Products from seaweeds

N. Kaliaperumal

Regional Centre of Central Marine Fisheries Research Institute
Marine Fisheries - 623 520, Ramnad District, Tamilnadu

Abstract

Seaweeds constitute one of the commercially important marine living renewable resources. They are the only source for the production of phytochemicals such as agar, agarose, carrageenan and algin which are widely used in various industries as gelling, stabilising and thickening agents. Seaweeds are good sources of food and medicine. Food products like jelly, jam, pickle etc. can be prepared from seaweeds. Many bioactive compounds can be extracted from seaweeds. Seaweed meal and seaweed liquid fertilizer are also manufactured from marine algae. The methods for manufacturing different phyto-chemicals and products from seaweeds are given in this paper.

Introduction

Seaweeds or marine algae are primitive non-flowering plants without true root, stem and leaves. They constitute one of the commercially important marine living renewable resources. They contain different vitamins, minerals, trace elements, protein, iodine, bromine and bioactive substances. Seaweeds are good source of food and medicine. They are the only source for the production of phytochemicals such as agar, agarose, carrageenan and algin. These phycocolloids are used as gelling, stabilising and thickening agents in food, pharmaceuticals, confectionery, dairy, textile, paper, paint and varnish industry etc. Marine algae are used as raw materials for the production of other chemicals such as mannitol, iodine, bromine, laminarin and fucoidin. Food products like jelly, payasam, jam, chacolate, salad, soup, curry etc. can be prepared from seaweeds. Seaweed meal and seaweed liquid fertilizer are also manufactured using marine algae. There are several medicinal properties in seaweeds. Many bioactive compounds can be extracted from seaweeds (Chapman and Chapman, 1980; Chennubhotla *et al.*, 1987a; Chennubhotla, 1996; Chennubhotla *et al.*, 1991; Kaladharan *et al.*, 1998; Chennubhotla and Kaliaperumal, 1999). The various products obtained from seaweeds, methods of manufacture and their used are given below.

Phytochemicals

Agar

Agar is the major cell-wall constitutent of certain red algae especially the member of families Gelidiaceae, Gelidiellaceae and Gracilariaceae. It is extracted from *Gelidiella acerosa, Gracilaria edulis, G.crassa, G. foliifera, G. verrucosa* and species of *Gelidium, Pterocladia* and *Ahenfeltia.* Agar consists of chain of 9-B galactopyranose units linked in 1, 4 bonds with a sulphated L. galactose. The method for production of agar on commercial scale (Kaliaperumal and Uthirasivan, 2001) is given in Annexure-I.

Annexure - I

Production of agar on commercial scale

Dried *Gracilaria edulis* (200 kg)
↓
Leaching in freshwater for 12-18 hours
↓
Washing two times with freshwater in agitator tank (3 washes-10 min. duration each)
↓
Softening of seaweed with HCl for ½ hr (pH 2-4)
↓
Washing with fresh water (7 pH)
↓
Cooking seaweed in digester for 2-3 hrs by passing steam at 50 lb pressure
↓
Settling agar gel for ½ hr
↓
Filtering agar gel through filter cloth
↓
Collection of agar gel in aluminium trays
↓
Cooling agar gel at room temperature for 1 - 2 hours
↓
Shredding agar gel with gel chopper
↓
Freezing agar for 24 hours (till temp. comes down to -20°C)
↓
Thawing agar after removal from freezing room
↓
Drying agar in sun on velon screen frames
↓
Bleaching agar in 10% chlorine water for 5-10 minutes
↓
Washing agar with fresh water for 2-3 times
↓
Drying agar in sun on velon screen frames
↓
Dried agar (15 kg)
↓
Packing dried agar sheets in polythene bags (1 kg packets)
↓
Sale

Agar is used for gelling and thickening in the confectionery and bakery industries and as stabilizer for the preparation of cheese and for salad dressings. In fish and meat processing industry, agar is applied for canned products as a protective coating against the effect of metal containers and against shaking during transport of these products. Agar is also used as a clarifying agent in wines, beer and liquors. In pharmaceutical industry, agar is used as a laxative for chronical constipation, as drug vehicle and as a medium for bacterial and fungal cultures. Agar is an ion exchanger and used in the manufacture of ion exchange resins. In cosmetic industry, agar serves as a contituent of skin creams and ointments. Agar is also employed in paper and textile industries as finishing and sizing agents.

Carrageenan

Carrageenan is a sulphated galactan polymer obtained from various red seaweeds belonging to the families Gigartinaceae, Solieriaceae and Hypneaceae. It differs from agar mainly in its higher sulphated fraction and higher ash content. The back bone of the carrageenan polymer consists of 1, 3 and 1, 4 linked D-galactopyranose units which vary in the degree and the location of sulphated esterification. Carrageenan can be separated into two fractions - k - carrageenan and λ-carrageenan whose 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.

Chondrus crisous, Gigartina stellata, Iridaea spp, *Eucheuma* spp and *Kappaphycus* spp are the chief raw materials used for extraction of carrageenan. The industrial method for the manufacture of Carrageenan (Kaliaperumal and Ramalingam, 2000) is given in Annexure - II.

Annexure - II

Industry method for production of carrageenan

Washed sun dried seaweed

↓ ← Steam

Boil the seaweed treating with 10% KOH (Caustic potash)

↓

Sun drying (or)

↓

Drying on sieve plates in indoor ← Hot Air

↓

Powdering

↓

Semiprocessed Carrageenan

Similar to Agar extraction → | ← Add 5-10% NaOH before hot extration

↓

Carrageenan

In food industry, carrageenan finds its use in bakery, confectionery and for culinary purposes especially in the preparation of condiment products, syrups, whipped creams, ice disserts, cheese etc. Carrageenan is used for clarification of beer, fruit juices and other beverages. Carrageenan improves the quality of wheat flour in spaghetti 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 for diseases of blood vessels. In cosmetics, carrageenan is applied as stabilizer and thickening agents in tooth paste, skin ointments and solid air freshners. In textile industry, hot water extracts of carrageenan is used in printing designs with dye and act as finishing and sizing agents. Carrageenan, also called "Painter Moss" has been used sometime in paint manufacturing as stabilizers for pigments. They are also good as film-forming agents.

Algin

Algin or alginic acid is a membrane mucilage and a major constituent of all alginates. The various salts of alginic acid are termed 'alginates' (for example sodium alginate, calcium alginate etc). The term algin is used as a collective name for alginic acid and alginates but also as a trade name for sodium alginate. Alginic acid and its salts with divalent and trivalent metal ions are generally insoluble in water, while alkali metal salts are water soluble.

Algin is obtained from brown seaweed species such as *Ecklonia, Macrocystis, Undaria, Laminaria* and *Durvillea* from temperate areas and *Turbinaria, Sargassum, Cystoseira* and *Hormophysa* from the topical areas. The industrial method for the manufacture of algin (Kaliaperumal and Ramalingam, 2000) is given in Annexure - III.

In pharmaceutical industry, algin is used as emulsifiers in watery emulsions with fats, oils and waxes, as fillers in the manufacture of tablets, pills and as base of any ointments. An alginate gauze is used as a blood stoping

Annexure - III

Method for production of sodium alginate on commercial scale

Sun dried seaweed
(Sargassum / Turbinaria)
↓
Wash in fresh water
↓
Treat with HCl
↓
Wash in fresh water
↓
Treat with sodium carbonate
↓
Settle for 2 hours
↓
Filter the supernatant solution
↓
Add chlorine solution
↓
Add HCl for alginic acid precipitation
↓
Dehydrate the precipitate using centrifuge
↓
Treat with sodium carbonate
↓
Drying in sun
↓
Powdering
↓
Sodium alginate

plaster. As a slimming agent, the alginate forms a jelly in the stomach which produces the feeling of saturation in stomach. Ammonium alginate wool is used as a filter for microorganisms for laminar flowhood.

In cosmetic, detergent and soap making industries, alginates serve as thickening and dispersing agents in the production of ointments, creams, liquid emulsions, lotions and tooth paste as well as an additive in hair dye, hair fixing tonics, shampoos etc. due to the ability of alginates to form films. Alginates increase the consistency of shaving creams. In dental technology, alginates are used for making denture mouldings as well as denture fixatives.

In food technology, alginates improve the baking properties and they are constituent of baking emulsions. Alginates are used to make sugar glazings, egg, fruit and other cream fillings and in confectionery for making imitation fruits. Jelly products are made with water insoluble alginates (calcium alginates). In a number of countries alginates are suggested as a gelating agent in marmalades and jams. In dairy products such as cheese, creams, milk shake mixed in chocolates, puddings, cold prepared pudding powder, soft cheese and custards, alginates are extensively used. Alginates act as stabilizers in milk mixes and impart uniform viscosity and good whipping ability.

In beverages, alginates act as clarifying agent for making wines and raw liquor of sugar and molasses. Alginates act as foam stabilizers in lager beer and malt beer. In meat and sausage industry, meat and sausage products are given a longer shelf life with an alginate film. Artificial casings with an alginate base have been developed for making small sausages particularly for vegetarians. For deep freezing of fish, meat and poultry products an alginate gel is used and this has been patented in many western countries.

Alginate filaments are used in the production of calcium alginate rayons. In ceramic and leather industries, addition of alginate stabilizes the pigment and glazing suspensions to ceramic, porcelain and Chinaware as well as leather goods. Alginates find extensive application in textile industry, particularly as a thickening agent for printing dyes and paints that prevents smudging and promote quick drying and evenness of prints.

Mannitol

Mannitol is an important sugar alcohol of the hexite series found in brown algae. Mannitol is a constituent of cell sap. It occurs also as mannitan. The chief raw materials for the extraction of mannitol are *Fucus vesiculosus, Laminaria hyperborea, Ecklonia radiata, Bifurcaria brassiformis, Sargassum* spp, and *Turbinaria* spp.

In the extraction of mannitol, the dried brown seaweed materials are pre-treated with dilute HCl (10-15%). The aqueous acid extract after neutralization is evaporated to dryness. From this mixture of salts, mannitol and soluble polysaccharides are extracted with boiling methonal for 5 hours in the Hannen and Badum extractor. The solution containing the extracted material is allowed to stand for 24 hours at 5°C and the precipitate- the cystalline mannitol is filtered and dried before weighing.

In pharmacy, mannitol is applied for the production of tablets. Mannitol is also used for making diabetic food, chewing gum etc. Mannitol is employed as dusting powder in the paint and varnish industry, leather and paper industry, pyrotechiniques and in making explosives. In organic systhesis and in plastic production, mannitol is used as plasticizers for the production of resins.

Iodine

Iodine is extracted in small quantities from brown seaweeds in Japan, Norway and France and from red seaweeds like *Phyllophora nervosa* in Russia. As seaweeds are good source to meet dietary requirement of iodine, goitre disease caused by iodine deficiency is less prevalent in countries where marine algae form part of the diet. The iodine occurs in seaweeds in readily available form and it is superior to the mineral iodine. Some species of seaweeds especially red and brown varieties, have the ability to accumulate iodine and have a more concentrated source of it. *Laminaria, Phyllophora* and *Ecklonia* are the seaweeds from which iodine is extracted in Japan, Britain and other countries (Kaliaperumal *et. al.*, 1987).

Protein

The protein content is high in green and red algae than in the brown algae. The seaweeds which form rich source of protein are *Ulva rigida, U.fasciata, U. stenophylla, Caulerpa scalpelliformis, Cladophora monumentalis, Bryopsis* spp, *Porphyra vietnamensis, Centroceras clavulatum* and *Acanthophora spicifiera*. These algal proteins have essential aminoacids including iodine containing aminoacids. Studies revealed that these seaweeds contain 16-30% of protein on dry weight basis and this amount is somewhat higher than that in other food materials such as cereals, eggs and fish. Protein can be extracted from these seaweeds and as such dry powders of *Ulva, Porphyra, Acanthophora* etc. can be added to various foods deficient in protein or taken along with other food stuffs in small quantities.

The protein is extracted by first treating the powdered seaweed with ether-water mixture (1:4 ratio) for about 3 hours and then with 1 N Sodium hydroxide solution. The protein is then precipitated with 10% solution by trichloroacetic acid at pH 4-5. The precipitated protein is washed, dried and powdered. Among the different precipitating agents, trichloroacetic acid gives best results giving a concentrate containing 60% of protein (Kaliaperumal *et. al.*, 1987).

Vitamins

Different vitamins such as Vitamin-B 12, Vitamin-C, Vitamin-D and Vitamin-E have been reported from marine algae growing in different parts of the world. In India, few studies were made on the Ascorbic acid content (Vitamin-C). The results obtained by Thivy (1960) on the algae of Mandapam showed that the quantity of ascorbic acid present in *Sargassum myriocystum* is high and it is more than that present in citrus fruit.

Bromine, laminarian and fucoidin are other carbohydrates isolated from green, brown and red seaweeds.

Human food

Seaweeds are not actually a sought after vegetable to most westerners. However, the orientals have been eating a variety of seaweeds for thousands of years. It is known that about 100,000 tonnes of seaweeds are eaten annually in Japan in the name of Nori, Kombu (konbu) and Wakame. Seaweeds are rich in protein, vitamins, aminoacids, growth hormones, minerals and other trace elements. Hypothyroidism (goitre) can be cured and controlled by intake of iodine rich seaweeds like *Asparagopsis* and *Sarconema* spp.

Nori

Nori is the name of various edible products derived from *Porphyra* after processing. Nori is prepared by harvesting *Porphyra,* pounded washed with water, drained, chopped and finally mixed with freshwater before being spread on bamboo mats for drying. When dried thin sheets of nori are obtained, these are pressed flat, stored, bundled and packed for marketing. Nori is used as a flavouring agent in soup, sauces, and broths or even soaked in soybean sauce and eaten with boiled rice. Nori is also used in well known dishes - tempura and sushi.

Kombu

Kombu is prepared from *Laminaria.* After harvesting and drying, *Laminaria* is separated from the stipe and holdfast for quality and sent to kombu factories. Kombu processing involves boiling the kelp in a green aniline dye solution, air drying, compressing in frames and then cutting into blocks which are shredded. Kombu is used as soupstock, boiled vegetable, snack or seasoning for rice dishes (as curry leaves are used in India).

Wakame

Wakame has become more popular in recent times. It is made from large brown seaweed *Undaria pinnatifida. Undaria* is processed as wakame by washing, desalting and drying. Desalting is achieved by boiling with water. Wakame is popularly known in the forms of roasted or sugar candied products.

Seaweed Recipes

Many seaweed food products and recipes can be prepared from different seaweeds and consumed (Chennubhotla *et. al.,* 1981; Kaladharan and Kaliaperumal, 2000 a).

Salad

The following seaweeds are used for making salads either singly or in combination of two or three seaweeds. *Caulerpa racemosa, C. sertularioides, Codium* spp, *Gracilaria verrucosa, G.eucheumoides, Hydroclathrus clathratus, Laurencia papillosa* and *Porphyra* spp.

Fresh seaweeds are cleaned of sand, debris, attached stones etc. and then washed in freshwater. Chopped tomatoes, carrot, onion, chilli and ginger are added and mixed. Salt is added to taste.

Seaweed masala

Cut onion and green seaweed *(Ulva lactuca)* into pieces and garnish them in low fire with oil, mustard and curry leaves. When about to turn grey, add chilli powder, coriander powder, turmeric powder, salt, ginger and tomato pieces and mix well. It can be eaten with rice and chappatis.

Seaweed pickle

Take cleaned fresh seaweed *(Gracilaria edulis)* and remove moisture with cloth. Cut into small pieces. Soak in vinegar for 2 days. Remove from vinegar, add gingelly oil, chilli powder, mustard and fenugreek powder. Season with asafoetida. Add peeled garlic. Mix throughly and bottle.

Seaweed wafer

Boil cleaned dried seaweed *(Gracilaria edulis)* in water. Filter through organdy cloth. Add rice paste, chilli paste and asafoetida powder. Add gingelly seed and cumin seed and mix well. Cook together. Dry the paste in open sun in small lumps on cloth. Store in air tight jar before serving fried in oil.

Seaweed porridge

Boil dried cleaned seaweed *(Gracilaria edulis)* in water for 20 minutes. Grind it into a fine paste. Boil the paste in water. Add sugar and milk and mix thoroughly. Add cashew nut raisins and cardomon. Serve hot.

Seaweed jelly

Boil cleaned and dried seaweed *(Gracilaria edulis)* in water for 45 minutes. Stir frequently. Filter through organdy cloth into a vessel. Add sugar, lime juice, food essence and food colour to taste in hot condition. Mix thoroughly. Pour in an enamel or stainless steel tray. Allow to set. Refrigerate for a minimum of 30 minutes. Cut into pieces and serve.

Seaweed jam

Prepare sugar syrup. Add seaweed powder *(Ulva lactuca)* and boil for 15 minutes with stirring. Add edible colour and essence. Ready to serve.

Some of the food stuff such as Ice-cream, Tomato sauce, Jams, Jelly, Marmalade, Blancmange (without corn flour) and Lime jelly requiring agar and their method of preparation are given by Thivy (1958).

Animal feed

Seaweed are utilised as animal feed in some countries. They are cheap sources of minerals and trace elements. Hence, the meal prepared from seaweeds can be given as supplements to the daily rations of cattle, poultry and other farm animals. Seaweed meal can be obtained by grinding cleaned and washed seaweeds such as *Ulva, Enteromorpha, Sargassum, Padina, Dictyota, Gracilaria* and *Hypnea.* Seaweed meal can also be mixed with fish meal and used as a poultry feed.

During the extraction of agar, the boiled extract is filtered to separate agar from the plant material. Indian seaweed industries can extract only 50-60% of the colloid content (10-20%) from the raw materials. Hence, the residue is known to contain considerable quantity of colloids, other carbohydrate, protein, vitamins and minerals. The residue remaining in the filter is normally discarded. This residue can be utilised as a feed for dairy, piggery and poultry or can be used as binder-cum carbohydrate substitute in the feed preparation for farm animals.

Seaweed meal prepared from *Gracilaria, Gelidiella* and *Hypnea* is added to the feed ingredients while making compounded feed for fish and prawns as excellent binders. The commercial binders are gelating and tapioca powders.

Use of seaweed meal as a binder in fish and prawn feeds can increase the phytochemicals standard of the feeds compared to those feeds manufactured with conventional binders. Feeds made of seaweed as binders help maintain water quality as the conventional binders get fermented easily. Because of the flavour of seaweeds, these feeds have more palatability and also they are enriched with minerals, aminoacids and carbohydrates (Kaladharan and Kaliaperumal, 2000 b).

Seaweed manure

The earliest record of utilisation of seaweed as manure was that of Palladius in 4th century AD as described by Chapman and Chapman (1980). It has been found that seaweeds contain many growth promoting hormones such as auxins, cytokinins etc. apart from macro and micro-nutrients. Hence, seaweeds can be used as eco-friendly manures either as compost or the extract as liquid seaweed fertilizer (L.S.F.).

Seaweed compost

Basal application of seaweeds as a green manure to coconut and other plantation crops along the Lakshadweep islands and coastal areas of Tamil Nadu and Kerala is still in practice. This treatment improves the water holding capacity of soil, besides supply of micro and macro nutrients upon decomposition. A method for composting seaweeds with cow dung has been described by Thivey (1960). Field experiments have been conducted in the Central Marine Fisheries Research Institute applying seaweed compost to bhendi, sweet potato, tapioca and brinjal plants and high yields were obtained from these vegetable crops.

Liquid seaweed fertilizer

Now, seaweed extract is made into mineral rich liquid seaweed fertilizer (LSF) and marketed under various trade names. Studies have proved that extracts of *Sargassum wightii, Ulva lactuca* and *Spatoglossum asperum* at 1% strength show favourable response on the germination, seedling vigour, fruit settling and on the weight of fruit in crops like groundnut, maize, gingelly, tomato and ber. Liquid seaweed extract was first patented in the year 1912. Another patent was offered in 1962 and exploited by Maxicrop Ltd and marketed as 'Maxicrop' and 'Bio-extract'. When foliar feeding became an orthodox method of plant nutrition in the 1950s 'Marinure', 'SM-3' and 'Trident' brands were made in the UK in the 1966s and 'algifert' in Norway. In India, SPIC is manufacturing and marketing LSF in the name of 'Cytozyme'.

The following steps are adopted in the preparation of liquid seaweed fertilizer - thoroughly wash the seaweed to remove sand, debris and other weeds. Dry seaweed and pulverize in a grinder. Soak the seaweed powder in water. Cook the seaweed for 2 hours with water in the ratio of 1:10. Filter and centrifuge the extract. The viscous filtrate is used as 'LSF'. The filtrate is dried at 65-70°C to get dry solid. The dry solid extract is powdered and packed in air-tight bottles. This powder can be used as LSF by making 0.5% to 1.5% (w/v) solution with water. This is used as a foliar spray on green canopy of leafy vegetables and other horticultural crops (Rama Rao, 1992 and 2000).

Fuel gas

Fuel gas for domestic use can be produced utilising the brown seaweed *Sargassum* as raw material. A mixture of about six micro-organisms mostly derived from marine environments can be used in diegesters. Addition of indole acetic acid stimulated anaerobic digesters. Salinity of the liquid above 20%

was stated to be detrimental to production of fuel gas (Chennubhotla *et. al.,* 1987 a).

Medicine

More than 600 secondary metabolites belonging to the categories of terpenes, alkaloids, fatty acids and nitrogenous compounds have been isolated from marine algae. Many of these compounds are therapeutically active and have been extensively studied using laboratory and pharmacological assays. Species of *Sargassum* were used for cooling and blood cleaning effect. They contain sargalin, a blood sugar reducing agent. *Hypnea musciformis* is employed as vermifuge and *Centroceras clavulatum* as cathartic agent. Seaweeds rich in iodine such as *Asparagopsis taxiformis* and *Sarconema furcellatum* can be used to check goitre disease.

Several red algae including *Gracilaria, Gelidium* and *Pterocladia* have been used to treat various stomach and intestinal disorders. The stipes of *Laminaria cloustoni* have been used to aid in child birth by distending the uterus during labour. Carrageenan is useful in ulcer therapy and alginates are found to prolong the rate of activity of certain drugs. A number of species of marine algae have been found to have anticoagulent and antibacterial properties. Though the importance of different seaweed products in pharmacology is known, the development of antimicrobial, antifungal and antiviral substances from seaweeds is still in an initial stage of research and development (Chennubhotla *et al.,* 1987a).

Conclusion

India has a long coastline of 7500 km with rich growth of different seaweeds in the south coast of Tamilnadu, Gujarat coast, Mumbai, Ratnagiri, Goa, Karwar, Varkala, Vizhinjam, Visakhapatnam and also in Pulicat Lake, Chilka Lake, Lakshadweep and Andaman Nicobar islands. About 271 genera and 1053 species of marine algae belonging to four groups namely Chlorophyceae, Phaeophyceae, Rhodophyceae and Cyanophyceae have been recorded from Indian waters of which more than 60 species are commercially important (Umamaheswara Rao, 1970; Chennubhotla *et al.,* 1987b; Kaliaperumal *et al.,* 1995). The total standing crop of seaweeds from intertidal and shallow waters of all maritime states and Lakshadweep was estimated as 91,333 tonnes (wet wt). The quantity of seaweeds estimated in deepwaters of Tamilnadu was 75,373 tonnes (wet wt) in an area of 1863 sq km from Rameswaram (Dhanushkodi) to Kanyakumari (Silas *et. al.,* 1986; Kaliaperumal, 1994, 2000a and 2002).

At present, in India, seaweeds collected from wild along Tamilnadu coast are used as raw material for the production of only agar and alginates. As seaweeds form a very good source of human food, animal feed, medicine, fertilizer and a variety of products, different kinds of seaweeds growing at various localities of our coast may be exploited in a rational way and used for these purposes. In addition, seaweeds can be cultured on large scale following various techniques (Kaliaperumal, 2000 b) in the lagoons of Gulf of Mannar islands, Lakshadweep and Andaman-Nicobar islands and in the bays and calm areas of the east and west coast of India to augment the seaweed resources for proper utilisation.

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