Conventional and alternative technologies for the extraction of algal polysaccharides

G. Hernández-Carmona, Instituto Politécnico Nacional, México, Y. Freile-Pelegrín, CINVESTAV-IPN, Unidad Mérida, México and E. Hernández-Garibay, Centro Regional de Investigación Pesquera de Ensenada, INAPESCA, México

DOI: 10.1533/9780857098689.3.475

Abstract: Alginates, agar and carrageenan are the main commercial water-extracted polysaccharides sourced from brown and red marine algae. These phycocolloids exhibit high viscosity, and stabilizing, emulsifying and unique gelling properties. Agar and carrageenan form thermoreversible gels while alginates form ionic non-thermoreversible gels; therefore they play an irreplaceable role in foods, pharmaceuticals and biotechnology. The phycocolloid industry uses seaweeds from different parts of the world, and phycocolloid production amounts to 86 100 tons annually; equivalent to US$ 1018 million. In this chapter we describe the conventional processes adopted in most factories for extracting and processing alginates, agar and carrageenan, and discuss the use of new eco-friendly extraction processes.

Key words: seaweeds polysaccharides, alginate, agar, carrageenan, phycocolloid process.

14.1 Introduction

The phycocolloids alginate, agar and carrageenan are the main commercial polysaccharides derived from seaweeds. These three hydrocolloids are widely used in the food industry, pharmaceutical industry and in biotechnology, among other applications, because of their ability to produce highly viscous solutions and/or gels. As the first phycocolloid used, agar was one of the first
food ingredients approved as GRAS (Generally Recognized as Safe) by the FDA (Food and Drug Administration).

The use of phycocolloids in the food industry as functional food products is largely based on their ability to form gels, and the unique properties of these gels. Agar and carrageenans produce thermoreversible gels, where agar melts at a higher temperature than carrageenans. Carrageenans further have the ability to bind proteins in milk and meat products, while the gels rendered by alginates are ionic non-thermoreversibles. The main commercial sources for alginate production are the brown seaweeds *Laminaria* (Europe and Asia), *Ascophyllum* (Europe) and *Lessonia* (Chile and Peru). For agar, *Gracilaria* and *Gelidium* are the preferred seaweeds, while *Kappaphycus*, *Eucheuma* and *Chondrus* are used for carrageenans. Agar is the most expensive colloid, at US$18 per kg, followed by alginates and carrageenan at US$12 per kg and US$10.5 per kg, respectively. The total volume of phycocolloid production in 2009 was 86,000 tons; equivalent to US$1,018 million. Of this total, carrageenans accounted for 50,000 tons (58%), producing an income of 527 million US$ (52%), alginates accounted for 26,500 tons and agar for 9,600 tons, representing 32% and 17%, respectively, of the total sales. The process of producing alginate involves pre-treatment of the seaweeds with HCl (pH 4), extraction of the alginate with Na$_2$CO$_3$ solution (pH 10, 80°C, 2 h), and dilution and filtration in a vacuum rotary filter. The recovery of the alginates is then carried out as the insoluble calcium-alginate. Conversion of the insoluble alginate to soluble is achieved by treating the fiber, first with acid, then with Na$_2$CO$_3$ to obtain sodium alginate. Quality control for alginates is focused on particle size distribution, viscosity, pH, ash and calcium content.

For agar, the conventional production process includes pre-treatment, extraction, filtration, concentration and dehydration. However, depending on the genus used, there are some differences in the pre-treatment step. For *Gelidium*, this stage consists of a corrective treatment with a mild alkaline solution. This eliminates phycoerythrine and prepares the seaweed for a more efficient extraction. For *Gracilaria*, the alkali treatment is performed before extraction to increase gel strength. However, the effluents produced by this conventional method constitute a pollution problem. In response to these problems, the use of ‘green’ technology to produce large quantities of agarophytes as Integrated Multitrophic Aquaculture (IMTA) systems, together with the use of eco-friendly agar extraction methods, are proposed as the key to the future of the agar industry.

In carrageenans the process is rather more complicated, and largely depends on the species used. There are two basic processing lines, one for the production of refined carrageenan, in which an extraction at high temperature is followed by filtration and precipitation with alcohol or potassium chloride (KCl), and the other is for the production of semi-refined carrageenan, in which the carrageenan is not actually extracted. In this process, the seaweeds are generally alkali treated and the gel strength increased by concomitant desulfation. Some impurities, such as proteins, pigments and minerals are
eliminated, and the seaweed are then dried and milled. There are some other mixed procedures available and, as previously mentioned, in order to diminish the environmental impact, the use of eco-friendly extraction techniques are necessary.

14.2 Alginates

Alginate is a structural phycocolloid of brown seaweeds. Alginate has the ability to form heat stable gels with some divalent metals. It is an ionic polysaccharide comprising salts of two residues: \(\beta\)-D-mannuronic acid (M) and \(\alpha\)-L-guluronic acid (G). These units are randomly distributed in a linear chain, where they can be arranged as homogeneous blocks MM or GG and alternates as MG. The physical properties of alginites depend on the proportion of the three types of blocks and are related to the seaweed source. Alginites with high G have higher gelling properties, whereas those with high M have higher viscosity. Alginites are obtained by acid pre-treatment, followed by an alkaline extraction. The extract is clarified by vacuum filtration in order to remove seaweed particles, and the alginate is recovered from the solution as insoluble fiber by precipitation with calcium salts. The insoluble calcium alginate is converted to soluble sodium alginate by treating it with acid first, followed by a sodium carbonate–ethanol treatment. The final product is dried, milled, and sold as powders of different mesh size. Alginites are widely used in industries to give consistency (viscosity) or to form gels. For example, it is used in baked foods, textile prints, beer foam stabilizers, welding rods, pill disintegrators, bandages and dental impression material, among many others.

14.2.1 Historical background

Alginate was discovered by Stanford in 1881, but it was not until 1923 that exploration of its potential really began when Thornley established a briquette business using alginate as a binder of anthracite dust. In 1927 he moved his company to San Diego, California, to produce alginate to seal cans. After some difficulties, the company changed its name to Kelp Products Corp and in 1929 it was reorganized as Kelco Company. Alginate production then started on a large scale in San Diego, California. Production in the United Kingdom was established in the period 1934–1939 and in Norway some years later, after World War II (McHugh, 1987).

14.2.2 Sources of alginophytes

The main commercial sources and amounts harvested per year (dry tons) up to 2009, in order of quantity, were: Laminaria spp. (30 500 t from: France, Ireland, United Kingdom, Norway); Lessonia spp. (27 000 t from Chile
and Peru); Laminaria spp. (20 000 t from China and Japan); Macrocystis pyrifera (5000 t from USA, Mexico and Chile); Durvillaea antarctica (4500 t from Australia), Lessonia flavicans (4000 t from Chile and Peru), Ecklonia maxima (2000 t from South Africa); Ascophyllum nodosum (from France, Iceland, Ireland, United Kingdom) (Fig. 14.1). A drastic reduction in the harvest of Macrocystis pyrifera has recently occurred. This was originally harvested on the west coast of North America, from the Monterey Peninsula in central California to the middle West coast of the Peninsula of Baja California (Mexico). The harvest was reduced from 35 000 t (1999) to 5000 t (2009), after the closure of the International Specialty Products facility in San Diego. Another dramatic case relates to Ascophyllum, production of which decreased from 13 500 t (1999) to 2000 t (2009), mainly because its alginate produces low strength gel (low G blocks) whilst the market is demanding high G alginate (Bixler and Porse, 2011). At present, the main alginate producers are: China (Bright Moon), Norway (FMC BioPolymer, previously Kelco and Pronova); France (Cargill, previously Degussa, and Danisco); Japan (Kimica and Chemifa Food), and Chile (Kimica). Only China, Japan and Chile are producing propylene glycol alginate (PGA). Total alginate sales for 2009 were 26 500 t, with a total value of US$318 million.

Fig. 14.1 Geographical distribution of commercial seaweeds used for phycocolloids production. Production and cost of phycocolloids in 2009. Data from Bixler and Porse (2011).
Technologies for the extraction of algal polysaccharides 479

(US$12/kg) (Fig. 14.1). The current price (2012) of sodium alginate increased to about US$17–19/kg and PGA is US$25–26/kg (Dennis Seisun, written communication; www.hydrocolloid.com).

14.2.3 Chemistry of alginate

The chemical compounds extracted from seaweeds which facilitate the formation of viscous solutions or gels are polysaccharides named phycocolloids. The main commercial phycocolloids are alginate from brown seaweeds, and agar and carrageenan from red seaweeds (McHugh, 1987). Alginates form part of the cell wall and inter-cellular matrix of all the brown seaweeds. In the seaweed, the alginate provides the flexibility and the mechanical strength required by the plant to survive in the sea. In their natural state, alginates are bonded with all of the salts present in the seawater, particularly Ca$^{2+}$, Na$^+$, Mg$^{2+}$, Sr$^{2+}$, and Ba$^{2+}$ ions (Haug, 1964).

Alginate is a linear polysaccharide co-polymer of (1–4)-linked β-D-mannuronic acid (M), and α-L-guluronic acid (G). The two residues are arranged in an aleatory way within the alginate molecule. Three types of segment or blocks can be distinguished within the alginate: two homopolymeric, MM and GG, and one heterogeneous or alternating MG. (Haug, 1964; Haug et al., 1966; Smidsrod and Draget, 1996; Draget et al., 2005; Murillo-Álvarez and Hernández-Carmona, 2007). Different raw materials feature different M and G content, and the alginate properties of a particular seaweed are dependent on both the M/G ratio and the block distribution within an alginate molecule (Haug et al., 1966).

14.2.4 Alginate in food applications and other uses

Alginates are widely used across a number of different industries. They give consistency and an appropriate appearance to dairy products and canned foods, help retain moisture, thus improving the texture of baked foods, and ensure a smooth texture and uniform dewatering in frozen foods. Alginates are used as ink paste thickeners for textile prints, whilst in the paper industry they provide a smooth surface with less fluff. More usual applications are as beer foam stabilizers, and as a material in welding rods. In medicine, alginates are used as pill disintegrators and for bandages that are absorbed by the body (and thus do not have to be removed). Alginates are also used as a component of dental impression material (McPeak and Glanz, 1984; Reyes-Tisnado et al., 2004).

14.2.5 New insights into alginate uses

Alginates are now used to treat gastric ulcers, lower cholesterol levels and inhibit the granulation of mast cells, which are involved in allergic reactions (Nagaoka et al., 2000). Alginates find novel applications in the immobilization
of beneficial microorganisms for waste water treatment, and as a plant growth promoter, (Iwasaki and Matsubara 2000; Yabur et al., 2007). More recent applications are as proteins carriers (Coppi et al., 2001), metal interchangers (Davis et al., 2004; De Stefano et al., 2005), new textiles (Gorenšek and Bukošek, 2006), yeast immobilization (Pajic-Lijakovic et al., 2007), micro beads (Schuldt and Hunkeler, 2007; Mørk 2008), UV ray absorption (Tavares-Salgado 2007) and control of ulcerative colitis (Alireza-Razavi et al., 2008).

Indirect uses are also found in the transformation of residuals from the alginate extraction for use as fertilizers, because the bacterium *Gracilibacillus (A7)* degrades the alginate to oligosaccharides during the composting process (Tang et al., 2009). These residues can also be used for bioethanol production, since they are rich in sugars such as manitol and laminaran, drastically reducing the cost of production (Moen et al., 1997; Horn et al., 2000).

### 14.3 Conventional alginate extraction methods

The foundation of alginate extraction from seaweeds is the conversion of all alginate salts into soluble sodium alginate, dissolution of the alginate in water and the removal of insoluble residues. Following this, a calcium salt is added to form calcium alginate, which is an insoluble fiber and can be easily removed from the residual water. The fibers are converted to alginic acid by treatment with a hydrochloric acid solution. The fibers are then separated and blended with alcohol and sodium carbonate to convert them to sodium alginate. Other salts like potassium can be used to obtain potassium alginate. The sodium alginate is pressed, dried and milled (McHugh, 2003) (Fig. 14.2). The extraction processes used by many authors employ chemical preparations at fixed concentrations (normal or percent), for example sodium carbonate at 1% for the extraction step (Nishigawa, 1985; Istini and Kusunose, 1994; Calumpong et al., 1999; Younis et al., 2000; Fenoradosoa et al., 2010). However, it has been found that it is better to control the process by controlling the pH in the different steps, to prevent the yield and quality of the alginate being produced.

#### 14.3.1 Reduction of the seaweeds

In order to facilitate the transport of the seaweeds and to speed up the chemical reactions, it is necessary to reduce the size of the raw material. The seaweeds must contain 83% dried matter (17% moisture), and less than 3% sand. Milling is usually carried out in a hammer mill, and is generally conducted when the dry seaweeds arrive at the factory. The milled product must meet the following size distribution: 100% less than 6 mm; 95% less than 3.3 mm; 2% less than 0.3 mm.

#### 14.3.2 Rehydrating the seaweeds

In order to soften the seaweed tissue and avoid alginate pigmentation, the seaweeds are rehydrated with 0.1% formaldehyde solution (37.5% purity), for 1 to 12 h, depending on the species. The solution reacts with phenolic compounds, polymerizing and making the coloring substances insoluble. The ratio is one part
seaweeds to nine parts water. This proportion should be minimized to the point that all water is absorbed by the seaweed and no water is left at the end of the hydration. The increase of alginate yield using formaldehyde treatment has been previously documented (Hernández-Carmona et al., 1999a; Davis et al., 2004).

### 14.3.3 Acid pre-extraction
Some authors mention that acid treatment is necessary to convert the alginate salts (Ca²⁺, Na⁺, K⁺, etc.) to insoluble alginic acid. This ionic exchange is not necessary for most species and the acid washing is useful only for the removal of external salts and residual formaldehyde. On the contrary, acid treatment at a pH lower than 4, as recommended by other authors (Haug,
Functional ingredients from algae for foods and nutraceuticals

1964; Myklestad, 1968; Hernández-Carmona and Aguirre-Vilchis, 1987), may produce depolymerization of the alginate and reduce the viscosity (Hernández-Carmona et al., 1999a). The hydrated seaweeds are placed in a tank with water, at a ratio of one part dried (starting weight) seaweeds to ten parts water. This amount of water should be enough to allow free agitation. Industrial hydrochloric acid (28% purity) is then added until pH 4 is reached in the solution. The seaweeds are stirred for 15 min at room temperature, and the residual solution is then drained. For best results, the seaweeds are washed with water (1:10) for 15 min (McHugh, 1987; Arvizu-Higuera et al., 1995; Hernández-Carmona et al., 1999a).

14.3.4 Extraction

To extract the alginate from the seaweeds, they are transported to an extraction tank (kettle with steam jacket), and water is added in the proportion of one part of the initial dried seaweeds to 16.6 of water. This volume may change depending on the species. For seaweeds that produce low viscosity alginates (i.e. Sargassum) less water is required (Rodríguez-Montesinos et al., 2008). The seaweed-water mixture is heated to 80°C, and enough sodium carbonate powder is added to reach pH 10. The amount of water may be adjusted to obtain a paste that can be mixed, but is still thick enough to produce high friction between the solution and the seaweeds, to favor the alginate extraction. It is useful to monitor the increase of the ‘process viscosity’ (Hernández-Carmona et al., 1999b) with a viscometer, as an indirect measurement of the reaction progress. The maximum viscosity will determine the maximum alginate yield to be obtained. A final viscosity value for some species, like M. pyrifera, would be 3000–4000 mPa·s after two hours. The pH may be reduced during this process, which should be counteracted by the addition of more sodium carbonate to maintain pH 10. This step can be used to control the required viscosity of the alginate. High temperatures and longer processing times will produce alginates with lower viscosity, because of depolymerization of the polymeric chain of the alginate (Truus et al., 2001). At the end of the extraction, the seaweed must be practically disintegrated (McHugh, 1987; Arvizu-Higuera et al., 1996; Hernández-Carmona et al., 1999b). The extraction time (2 h) was confirmed for Laminaria digitata (Vauchel et al., 2008b), and the increase of alginate yield using a temperature of 80°C has also been demonstrated for the genus Sargassum (Davis et al., 2004).

14.3.5 Dilution and filtration

The paste obtained after the extraction step is pumped into a heated tank fitted with an agitation device. To allow the filtration process to occur, water is added to reduce the viscosity to 45 mPa·s (at 75°C). For species like M. pyrifera, the volume of water needed to reach 45 mPa·s corresponds to one part of the initial dried seaweeds to 55 parts of water. After the viscosity
and temperature have been adjusted, the solution is pumped to a rotary vacuum drum filter (http://www.alarcorp.com/equipment/auto-vac) that effectively removes solid particles from the sludge, producing dewatered, dry seaweed residue and a clear alginate solution. The filter consists of a hollow cloth-covered drum rotating on a hollow shaft, while partially immersed in a pan. The shaft is connected to a vacuum pump, and the filter is pre-coated by feeding a suspension of filter aid in water into the pan. The vacuum pulls the filter aid onto the cloth, building up a layer of filter aid. The alginate solution is then fed into the pan, pulled through the filter aid by the vacuum, and fed out via the hollow shaft. As the solution is pulled through this layer of filter aid, the fine solid particles in the solution are deposited on the surface. A knife blade is arranged to move slowly and automatically on the surface of the filter aid, shaving off a thin layer as the drum rotates and leaving a clean surface for rapid filtration (modified from Alar, 1991). Some of the best filter aids are the diatomaceous earth (Celite 545) and the expanded lava (perlite), which is more economical (McHugh, 1987; Hernández-Carmona et al., 1999b).

14.3.6 Calcium alginate precipitation
The clarified alginate solution is pumped from the filter into the precipitation tank. A shower nozzle should be installed at the end of the pipe to spray-discharge the solution in drops. At the same time, a 10% calcium chloride (CaCl₂) solution is added. The total amount of calcium to be added corresponds to two times the total alginate in solution to be precipitated. Both solutions are added simultaneously at a synchronized speed, so both solutions are programmed to finish at the same time. The agitation speed is important; a speed that is too slow will produce a clot-type precipitation, while a speed that is too fast will produce small fibers, increasing the difficulty of separating the alginate from the solution. The agitation speed should be increased as the solution volume in the tank increases. It is therefore necessary to be equipped with a variable speed agitator. The calcium alginate fibers are left in the tank for 15 minutes to allow the reaction to proceed. The fibrous calcium alginate can then be recovered by passing the suspension through a stainless steel screen (McHugh, 1987; Hernández-Carmona and Casas-Valdez, 1985; Arvizu-Higuera et al., 1997; McHugh et al., 2001).

14.3.7 Conversion of calcium alginate to alginic acid
The fibers of calcium alginate are transformed into alginic acid via acid treatment. This step is carried out in three counter-current steps, using three square tanks with stirrers. The calcium alginate is transported to the first tank, which contains acid previously used in the second tank. After stirring for 15 min, the solids are transported to the second tank using an endless screw with mesh at
the bottom. This second tank contains acid previously used in the third tank. The stirring and transportation are repeated, and the solids are fed to the third tank which contains new, diluted hydrochloric acid. The pH is adjusted to 2 in the first tank, and pH 1.8 in the second and the third tanks (McHugh, 1987). If water is not limited, the alginic acid fibers could then be washed with water for 15 min. The alginic acid must be almost free of calcium ions. However, if calcium is required in the final product (to increase the viscosity of the alginate solution), the pH in the tanks should be increased to pH 2, 2 and 1.8, respectively, limiting the ionic exchange. The alginate viscosity of a 1% solution is measured during quality control testing, before and after adding a calcium-sequestering agent (sodium hexametaphosphate). Viscosity will be reduced after adding the salt, but the reduction should not be more than 40%, so the amount of calcium in the final product should therefore be limited (Arvizu-Higuera et al., 1997; McHugh et al., 2001; Rodríguez-Montesinos et al., 2005).

14.3.8 Pressing and conversion of alginic acid to sodium alginate

The alginic acid is pressed to remove excess water using a screw press or S-press. Materials like alginic acid that tend to pack or are otherwise considered unpressable can be successfully processed using this equipment. The water is continuously drained from three areas of the press, reducing the hydraulic load. The screw press is equipped with a separate main drive and cone motors for independent speed control and retention time in the press. The alginic acid should contain 25% solids for the next step (modified from Bepex: http://www.bepex.com/spress.htm)

The alginic acid fibers are placed in a double planetary mixer, and enough alcohol is added to maintain a 55:45 alcohol:water ratio. For an estimation of the appropriate alcohol level to be used during neutralization, it is necessary to determine the amount of water remaining in the alginic acid fibers. This is obtained by subtracting the expected weight of the dry alginate (based on prior analysis in the laboratory) from the weight of the wet alginic acid. An additional option is to determine the moisture content of alginic acid. For example, a sample of pressed alginic acid (wet) with a starting weight of 23 kg contains 2.3 kg of sodium alginate, and is estimated to contain 20.7 L of water. This accounts for 55% of the content, so the volume of alcohol needed to obtain a proportion of 45% is found as follows: V = (45 × 20.7) / 55 = 16.9 L. Therefore 16.9 L of alcohol should be added to the fibers.

The next step is to add enough Na₂CO₃ powder to achieve a pH of 8 in the fibers. After stirring for 15 minutes the pH is measured; a sample of the fibers is dissolved in water and the pH is measured in the solution with pH paper. Alcohol may cause some interference in the pH measurement, and generally the pH of the alginate in solution will be one point lower than the pH measured in the fibers with alcohol. The approximate amount of Na₂CO₃ to add
is 0.25 parts per one part of the sodium alginate to be obtained. In this step the \( \text{Na}_2\text{CO}_3 \) can be replaced for \( \text{K}_2\text{CO}_3 \) to obtain potassium alginate. At this stage, the function of the alcohol is to keep the sodium alginate insoluble during the conversion process. Because alcohol is expensive, this must subsequently be recovered by distillation to reduce costs. It is estimated that only 2% of alcohol will be lost in the recovery operation.

Sodium alginate can also be obtained without the use of alcohol. To do this, the alginic acid is directly mixed with sodium carbonate. However, in this case the fibrous consistency is lost and the product must be passed through an extruder to obtain pellets. These pellets are subsequently dried and pulverized (McHugh, 1987; Arvizu-Higuera et al., 2002; Hernández-Carmona et al., 2002).

### 14.3.9 Drying, milling and blending

Drying is carried out on trays in a hot-air oven at 60°C until the alginate reaches 12% moisture. On a large scale, it is better to use a fluidized-bed dryer with a vibrating screen and hot air blowing up through the screen (McHugh, 1987). Milling is carried out in a turbine mill or fixed hammer mill. Most alginate products require a particle size lower than 60 mesh (250 microns), which can be achieved using a 3 mm mesh on the miller. To obtain a smaller particle size, the fine particles are separated and the coarse particles are milled with a 0.5 mm mesh size. In some cases a smaller size is required, and a third milling is then necessary. To separate the alginate by size, a five vibration mesh system is used with the follow size meshes: 30 (0.594 mm), 60 (0.250 mm), 80 (0.177 mm), 100 (0.149 mm) and 120 (0.125 mm). If the alginate is fluffy, it is harder to obtain fine alginate particles. Even after a third milling, 16% of the particles still will not pass through mesh 30 (Hernández-Carmona et al., 2002). More expensive modern equipment for drying, milling and screening is available (Fig. 14.2).

### 14.3.10 Quality control

The alginate obtained is analyzed in the laboratory to determine the viscosity of the product in 1% solution. The quality of the alginates (in terms of viscosity) varies according to various biological, environmental and processing factors. Therefore the products obtained may have different viscosities and should be blended to provide consistent quality. For blending the alginate a ‘V’-type blender can be used. The varied viscosities obtained from different batches can be combined to produce a specific viscosity: alginates with viscosity of 800 mPa·s can be produced by blending batches from 600 to higher than 1000 mPa·s. Alginates with mPa·s are produced by blending batches from 150 to 600 mPa·s; alginates with 80 mPa·s are obtained by blending batches from 40 to 150 mPa·s and products with 30 mPa·s are prepared by blending batches from 10 to 80 mPa·s. Generally, the final product is packaged in cardboard.
kegs of 22.5 kg with a plastic bag inside. Alginates are analyzed for the following properties:

- Viscosity in 1% of the solution, both before and after the addition of 0.5% of sodium hexametaphosphate. Viscosity is measured with a viscometer and the product is classified for sale by its viscosity according to the following ranges (mPa·s): very low (25–35), low (70–100), medium (340–460) and high (680–920).
- The pH of the alginate solution, which, at 1%, should be 6.1–7.8.
- Particle size distribution. The regular products are sold at particle sizes between 30 and 60 mesh and the refined between 100 and 150 mesh.
- Moisture, which must be less than 12%.
- Ash, the standard is in the range 18–27%.
- Calcium content, the standard is between 0.3% and 1%.
- Purity, which should be between 96% and 98% (Food Chemical Codex, 1981; Kelco, 1996).

### 14.3.11 Future trends in alginate extraction

An alternative method proposed for the alkaline extraction step employs a twin-screw extruder, and is called reactive extrusion. This technique appears to be more efficient than batch processing in a number of ways: process time is reduced to a few minutes, water and reactant are reduced, yield may be increased by 15%, and rheological properties are enhanced. All of these enhancements are due to the high level of shearing and mixing efficiency with the reactant. The reduced processing time lowers the level of depolymerization phenomena, thus increasing the alginate quality. This is a continuous process that makes the alginate extraction interesting from both an economic and an environmental perspective (Vauchel et al., 2008a, 2008b). Yield is also increased because of the reduced quantity of seaweed particles in the process (Vauchel et al., 2009).

### 14.4 Agar

Agar is a strongly gelling hydrocolloid from marine red algae. Its main structure is chemically characterized by repetitive units of D-galactose and 3,6-anhydro-L-galactose. Substitution with sulfates, methyl ethers, and/or pyruvate ketal can occur at various sites in the polysaccharide chain. The substitution pattern of these groups depends on both the algae species and the extraction method used which can promote desulfation, causing an increase in agar quality. In *Gelidium* and *Pterocladi a*, desulfation occurs as a natural internal transformation through an enzymatic process, whereas in *Gracilaria* it is not converted in the needed amount during the seaweed’s lifetime. Therefore when agar is
produced at an industrial level, it is necessary to promote desulfation by means of a chemical method before extracting the agar. The conventional agar production process can be described in key stages of pre-treatment, extraction, filtration, concentration, and dehydration. In the current industrial practice of producing agar, large quantities of sodium hydroxide at elevated temperatures are used for several hours. Agar, being a viscous material, transfers energy poorly and large thermal gradients can result in sub-optimal conversions and result in loss of product. In this context, new extraction techniques have been tested in the last decade to accelerate the reaction based on microwave-assisted extraction (MAE). The MAE requires less energy and solvent than conventional processes while generating fewer wastes and can be designed as an alternative eco-friendly agar extraction method.

14.4.1 Historical background

Agar is a mixture of polysaccharides that occur in the cell matrix of marine red algae (Rhodophyta). The biological function of agar is to give a flexible structure to the seaweeds, helping them stand the varying stresses of currents and wave motion (Craigie, 1990). Our ability to exploit the ‘inventions’ of nature for our own benefit has led to the use of agar as a gelling agent in a large number of food and industrial applications. The Japanese were the first to accidentally discover the original manufacturing method for extracting and purifying agar in 1658. The documented story described by Armisén and Galatas (1987) tells that a Japanese officer arrived at a little inn where the innkeeper, Minoya Tarozaemon, offered him for dinner a traditional seaweed jelly dish, which had been prepared by cooking Gelidium with water. After dinner the surplus jelly was thrown outdoors by the innkeeper. The jelly froze during the night, then thawed and dried in the sun, leaving a dry, white residue. Tarozaemon found that when this was boiled in water and cooled, it produced a clearer jelly than was originally produced. This was named ‘kanten’, which literally translates as ‘frozen sky’. This name describes figuratively the natural method of freeze-thawing which has been used since its discovery right up to the present day.

The use of agar in foods was widespread throughout the Far East, including Japan, China, Taiwan, Korea, the Philippines and Indonesia. In fact, the name agar-agar (nowadays called solely ‘agar’) is Malayan, where agar means jelly. In the Polynesian languages, the repeated word gives added emphasis; agar-agar is therefore translated as pure-jelly. Upon its later introduction into Europe, the Malayan term became attached to the Japanese seaweed extract (UNDP/FAO, 1990). As the first phycocolloid used (200 years prior to alginate or carrageenan) agar was one of the first food ingredients approved as GRAS (Generally Recognized As Safe) by the FDA (Food and Drug Administration) in 1972. It also passed all other toxicological, teratological and mutagenic tests (Armisén, 1995). Popular culture associates agar consumption with longevity. In addition, because it consists of around 80%
fiber, this phycocolloid is consumed to serve as an excellent intestinal regulator, playing an important role in the functional food market (Maeda et al., 2005). Although the processed food industry is still the primary market for agar, there is an attractive market for the derivative products bacteriological agar and agarose, as microbiological and electrophoresis media respectively. Among the seaweed hydrocolloids agar, carrageenan and alginate, agar has the higher price, currently estimated at US$18/kg in 2009 (Bixler and Porse, 2011).

14.4.2 Sources of agarophytes

The world agar industry mainly uses the following genera: Gelidium, harvested from wild beds in Spain, Portugal, Morocco, Japan, Korea, Mexico, France, USA, China, Chile and South Africa; Gracilaria, the only agar source that is commercially cultivated at present in Indonesia and Chile and to a far lesser degree in Malaysia, Thailand and China; and Pterocladia, harvested from wild beds in the Azores (Portugal) and New Zealand (Fig. 14.1). The genera Gracilaria and Gelidium are the dominant industrial seaweeds for agar extraction. Gelidium species were the original materials used in Japan, but shortages during World War II led to the employment of Gracilaria species, to counteract the lack of Gelidium. About 9600 tons of agar (valued at US$173 million) were produced worldwide in 2009 (Fig. 14.1) and Gracilaria has become the preferred seaweed for the production of food grade agar. This is due to the success of its cultivation, the increase in its availability and subsequent competitive prices (Bixler and Porse, 2011). The data obtained by the same authors show an increase of 69% in Gracilaria harvesting for the period of 1999 to 2009 and a decline of 73.3% of Gelidium in the same period. For further details see McHugh (2003).

14.4.3 Chemistry of agar and mechanism of gelation

Agar is composed of a heterogeneous mixture of molecules, built on a disaccharide repeating unit of 3-linked β-D-galactopyranosyl and 4-linked 3,6-anhydro-α-L-galactopyranosyl residue. Substitution with sulfate hemi-esters, methyl ethers and/or pyruvate ketals can occur at various sites in the polysaccharide chain. The pattern of substitution depends on various aspects: environmental factors, such as hydrodynamic conditions, availability and quality of light and nutrients; physiological factors such reproductive stage and nutritional state; and the extraction and isolation conditions of agar. Agar polysaccharides isolated from Gracilaria are typically more sulfated than those obtained from Gelidium and Pterocladia, with the pattern of sulfation dominated by the esterification of C-6 of the linked galactose L-unit. This L-galactose 6-sulfated residue is synthesized in Gracilaria as a biological precursor of the 3,6-anhydro-L-galactose, and is enzymatically converted to the anhydrous form by sulphohydrolases (Murano, 1995). However, this enzymatic activity seems to be lower than that which occurs in Gelidium and
Pterocladia. A higher number of unfinished 6-sulfated molecules are therefore found in agars from Gracilaria, producing none gelling or weak gel-forming polysaccharides. Thus, the physical properties of the resulting agar (gel strength, gelling and melting temperatures) are linked to their chemical structures. The gelling ability of agars from most Gracilaria species can be considerably improved by adopting an alkali treatment before extraction, which increases the proportion of 3,6-anhydrogalactose. This reaction occurs when 6-sulfated-L-galactose units are present; by heating the polysaccharide in strong alkaline media, the 3-OH group can be ionized, producing an intramolecular nucleophilic displacement of the sulfate group in position 6. This reaction is highly specific and no other sulfate group is affected (Murano, 1995).

Agar gelation occurs through a helical conformation of agar polysaccharides. These helices can be aggregated by hydrogen bonds. Consequently, the typical hysteresis of the thermoreversible order-disorder transition of agar can be highly perturbed by the presence of charged groups, which can interfere with intermolecular hydrogen bonding (Lahaye and Rochas, 1991). For further details on the agar gelation mechanism, see Armișen and Galatas (2000).

One of the most remarkable features of agar gels is their thermoreversibility. Agar melts by heating to a temperature over 85°C, depending on the algal species, but becomes a gel again upon cooling. The gelling temperature is affected by the methoxyl groups, which vary depending on the algal species used (Guiseley, 1970). In particular, the extent of methoxylation of agar polymers from Gracilaria is significantly higher than Gelidium and Pterocladia, and this difference is reflected in their gelling temperatures, which are in the range of 40–42°C in Gracilaria species, compared to 34–36°C for Gelidiaceae.

14.4.4 Agar for food applications

Traditionally three grades of agar with different gelling characteristics are recognized: food-grade, bacteriological agar and agarose (a neutral fraction of agar which has widespread use today for gel electrophoresis analysis). Bacteriological agars are usually prepared from Gelidium and Pterocladia, because agars from Gracilaria have gelling temperature above 40°C. Agarose is usually obtained from Gelidium, although some preparations of this more neutral molecule can be produced from certain select Gracilaria species (Murano, 1995).

Agar is employed as a vegetarian gelatin with high fiber content, and is also used as a replacement in icings, glazes, processed cheeses and sweets. The use of agar in food applications is based on its ability to form gels, and the unique properties of these gels. Agar dissolves in boiling water and, when cooled, forms a thermoreversible, clear, colorless and odorless gel. In contrast to gelatin gels that melt around 37°C, agar gels do not melt until heated to 85°C or higher. The large difference between the gelling and melting temperatures (temperature hysteresis) is unusual, and unique to agar. In spite of agar having a very similar structure to carrageenan, it melts and gels at higher
temperatures, and many of its applications take advantage of this difference. As an example, agar is found to have specific uses in pastry fillings and glazes, which can be applied before the pastry is baked without melting in the oven. The agar consumption for this segment of the market was 6050 tons during 2009 (Bixler and Porse, 2011). The same authors highlight the fact that although in processed meats carrageenan is the preferred water binder or texturing agent of choice, agar holds on to the gelatin replacement market in canned meats and aspics, with a market of 150 tons during 2009. The texture of agar in fruit jellies also helps it compete with kappa-carrageenan jellies, and the agar texture is preferred in Asia, particularly in Japan, where agar is a traditional ingredient which has been in use for hundreds of years. In the modern day it is one of the hydrocolloids that is available in many Asian grocery stores, and is sold as strips, in square form and more recently in tablet form. In western countries agar is sold through specialized stores as a ‘natural food and functional seaweed product’ with a market of 2000 tons in 2009 (Bixler and Porse, 2011).

Though species of *Gracilaria* generally produce agars with low gelling capacity or low gel strengths, they are considered the most important source of commercially valuable agar for the food industry, mainly due to the availability of the biomass due to culturing, and the improved quality that can be obtained via the use of the alkali treatment. Furthermore, new dimensions in the application of *Gracilaria* agars are opening thanks to the discovery of its sugar-reactive property, an important effect by which an agar may increase the gel strength after the addition of sucrose (40–60%), increasing its commercial interest (Matsuhashi, 1990). However, since sugar consumption is directly related to diabetes and obesity, there is an increased interest in sugar-free products. This presents a different set of challenges, as low sugar content leads to difficulties in gel formation of this kind of agar, with a decrease in texture, stability and uniformity. However, in response to this, a recent study demonstrated that by replacing sucrose with inulin-type fructans the strength of the agar gel may also increase (Kronberga *et al*., 2011). Since oligosaccharides produce a lower caloric content (around 2 kcal/g) the authors stated that sugar may be replaced by inulin for those who like to consume agar jelly (where sugar is used) and have weight problems.

### 14.4.5 New insights into agar uses and potential markets

About 90% of the agar produced is used in food applications, with the remaining 10% put to bacteriological and biotechnological uses. For further details on these different uses and the corresponding type of algae required, see Armisén and Galatas (2000) and Bixler and Porse (2011). Though food applications continue to grow, non-traditional uses of agar are continuously being tested. In the biomaterials field, agar, either by itself or in blends with other biopolymers, appears to impart favorable properties to plastic films, improving resistance, clarity and increasing biodegradability (Madera-Santana
et al., 2009, 2010; Madera-Santana et al., 2011). Nevertheless, agar is more expensive than starch (commonly used for this application), which limits its large-scale use. Recently, the development of materials formed with magnetic particles inside an organic matrix have received great attention due to the possibility of inducing, by external magnetic fields, controlled changes in temperature and physical properties of the material. In biomedicine, such hybrid compounds with micro- or nanoparticles can be used as auxiliary elements for the diagnosis and treatment of diverse diseases. They also exhibit properties that are desirable in the development of smart materials for biodegradable matrices. The application of alternating magnets to the electromagnetic fields could induce heating of the magnetic particles inside a biocompatible polymeric matrix, and the effects of such magnetic particles in agar are already being explored with promising results (Hsieh et al., 2010; Chang et al., 2011).

14.5 Conventional agar extraction methods

The production process of agar can be separated into certain key stages: pretreatment, extraction, filtration, concentration and dehydration (Fig. 14.3). Details of each stage are given in Matsuhashi (1990, pp. 6–14), McHugh (2003, pp. 17–21) and Armisén (2000, pp. 23–26).

14.5.1 Pre-treatments

In order to obtain the purest possible extraction, seaweeds are first washed to remove sand, salts, shells and other foreign matter. There are some differences in the pre-treatment depending on the genus used. For Gelidium, this stage consists of a corrective treatment with a mild alkaline solution (usually sodium carbonate) to eliminate the pigment phycoerythrin and to macerate and prepare the seaweed for a better extraction. For Gracilaria, alkali treatment before extraction is performed to increase gel strength. The seaweeds are heated at 85–90°C in a sodium hydroxide solution, at concentrations ranging from 0.5% to 7% NaOH, for 1–2 hours. The concentration of the alkali, as well as temperature and time, must be adapted to each species of Gracilaria to obtain as much desulfation as possible while avoiding the yield losses that this process can cause (Freile-Pelegrin and Robledo, 1997; Freile-Pelegrin and Murano, 2005). After removal of the alkali, the seaweeds are washed with water and, occasionally, with very weak acid to neutralize any residual alkali.

14.5.2 Extraction and filtration

Agar extraction necessarily involves cooking the seaweeds in an excess of water at boiling point. To promote a good extraction, careful addition of acid to adjust the pH to 6.3–6.5 is generally required. Extraction under pressure reduces processing time and increases the yield of agar. However, whilst both the pressure method and acid cooking are effective for agar extraction,
both of these conditions are potentially destructive to the extracted agar. Therefore optimum extraction conditions have to be established for each kind of seaweed. The agar dissolved in the water must be filtered to remove the residual seaweed, and the hot filtrate is cooled to form a gel. Depending on the agar quality sought, the gel may be treated with bleach (usually sodium hypochlorite) to reduce any color. Following such a treatment, the gel must be washed to remove the bleach, leaving a gel which contains about 1% agar. The remaining 99% is water and must be removed from the gel, either by a freeze-thaw process or by squeezing it out using pressure.

14.5.3 Concentration by freezing-thawing method

The traditional technique adapted by Minoya Tarozaemon based on freezing and thawing is still in use to a small extent to produce ‘natural agar’ in the oriental craft industry (Matsuhashi, 1990). This technique begins with careful washing of Gelidium amansii, employing devices similar to those used to wash tea-leaves. In the past, the adjustment of pH during extraction was conducted with vinegar or sake but now diluted sulfuric acid is more commonly employed. The liquid extract is filtered while hot through cotton bags, poured into wooden trays and allowed to gel by cooling. Depending of the volume of gel, it can be cut into square bars or extruded to produce strips 25–40 cm long before the natural freeze-thaw process is used to dewater and concentrate the gel prior to drying. The seaweed extract, which normally contains 1–1.2% of agar during the process, is concentrated after thawing and straining (normally by centrifugation) to contain 10 to 12% agar – a tenfold increase. The eluted water carries away oligomers, organic and inorganic salts, and proteins from the algae, including the phycoerythrins responsible for producing the red color of the Rhodophyceae family.

14.5.4 Concentration by syneresis method

An alternative method to reduce water content in the gel is based on syneresis. The agar gel is placed between porous filter cloths and squeezed in a hydraulic press to remove water. This syneresis technique has spread rapidly all over the world due to the reduction in energy costs it facilitates. As a comparative example, the freezing method requires ice production of c. 100 tons to produce one ton of agar, which requires far greater energy than the low energy consumption of the syneresis method. Furthermore, agar purity increases in the syneresis method because a greater quantity of water and soluble impurities can be removed (Fig. 14.3).

14.5.5 Future trends in agar extraction: eco-friendly agar extraction as an alternative to conventional methods

Agar extraction is a relatively mature industry in terms of manufacturing methods and applications. Today, most processors are using press/syneresis technology, although some still favor freezing/thawing technology or a
mixture of these approaches. While the basic processes may not have changed, improvements in presses and freezing equipment are being implemented to improve efficiency and reduce energy requirements (Bixler and Porse, 2011). However, in the current industrial practice of agar extraction, large quantities of solvents are still used during bleaching, pre-treatment and during alkaline modification. These steps must be carefully controlled to avoid the considerable pollution generated by outflows of bleaching agents, alkaline residues and large quantities of ‘sodium agarpectinates’. Moreover, if an agar for
industrial purposes can be obtained without the need for an alkaline treatment step, it may be more attractive from both an ecological and an economic point of view. This has been made possible for algae cultured through a special enzymatic process. This process is activated by darkness and salinity treatments to the biomass before being harvested (Yu and Pedersén, 1990; Rincones et al., 1993; Freile-Pelegrin et al., 2002). In this context, ‘green’ technologies used to produce biomass, together with eco-friendly agar extraction methods, have arisen as alternatives to those used conventionally.

**Photobleaching extraction process**

The chloride gas produced by the bleaching process, which is conducted to achieve the pure white color of agar, can adversely affect the health of workers (Warburton, 2005). Furthermore, the effluents produced by bleaching constitute a pollution problem. In response to these problems, a novel agar photobleaching extraction process has recently been developed and patented by Jin et al. (2006) and Li et al. (2008). This process exploits the ‘green’ energy of sunlight and is based on the photochemical degradation of colored organic matters (CDOM). The authors claim that when solar radiation is absorbed by the CDOM in surface water, a rich variety of photochemical reactions will ensue. Such reactions are involved in energy transfer, electron transfer, and free radical reactions that lead to the cleavage of a variety of photoproducts, and to a reduction of average molecular mass. Furthermore, the enhanced mineralization produced helps to reduce dissolved inorganic compounds (DIC), such as carbon monoxide, carbon dioxide, and other forms of dissolved organic carbon (DOC).

The CDOM photolysis is accompanied by a reduction in the absorption coefficients of the dissolved organic matter across the ultraviolet and visible spectral regions. This reduction in absorbance of light is termed ‘photobleaching’ (Gao and Zepp, 1998, cited in Li et al., 2008). *Gracilaria lemaneiformis* and *Gracilaria asiatica*, growing as aquaculture bioremediation along the coasts of Liaodong Peninsula, China, were investigated in relation to agar production using the photobleaching extraction process (Li et al., 2008). The duration of photobleaching was demonstrated to have a significant impact on agar gel strength. To explain this response, the authors suggest that ‘agar with repeating sulfate-connected disaccharides underwent photolysis with the free radicals during the photobleaching process in water, which improved the gel strength by decreasing the sulfate content and increasing the 3,6-anhydro-L-galactose levels’. The above results indicate that the agar photobleaching extraction process is a feasible method for *Gracilaria* species and has good potential as an application of green technology.

**Microwave-assisted extraction**

In the last decade, microwave-assisted extraction (MAE) has been successfully applied to various fields of analytical chemistry. This technique involves the use of microwave energy to heat solvents in contact with a sample.
algal matrix is highly susceptible to microwave irradiation, owing to the high natural moisture content. Rapid internal heating of these structures brings about effective cell rupture, releasing the analytes into the cold solvent (Mandal et al., 2007). The main advantages of the proposed procedure are the reduced consumption of solvents (in comparison to solvent consumption of traditional methods), the lower level of energy required and the reduced extraction time.

Recently, Sousa et al. (2010) reported the first extraction of an agar using MAE from Gracilaria vermiculophylla, from an integrated multitrophic aquaculture (IMTA) system. The authors obtained higher yields and reproducibility, as well as higher gel strength, in comparison to conventional extraction methods. The MAE approach supports sustainable development, as it requires less energy and solvent than conventional processes, whilst generating fewer waste products. This research suggests the feasibility of using MAE as a ‘green’ technology for the production of superior quality agar gels.

In the so-called integrated polyculture systems, recently grouped under the term IMTA systems, the wastes generated during the growth of a species are ‘recycled’ to become ‘food’ for another, so that different aquatic resources are interacting positively with each other (Robledo and Freile-Pelegriń, 2011). The implementation of this concept in the context of fish farming is to improve the utilization of marine resources, increase the profitability of these activities and ensure the sustainability of aquaculture. In this context seaweeds play a critical role, as they are primary producers capable of converting dissolved substances that have been excreted by organisms of other trophic levels into additional crops.

In addition to its biofiltration efficacy, the economic value of the biomass should be considered when choosing the seaweed species to work with in IMTA systems. Gracilaria is one of the most cultivated and valuable seaweeds worldwide. Adopting the IMTA approach with this genus has already produced good examples of significant revenues for the fish aquaculture industry (Neori et al., 2000; Chopin et al., 2001; Abreu et al., 2011). Green technology for the large-scale production of important agarophytes as IMTA systems, together with the use of eco-friendly agar extraction methods, are key to the future of the agar industry.

14.6 Carrageenan

Carrageenan is a phycocolloid, extracted from different genera of red seaweeds, where this substance plays a structural function. It is a strongly ionic polysaccharide, composed of galactose with different degree and pattern of sulfates distributed in the polymeric chain, which impart characteristic solubility properties. Some carrageenans are soluble in cold water, with only viscosifying properties, whereas others are soluble only in hot water and have the ability to form a thermoreversible gel, with potassium or calcium ions. It is widely used in the food and pharmaceutical industries. The extraction
process of carrageenans from seaweeds is divided into two process lines based on the purity of the product obtained. In the first method, it is necessary to dissolve the polysaccharide in the solution, then it is filtered to remove solid particles, and the carrageenans are recovered from the solution and impurities by precipitation with an organic solvent or with potassium salts. In the second method, the carrageenan is actually not extracted – seaweed is treated usually with alkaline solution, then soluble impurities are removed, leaving mostly carrageenan and cellulose, which are dried and milled. Although with this second process the carrageenan is more impure, it is cheaper, making it more attractive and favoring the development of new uses. Recently the market for carrageenans is growing, making it essential to search for new raw materials and improved technologies with less impact on the environment.

14.6.1 Historical background
Carrageenan is the generic name of a family of natural, water soluble polysaccharides, isolated from several kinds of red seaweeds. Carrageenan, composed of sulfated galactans, have both gel-forming abilities and viscousifying properties. In addition to forming thermoreversible gels, they are labile at high temperatures in acidic conditions. Historical use of carrageenan can be tracked back in Europe, where for about 600 years a substance obtained by cooking certain red seaweeds has been used as a thickening and stabilizing agent in foods. In Europe and North America, a kind of flan (blancmange) was made by cooking red seaweeds as Chondrus crispus or Gigartina stellata in milk (van de Velde and de Ruiter, 2002). The name ‘carragee’ seems to have been introduced around 1829, derived from the Irish word, carraigeen, meaning ‘rock moss’ in reference to the seaweed Chondrus crispus or ‘Irish moss’ (Mitchell and Guiry, 1983). The name carrageenin was first used by Stanford in 1862 to refer to the gelatinous water extract from Chondrus crispus (Tseng, 1946). Nowadays, the term ‘carrageenan’ has become accepted, in agreement with the use of the -an suffix, within the polysaccharide nomenclature (Stanley, 1987).

Formerly, the carrageenan process was based on the direct use of sun-bleached seaweeds. The first procedure for obtaining carrageenan was developed by Schmidt in the USA in 1844 (Armité, 2000). Commercial carrageenan production was then initiated in Maine, USA (1937), where Chondrus crispus from Maine and the Maritime Provinces Canada, was used as the main raw material. It was known that carrageenan was a heterogeneous compound, made up of galactose and ester sulfate, but very little was understood about its structure. In 1953, Smith and Cook, using crude carrageenan from Chondrus crispus, were able to separate two fractions based on their solubility in potassium chloride solution. One fraction precipitated selectively by potassium ions (Kappa), while the other fraction remained in the solution, as it was non-sensitive to potassium ions (Lambda).

The existence in carrageenans of more than two fractions within a Chondrus crispus extract was demonstrated by Pernas et al. (1967). They carried out a
fractional precipitation with KCl and found not only kappa and lambda fractions, but instead a continuous spectrum of carrageenans, each with different chemical compositions and properties. Further studies, derived from the red seaweed *Eucheuma spinosum*, elucidated a third type of carrageenan; the iota-carrageenan (Rees, 1969). Many carrageenan types have now been described (mu, kappa, nu, iota, theta and lambda among others), each of them with specific physicochemical properties, differing in amounts of 3,6-anhydro-D-galactose, and degree and pattern of sulfation (Painter, 1983; Craigie, 1990). Despite the wide carrageenan variety found in nature, from a commercial point of view there are three main commercial carrageenans: kappa, iota and lambda. They are differentiated by their sensitivity to potassium ions, and their uses are related to their ability to form viscous solutions or gels (Table 14.1).

### Table 14.1 Main commercial carrageenans and their functional properties

<table>
<thead>
<tr>
<th>Carrageenan type</th>
<th>General properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kappa</td>
<td>Form strong and rigid gel with potassium salts. Brittle gels with calcium salts. Shown syneresis. Synergy with locust bean gum.</td>
</tr>
<tr>
<td>Iota</td>
<td>Form strong gels with calcium salts. Elastic and clear gels. Gel is freeze-thaw stable. Gels without syneresis.</td>
</tr>
<tr>
<td>Lambda</td>
<td>Non gelling with potassium ions, form high viscosity solutions. Soluble in concentrated salt solutions.</td>
</tr>
</tbody>
</table>

*Source: Modified from Moirano, 1977.*

14.6.2 Sources of carrageenophytes

*Chondrus crispus*, commonly known as ‘Irish moss’, was the original raw material for carrageenan production. However, as demand increased and new applications appeared, it was necessary to find a new supply of raw materials. Since different species produce different types of carrageenan, new seaweed species were incorporated into carrageenan manufacture (Table 14.2). Thus the availability of particular seaweed species determines their commercial use (McHugh, 2003).

It is unusual for one seaweed to be reported as containing a single carrageenan type, as seaweeds generally contain molecules of the hybrid type, in which repeating units of different carrageenans exist in the same molecule (i.e. kappa-iota hybrids) (Usov et al., 1980; Usov, 1998; Craigie, 1990; van de Velde, 2008). In seaweeds which are members of Gigartinaceae, carrageenans of the kappa family (hybrids kappa-iota) are produced by gametophytes, whereas hybrids of the lambda family (lambda, xi and pi) are produced by
Functional ingredients from algae for foods and nutraceuticals

Table 14.2  Main seaweeds used in carrageenan production and carrageenan type produced

<table>
<thead>
<tr>
<th>Seaweed</th>
<th>Life stage</th>
<th>Carrageenan type</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Chondrus crispus</em>¹</td>
<td>Gametophyte</td>
<td>Kappa/iota (κ/ι)</td>
</tr>
<tr>
<td></td>
<td>Tetrasporic</td>
<td>Lambda (λ)</td>
</tr>
<tr>
<td><em>Chondracanthus</em></td>
<td>Gametophyte</td>
<td>κ/ι</td>
</tr>
<tr>
<td><em>canaliculatus</em>³</td>
<td>Tetrasporic</td>
<td>λ</td>
</tr>
<tr>
<td><em>Mastocarpus stellatus</em>¹</td>
<td>Gametophyte</td>
<td>κ/ι</td>
</tr>
<tr>
<td></td>
<td>Tetrasporic (absent phase)</td>
<td></td>
</tr>
<tr>
<td><em>Gigartina skottsbergii</em>²</td>
<td>Gametophyte</td>
<td>κ/ι</td>
</tr>
<tr>
<td></td>
<td>Tetrasporic</td>
<td>λ</td>
</tr>
<tr>
<td><em>Sarcothalia crispata</em>⁵</td>
<td>Gametophyte</td>
<td>κ/ι</td>
</tr>
<tr>
<td></td>
<td>Tetrasporic</td>
<td>Deviant λ</td>
</tr>
<tr>
<td><em>Furcellaria lumbricalis</em>⁶</td>
<td></td>
<td>Kappa/beta (κ/β)</td>
</tr>
<tr>
<td><em>Kappaphycus alvarezi</em>²</td>
<td></td>
<td>Mainly kappa (κ/ι)</td>
</tr>
<tr>
<td><em>Eucheuma denticulatum</em>¹</td>
<td></td>
<td>Mainly i</td>
</tr>
<tr>
<td><em>Betaphycus gelatinum</em>⁸</td>
<td></td>
<td>Mainly beta (β)</td>
</tr>
<tr>
<td><em>Hypnea</em>⁹</td>
<td></td>
<td>κ/ι</td>
</tr>
</tbody>
</table>


The genus *Eucheuma* produces different types of carrageenan depending on the species, with no differences between life cycles (Craigie, 1990) (Table 14.2). Nowadays the carrageenan industry uses a wide number of seaweed species; all of these belong to seven Rodophyta families: Gigartinaceae, Solieraceae, Rhabdoniaceae, Hypnaceae, Phyllophoraceae, Furcellariaceae and Rhodophyllidaceae (Dawes *et al.*, 1977; Deslandes *et al.*, 1985).

*C. crispus* continues to be used in the industry, but only in limited quantities. It is mainly harvested from natural stocks in the USA (coast of Maine and Massachusetts), Canada (Nova Scotia and Prince Edward Island) and France. In the mid 1960s, there was an increased interest in *Eucheuma* species from the Philippines and Indonesia, such as *Kappaphycus alvarezi* (formerly *E. cottonii*) and *E. denticulatum* (formerly *E. spinosum*). These were first harvested from natural stocks, but by the early 1970s *Eucheuma* farming was being developed in both countries. Cultivation also spread to Tanzania (Zanzibar), Vietnam and some of the Pacific Islands, such as those of Kiribati. Wild *Betaphycus gelatinum* (formerly *E. gelatinae*) is mainly harvested in China, Taiwan Province of China and the Philippines, and it is both harvested and cultivated on Hainan Island (McHugh, 2003) (Fig. 14.1). Several *Gigartina* species from natural stocks are harvested in South America, particularly in Chile, Argentina, Peru and Mexico (Fig. 14.1, Table 14.3).

In the last decade, seaweed production increased by 17%, exceeding 202 000 dried tons per year, and valued at over 70 million USD. Recent data
has shown that *K. alvarezii* accounts for roughly 80% of the total production. By 2009, carrageenans had the highest production level among the phycocolloids (50 000 tons). Despite the lower unitary price, carrageenans account for roughly 50% of phycocolloids sales (Fig. 14.1). The current price of carrageenans (2012) is related, among other characteristics, to the purity of the product; regular products are about US$6–15/kg. Table 14.3 shows the different carrageenan sources used in carrageenan manufacture (Stanley, 1987; McHugh, 2003, 2006).

### 14.6.3 Chemistry of carrageenan

Carrageenan, together with agar and furcellaran (formerly Danish agar), belong to the family of linear polysaccharides derived from red seaweeds called sulfated galactans. Instead of some structural particularities, they are broadly differentiated from each other by their sulfation degree, where agar yields 3–4% sulfate, furcellaran yields 8 to 19% (actually belonging to the carrageenan family), and carrageenan more than 20% (Moirano, 1977). The carrageenan molecule has a repeating structure of alternating 1,3-linked

<table>
<thead>
<tr>
<th>Seaweed species</th>
<th>Old name</th>
<th>Source</th>
<th>Country</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Chondrus crispus</em></td>
<td></td>
<td>Natural stocks</td>
<td>United States, Canada, France, Spain, Portugal</td>
</tr>
<tr>
<td><em>Furcellaria spp</em></td>
<td></td>
<td>Natural stocks</td>
<td>Denmark, Russia</td>
</tr>
<tr>
<td><em>Mastocarpus stellatus</em></td>
<td><em>Gigartina stellata</em></td>
<td>Natural stocks</td>
<td>Spain, Portugal, Morocco.</td>
</tr>
<tr>
<td><em>Kappaphycus alvarezii</em></td>
<td><em>Eucheuma cottonii</em></td>
<td>Mostly farming</td>
<td>Philippines, Indonesia, Tanzania, Vietnam, Kiribati Islands</td>
</tr>
<tr>
<td><em>Eucheuma denticulatum</em></td>
<td><em>Eucheuma spinosum</em></td>
<td>Mostly farming</td>
<td></td>
</tr>
<tr>
<td><em>Betaphycus gelatinum</em></td>
<td><em>Eucheuma gelatinae</em></td>
<td>Farming and Natural stocks</td>
<td>Hainan Island, Philippines, China and Taiwan</td>
</tr>
<tr>
<td><em>Gigartina skottsbergii</em></td>
<td></td>
<td>Natural stocks</td>
<td>Chile, Argentina</td>
</tr>
<tr>
<td><em>Sarcothalia crispta</em></td>
<td><em>Iridaea ciliata</em></td>
<td>Natural stocks</td>
<td>Chile</td>
</tr>
<tr>
<td><em>Mazzella laminaroides</em></td>
<td><em>Iridaea laminaroides</em></td>
<td>Natural stocks</td>
<td>Chile</td>
</tr>
<tr>
<td><em>Hypnea musciformis</em></td>
<td></td>
<td>Natural stocks</td>
<td>Brazil</td>
</tr>
<tr>
<td><em>Chondracanthus canaliculatus</em></td>
<td><em>Gigartina canaliculata</em></td>
<td>Natural stocks</td>
<td>Mexico</td>
</tr>
</tbody>
</table>

β-D-galactopyranosyl and 1,4-linked α-D-galactopyranosyl units, where the 3-linked unit can be unsulfated, 2-sulfated or 4-sulfated. The 4-linked unit can occur as 2-sulfate, 6-sulfate, 2,6-sulfate, 3,6-anhydride or 3,6-anhydride 2-sulfate (Stanley, 1987, Craigie, 1990).

There are many individual carrageenan types, each one named in Greek letters, following the originally proposed nomenclature (Smith and Cook, 1953). The carrageenans are then grouped into three main families: the Kappa family, including kappa (κ) and iota (ι) carrageenans; the Beta family including beta (β) and omega (ω), and the Lambda family which include theta (θ) and pi (π) (Table 14.4). In each of these families there are different related precursor structures. For more information on this classification, see Greer and Yaphe (1984) and Craigie (1990). Because of the large number of carrageenan structures defined at present, the carrageenan nomenclature is becoming more confusing. To reverse this, Knutsen et al. (1994), proposed a more systematic nomenclature for carrageenan and agars, based on the IUPAC (International Union of Pure and Applied Chemistry) nomenclature. However, for the purpose of this work we will continue using the Greek prefix letters. The different carrageenan structures differ in the 3,6-anhydrogalactose and ester sulfate contents. Variations in these components influence hydration, gel strength and texture, melting and setting temperatures, syneresis and synergism. These differences are controlled and created by seaweed selection, processing and blending of different extracts (Imeson et al., 1977, 2000).

### 14.6.4 Carrageenan for food applications

Traditionally, the main applications of carrageenan are in the food industry. In order to explore why carrageenan is so well suited to these applications, we will first briefly describe the properties of the main commercial types. In the fields of food, drugs and cosmetics, these are generally used at concentrations as low as 0.01 to 1.0% (Hansen, 1987). Kappa and iota carrageenan have the ability to form gels with potassium and calcium ions. Kappa carrageenan forms the strongest gel, while gels of iota are more elastic. The binding of cations in carrageenans reduces the effective charge density of the helical chains, subsequently promoting helix aggregation and the formation of a three-dimensional gel structure (Williams, 2009). Kappa reacts with potassium ions to form strong, rigid gels, while the reaction with calcium ions produces gels that are brittle (Table 14.1). Kappa gels can be set with as little as 0.5% in water and 0.2% in milk (Imeson, 2000). Gels with only kappa carrageenan can suffer syneresis (water bleeding), but this problem can be solved by using appropriate blends of kappa with iota or lambda carrageenan, which reduce the rigidity of the gel, improving the water retention ability (Imeson, 2000).

Another way to eliminate the syneresis of kappa gels is by making blends with different gums, such as locust bean gum or konjac flour. Such gums produce a synergistic effect, improving the elasticity and the gel strength. This, in turn, allows a reduction in the amount of kappa carrageenan needed to
maintain the required gel strength, rendering the gels more elastic, clear and free of syneresis (Williams, 2009). Iota carrageenan has the ability to form stronger gels with calcium ions than potassium; the iota gels are elastic and free of syneresis. These iota gels also exhibit thixotropic flow behavior, meaning that the gel can be stirred and will flow like a thick liquid (syrup), before, in repose again, gradually re-forming back into a gel. The iota carrageenan has vast uses in frozen desserts, where it gives a smooth, creamier texture to the final product. Lambda carrageenan is a very soluble polysaccharide in cold or hot solutions and is soluble with all salts at any concentration, with low concentrations imparting high viscosity to solutions.

Until the late 1970s, carrageenan use in food products was mainly confined to milk products, due to the unique ability of carrageenan to interact with the casein in milk. A very low carrageenan concentration can keep milk solids in suspension and stabilize them. This prevents whey separation in cheese products and enhances the formation of fine crystals in milk ice cream, producing a creamier texture in the mouth. Such properties mean these carrageenans have been used widely in milk product applications, including in cheese production, cocoa suspensions, chocolate milk products and milk gel flans, amongst others. In this line of applications, kappa and lambda carrageenan obtained from Gigartinales give excellent results.

Another area that has been positively drawing on carrageenan production since the early 1980s is the meat industry, where carrageenans are now extensively used, particularly those obtained from *Eucheuma* species. The great ability of kappa carrageenan to hold water makes this product very suitable as a replacement for fat in meat products, where it improves the final texture. Kappa carrageenan are employed in the production of ham, lean ham and hamburgers, processed meat, reconstituted seafood and poultry products. To obtain the optimum results, the carrageenans are commonly blended with others gums, such as locust bean gum or konjac flour, improving the characteristics of the product and making an important reduction to the amount of carrageenan needed. As a part of the commercialization of carrageenan, producers now make gum blends which are appropriately tailored for the specific applications required.

Carrageenans also have important uses in water gel applications, such as gummy candies, fruit gels, fruit juices and marmalades, for example, as well as in toothpaste, bakery products and slow release capsules (Imeson, 2000; Bixler and Porse, 2011).

### 14.6.5 New insights for carrageenan uses and potential markets

Following the initial success of commercial carrageenan production for food product applications, diverse new uses are continuing to emerge across a range of areas, including water applications, candies, freshener gels, cosmetics and in the meat industry, for example. Nowadays the food uses account for 90% of commercially produced carrageenan (Bixler and Porse, 2011),

© Woodhead Publishing Limited, 2013
Table 14.4  Idealized molecular structures of different carrageenan families

<table>
<thead>
<tr>
<th>Family</th>
<th>Precursors</th>
<th>Idealized terminal structures</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Beta carrageenan</strong></td>
<td><img src="image" alt="Beta" /></td>
<td><img src="image" alt="Beta" /></td>
</tr>
<tr>
<td></td>
<td><img src="image" alt="Gamma" /></td>
<td><img src="image" alt="Gamma" /></td>
</tr>
<tr>
<td></td>
<td><img src="image" alt="Psi" /></td>
<td><img src="image" alt="Psi" /></td>
</tr>
<tr>
<td><strong>Kappa carrageenan</strong></td>
<td><img src="image" alt="Mu" /></td>
<td><img src="image" alt="Mu" /></td>
</tr>
<tr>
<td></td>
<td><img src="image" alt="Kappa" /></td>
<td><img src="image" alt="Kappa" /></td>
</tr>
<tr>
<td></td>
<td><img src="image" alt="Iota" /></td>
<td><img src="image" alt="Iota" /></td>
</tr>
</tbody>
</table>
Lambda carrageenan family

Source: Modified from Greer and Yaphe, 1984.
with the dairy and meat industries the main application sectors (Table 14.5). In the last decade a production increase of 18% (from 42 000 to 50 000 m tons) was observed in the carrageenan market, mostly reflected in meat and water gel applications (Bixler, 1996; Bixler and Porse, 2011). It is difficult to predict how future substantial changes could alter the carrageenan market. However, emerging economies such as China and Brazil are already having an important impact on the raw materials; increased use of these raw products is reflected in the current seaweed and carrageenan prices, in turn affecting the expansion of the carrageenan market.

Further increases in carrageenan use and new applications can be expected as understanding of their value as bioactive compounds develops. This bioactivity is associated with the sulfate content, and some novel commercial products are using it for its antiviral properties. Carraguard™, for example, is used as a sexual lubricant and microbicide, and it is further suspected that it may have a protective effect against the human papilloma viruses (HPV), herpes simplex viruses (HSV) and against human immunodeficiency virus (HIV). Despite the presence in the market of some commercial products, more trials must be conducted with this kind of application before the full potential in this area can be assessed.

### 14.7 Conventional carrageenan extraction methods

Carrageenan is present in some types of red seaweeds as a water soluble anionic polysaccharide. In the plant, it is mostly found immersed in the cell wall and cell matrix, functioning as a structural polysaccharide and contributing to the rigidity and flexibility of the plant (Lobban and Harrison, 1994). In the cell wall, carrageenans have strong interactions with proteins, pigments, minerals and others polysaccharides, such as cellulose and hemicelluloses, alongside various other seaweed components.

In order to use the functional properties of the carrageenans as a product, there are two main lines of processing: a) refined carrageenan, which involves extraction in aqueous solution, filtration and precipitation and b) semi-refined carrageenan, where the carrageenan is retained in the seaweed while other seaweed components are eliminated (Schweiger et al., 1992).
14.7.1 Refined carrageenan

**Alcohol process**

This is the first commercial process used. The objective is to get the carrageenan free of the other seaweed components, before further separating the carrageenan from the cell wall materials, solubilizing it in an aqueous solution. Firstly, in order to remove sand, salts, shells and other foreign matter, the dry seaweeds are washed with running water. The extraction is then carried out with a mild alkaline solution (sodium bicarbonate) at pH 8 to 9, at a ratio of 1:50 (solid:liquid) which is boiled for two hours. When the carrageenan is in solution, the cellulose and other insoluble material are discarded via different clarification processes, most commonly by filtration using a filter aid on a pressure filter (Fig. 14.4).

To recover the carrageenan from the solution, and to reduce the alcohol needed to produce a precipitate, the clear solution is vacuum evaporated to approximately a third of the original volume. The precipitation is carried via an organic solvent, commonly isopropyl alcohol (proportion 2:1, solvent:extract), and the carrageenan is precipitated whilst the water and soluble impurities remain in solution. This process produces the so-called ‘refined carrageenan’. Already successfully applied to the processing of *C. crispus* and different *Gigartina* species, this methodology can be used to

![Flow chart for refined carrageenan production](image-url)

**Fig. 14.4** Flow chart for refined carrageenan production, where the three left options (a, b and c) can be used to process any kind of seaweeds (Gigartinales species) while the KCl (d) option is only for kappa carrageenan-producing species (i.e. *Kappaphycus* and gametophytes from Gigartinales).
Functional ingredients from algae for foods and nutraceuticals

process any seaweed. Importantly, this means it can be used to produce any kind of carrageenan (Fig. 14.4c). Until now this methodology is the only alternative for obtaining the highly soluble lambda carrageenan. The disadvantage of this method is the high cost involved in the distillation of large volumes of alcohol and the purchase of the necessary explosion-proof equipment.

Potassium chloride process
This is a variant of the alcohol process which also involves the carrageenan initially being in a solution. However, the difference is in the precipitation method used; instead of using alcohol, KCl to 1% (w/v) is added, and a gel is formed by lowering the temperature on a counter current pipe. Dewatering is achieved via a freeze-thaw process or by pressing the gel, as in the agar process. While this process is cheaper than the alcohol-based method, it is exclusive to the production of kappa carrageenan. This is, however, an appropriate methodology for processing gametophytes of the Gigartinaceae family and such kappa carrageenan-bearing seaweed as *Kappaphycus alvarezii* and other *Eucheuma* species (Fig. 14.4d).

Drum drying process
A third alternative for producing refined carrageenan differs from the other methods in that the carrageenan is recovered directly from the aqueous solution. Instead of precipitation, the water is removed by evaporation. This can be accomplished through the use of a steam heated, single or double drum dryer. The best performance is achieved in a vacuum chamber, which speeds up the process and prevents excessive thermal breakdown of the carrageenan molecule. The carrageenan is then recovered as flakes which contain some soluble impurities (Fig. 14.4a). In order to equal the quality produced by the alcohol precipitation method, these impurities need to be removed, which can be achieved by solubilization with an alcohol: water mixture (≥ 60:40). This process is cheaper and uses much less alcohol than the aforementioned alcohol precipitation method. However, the economy of the process is similarly influenced by the alcohol recovery efficiency. This process can be applied to the production of any carrageenan type (Fig. 14.4b).

14.7.2 Alternative carrageenan extraction methods
After the success in *Eucheuma* farming in Philippines, further developments led to the production of *E. cottonii* flour, which was applied in the manufacture of canned pet food. By the early 1980s, the quality of the flour had improved to a level that allowed its use in food applications, especially in areas where clarity was not a requisite, as in the meat industry, for example. The products used for such applications, known as Semi-refined Carrageenan

© Woodhead Publishing Limited, 2013
Technologies for the extraction of algal polysaccharides 507

(SRC), Philippines Natural Grade (PNG) or Philippines *Eucheuma Seaweed* (PES), were subsequently accepted by the FDA in the USA.

### 14.7.3 Semi-refined carrageenan

In this process the carrageenan is never actually extracted from the seaweed. Instead, it is retained in the seaweed, but all other components (including soluble proteins, minerals, pigments and fats) are, as far as possible, eliminated from the seaweed. The process for producing this kind of product involves obtaining fresh or dried seaweed, such as *Kappaphycus alvarezii* or *Eucheuma denticulatum*, which is then subjected to an alkali treatment with a hot alkali solution: KOH or Ca(OH)$_2$ at $\geq 5\%$ in seawater at 70–80°C for over 1 h. After this treatment, some of the sulfate groups are released, and 3,6-anhydro-galactose is formed, improving the gel strength of the product. The hot alkali and subsequent washing removes residual minerals, proteins and fats, leaving the carrageenan and some residual cellulose in the seaweeds. The alkali-treated seaweed is chopped into small pieces, bleached, dried and milled. Sometimes the dried product is chopped into pieces but not milled, and is sold as a raw material for the production of refined carrageenan. This

Fig. 14.5 Flow chart of semi-refined carrageenan production, where the carrageenan actually is not extracted from the seaweed. Usually the seaweeds are alkali treated in order to increase the gel strength (a) in alkaline water solution for *Eucheuma* species or (b) for *Gigartina* in alkaline alcohol media; the final product in all cases contains seaweed particles.
product is called alkali-treated cottonii (ATC), alkali-treated cottonii chips (ATCC), or even simply cottonii chips (Fig. 14.5a) (McHugh, 2003).

14.7.4 Mixed carrageenan extraction methods
A hybrid process has been developed in which raw materials are treated in the same manner as in the semi-refined process, retaining carrageenan in the seaweed, but instead of using the water alkaline solution, the alkali treatment is carried out in an alcohol slurry (Fromholt, 1998). The proportion of alcohol in the alcohol:water mixture used for the treatment should be high enough to inhibit carrageenan dissolution. This proportion is usually above 60:40 at 80°C at high alkali concentration (commonly KOH ≥ 5%), which is usually sufficient to dissolve such impurities as pigments, fats, minerals and other components. Although this process is more expensive than the semi-refined process, the alcohol used can be recovered efficiently (Fig. 14.5b). The advantage of this process is that it can potentially be used to process any seaweed.

The other processing line commonly used in carrageenan extraction is called selective extraction. In this process, the carrageenans are selectively extracted by inhibiting the solubility of one type of carrageenan and increasing the solubility of others. In mixtures of kappa–lambda species, kappa carrageenan is kept in the seaweed using an optimum KCl concentration and low temperature (20–30°C) treatment (Fig. 14.6). This allows the extraction of lambda carrageenan and/or precursors as mu and nu carrageenans (Stancioff, 1965). Soluble lambda carrageenan and precursors are separated and precipitated with alcohol (Fig. 14.6a), while kappa is processed as semi-refined via drying and milling (Fig. 14.6b). Alternatively, the kappa carrageenan can be extracted into a solution by increasing the temperature; after filtration, it is recovered with alcohol or KCl as refined carrageenan (Fig. 14.6c). This process can be modified by applying alkali treatment to raw seaweeds.

14.7.5 Future trends in carrageenan extraction
The development and employment of innovative MAE techniques can have a favorable effect on process efficiency to reduce the cost of algal polysaccharide extraction. The microwave method allows selective and localized heating of materials without requiring the application of excessive energy. This technology involves the use of non-refractive materials and clear transport pipes, which allow the heating process to be successfully achieved (Kluck, 1970). Another advantage of this methodology is that less heat damage is done to the carrageenan molecule, as the heat is applied over a shorter period of time (Scott, 1984). In addition, smaller amounts of water and alkali are needed for this method, due to the improved efficiency, leading to a reduction in the environmental impact.
14.8 Conclusions

The search for new functional ingredients from natural sources is one of the most important challenges in food science and technology. It is driven by a social demand for new functional foods with scientifically demonstrated health properties. Marine algae are well known natural sources of gums, such as alginate, agar and carrageenan. Once their usefulness in the food, pharmaceutical and other industries has been well demonstrated, it will be necessary to overcome the scarcity and poor quality of some raw materials. This may be achieved through the development on an industrial scale of the so-called integrated polyculture systems, and improved processing technology for the production and purification by environment-friendly extraction processes in a fast, cost-effective and non-aggressive way.

14.9 References

510 Functional ingredients from algae for foods and nutraceuticals


© Woodhead Publishing Limited, 2013
Technologies for the extraction of algal polysaccharides 511


HENDRÉZ-CARMONA, G, MCHUGH, DJ, ARVIZU-HIGUERA, DL and RODRÍGUEZ-MONTESINOS, YE (2002), ‘Pilot plant scale extraction of alginites from Macrocystis
Functional ingredients from algae for foods and nutraceuticals


Technologies for the extraction of algal polysaccharides


SOUSA, AMM, ALVES, VD, MORAIS, S, DELERUE-MATOS, C and GONÇALVES, MP (2010), ‘Agar extraction from integrated multitrophic aquacultured *Gracilaria vermiculophylla*: 

© Woodhead Publishing Limited, 2013
Technologies for the extraction of algal polysaccharides


