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Recovery of carrageenan from Solomon Islands red seaweed using ionic liquid-assisted subcritical water extraction

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ABSTRACT

The subcritical water extraction (SWE) was employed to extract κ -carrageenan from the red marine macroalgae *Kappaphycus alvarezii*. A series of extractions using different conditions were carried out with different ionic liquids (ILs) as catalyst, and 1% 1-Butyl-3-methylimidazolium acetate (BMIMAc) at 150 °C/5 MPa with 1:80 gmL⁻¹ (solid to liquid ratio) exhibited the highest yield (78.75%). Extracted material was compared with samples obtained by aqueous SWE and the conventional method. Characterization of the extracts was performed using Fourier transform infrared spectroscopy (FTIR), thermal gravimetric analysis (TGA) and X-ray diffraction (XRD). Hence, the results showed comparability to the standard confirming the extracted material as typical crude κ -carrageenan. Physical properties including gel strength and viscosity were minimal but emulsification index was relatively high for the sample obtained by SWE with IL catalyst. Antioxidant activity however was low compared to the other samples due to the low sulfate content but monosaccharide composition was close to the standard. The molecular weights of all samples were directly impacted by thermal degradation and IL dissolution which enhanced their bioavailability and functional properties. The SWE with IL catalyst is a potential technology that can be utilized for extraction of κ -carrageenan for commercial use in different industrial sectors.

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1. Introduction

The use of polysaccharides from natural sources in various industrial applications has been continuously growing in the past decades. Recently, marine microalgae and seaweeds were identified as some of the most abundant storage and largely untapped natural stocks of essential polysaccharides such as alginate, agar and carrageenan [1]. Carrageenan is a general name for a family of linear sulfated polysaccharides obtained by extraction from certain species of red marine macroalgae [2]. Commercially, carrageenans are extensively used in the food industry for their excellent physico-chemical properties such as stabilizing, thickening and gelling agents and have also been utilized in a variety of non-food products such as pharmaceutical, cosmetics, printing and textile formulations [3]. In addition, these sulfated polysaccharides also exhibited an important role as natural antioxidants that prevent oxidative damage in living organisms and are also important sources of soluble dietary fibers that come into contact with the immune system of the large intestine.

The structure of carrageenans is normally sorted into three major groups namely; (κ) κ -carrageenan, (ι) ι -carrageenan, and (λ) λ -carrageenan. Variation in the orientation of the basic structure is due to the number and location of ester sulfate substitutions and occurrence of the 3, 6-anhydrogalactose residues on the carrageenan backbone. κ -Carrageenan is characterized by an alternating disaccharide unit of 1, 3-linked β -D-galactose-4-sulfate and 1, 4-linked 3, 6 anhydro- α -D-galactose. Similarly, ι -carrageenan differs only by addition of a sulphated group at carbon 2 of 1, 4 linked galactose unit, while λ -carrageenan includes a third sulphated group at carbon 6 of 1, 4 linked galactose unit. Basically in the presence of cations and in aqueous solutions, both κ - and ι -carrageenans can easily form thermo-reversible gels upon cooling, whereas λ -carrageenan is a non-gelling agent [4].

Since the previous decades, global production of primary raw materials for κ - and ι -carrageenans specifically, *K. alvarezii* and *Eucheuma denticulatum* has increased quite drastically due to the growing demand for their thickening and gelling properties with increasing consumption of processed food. There was a rapid expansion of experimentation of cultivating carrageenan seaweeds from 944, 000 wet metric tonnes in 2000 to 5.6 million wet metric

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tonnes in 2010 (63%) [5,6]. The major carrageenan producers are Indonesia, Philippines, Tanzania, Kiribati, Fiji, and most recently India, Mexico and Solomon Islands. According to Kronen [7], production of *K. alvarezii* in Solomon Islands steadily increased from the first export in 2002 up to the latest record in 2009. The major producers are seaweed farmers in Wagina, located (latitude 7° 26' 00" S, longitude 157° 46' 00" E) in the Katupika region of Choiseul province [8].

The significant increase in the demand for carrageenan from different industrial sectors has created a need for a fast, efficient, and eco-friendly technology that will produce maximum yields. The sub-critical water extraction (SWE) with ionic liquid (IL) catalyst was selected because of the efficiency of the technology and environmentally benign nature of ILs [8,9]. The SWE is characterized by processing the sample at temperatures ranging from 100 °C to 374 °C and a pressure up to 22.1 MPa. This region where water is pressurized to a temperature and pressure below its critical level conditions is described as the subcritical region. Here water is maintained in the liquid state by keeping the pressure constant above the vapor pressure [10]. The IL catalyst is added to enhance the yield and increase dissolution of κ -carrageenan from the original seaweed matrix. According to Prasad [9] and Izawa [11], ILs are suitable for solvent dissolution and are also considered efficient for producing new polysaccharides because of their specific properties. Basically ILs have gained widespread recognition as eco-friendly alternatives to traditional organic solvents because of their distinctive physical and chemical properties such as; the ability to dissolve an extensive range of organic and inorganic compounds, their negligible vapor pressure and their high chemical and thermal stabilities. So far not much work has been done to extract carrageenan directly from seaweeds using ILs although many studies have already been conducted on extraction and analysis of cellulose from various substrates with different ILs including 1-Butyl-3-methylimidazolium Chloride (BMIMCl) and 1-Butyl-3-methylimidazolium acetate (BMIMAc) [12–17].

In this study, the best condition and IL catalyst that enhanced κ -carrageenan yield by SWE was identified and the crude κ -carrageenan recovered from the seaweed matrix was characterized and analyze for various physical and biological properties. Characterization to investigate absorption of different components in the κ -carrageenan, its thermal stability and crystalline structure was carried out using Fourier transform infrared spectroscopy (FTIR), thermal gravimetric analysis (TGA) and X-ray diffraction (XRD) respectively. The IL assisted SWE technology is a green approach that facilitates a comprehensive utilization of *K. alvarezii* as the natural source of κ -carrageenan.

2. Materials and methods

2.1. Materials and sample preparation

K. alvarezii sample was collected from seaweed farms in Wagina, Solomon Islands in August 2015, high purity nitrogen gas (99.99%) was supplied by KOSEM (Republic of Korea) and standards such as sodium sulfate, D-(+) - glucose, D-(+)-galactose, 3, 6-anhydrogalactose and κ -carrageenan were purchased from Sigma-Aldrich Chemical Co. (USA) for comparison. The series of ILs including 1-Butyl-3-methylimidazolium acetate (BMIMAc), 1-Butyl-3-methylimidazolium dibutyl phosphate ([BMIM][PO₄]), 1-Butyl-3-methylimidazolium tetrafluoroborate (BMIM-BF₄), 1-Ethyl-3-methylimidazolium Bromide (EMIM Br), 1-Ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF₄), 1-Butyl-3-methylimidazolium Chloride (BMIMCl) and Choline chloride (ChCl) were acquired from C-Tri (Chem Tech research incorporation, South Korea). The seaweed sample was prepared from our previous work [8].

2.2. Subcritical water extraction (SWE) of κ -carrageenan

SWE of κ -carrageenan was carried out in a 200-cm³ C276 batch reactor made of Hastelloy (continuous-type supercritical water system, Phosentech, South Korea) with a temperature control as described in our previous work [8]. Dried ground seaweed material was loaded into the reactor with 160 mL of 1% IL or deionized water. The vessel was closed tightly and heated using an electric heater to the desired temperature (60 °C to 180 °C). Pressure was determined based on saturated vapor to be 5 MPa for the temperature condition studied. Temperature and pressure in the reactor were controlled using a temperature controller and pressure gauge, respectively. The sample was agitated using a four-blade stirrer at 200 rpm with a reaction time of 5 min, maintained after reaching the desired temperature. The extracted hydrolysate was collected and centrifuged (8000 rpm, 10 min, 25 °C) to separate the supernatant from the insoluble residue.

The resultant supernatant was then precipitated with isopropanol alcohol (1:3, v/v) as described by Stengel [18] with some modifications. Recovery of the polysaccharide precipitate was carried out by centrifugation (8000 rpm, 10 min, 25 °C) and dried to constant weight at 35 °C to determine the mass and then ground in a mechanical blender (PN SMKA-4000 mixer, PN Co., Korea) and stored in a dry place at room temperature. The percentage yield was determined following our previous work [8] using the equation below:

$$\text{Yield}(\%) = \frac{\text{Weight of dry extract}}{\text{Initial weight of sample}} \times 100 \quad (1)$$

2.3. Extraction of κ -carrageenan by conventional method

Extraction of κ -carrageenan was performed using the conventional method described by Das [12] with slight modifications. *K. alvarezii* powder (10 g) was soaked for 2 h in a 200 mL solution of 0.5% calcium hydroxide. To the soaked seaweed, 200 mL of deionized water was added and autoclaved for 1.5 h at 107 °C. The hot mixture was ground in a mechanical blender (PN SMKA-4000 mixer, PN Co., Korea) and centrifuged, and the supernatant was slowly added under constant stirring to isopropanol alcohol (1:3, v/v). The precipitated κ -carrageenan was then oven dried to a constant weight, ground and stored at room temperature.

2.4. Characterization

κ -Carrageenan samples were mixed with potassium bromide and analyzed on a spectrum GX FTIR (Perkin Elmer, Inc., USA) equipped with a DTGS detector, in the range of 400–4000 cm⁻¹ as described by Saravana [19] with minor modifications. The TGA was performed on a TGA-50 (Shimadzu Corporation, Kyoto, Japan) instrument in a nitrogen atmosphere where 10–13 mg of sample was heated at a rate of 10 °C min⁻¹ from room temperature to 700 °C. XRD patterns of κ -carrageenan powder were recorded on a Brüker D8-Advance diffractometer (Brüker, Germany). A step size of 0.05° and a counting time of 5 s/step was used to collect data in the 2 θ range of 5–80°.

2.5. Physical properties of κ -carrageenan

Hot κ -carrageenan solution (1.5% w/v) in 0.005 M potassium chloride (KCl) was allowed to gel overnight at 25 °C and the gel strength was measured using a Brookfield CT3 4500 (Brookfield Engineering Laboratories, Inc., Middleboro, MA, USA) texture analyzer with a TA11/1000 probe at a speed of 0.5 mm s⁻¹ as described by Murano and Rhein-Knudsen [20,21] with minor modifications.

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