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Commercial scale production of carrageenan from red algae

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ABSTRACT

Carrageenan is one of the commercially important water soluble polysaccharides extracted from certain red algae and it is widely utilised in foods, dairy products and pharmaceuticals. In India, there is no carrageenan manufacturing unit and knowledge on the processing technologies of this phytochemical is very limited. Various methods available for the extraction of different types of carrageenan are reviewed in this paper.

Introduction

Carrageenan is a sulphated polymer obtained from some red seaweeds belonging to the families Gigartinaceae, Solieriaceae and Hypneaceae. It differs from agar mainly in its higher sulphated fraction and higher ash content. As our knowledge on the carrageenan yielding plants is very limited, information available on different aspects of this sulphated polysaccharide is summarised here.

Carrageenophytes

In recent years much attention has been paid to the carrageenan contents of various species of *Chondrus, Gigartina, Eucheuma, Kappaphycus, Hypnea, Laurencia, Solieria, Agardhiella* and *Sarconema* (Chen *et.al.*, 1973; Parekh *et.al.*, 1979 and 1988 a, b; Rama Rao, 1982; Mc Candles *et al.*,1982 and 1983; Mollion, 1983; Cheney *et.al.*, 1987; Chiovitti *et.al.*, 1988; Murano *et.al.*, 1997; Mollet *et.al.*, 1998; Seema Pasricha *et.al.*, 1998). The type of yield of carrageenan obtained from Indian red algae are given in Table-1. Seasonal variation in the carrageenan content were also recorded by few workers (Krishnamurthy and Rama Rao 1968; Fuller and Mathieson, 1972; Breden and Bird, 1994; Reani *et.al.*, 1998).

Chondrus crispus, Gigartina stellata, Iridaea spp, *Eucheuma* spp and *Kappaphycus* spp are the chief raw materials used for carrageenan extraction. The production of carrageenan was started in 1930's in the United States. In China, the production of carrageenan was started in 1970's using *Eucheuma gelatinae* and *Hypnea* as raw material. The major carrageenan producing countries are U.S.A., Denmark,

France, Japan, Spain, China, Korea, Brazil and Philippines. The annual world production is about 15,000 tons including 600 tons of carrageenan produced by China (Ji Ming Hou, 1990). The crude unrefined carrageenan is produced in Philippines and there is heavy demand for the unrefined carrageenan in the meat industries in the United States. Philippines is the leading country exporting the crude carrageenan to Europe, Japan and America (Gopakumar, 1997). But there is no carrageenan manufacturing unit in our country. Carrageenan production must be commenced in India using algal resources available in our country.

Types of carrageenan

Carrageenans are linear polysaccharides consisting of alternating 1, 3-1 linked β-D-galactophyranosyl and 1, 4-1 linked a-D-galactopyranosyl units. The three linked units occur as the 2- and 4- sulphate or not sulphated at all while the 4-linked units occur as the 2- sulphate, the 2, 6-disulphate, the 3,6-anhydride or as the 3,6-anhydride 2 sulphate. The presence of sulphate at C_3 has never been recorded. According to Greer and Yaphe (1984) carrageenans can be divided into three main groups. The Kappa family (k) in which the 1,3-linked galactopyranosyl groups are sulphated at C_4 (kappa, iota, mu and nu carrageenans), the lambda (λ) family where the sulphation is at C_2 (lambda, xi and pi carrageenans) and the beta (β) family (beta and gamma carrageenans) in which the 1,3-linked units are not sulphated (Greer and Yaphe, 1984). Another type of carrageenan which has sulphate groups on the C_6 of the I, 3-1 linked galactopyranosyl units, is named as Omega carrageenan (Mollion *et.al.*, 1986). Alpha carrageenan is not sulphated at C_4 of the I, 3-linked galactopyranosyl units but the sulphation occurs only at C_2 of the 3, 6 anhydrogalactose groups. So it was included in the beta family of carrageenans. In delta carrageenan, the precursor is sulphated at C_2 and C_6 of the 1, 4- linked units which upon treatment with strong alkali is converted into alpha carrageenan (Zablakis and Santos, 1986).

In k-carrageenan and λ- carrageenan polymer chain is branched in the former and linear in the latter. K- fraction is separated from λ–fraction by precipitation with potassium chloride and amounts to 40% of the carrageenan, the balance being the λ -fraction. The fraction soluble in hot water stands for k-carrageenan and the cold water soluble fraction to be λ–carrageenan.

Uses of carrageenan

The uses of carrageenan extracted from *Chondrus crispus* were reported in 1837. In food industry, carrageenan finds its use in bakery, confectionary and for culinary purposes especially in the preparation of condiment products, syrups, whipped creams, ice desserts, cheese etc. Carrageenan is used for clarification of beer, fruit juices and other beverages. It improves the quality of wheat flour in Chappatti and Parotta making. The food sector accounts for nearly 70% of world market for carrageenan. In pharmaceutical industry, carrageenan is used as emulsifiers in cod liver oil and emulsions as granulation and binding agents to tablets, elixirs, cough syrups etc. It is used extensively in ulcer therapy and diseases of blood vessels. In cosmetics, carrageenan is applied as stabilizer and thickening agents in tooth-paste, skin ointments and soaked air freshners. In textiles industry, hot water extracts of

Table 1. *Data on the type and yield of carrageenan obtained from Indian red algae*

Species	Type of carrageenan	% yield (dry wt)	Authors
Acanthophora spicifiera (Vahl.) Boergs.	Lambda	18.20	Parekh et. al., 1989
Grateloupia indica Boergs.	do	25-30	Parekh et. al., 1989
Halymenia porphyroides Boergs.	do	25-30	Parekh et. al., 1989
H. venusta Boergesen	do	35-40	Parekh et. al., 1987
Hypnea musciformis (Wulf.) Lamour.	Kappa	30-35	Parekh et. al., 1988 b
H. valentiae (Turn.) Mont.	do	25-30	Parekh et. al., 1988 a
Laurencia papillosa (Forssk.) Grev.	Lambda	22-25	Doshi et. al., 1987
Sebdenia polydactyla (Boergs.) Balak.	Iota	20-25	Doshi et. al., 1988
Sebdenia polydactyla (Boergs.) Balak.	Lambda	25-30	Doshi et. al., 1988
Solieria robusta (Grev.) Kylin	Iota	20-22	Doshi et. al., 1990

carrageenan are used in printing designs with dye and they also act as finishing and sizing agents. Carrageenan also called "painters moss" has been used for sometime in paint manufacturing as stabilizers for pigments. It is also used as good film-farming agent (Bhakuni and Silva, 1974; Guiseley *et.al.*, 1980; Parekh *et.al.*, 1992; Neushul, 1993; Kaladharan *et.al.*, 1998).

Industrial methods for manufacture of carrageenan

Kappa, Iota and Lambda carrageenans are having their own peculiar properties. The food industries are utilizing Lambda carrageenan because of its non gelling and high viscosity properties. The kappa carrageenan is widely used in the industries where it is required as gelling agent. In the same way, the iota carrageenan is also used in different industries.

Kappa carrageenan extraction

The different steps in the processing of kappa carrageenan is more or less similar to that of agar extraction. Species of *Eucheuma, Hypnea, Chondrus* and *Furcellaria* can be used as raw material. In India, *Hypnea musciformis* and *H.valentiae* are the good source of raw material for the manufacture of kappa carrageenan with an yield of 30-35% and 25-30% respectively (Table-1). The processing of kappa carrageenan is given in the Annexure-1 (Ji Ming Hou, 1990). The sun bleached dry seaweed is treated with 5-10% of NaOH at 80-90° C for a particular time depending upon the texture of the alga. Then, the seaweed is boiled and the extract is collected in a evaporator to reduce the volume of gel solution. In the case of seaweeds such as *Furcellaria* and *Eucheuma,* KCl precipitation process is applied. In this case, the filtrate after hot extraction is evaporated to reduce the volume of filterate and then the filterate is extruded through the spinnerets into cold 1-1.5% KCl solution. The gelled threads are washed again within the KCl solution. Then it is dehydrated by pressing method, dried and milled to get k-carrageenan powder.

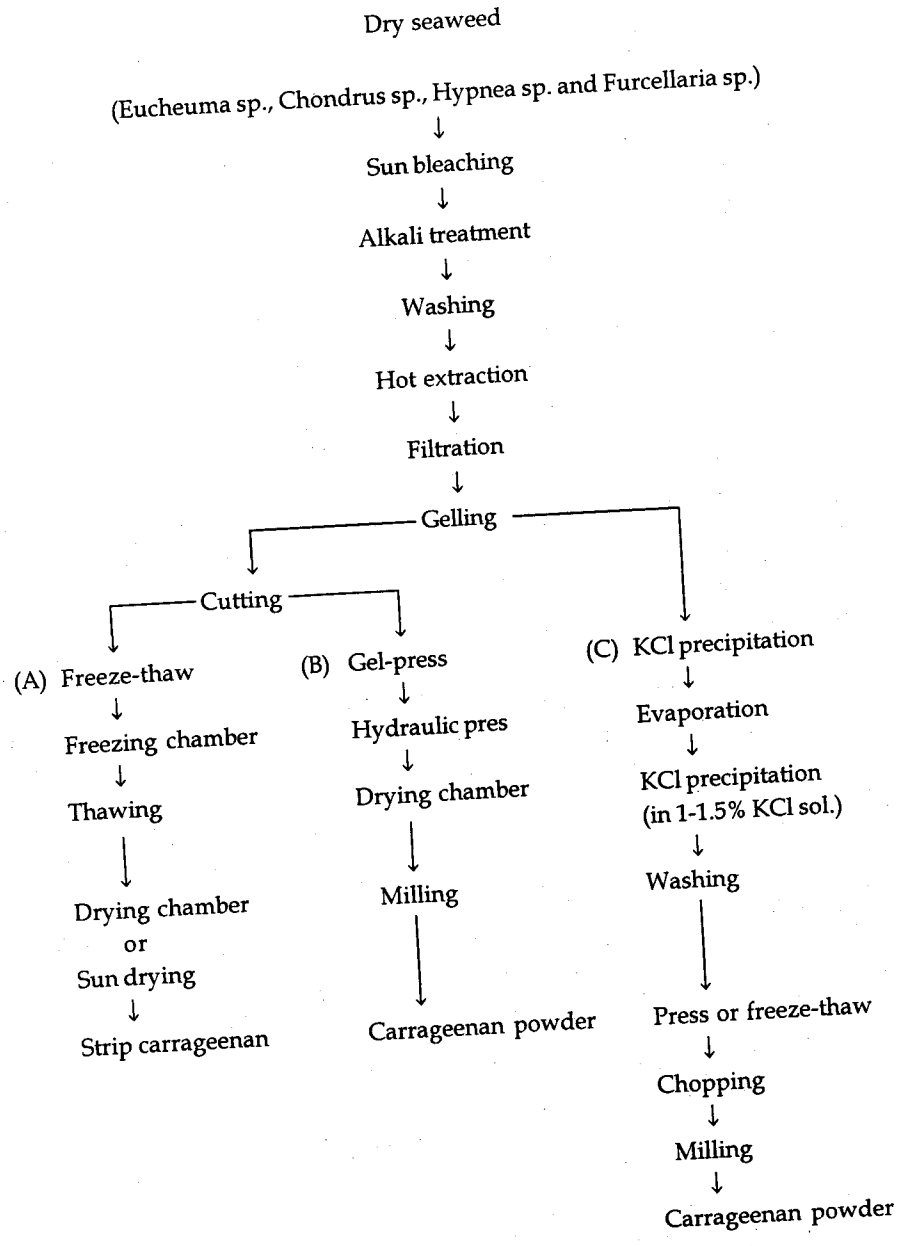
Lambda carrageenan

It contains about 35% sulphate and 0% 3,6-AG; exhibits no gelling ability at all and is more hydrophilic. Thus it could be dried by using drum dryer or alcohol precipitation process. The drum dryer method degrades the product. So,

Annexure-1

Processing technology for Kappa - carrageenan production

(Ji Ming Hou, 1990)



generally alcohol preciptitation method is practised. Propyl alcohol or ethyl alcohol is used as dehydrating agent (Annexure-2).

Iota carrageenan

This type of carrageenan has gelling properties in the presence of calcium ions but contains 30% 3,6-AG and 32% sulphate. It is more hydrophilic than k-carrageenan and difficult to produce by the freeze-thaw or gel process. So, alcoholic precipitation technique is used similar to that of lambda carrageenan. After hot extraction, the pH of the alkaline liquor is adjusted and subjected to coarse and fine filtration. The filtrate is then concentrated with double-effect evaporator to reduce the volume (Annexure - 2).

Semi processed / Semi refined carrageenan

The semiprocessed carrageenan is produced by alkali treatment of *Eucheuma cottonii* and drying in the farm itself. A basket of seaweeds is immersed and cooked in hot aqueous KOH at 100 °C and then soaked in fresh water to extract the alkali. The produce is dried and ground to powder. By this process, the quantity of water required to produce the final product is minimised, thereby reducing the cost of the product. This product usually can be substituted for extracted carrageenan where a little cloudiness due to small amount of cellulose present does not interfere (Annexure-3). The processing technology for semi-processed/crude carrageenan given by Gopakumar (1977) and Kaliaperumal (1984) is shown in Annexures 4 and 5 respectively.

Annexure-2

Processing technology for Iota and Lambda carrageenan production

(Ji Ming Hou, 1990)

Dried seaweeds

(*Gigartina* sp.,

Eucheuma sp.)

↓

Sun bleaching

↓

Washing

↓

Hot extraction

↓

Filtration

↓

Evaporation

↓

Alcohol precipitation

↓

Centrifuge

↓

Drying

↓

Milling

↓

Iota or Lamda Carrageenan powder

Annexure-3

Processing technology for semi-processed carrageenan

(Ji Ming Hou, 1990)

Dried seaweeds
(*Kappaphycus alvarezii, Eucheuma cottonii*)

↓

Cutting

↓

Alkali treatment
(8.5% KOH)

↓

Rinsing

↓

Sun drying

↓

Milling

↓

Semi-processed carrageenan product

Annexure-4

Processing technology for crude carrageenan

(Gopakumar, 1997)

Washed and sundreid seaweed
(*Eucheuma* sp)

↓

Digestion with 0.5% KOH at 90°C for 60 minutes

↓

Alkali digested seaweed

↓

Washing with clean water

↓

Alkali free digested seaweed

↓

Sun drying

↓

Pulverisation in grinding mill / or Milling

↓

Powdered seaweed
(yellow colour)

↓

Crude carrageenan

Annexure-5

Processing Technology for semi-refined carrageenan

(N. Kaliaperumal, 1984)

Cleaned dried *Euchema*

↓

Washing the cleaned seaweed in fresh water

↓

Boil the seaweed

↓

Treat with 10% potassium hydroxide (caust ic potash)

↓

Sundrying

↓

Grinding

↓

Powdered semi-refined carrageenan

Resources and Prospects

In India, *Hypnea musciformis* and *H.valentiae* occur in large harvestable quantities in the intertidal, subtidal and deepwater regions. The standing crop estimated for these species from the intertidal and shallow waters of Gulf of Mannar and Palk Bay in Tamilnadu was 900 tons wet wt (Subba Rao *et.al.*, 2001) and 5263 tons (wet wt) from deep waters of Tamilnadu coast (Kaliaperumal *et al.*, 1998). The quantity of *Hypnea* spp estimated from Lakshadweep islands was 32 tons wet wt (Subba Rao *et.al.*,2001). Further, mariculture of *Hypnea* has been successfully achieved (Rama Rao *et.al.*, 1985; Rama Rao and Subbaramaiah, 1986; Subba Rao *et.al.*, 2001).

The huge quantities of *Hypnea* and other carrageenophytes available in Indian waters can be utilised for the manufacture of carrageenan. Further, in recent years the carrageenan yielding red alga *Kappaphycus alvarezii* has been successfully cultured on commercial scale in our waters (Eswaran *et.al.*, 2002; Subba Rao *et.al.*, 2001). This red alga can also be used as raw material along with *Hypnea* for production of processed / semiprocessed carrageenan. Now, the country's domestic need of about 40 tons per annum is met through imports at considerably high prices. By establishing carrageenan industry, the country's demand for carrageenan can be met and it will save valuable foreign exchange and provide additional employment opportunities to the people living in the coastal villages.

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