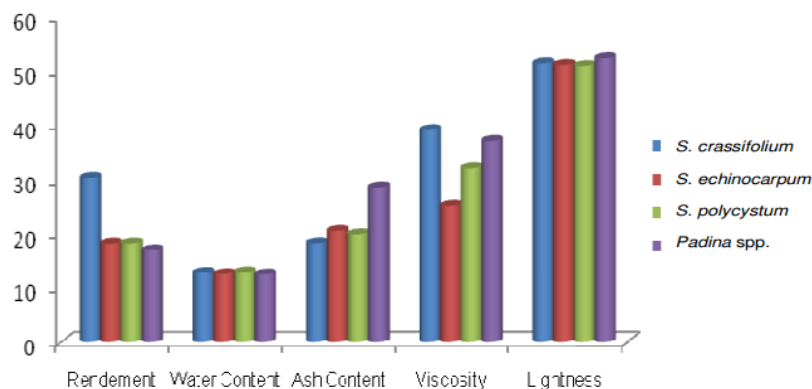


Figure 8. Alginate characteristics (source; Mushollaeni, 2011)

Based on the results of alginate extraction, the brown seaweed used in Moshollaeni's research (2011) has the potential to produce alginate, with moisture content ranging from 12.5% - 13.43%, ash content 18.2% - 28.59%, Pb is 0.083 ± 0.01 - 0.36 ± 0.04 ppm and Hg is 0.3 ± 0.05 ppm. Viscosity of 25 - 39 cps and brightness of 46.2 - 52.3. All of these characteristics have qualify the minimum criteria set (Winarno 1996) and the *Food Chemical Codex* (1981).

APPLICATION OF ALGINATE

Alginate can be applied in the process of developing food products, for example, as an emulsifier in making kamaboko, as a stabilizer in making ice cream, and can be used to inhibit quality deterioration for food products. The following are some of the results of using alginate as a food additive:

Alginate as an Emulphisier in The Manufacture of Fish Kamaboko.

One of the functions of alginate is as an emulsifier, in the research of Utomo et al., (2014) with the title "Application of Alginate as Emulsifier in Making Kamaboko Fish Kuniran (*Upeneus sulphureus*) at Room Temperature Storage". Alginate is used as an emulsion in the manufacture of food products, namely fish kamaboko, kamaboko is a product of processed fish meat in the form of a gel. invalid and elastic. This product comes from Japan. In Indonesia, there are known a kind of kamaboko products, namely fish balls, *otak-otak* (traditional food), and *empek-empek*. Kamaboko can be served as a food complement., Kamaboko fish is a fishery product that requires emulsion stability resistance, one of the fish that can be used in the process of making kamaboko is kuniar fish, turmeric fish is a fish that has high economic value and is also easily found in the market along years, turmeric fish is a fish that has a low fat content, has a distinctive taste, is delicious and also savory, so that this fish is a fish favored by the community (Subagio et al., 2004). In making kamaboko, alginate is needed as an ingredient to maintain emulsion stability, alginate is a linear copolymer consisting of two monomeric units, namely *Dmannuronic* and *acidL-guluronic acid* which are found in all types of brown algae (*phaeophyta*) which are the main components in the formation of cell walls. consists of the salts of *calcium*, *magnesium*, *sodium* and *potassium* alginate (Kirk and Othmer, 1994).

From this research, alginate can be used to increase emulsion stability in kamaboko turmeric fish products, in the substitution of alginate 2.55 and 7.5% tapioca flour. The stability value of kamaboko emulsion with alginate substitution on day 0 to day 3 stored at room temperature was higher than kamaboko without alginate substitution, and it can be concluded that alginate can be used as a food additive to be used as an emulsifier.

Alginate as a Stabilizer in Making Ice Cream

Alginate can be used as a stabilizer in making ice cream. Ice cream is a food product that comes from milk processing combined with the composition of ice cream-forming ingredients such as cream, sweetener, emulsifier, stabilizer, skim and also the addition of flavor. In the process of making ice cream, alginate functions to prevent large ice crystals from forming a thickness so that an ice cream product with a smooth and soft texture is obtained. Alginate is also used in the manufacture of ice cream used as a stabilizer and emulsifier. The stabilizer is a surface active material that can reduce the tendency of droplets in the emulsion to combine, the stability occurs due to surface tension (Makhfoeld et al 2002). The use of alginate as a stabilizer in making ice cream has been widely used, which is expected to be an innovation in the development of ice cream products that have high nutritional value, are safe for consumption and guaranteed halalness. Research reported by Mulyani et al., (2017) states that sensory analysis of ice cream with the addition of alginate generally produces a high value for each parameter, and it can be concluded that alginate can be used as a stabilizer in making ice cream.

Alginate as an Inhibitor of Deterioration of Product Quality

Alginate can be used as an inhibitor in the process of decreasing food products or it can be called a deterioration of product quality. In the research of Nasyiah et al., (2014) entitled "Application of *Edible Coating Sodium Alginate* in Inhibiting Quality Decrease of Seaweed Dodol". Alginate is used to inhibit the deterioration of the quality of seaweed lunthead, dodol is a popular traditional food product in Indonesia which has a tough and sweet taste, seaweed can be used as a raw material for making lunthead and has been liked by many people. From this study, it was found that the difference in the concentration of sodium alginate edible coating had an effect on the deterioration of the quality of seaweed dodol based on several parameters such as the value of TPC, water content, Aw, pH, and organoleptic, 2.5% sodium alginate edible coating was the best concentration capable. maintain the quality of seaweed lunthead products until the 8th day with a TPC value of 5×10^4 CfU / g, a water content of 29.03%, Aw of 0.86, a pH of 6.21 and an organoleptic value of $7.00 < \mu < 7$, 47. It can be concluded that the algiant can be used as an inhibitor of deterioration in the quality of food products.

CONCLUSION

Based on the above analysis, alginate can be extracted from the types of seaweed *Sargassum* sp and *Turbinaria* Sp. The alginate extraction method can be done in 7 methods. The quality of alginate is regulated in JECFA (*The FAO / WHO Joint Expert Committee on Food Additives*) standards. Alginate has been widely applied as a food additive in the manufacture of comaboko (as an emulsifier, ice cream (as a stabilizer) and dodol (as an edible coating to slow down decline food).

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