Physicochemical properties of carrageenan originated from Lermatang Village, Southwest Maluku District

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Abstract. Lermatang Village is situated at Southwest Maluku Regency and is known as a producer of seaweed. Generally, the seaweed produced in this village belongs to Eucheuma cottonii, which is a source of carrageenan and has high economic value. Carrageenan is known as raw material for the pharmaceutical, cosmetic, food and other industries, as gelling agents, material binders, emulsifiers, and stabilizers. The most common problem faced by the seaweed grower was they haven’t been able in optimizing the processing technologies yet. The seaweed farmer is still selling the seaweeds in form of dry seaweed without further processing and this cause a low price. The aim of this research was to study the physicochemical properties of carrageenan of Eucheuma cottonii originated from Lermatang Village fo Southwest Maluku Regency. Seaweed was extracted by using sodium hydroxide then physicochemical properties of carrageenan were observed. The results showed that physicochemical properties of carrageenan were indicated by yield 34.50–44.25 g, gel strength 500–850 g/cm², viscosity 35.2–40.89 cP, water content 14.32–25.73%, ash content 21.34–22.62% and sulphate content 14.85–16.50%.

1. Introduction
Seaweeds are benthic macroalgae which belongs to the group of plants that live either in marine or brackish water environment. Seaweeds become an important and potential export commodity since they contain different vitamins, minerals, trace elements, protein, iodine, bromine and bioactive substances which are a good source of food and medicine [1, 2]. The simplest classification of marine algae is based on the pigment they have i.e. the green algae (Chlorophyta), the brown algae (Phaeophyta), the red algae (Rhodophyta) [2, 3]. Some of the high economic value seaweeds found in Indonesia are Eucheuma spp., Glascillaria sp., Gelidium sp., Sargassum sp., and Hypnea sp. Two main species from red algae which have high carrageenan content and highly contribute to Indonesia seaweeds product are E. cottonii and E. spinosum [4].

Carrageenan is a sulphated linear polysaccharide of D-galactose and 3,6-anhydro-D-galactose isolated from several species of red seaweeds from the family of Rhodophyceae. Carrageenan widely used in food industrious as it has functional and physics properties like a thickener, gelling agent, stabilizer, protein suspended. Carrageenan also widely used in the pharmaceutical field as encapsulation material and cosmetics, other purposes are printing and textile [5, 6].

For more than four decades, carrageenan has been used as important raw material in many industrial fields. Carrageenan has been produced mostly by the countries around Southeast Asia, and 96.5% of total carrageenan production was extracted from the red seaweeds. From total carrageenan produced, 55% come from the Philippine, 38% from Indonesia and 2.5% from Malaysia [7].

Carrageenan can be used as a thickening, emulsifying, suspending, and stabilizing. In the food industry, carrageenan has been used to improve the appearance of coffee, beverage, sausage, salad, ice
cream, condensed creamer, chocolate, and jelly. The pharmaceutical industry uses carrageenan as raw material for medicine, syrup, tablet, toothpaste, shampoo, etc. Cosmetics industry uses it as a gelling agent or binding agent. While, the non-food industry uses it as raw material for textile, paper, water paint, crude oil transportation, air freshness, ceramic sealer, printer paper, printing machine and carpet [8, 9, 10, 11].

In order to improve the utilization of red seaweeds of the species *E. cottonii* to be more valuable economically, it can be transformed to be carrageenan. Carrageenan has been extracted by using hot water and hot alkali solution [12]. Alkalis atmosphere can be obtained by added the solution of NaOH, Ca(OH)2 or KOH. Alkalis solution have a purpose to support the polysaccharide extraction more properly and accelerate 6-sulphate elimination from monomer form 3,6-anhydro-D-galactose, increase gel strength and product reactivity on the protein [13].

There has been reported of an alkali solution (KOH) used to extract seaweeds that can increase the yield of carrageenan [14]. Moreover, study has shown that a concentration of KOH 0.5% with extraction period of 2 hours can produce carrageenan with the best quality [15]. The aim of the present, therefore, was to evaluate the effect of different KOH concentration on the quality of carrageenan resulted from seaweed extract.

2. Materials and Method

2.1. Time and study site
This study was conducted for six months from November 2016 to April 2017 at Lermatang Village, Southwest Maluku Regency.

2.2. Materials
Material used in this study was seaweed of species *E. cottonii*. Chemical materials used in carrageenan process vis. KOH, KCL, and distilled water, while for carrageenan analysis was HCl, KCl, BaCl2, BaSO4, and K2SO4. Apparatus used to extract carrageenan was boiling pan, analytical balance, basin, gelling basin, dryer rack, filter, powder machine, pH-paper, stopwatch, and stove. The instrument for carrageenan quality analysis comprises of a porcelain cup, desiccator, Erlenmeyer flask, beaker glass, stirrer, funnel, spatula, oven, furnace oven, filter paper, thermometer, curd tension, cast, and Brookfield Viscometer.

2.3. Extraction of carrageenan.
Two different KOH concentration i.e. 0.37% and 0.75% was used to extract carrageenan from dry seaweed at the temperature of 90-95°C for 1 hour then filtered and washed. The HCL solution was then added to the two residues and heated at 90-95°C for another 1 hour. The carrageenan was then filter using nylon filer then placed in the pan and left overnight to form gel. The gel tube carrageenan was then sliced for about 1 cm thick, wrapped in the gauze and pressed overnight by using pressing equipment to remove water as much as possible. Wet carrageenan sheet was then sun-dried to obtain dry carrageenan sheet. This dry carrageenan sheet was then ground to get a powder carrageenan.

2.4. Chemical-Physical Analysis
Chemical and physical analysis covered yield, gel strength, viscosity, water content, ash content, and sulphate content, and the analysis procedure for yield, gel strength, viscosity, and sulphate content referred to FMC Corp. 1977[13], while water and ash content was referred to AOAC 1995 [14].

3. Results and Discussion
Table 1 shows the physical-chemical properties of carrageenan extracted using 0.35% and 0.75% KOH concentration. This table shows that there are differences in yield, moisture, ash, viscosity, gel strength and sulphate of carrageenan resulted from this two KOH concentration.
Table 1. Yield, moisture, ash, viscosity, gel strength, and sulphate of carrageenan extracted from two different KOH concentration.

| Parameters       | Concentration of KOH |
|------------------|-----------------------|
|                  | 0.35%  | 0.75%  |
| Yield (%)        | 34.50  | 44.25  |
| Moisture (%)     | 25.73  | 14.32  |
| Ash (%)          | 22.13  | 21.34  |
| Viscosity cP     | 14.85  | 16.50  |
| Gel strength g/cm² | 500.00 | 850.00 |
| Sulphate (%)     | 35.20  | 40.20  |

3.1. Yield.
Yield is an important parameter to monitored whether the carrageenan extract processing is running effective or not, and this is indicated by the ratio between extracted and raw seaweeds. The result showed that yield is increasing due to the increasing of KOH concentration. There have been reported that the higher KOH concentration, obtained the higher the carrageenan yield [15]. Factors affecting carrageenan yield is the increase of pH due to the KOH increment. Carrageenan yield is also influenced by temperature. As temperature increase, carrageenan yield is increasing too because the seaweeds can be extracted completely. Moreover, alkali treatment accelerate 3,6-anhydrogalactosa during extraction process [16,17,18]. SNI 01-2690-1998 requires the water content of carrageenan should not more than 25%. Refers to the result of carrageenan obtained, the moisture content was within the range of standard required.

Carrageenan yield obtained is also affected by climate, extraction method, harvest time and culture location [19]. Moreover, the scale of seaweeds production can affect the yield of carrageenan. The yield of carrageenan reported by FAO [20] was in the range from 18 – 35%, whilst the carrageenan yield obtained from this work was 34.50-44.25% which is higher than that report.

3.2. Viscosity
Viscosity is an important physical property of carrageenan. Viscosity monitoring is aimed to study the carrageenan consistency at a certain concentration and temperature level. Viscosity is usually measured at the temperature of 75°C with 1.5% concentration [21].

Carrageenan viscosity obtained through extraction method by using 0.35% and 0.75% KOH was 20.04 and 37.70 cP respectively. Minimum standard viscosity allowed by FAO is 5 cP, hence the carrageenan therefore carrageenan resulted is qualify to that standard suggested by FAO. The higher the KOH concentration, the higher the viscosity obtained. KOH solution can dissolve salted content in seaweeds and as a result, viscosity will increase [22].

There have been reported when the sulphate content was fewer, the viscosity decrease, however, followed by the consistency enhancement [23]. The presence of dissolved salt in carrageenan decreases the charge along the polymer chain. This circumstance leads to the repulsion decrease between the sulphate group, and this will cause hydrophilic polymer profile to be weak and viscosity of dissolve decreased. Carrageenan solution viscosity will be decreased as the temperature increase which will cause carrageenan degradation [23]. According to carrageenan standardization, the minimum viscosity of carrageenan is 5 cP, hence this viscosity value obtained from this study has met the quality standard.

The viscosity of the carrageenan is produced by repulsion of sulphate group of negatively charged along the polymer chain, which will cause the polymer chain to be rigid and strong [24]. The hydrophilic profile leads to that surrounded molecule by stopping the water and will result in the
increase of viscosity.  Carrageenan viscosity was increasing based on the increase of KOH concentration. Carrageenan viscosity is influenced by carrageenan concentration, temperature, dispersion value, sulphate concentration, and carrageenan molecule weight [10, 21]. There is reported the increasing of gel consistency caused the viscosity decreased [25].

3.3. Gel strength
The unique carrageenan property is its ability to change the form of liquid into a solid and to change the form of sol to be gel reversible. This unique properties of carrageenan enlarge to the widely used of carrageenan for both food and pharmaceutical industry. Gel strength of carrageenan obtained through extraction method using 0.35% and 0.75% KOH concentration was 500 and 850 g m\(^{-2}\) respectively.

Research on the effect of liquid potassium hydroxide concentration towards carrageenan sheet quality shows that the increase of sulphate compound will reduce the gel strength, but will higher the viscosity [26]. Time of extraction is also known to influence gel strength where faster extraction time causes sulphate compound to be bigger and lower the gel strength.

Comparing gel strength obtained from this result with gel strength obtained from other results with the value range from 191.09 to 208.96 [27], and 18.33 to 168 to 168.86 [20], carrageenan obtained in this research was considered as a good quality carrageenan.

3.4. Moisture content
The moisture content of the carrageenan significantly influences the shelf life. Moisture content in food affects the metabolism of the enzyme, microbe activity, and chemical activity [28]. This research showed that a higher concentration of KOH caused the decreased of moisture content within the carrageenan. Previous research shows that an increase in KOH solution will reduce mineral salts and moisture content [22]. According to the commercial quality requirement for carrageenan, permitted moisture content should below 15%. Based on this carrageenan standard requirement, carrageenan moisture content obtained from this study through 0.75% KOH concentration was 14.32% which fulfill the standard moisture content requirement.

3.5. Ash content.
The analysis of ash content within the carrageenan was performed in order to know the mineral content of the carrageenan [29]. Mineral exists within the material can be divided into two kinds of mineral namely organic and inorganic mineral [30]. Seaweeds are known to contain the high mineral. Ash content within carrageenan is influenced by the salinity of seawater where it grows. During research, the salinity of the waters was at the range from 32 to 35 ppt.

According to the international standard requirement for carrageenan, the ash content permitted is at the range from 14 to 40 %. Based on this requirement, carrageenan produced from this study was on the range permitted by international standard. The existence of ash in carrageenan was originated from hydrocolloid which contain ester sulphate, potassium, sodium, calcium, magnesium, and ammonium from galactose, and 3,6 anhydro-D-galactose [26, 31].

3.6. Sulphate
Sulphate was used to indicate the quality of carrageenan, and carrageenan quality usually distinguished based on the sulphate content [32, 33]. Sulphate content of the carrageenan obtained by extraction method using KOH concentration of 0.35 % and 0.75% was 35.2 % and 40.2 % respectively. According to carrageenan quality standard based on the FAO requirement [34], the sulphate content of carrageenan should be ranged from 15-40%. Extraction of carrageenan with 0.35% and 0.75% KOH concentration produce sulphate content of 35.2% and 40.2% respectively. These values can be considered to be in accordance with FAO standard requirement.
4. Conclusion

Differences in KOH concentration showed the different on yield, moisture, total ash, viscosity, gel strength, and sulphate content. According to quality standard requirement proposed by FAO, all the parameters of carrageenan resulted from this study can be said to be in accordance to FAO standard except for sulphate content at 0.35 KOH concentration.

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